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The role of commodity science in quality management in a knowledge-based economy

Innovations in quality development of products and services, vol. 2

Innowacje w kształtowaniu jakości wyrobów i usług, tom 2

Red. Millena Ruszkowska

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pod redakcją Milleny Ruszkowskiej

Gdynia 2022

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ANTIOXIDANT ACTIVITY OF KAKADU PLUM (*TERMINALIA FERDINANDIANA*) EXTRACT AND SELECTED ASCORBIC ACID DERIVATIVES AS COSMETIC RAW MATERIALS

JUSTYNA KIEWLICZ[1], DOBRAWA KWAŚNIEWSKA[2]

[1] *Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economics and Business*
e-mail: justyna.kiewlicz@ue.poznan.pl
[2] *Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economics and Business*
e-mail: dobrawa.kwasniewska@ue.poznan.pl

Abstract
On the cosmetic market, for several years, products with vitamin C or its derivatives are very popular with consumers. This popularity is due to the antioxidant activity of these compounds, but also to the influence of vitamin C on the synthesis of collagen. However, the pro-ecological trend observed on the cosmetics market makes manufacturers more willing to replace synthetic compounds with products of natural origin. This research shows that the analyzed vitamin C derivatives can be replaced with Kakadu plum fruit extracts. The antioxidant properties were determined using: 1,1-Diphenyl-2-picrylhydrazyl (DPPH), Ferric Reducing Antioxidant Power (FRAP) and Trolox Equivalent Antioxidant Capacity (TEAC) assays.

Keywords: quality, antioxidant activity, L-ascorbic acid derivatives, Kakadu plum

Introduction

Functional cosmetics are described in scientific literature as cosmetics ensuring comprehensive action in terms of skin whitening and protection skin against wrinkle, ultraviolet or burned skin [Pan-Jin & Le 2016]. The above-mentioned product category includes cosmetics with vitamin C, which are still gaining popularity

on the market as products recommended especially for the people with mature skin. Cosmetics containing vitamin C exhibit broad spectrum of activity. The regular application of this preparations causes slowing down the process of wrinkle formation, protects skin against UV radiations, brightens discolorations, maintains activity of vitamin E in the skin and stimulates the synthesis of ceramides, which are a natural component of the skin [Winkler 2019; Gref et al. 2020]. The care properties of vitamin C are based in part on its strong antioxidant activity. Vitamin C protects skin against oxidative damage by neutralizing reactive oxygen species (ROS). On the other hand, it may also participate in protection of cosmetic emulsion against undesirable changes caused by lipid oxidation leading to deterioration of overall quality of products, which are produced from plant oils rich in unsaturated fatty acids [Telang 2013].

The factor limiting the use of vitamin C is its rapid degradation, namely oxidation under the influence of air, which may lead to partial loss of care properties of cosmetics and lowers their quality in terms of utility value. Due to the hydrophilicity, difficulty in penetrating stratum corneum and limited stability, vitamin C is often replaced by synthetic derivatives of ascorbic acid [Winkler 2019]. Despite of undeniable benefits of their use, observed over the last years turn towards ecology and natural products prompts the manufacturers to focus on formulating and developing the high quality products with organic and natural components rich in vitamin C as a substitute for synthetic antioxidants [Fonseca-Santos et al. 2015]. The literature data [Kenalemang-Palm & Eriksson 2021; Ringrow 2016] indicates that the use of marketing strategies emphasized a lack of chemicals and more ecological approach to skin care, has a positive effect on purchase decisions of the female consumers, who cares about their looks and well-being as well as also care about their safety and ecological footprint.

Around 250 species of the genus *Terminalia* of the *Combretaceae* family can be found worldwide in regions with tropical climates, of which 30 species or subspecies Terminalia are endemic to Australia [Saleha et al. 2019; Cozzolino et al. 2021]. The name of the species comes from the Latin "terminus" which can be translated as a leaf at the end of a branch. Since 1930, research has been carried out to determine the chemical composition of the genus *Terminalia*. So far, 39 *Terminalia*

species have been tested in terms of phytochemicals, finding their presence of terpenes, tannins, flavonoids, lignans, glycosides and phenols. Due to the richness of active ingredients, it is not surprising that plants belonging to this type are attributed anti-inflammatory, antibacterial and anticancer properties [Zhang et al. 2019; Akter et al. 2021].

Terminalia ferdinandiana, commonly known as the Kakadu plum, is an endemic Australian plant. It takes the form of a semi-deciduous tree with wide, light green leaves, the fruits are smooth-skinned, fleshy ovoid drupes with a short beak and green-yellow in colour [Konczak et al. 2014; Saleha et al. 2019]. Aboriginal Australians have been using fruit for thousands of years as food, while the bark and leaves have been using it to treat ailments of various etiologist [Akter et al. 2018]. In recent years, there has been an increase in demand for fruit *Terminalia ferdinandiana*, there are various product lines available on the market, including fruit pulp or powdered fruit and seeds [Akter et al. 2021], additionally, the Kakadu plum is included in dietary supplements, pharmacological products, jams and pickles [Konczak et al. 2014].

The interest in the Kakadu plum is not surprising as it is a source of phenolics and flavonoids, α-tocopherol, γ-tocopherol, δ-tocopherol, lutein, chlorophyll a and b, antioxidants, nutrients, and ellagic acid [Emy et al. 2021; Bobasa et al. 2021]. The literature also states that the fruit of the Kakadu plum has an extremely high vitamin C content, ranging from 406 mg to 5320 mg per 100 g of the edible part of the fruit [Sommano et al. 2011]. Therefore, the consideration of the Kakadu plum as a raw material for the production of cosmetic extracts seems to be obvious.

The appropriate selection of antioxidants for cosmetic formulations determines the quality of final products in different ways. The high antioxidant activity improves both the functional value as well as extends the shelf life of cosmetic emulsions. In this study, we compared the antioxidant activity of popular vitamin C derivatives: 3-O-ethyl ascorbic acid, ascorbyl glucoside, and self-prepared Kakadu plum extract, which is considered to be the greatest natural source of vitamin C. The total antioxidant capacity was determined using: 1,1-Diphenyl-2-picrylhydrazyl (DPPH) , Ferric Reducing Antioxidant Power (FRAP) and Trolox Equivalent Antioxidant Capacity (TEAC) assays.

1. Material and methods

1.1. Materials

Lyophilized Kakadu plum (*Terminalia ferdinandiana*) powder (Kakadu plum Co., Australia), ascorbic acid and its selected commercially available derivatives, such as ascorbyl glucoside and 3-O-ethyl ascorbic acid were purchased from internet retailers. The details of investigated commercially available ascorbic acid and its derivatives are shown in table 1. All forms of vitamin C investigated were distributed as components for self-production of cosmetics.

Table 1. Description of ascorbic acid and its derivatives

Trade name	INCI	Concentration of active ingredient	Supplier
Kwas askorbinowy witamina C	ASCORBIC ACID	99.8%	Zrób Sobie Krem
Witamina C glukozyd askorbylu	ASCORBYL GLUCOSIDE	100% pure	Ecospa
Stabilna forma witaminy C	3-O-ETHYL ASCORBIC ACID	100% pure	Zrób Sobie Krem

Source: manufacturer's declarations.

1.2. Sample preparation

The extraction of antioxidants from Kakadu plum powder was conducted according to the method described by Ramful et al. [2011] with further modifications. The selection of the extraction solvent was based on the analysis of literature data which suggest that pure solvents (water or ethanol) exhibit much lower extraction power than some their mixtures [Kiewlicz & Zieliński 2017]. 200 mg of Kakadu plum powder was weighed into a plastic screw-capped tube and 10 mL of 80% ethanol (v/v) was added. The content was vortexed and left to macerate overnight at room temperature. Then, samples were centrifuged (MPW M-Science, Warsaw, Poland) at 10000 rpm for 10 min and the clear supernatant obtained was decanted for further analysis**.**

Before the analysis, water solutions of vitamin C and ascorbic acid derivatives investigated were prepared. Each solution was separately diluted appropriately for the assays. The concentrations used were experimentally determined. The final concentrations of ascorbic acid and its derivatives in working solutions used for DPPH and TEAC assays were: 0.240 mg/mL (ascorbic acid), 0.625 mg/mL (3-O-ethyl ascorbic acid) and 0.950 mg/mL (ascorbyl glucoside) while for FRAP assay it was respectively, 0.240 mg/mL (ascorbic acid), 0.625 mg/mL (3-O-ethyl ascorbic acid) and 35 mg/mL (ascorbyl glucoside).

1.3. Ferric Reducing Antioxidant Power (FRAP) assay

FRAP assay procedure used in the study was adapted from Benzie & Strain [1996] with further modifications [Malinowska et al. 2014]. Before the test, FRAP reagent was prepared by mixing: 10 mM 2,4,6-tris-(2-pyridyl)-s-triazyne (TPTZ) in 40 mM hydrochloric acid solution, 20 mM ferric chloride (III) solution, and 300 mM acetic buffer solution (pH 3.6) in a ratio of 1:1:10. Then, 30 µL of sample was added into 2970 µL of FRAP reagent and allowed to stand for 4 min. Subsequently, the absorbance with spectrometer UV-VIS (Metertech SP-8001, Taipei, Taiwan) was measured at 593 nm against blank. $FeSO_4 \cdot {}^{V}H_2O$ was used as a standard. FRAP value was expressed as mmol of Fe^{2+} per 1 g of the sample.

1.4. Trolox Equivalent Antioxidant Capacity (TEAC) assay

The Trolox Equivalent Antioxidant Capacity (TEAC) was determined according to the method described by Re et al. [1999]. For this purpose, $ABTS^{\cdot+}$ radical cation was generated by mixing 7.7 mg of 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid with 0.2 mL of 24.5 mM potassium persulfate solution and 1.8 mL of distilled water. The solution was kept for 14-16 h in the dark place at room temperature and subsequently diluted with methanol to an absorbance about 0.8-0.9.

Then, 2970 µl of $ABTS^{\cdot+}$ solution was placed in the measuring cuvette, 30 µl of sample was added and allowed to stand for 6 min. The decrease of absorbance caused by different concentrations of sample was measured with spectrometer

UV-VIS against methanol at 734 nm [Karamać et al. 2019]. The TEAC value was calculated as the ratio of the slope of the linear plot for scavenging of $ABTS^{\cdot+}$ radical cation by the sample to the slope of the plot for $ABTS^{\cdot+}$ radical cation scavenging by Trolox. The TEAC values were expressed as mmol of Trolox per 1g of the sample.

1.5. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) method

Before the test, 100 μM working solution of $DPPH^{\cdot}$ in methanol was prepared [Enko & Gliszczyńska-Świgło 2016]. The reaction was carried out directly in the measuring cuvette. 30 μl of sample was added to 2970 μl of working solution of $DPPH^{\cdot}$. The decrease of absorbance was measured after 15 min at 517 nm against methanol. The results were expressed in terms of IC_{50} value, defined as the concentration of the sample (as μg/mL) necessary to scavenge 50% of $DPPH^{\cdot}$ radical. IC_{50} value was calculated by linear regression.

1.6. Statistical analysis

All results were expressed as mean ± standard deviation for triplicate determinations. The one-way variance analysis (ANOVA) and Tukey's post-test at α=0.05 (Statistica 12.0 software, StatSoft, Inc. 2013) were conducted to identify differences among means.

2. Results

Ferric Reducing Antioxidant Power (FRAP) method enables the determination of the antioxidant activity of the sample using the reduction of TPTZ-Fe^{3+} complex to intensively blue-colored TPTZ-Fe^{2+} complex (Benzie & Strain, 1996). As can be seen in Fig. 1, the FRAP values of ascorbic acid and its derivatives investigated ranged from 0.07 mmol Fe^{2+}/g for ascorbyl glucoside to 9.63 mmol Fe^{2+}/g for ascorbic acid. Surprisingly, Kakadu plum extract (0.72 mmol Fe^{2+}/g) showed the ferric-reducing activity comparable to 3-O-ethyl ascorbic acid (0.78 mmol Fe^{2+}/g). The significant differences among both mean values were not observed. The large variation in FRAP values between the forms of vitamin C investigated is also worth

to emphasized. Ascorbyl glucoside had more than ten-fold lower FRAP value than 3-O-ethyl ascorbic acid and more than hundred-fold lower than ascorbic acid.

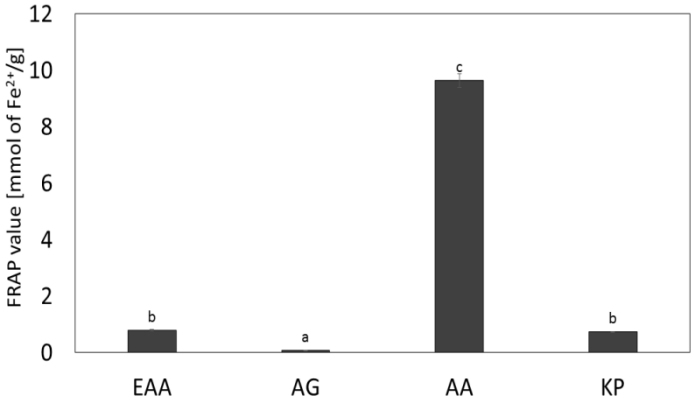

Fig. 1. FRAP values of lyophilized Kakadu plum powder, ascorbic acid and its selected derivatives investigated

EAA - 3-O-ethyl ascorbic acid, AG – ascorbyl glucoside, AA – ascorbic acid, KP – Kakadu plum extract

Values marked the different letter are significantly different ($p<0.05$, $n=3$)

Source: authors own studies.

The TEAC values were obtained from the capacity of antioxidants present in the samples to inhibit the $ABTS^{\cdot+}$ radical cation at a defined time point, relative to Trolox (Re et al. 1999). TEAC values of Kakadu plum extract, ascorbic acid and its selected derivatives investigated are presented in Fig. 2. Ascorbic acid had the highest TEAC value among all materials investigated and it was 30.60 mmol Trolox-/g. Moreover, both ascorbic acid derivatives investigated in this study demonstrated similar antiradical activity in TEAC assay. No significant differences in the TEAC values between ascorbyl glucoside (3.28 mmol Trolox/g), and 3-O-ethyl ascorbic acid (3.61 mmol Trolox/g) were observed. The lowest antiradical activity was found for Kakadu plum powder (0.82 mmol Trolox/g).

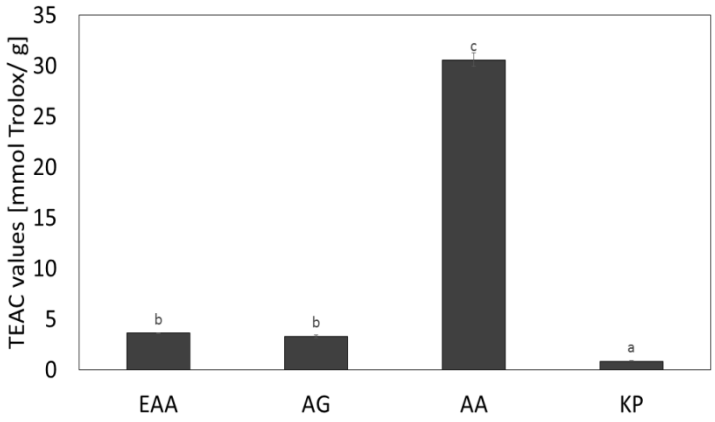

Fig. 2. TEAC values of lyophilized Kakadu plum powder, ascorbic acid and its selected derivatives investigated

EAA - 3-O-ethyl ascorbic acid, AG – ascorbyl glucoside, AA – ascorbic acid, KP – Kakadu plum extract

Values marked the different letter are significantly different ($p<0.05$, $n=3$)

Source: authors own studies.

IC_{50} value is defined as the concentration of the sample necessary to decrease the initial $DPPH^{\bullet}$ concentration by 50%. Therefore, the lower IC_{50} value, the higher antioxidant activity. As can be seen in Fig. 3, large variation in IC_{50} values was found. The mean values increased in the following order: ascorbic acid (4.15 μg/mL) < 3-O-ethyl ascorbic acid (8.02 μg/mL) < ascorbyl glucoside (13.32 μg/mL) < Kakadu plum (33.64 μg/mL).

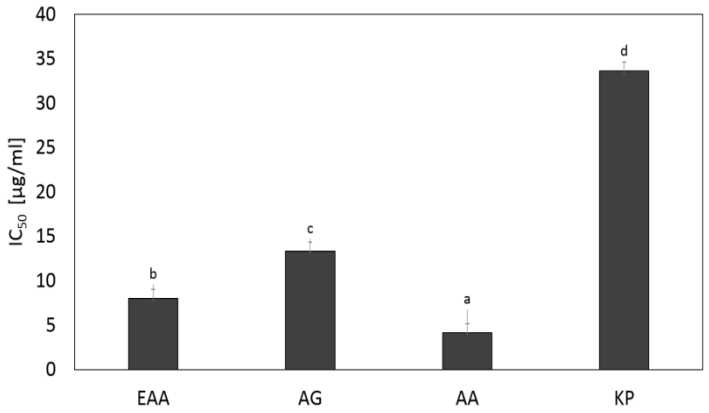

Fig. 3. IC_{50} values of lyophilized Kakadu plum powder, ascorbic acid and its selected derivatives investigated

EAA - 3-O-ethyl ascorbic acid, AG – ascorbyl glucoside, AA – ascorbic acid, KP – Kakadu plum extract

Values marked the different letter are significantly different ($p<0.05$, $n=3$)

Source: authors own studies.

3. Discussion

Kakadu plum is one of the most common Australian native fruits on the marketplace [Richmond et al. 2019]. Recently, it is getting worldwide popularity in cosmetic industry as a rich source of valuable active ingredients, of which special attention is paid to antioxidants. Our results of FRAP assay showed that even one gram of Kakadu plum powder can be used to obtain an extract with ferric-reducing activity higher than ascorbyl glucoside and comparable to 3-O-ethyl ascorbic acid. Although, the TEAC and IC_{50} values indicated lower antioxidant activity of Kakadu plum than the forms of vitamin C investigated, it should be emphasized, that Kakadu plum as plant material considering in terms of potential source of antioxidants in cosmetic industry exhibit relatively high antioxidant activity compared to both derivatives of ascorbic acid. For greater demonstration of the potential of Kakadu plum as cosmetic raw material it is worth to notice that other popular fruit raw materials

had following TEAC values in different studies: acerola 1.2 mmol Trolox/g [Rufino et al. 2010] and rose hip 0.35 mmol Trolox/g [Rybicka et al. 2021].

The literature data provided [Richmond et al. 2019] that Kakadu plum is particularly appreciated for its vitamin C content, which is considered as the highest vitamin C concentration in already known plant material. In dermatology, vitamin C is one of the non-enzymatic antioxidants, which protects skin from oxidative stress and its effects [Chen et al. 2021]. Moreover, it exhibits photoprotective properties, influences collagen biosynthesis, act as depigmenting agent and has a potentially anti-inflammatory activity [Telang 2013]. Konczak et al. [2014] revealed that vitamin C levels in Kakadu plum ranged from 0.5 mg/g of lyophilized pulp, to 322.2 mg/g, depending on genetic differences and environmental conditions. The other studies [Konczak et al. 2010] reported that acerola fruits, which are commonly used in the production of cosmetic extracts [Malinowska et al. 2014], contains about 10 mg of vitamin C per g of fresh weight and it is about 80% of the vitamin C level in Kakadu plum. Besides vitamin C, Kakadu plum is also good source of phenolic antioxidants, which largely affect its overall antioxidant activity. Bobasa et al. [2021] revealed that the main bioactive compound in Kakadu plum is ellagic acid (4 g/100 g), but their studies suggested also the presence of nine other main phenolic compounds in different Kakadu plum extracts. The identified phenolic compounds in Kakadu plum include quercetin/hesperidin-based glucosides and kaempferol/luteolin-based glucosides [Konczak et al. 2010] as well as ellagitannins, gallotannins and phenolic acids [Akter et al. 2021; Akter et al. 2022; Bobasa et al. 2021]. The correlation between TPC or vitamin C content and total antioxidant capacity is commonly known and has been already proved in various investigations [Elkhatim et al. 2018; Muflihah et al. 2021]. Moreover, Konczak et al. [2014] have shown the strong positive correlation between TPC values and total antioxidant capacity (expressed as: FRAP and ORAC) of *T. ferdinandiana* fruits collected in different locations while the lowest correlation was observed between vitamin C content and ORAC. The literature data [Enko et al. 2016] indicates also the occurring of synergism between vitamin C and some phenolic compounds, what is beneficial factor in the context of antioxidant activity. Thus, it can also have a positive effect on prolonging oxidative

stability of cosmetics containing plant oils rich in unsaturated fatty acids. However, it should be remembered that due to so-called "polar paradox" the polar antioxidants are more active in bulk lipid than non-polar ones and analogously less effective in oil-in-water emulsions [Battista et al. 2019]. Furthermore, due to the hydrophilicity, it may be necessary to use carriers (e.g. liposomes) in cosmetics to improve the absorption [Winkler 2019] of active compounds contained in Kakadu plum extract.

It is also worth paying attention to socio-economic aspect of cultivation and processing of Kakadu plum. Kakadu plum is natural raw material, particularly attractive in view of global turn towards ecology and policy of enhancement the sustainable development [Gorman et al. 2019; Kenalemang-Palm & Eriksson 2021]. It is also identified as "functional food" associated with potentially positive effect on the health. The right marketing approach and multiple using of products from the fruit and leaves of *T. ferdinandiana* may improve the overall commercial attention and profitability of production on scale. On the other hand, *T. ferdinandiana* is an endemic plant [Saleha et al. 2019], which may be associated with various limitation, e.g. the risk of limited availability or high logistic costs. However, it does not change the fact that, *T. ferdinandiana* is described in the literature as Indigenous agribusiness which has potential be sustainably commercialized, as evidenced by the economic development programs for producers of *T. ferdinandiana* [Gorman et al. 2019].

Due to the worldwide trend in cosmetic industry regarding formulating and developing the products with organic or natural ingredients, Kakadu plum may provide an attractive substitute for synthetic forms of vitamin C. Nevertheless, in recent years, ascorbic acid and its derivatives became a popular cosmeceutical agent and more stable ascorbic acid derivatives are still under development [Al-Niaimi & Chiang 2017]. The obtained results showed that ascorbic acid, demonstrated much the highest antioxidant activity among all forms of vitamin C investigated. The FRAP, and DPPH values found in our studies for ascorbic acid were consistent with those obtained by other researchers [Enko & Gliszczyńska-Świgło 2016] (respectively, 10.69 Fe^{2+}/g and 3.59 μg/mL). The theoretical studies conducted by Liu et al. [2020] revealed that in the process of radical quenching, the most likely reaction sites of ascorbic acid and its derivatives are on the double bond of lactone ring.

Nevertheless, the differences in antioxidant activity between ascorbic acid and its derivatives might be due to the presence of two oxidizable hydroxyl group on the lactone ring of ascorbic acid, while 3-O-ethyl ascorbic acid or ascorbyl glucoside have only one such group in the molecules. This proves, that the process of optimizing the chemical structure of vitamin C, results a partial loss of their antioxidant properties.

4. Conclusions

Ascorbic acid is a popular antioxidant used in cosmetics, but its use is limited due to its rapid degradation, which in turn shortens the shelf life of cosmetics with its content and lowering their quality. As a result, in cosmetic formulations it is readily replaced with more stable derivatives, among others: ascorbyl glucoside and 3-O-ethyl ascorbic acid. Another observed on the cosmetics market trend is to return to nature and reaching for cosmetic raw materials of natural origin. The results presented above suggest that 3-O-ethyl ascorbic acid will be a better vitamin C substitute in cosmetics than ascorbyl glucoside. Considering that natural antioxidants such as vitamin C or phenolic compounds constitute a small proportion of the dry weight of the plant material, it is not surprising that Kakadu extract demonstrated lower antiradical activity than ascorbic acid and its derivatives. Nevertheless, comparing with literature data, Kakadu plum exhibit antioxidant activity similar or even better than the other fruit raw materials. Therefore, Kakadu plum may be considered as a valuable raw material for the production of the high-quality cosmetic extracts rich in natural vitamin C. The results obtained and the observed consumer trends suggest that products with Kakadu plum extracts will continue to be in demand among consumers for a long time to come.

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KAKADU PLUM (*TERMINALIA FERDINANDIANA*), CAMU CAMU (*MYRCIARIA DUBIA*), ACEROLA (*MALPIGHIA EMARGINATA*) AND ROSEHIP (*ROSA CANINA*) AS A SOURCE OF ANTIOXIDANTS

JUSTYNA KIEWLICZ[1], DOBRAWA KWAŚNIEWSKA[2]

[1] *Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economics and Business*
e-mail: justyna.kiewlicz@ue.poznan.pl
[2] *Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economics and Business*
e-mail: dobrawa.kwasniewska@ue.poznan.pl

Abstract
Ones of the main exogenous factors contributing to skin aging are free radicals, reactive oxygen species (ROS) and reactive nitrogen species (RNS) reacting with DNA, proteins and fatty acids which are extremely sensitive to the oxidation process. Fruits of Kakadu plum (*Terminalia ferdinandiana*), camu camu (*Myrciaria dubia*), acerola (*Malpighia emarginata*) and rosehip (*Rosa canina*) are described as natural source of antioxidants, especially vitamin C and phenolic compounds. For this reason, their use is attributed to an anti-aging, photoprotective, brightening, and regenerating effect. In this study the total phenolic content (TPC) and total antioxidant capacity of above-mentioned fruits were evaluated and compared.

Keywords: acerola, antioxidant activity, camu camu Kakadu plum, rosehip

Introduction

Skin is a complex structure, which is composed of several layers and possess the largest area in the body. Due to constant exposure to external factors it is also particularly vulnerable to oxidative stress. The effects of the activity of reactive oxygen (ROS) and nitrogen (RNS) species are ones of the major factors determining premature skin aging, skin disorders and skin diseases [Kohen 1999]. The unfavourable

aspect of their action on the skin is the peroxidation of intercellular cement lipids and cell membrane phospholipids, which can lead indirectly to protein damage and release of inflammatory mediators as well as contribute to the disturbances in the functioning of the epidermal barrier and consequently increase the transepidermal water loss (TEWL) [Ratz-Łyko 2013]. It should be remembered that exposure of the skin to UV radiation may induce the formation of free radicals which damage cellular structures. Moreover, it may also cause elastosis that is an accumulation of tropoelastin aggregates in the skin [Zduńska-Pęciak et al. 2022]. This effect is strictly related to photoaging and its visible symptoms such as wrinkles, dryness, telangiectasia, loss of firmness of the skin and hyperpigmentation [Papanagitou 2009; Ratz-Łyko 2013; Zduńska-Pęciak et al. 2022].

The counteracting of the negative oxidative stress effects takes place in the body with participation of enzymatic and non-enzymatic antioxidant defence systems. The firs of them includes, the superoxide dismutase, glutathione peroxidase and catalase. Among non-enzymatic antioxidants are endogenous (e.g. glutathione) and exogenous antioxidants. The latter ones, such as phenolic compounds (e.g. phenolic acids, flavonoids), vitamin C and E, carotenoids (e.g. β-carotene, α-carotene, lutein, lycopene) and trace elements (e.g. zinc, selenium) require oral administration or are applicate topically on the skin for achieving favourable effect [Lohan et al. 2015].

Plant extracts rich in various active compounds are used in healing dermatological disorders since ages. The herbal raw materials can be leaves, flowers, fruits, seeds, roots, rhizomes, bark or whole plants. The active compounds are isolated from plant tissues by extraction from the comminuted raw material with the use of a properly selected solvents. Fruit extracts have already been the subject of different scientific research in terms of the use in cosmetic industry. Malinowska [2015] carried out the screening of antioxidant activity of commercially available liquid extracts from following fruits: apricot (*Prunus armeniaca)*, grape (*Vitis vinifera)*, peach (*Prunus persica)*, muskmelon (*Cucumis melo)* and pomelo (*Citrus grandis)*. The highest antioxidant activity among extracts investigated exhibited apricot extract. In other research, the same author and co-workers [Malinowska et al. 2014] studied protective effect of selected commercial extracts (e.g. acerola extract)

of cosmetic emulsions. Generally, literature data show that fruit extracts are particularly appreciated in cosmetology for antioxidant [Malinowska et al. 2014], antimicrobial [Vaillant 2020] and anticancer [Jain et al. 2022] activity.

The sustained growth of consumers interest in natural products and biodiversity causes the striving for continuous development of new products made of organic and natural ingredients, which may successfully replace synthetic components [Ogonowski & Kołkowska 2011]. Acerola (*Malpighia emarginata*), camu camu (*Myrciaria dubia*), Kakadu plum (*Terminalia ferdinandiana*) and wild rose (*Rosa canina*) are medicinal plants, whose fruits are especially appreciated for high content of vitamin C. Of above-mentioned (excluding rosehip) only acerola fruits are well known to Polish consumers and marketed in different form such as an ingredient of dietary supplements, functional foods as well as cosmetic products. Relatively less known camu camu is a native shrub growing as wild populations in the tropical rainforests of the Amazon. Camu camu fruits are globular with the reddish-green colour of peel. Their diameter and length are 1.0-3.2 cm and 1.2-2.5 cm, respectively. According to literature data camu camu products are exported to European Union as pulp, extract and juice [Akter et al. 2011; Castro et al. 2018]. Kakadu plum is in turn the Australian native tree with yellow-green coloured fruits. The barks and leaves of this plant have been used to treatment ailments by indigenous Australians since generations. Nowadays, Kakadu plum products are distributed as ingredients of food supplements, beverages, cosmetic, preservatives and anti-aging products [Bobasa et al. 2021]. According to literature data the vitamin C content in fruits of acerola, camu camu, Kakadu plum and rosehip increased in the following order: rosehip (from 839.18 to 1972.63 mg/ 100 g) [Medveckien et al. 2021] < acerola (from 1190 to 2187 mg/100 g) [Pereira de Moraes et al. 2019] < camu camu (from 1882 to 2780 mg/ 100 g) [Nemirovsky et al. 2014; Rufino et al. 2010] < Kakadu plum (from 406 to 5320 mg/100 g) [Sommano et al. 2011]. They are also considered as abundant source of phenolic compounds. Due to the richness of health-promoting phytochemicals, it is not surprising that these fruits are attributed the antioxidant, anti-inflammatory, antihyperglycemic, anti-obesity, hypolipidemic, antibacterial and anticancer properties [Zhang, et al. 2019; Akter, Sultanbawa; & Cozzolino 2021; Belwal et al. 2018;

Castro et al. 2018; Fascella et al. 2019]. The anti-aging, photo-protective, brightening and regenerating activity makes them also a promising cosmetic raw material.

The aim of this study was determination of total phenolic content and total antioxidant capacity expressed as FRAP value of acerola (*Malpighia emarginata*), camu camu (*Myrciaria dubia*) and Kakadu plum (*Terminalia ferdinandiana*) freeze-dried fruits. The research on the antioxidant activity of above-mentioned fruits were carried out using rosehip as a standard. The *Rosa* genus due to non-selectivity with regard to the pedoclimatic exigencies is commonly cultivated in many areas of the world including Central Europe region. Therefore, the rosehip have been already widely studied in terms of morphological characteristics, biochemical composition and antioxidant activity [Fascella et al. 2019]. Moreover, native rosehip and its preparations are also considered as one of the most abundant source of vitamin C among fruits growing at this latitude. The obtained results enabled comparing and describing fruits investigated as potential raw materials for the production of cosmetic extracts.

1. Material and methods

1.1. Materials

The freeze-dried acerola (*Malpighia emarginata*), camu camu (*Myrciaria dubia*), Kakadu plum (*Terminalia ferdinandiana*) and rosehip (*Rosa canina*) powders were purchased from internet retailers. All fruits were purchased from the same company. 2,4,6-tris-(2-pyridyl)-s-triazyne (TPTZ) used in this study was supplied by Sigma-Aldrich (Saint Louis, USA). Hydrochloric acid, sodium acetate trihydrate, sodium carbonate, acetic acid, ferric chloride (III) anhydrous, Folin-Ciocalteau reagent and the solvents used in this study were obtained from Chempur (Piekary Śląskie, Poland). All used chemicals were analytical grade.

1.2. Sample preparation

For extraction of antioxidants from acerola, camu camu, Kakadu plum and rosehip powders the method described by Ramful et al. [2011] with further modifications was used. 100 mg of each fruit powder was weighed into a screw-capped tubes and 10 ml of 80% (v/v) ethanol was added. Subsequently, the samples were vortexed and left to macerate at ambient temperature overnight. Then, each sample was centrifuged (MPW M-Science, Warsaw, Poland) at 10000 rpm for 1 min and the supernatant was decanted for further analysis.

1.3. Total phenolic content (TPC) evaluation

Total phenolic content was evaluated with the Folin-Ciocalteau method [Singleton & Rossi 1965; Rybicka et al. 2021]. For this purpose 0.1 mL of the sample was mixed with 0.5 mL of Folin-Ciocalteau reagent and 5 mL of distilled water. After 5 min 1.5 mL of 20% sodium carbonate (Na_2CO_3) was added and the volume was made up to 10 mL with distilled water. The samples were left in the dark for 2 h and then the absorbance at 765 nm was measured using spectrophotometer UV-VIS (Metertech SP-8001, Taipei, Taiwan). At least three determinations were performed for each independent extract of the fruit powder. The total phenolic content (TPC) was expressed as mg of gallic acid equivalents per 1 g d.m. of fruit (mg GAE/g d.m.) using the calibration curve.

1.4. Determination of total antioxidant capacity expressed as the FRAP value

The FRAP (Ferric Reducing Antioxidant Power) assay was carried out according to the method described by Benzie & Strain [1996] with further modifications [Malinowska et al. 2014; Enko & Gliszczyńska-Świgło 2016]. 0.03 mL of the sample was added to 2.97 mL of FRAP reagent, which was prepared before the test as a mixture of 10 mM 2,4,6-tris-(2-pyridyl)-s-triazyne (TPTZ) in 40 mM hydrochloric acid solution, 20 mM ferric chloride (III) solution, and 300 mM acetic buffer solution

(pH 3.6) in a ratio of 1:1:10. The reaction was carried out in the measuring cuvette for 4 min. Then, the increase in absorbance was measured at 593 nm with spectrometer UV-VIS (Metertech SP-8001, Taipei, Taiwan). $FeSO_4 \cdot 7H_2O$ was used as a standard. Three independent determinations were performed for each extract. Total antioxidant capacity of fruit was expressed as FRAP value (mmol Fe^{2+}/g d.m.).

1.5. Statistical analysis

All results were expressed as mean±standard deviation. The one-way variance analysis (ANOVA) and Tukey's post-test at α=0.05 were conducted to identify significance of differences between means obtained for the products. The statistical analyses were carried out using Statistica 13.0 version (StatSoft, Inc).

2. Results

The Folin-Ciocialteau method is based on the colorimetric reaction which enable measuring the total concentration of phenolic hydroxyl groups in the plant extracts. Polyphenols react with the specific redox reagent to form an intense blue complex that could be quantified using spectrophotometry UV-Vis. This method is easy to perform, applicable in routine laboratory use, and low-cost [Blainski et al. 2013]. As can be seen in fig. 1. the TPC values of tested fruits ranged from 28.8 mg GAE/g d.m. for rosehip to 82.6 mg GAE/g d.m. for camu camu. Acerola and Kakadu plum had TPC values respectively, 37.1 mg GAE/g d.m. and 62.9 mg GAE/g d.m.

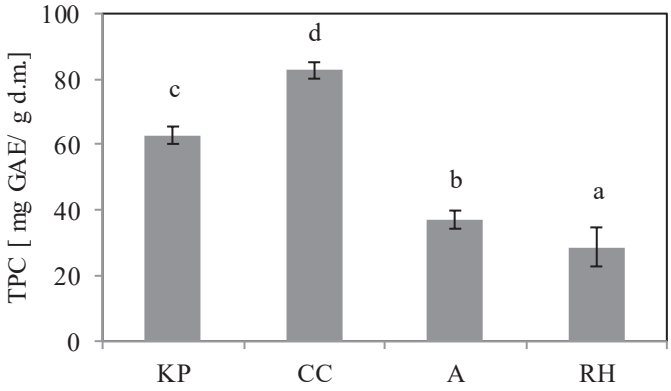

Fig. 1. Total phenolic content of fruits investigated

KP – Kakadu plum, CC – camu camu, A – acerola, RH – rosehip
Values marked the different letter are significantly different ($p<0.05$, $n=3$)
(sorted from the lowest to highest values)
Source: authors own studies.

Ferric Reducing Antioxidant Power assay is a method which has been developed using reduction of colourless TPTZ-Fe^{3+} complex into intense blue coloured TPTZ-Fe^{2+} once it interacts with an antioxidant [Jabbari & Jabbari 2016, Spiegel et al. 2020]. FRAP values of fruits investigated has been shown in fig. 2. The FRAP values increased in the following order of fruits investigated: rosehip (0.41 mmol Fe^{2+}/g d.m.) < Kakadu plum (0.73 mmol Fe^{2+}/g d.m) < acerola (1.35 mmol Fe^{2+}/g d.m) < camu camu (1.68 mmol Fe^{2+}/g d.m.).

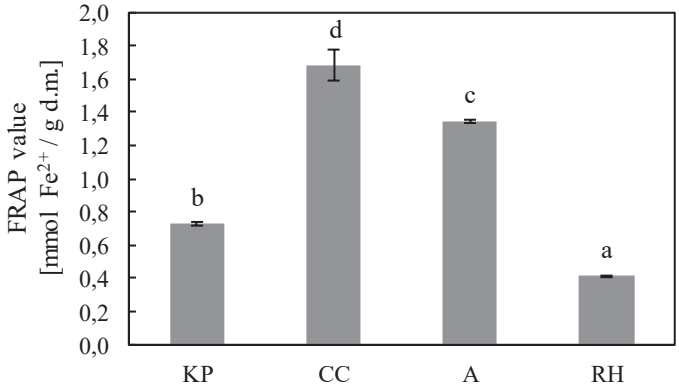

Fig. 2. FRAP values of fruits investigated

KP – Kakadu plum, CC – camu camu, A – acerola, RH – rosehip

Values marked the different letter are significantly different ($p<0.05$, $n=3$)

(sorted from the lowest to highest values)

Source: authors own studies.

3. Discussion

In this study total phenolic content and total antioxidant capacity expressed as FRAP value were evaluated and compared. The analysis of literature data available indicates that our results are in line with the findings of other authors, nevertheless the direct comparison of data was difficult due to different extraction solvents and conditions or standard to express TPC and FRAP values used by various researchers. Fujita et al. [2017] reported that TPC values obtained for freeze dried camu camu pulp ranged from 89.0-97.1 mg GAE/ g d.m. The convergence of these values with our results may be related to the similar solvent used for the extraction of phenolic antioxidants. The high accordance of our findings with literature data was also observed for rosehip. In the studies conducted by Rybicka et al. [2021] the TPC and FRAP values obtained for dried fruit were respectively, 3097 mg GAE/100 g d.m. and 42.1 mmol Fe^{2+}/100 g d.m. Similarly, Demir et al. [2014] found that the FRAP

values of different species of rosehip varied from 301.80 to 589.78 μmol Fe^{2+}/g d.m. Akter et al. [2019] determined total phenolic content in Kakadu plum fruit using methanol, ethanol, water, acetone and hexane for extraction of antioxidants. The TPC values obtained in their study ranged from 0.40 mg to 122 mg GAE/g d.m., while corresponding result of our research (using 80% ethanol as a solvent) was 62.9 mg GAE/g d.m.

It is also worth to notice that positive correlation between TPC and FRAP values in our studies was observed. It may suggests that the phenolic compounds were the main components responsible for antioxidant activity of fruits investigated. According to literature data the major phenolic compounds found in camu camu fruits were: quercetin, cyanidin-3-glucoside, ellagic acid and ellegitannin [Fujita et al. 2015]. Ellagic acid was also identified as main bioactive compound contained in Kakadu plum fruits, but different studies showed additionally presence of other important phenolic compounds such as e.g. quercetin/hesperidin-based glucosides and kaempferol/luteolin-based glucosides [Bobasa et al. 2021]. On the other hand, each fruits investigated are described in the literature as abundant source of vitamin C which is strong water-soluble antioxidant and should be considered as another compound determining their total antioxidant capacity. The literature data [Enko & Gliszczyńska-Świgło 2016] show also the synergistic antioxidant activity of mixtures of vitamin C and some phenolic compounds. Therefore, the fruit extracts rich in both, phenolic compounds and vitamin C can be applied in cosmetic industry as active ingredients which protect skin against undesirable effects of oxidative stress and may prolonging products stability. Additionally, the literature data show that phenolic compounds exhibit anti-inflammatory, anti-microbial and estrogen-like properties as well as complex forming, sealing of capillary vessels and induction or inhibition of some enzyme functions in the skin [Malinowska et al. 2014]. Considering the benefits of using vitamin C the anti-wrinkle, photoprotective, and brightening activity should be emphasized. Moreover, it also maintains activity of vitamin E and stimulates the synthesis of ceramides [Gref et al. 2020]. Therefore the cosmetics containing plant extracts rich in phenolic compounds and vitamin C are particularly getting popularity among the consumers with mature skin.

4. Conclusions

Camu camu (*Myrciaria dubia*), Kakadu plum (*Terminalia ferdinandiana*), acerola (*Malpighia emarginata*) and rosehip (*Rosa canina*) fruits are appreciated for high content of vitamin C which is one of the most valuable active ingredients in cosmetics dedicated for the mature skin. We confirmed in this study that all tested fruits are the rich source of phenolic compounds. Camu camu fruits had the highest total phenolic content and total antioxidant capacity expressed as FRAP value among all fruits investigated. Whereas, Kakadu plum had a slightly lower total phenolic content than mentioned fruit. A global trend regarding a rising of the interest on natural products and biodiversity stimulate of the research for the natural, renewable and sustainable production. Increasingly more consumers expect that "eco-friendly" products will replace on the market cosmetics made of synthetic ingredients. Therefore, it can be concluded that fruits investigated, with particular emphasis on camu camu, can be considered as excellent raw material for production of cosmetic extracts, which may be a substitute for synthetic vitamin C.

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ASSESSMENT OF USAGE PROPERTIES OF BODY CARE EMULSIONS CONTAINING OILS FROM WASTE RASPBERRY AND PUMPKIN SEEDS

ANNA MAŁYSA, MONIKA ZATORSKA

Department of Industrial Chemistry, Faculty of Chemical Engineering and Commodity Science, University of Technology and Humanities in Radom,
e-mail: a.malysa@uthrad.pl

Abstract
The influence of oils obtained from waste raspberry and pumpkin seeds on usage properties of body care emulsions has been assessed in this paper. The subject is a part of sustainable development trend by using waste seeds from food industry as a source of vegetable oils used as emollients in cosmetic emulsions. On the basis of available literature data and own research, recipes of 7 prototypes of body creams containing 1 to 3 wt.% of refused additives have been worked out. The following properties of the cosmetics were evaluated: stability, pH, viscosity, skin moisturization level, transepidermal water loss (TEWL) and yield stress. The obtained results were compared to the base sample and commercial products. The addition of raspberry seed and pumpkin seed oils did not significantly affect changes in pH values of the preparations, resulted in better skin moisturize, reduced TEWL values in relation to the base, and improved sensory properties. On the other hand, an increase in the concentration of oils in emulsions resulted in a decrease in the yield stress, which had a beneficial effect on the cosmetic's application properties, mainly spreading the cream over the skin. On the basis of studies it can be concluded that the obtained original formulations were stable, had comparable usage properties to commercial products and showed skin-care properties.

Keywords: body care emulsions, raspberry seed oil, pumpkin seed oil

Introduction

Plant-based raw materials and natural cosmetics have become a major trend in recent years. Already in ancient times plant fats were used in personal care cosmetics in pure form or as ingredients in various forms. Most of them occur as basic

ingredients, included in the fatty phase of cosmetic emulsions, while additionally, thanks to their biocompatibility with human skin, they are used as biologically active substances [Athar & Nasir 2005], [Schäfer-Korting et al. 2007]. Vegetable fats are used as the basic form of delivery through the skin of nutrients and vitamins soluble in them. They act as neutral carriers and solvents for other active substances [Baranowska et al. 2015]. The latest trends include the use of plant ingredients with multifunctional effects, avoidance of petroleum derivatives, and the so-called "zero-waste trend", i.e. the use of zero-waste technologies or management of already generated waste [Bergfeld et al. 2004], [Stamataset et al. 2008]. The food industry is one of the largest resources for the recovery of potential sources of raw materials for cosmetic purposes, including peels, pulp, seeds, seeds as by-products in the industrial production of jams, juices, and many other food articles [Fruhwirth, & Hermetter 2007], [Prior et al. 2005].

In this study, we used oils obtained from waste seeds of food industry, i.e. raspberry seed oil and pumpkin seed oil, which is in line with the trend of sustainable development through the use of waste materials as valuable and active cosmetic ingredients.

Raspberry seed oil is used in sunscreen preparations because it reduces the effects of radiation. It soothes irritations, which helps the epidermis regenerate faster. It shows antioxidant and antimutagenic properties, eliminates free radicals. This oil makes the skin elastic and rejuvenates it, but it also soothes inflammations, that is why it is also used in toothpastes. Thanks to its greasing and moisturizing properties, raspberry oil is used in creams, lotions, milks, emulsions, ointments, and also in massage oils. It has a delicate wrinkle-reducing effect and is therefore used as an ingredient in creams for aging skin [Oomaha & Ladet 2000].

On the other hand, pumpkin seed oil is used in skin care products for dry, flaky and cracked skin. Thanks to its lubricating, moisturizing and smoothing properties it is used in the fight against stretch marks [Fruhwirth & Hermetter 2007], [Nederal et al. 2012]. It is also used in massage oils, creams and scrubs. Pumpkin seed oil contains potassium, which has a purifying and brightening effect on the skin. The presence, location and distribution of hydroxyl groups affect the antioxidant properties.

Phenolic acids also prevent photo-oxidative damage to the skin [Vujasinovic, et al. 2010], [Salgin & Korkmaz 2011].

1. Materials and Methods

1.1 Materials

The research material consisted of original body care emulsions prepared on the basis of literature data and own research and commercial emulsions.

The formulations of the original emulsions are presented in table 1. Raspberry seed and pumpkin seed oils were used in the emulsion prototypes in concentrations: 1,2,3 wt. % in the product. The designation of the various emulsions is shown in the Table 1. The samples containing raspberry seed oil were designated by the letters **M1,M2,M3**, these samples contained 1,2,3 wt. % of raspberry seed oil. Similarly, the samples containing pumpkin seed oil were designated with letters **D1,D2,D3**, these samples contained 1,2,3 wt. % of the oil. The samples contained a total of 3% by weight of fat base, including caprylic/capric triglycerides. The base sample (**Base**) contained only added caprylic/capric triglycerides and did not contain raspberry seed oil or pumpkin seed oil.

Table 1 Formulations of original body care emulsions

INCI NAME	wt. %						
	Base	**M1**	**M2**	**M3**	**D1**	**D2**	**D3**
Cetearyl Olivate	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Cera Alba	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Cetearyl Alcohol	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Glycerin	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Caprylic/Capric Triglyceride	3	2.0	1.0	0	2.0	1.0	0
Rubus Idaeus (Raspberry) Seed Oil	0	1.0	2.0	3.0			
Cucurbita Pepo (Pumpkin)Seed Oil					1.0	2.0	3.0
Aqua	up 100	up 100	up 100	up 100	up 100	up 100	up 100
Preservative	q.s	q.s	q.s	q.s	q.s	q.s	q.s

Source: own study.

The technology to produce the emulsion was as follows: the components of the oil phase were measured and mixed on a magnetic stirrer using a water bath at 70ºC until the components dissolved. Then, the weighed water and glycerin heated on a water bath to 70ºC were added to the oil phase while continuing to stir on a magnetic stirrer until completely cooled. At about 30ºC, the preservative was added.

The reference point in the evaluation was two commercial products. Characteristics of market emulsions designated as **PHM** (containing raspberry seed oil), **PHD** (containing pumpkin seed oil) are presented in the table 2.

Table 2 Characteristics of commercial body care emulsions

Designation	Capacity [ml]	Properties declared by the manufacturer on the label
PHM	50	A light, vegan cream for skin that needs effective hydration and soothing, also for sensitive skin. It intensively moisturizes and refreshes the skin, rebuilds its hydrolipid coat, preventing water loss from the epidermis. It promotes soothing and calming effects. Its light, dessert formula does not weigh down the skin, is perfectly absorbed and takes care of your complexion. The cream contains effective active ingredients: raspberry extract supports hydrolipidic barrier of the epidermis, intensively moisturizes and nourishes the skin. Hyaluronic acid deeply moisturizes and revitalizes the epidermis. The cream contains 98% ingredients of natural origin (ISO 16128),
PHD	200	Nourishing pumpkin body balm strengthens, intensively nourishes and smoothes the skin, additionally making it firmer and more toned. Pumpkin seed oil contained in the balm cares for dry skin with reduced elasticity, strengthening its lipid barrier and nourishing it deeply. The abundance of valuable fatty acids contained in linseed oil helps reduce water loss and support the skin's regeneration processes. Phytosterols occurring phytosterols contained in the oil have the ability to stimulate collagen synthesis and vitamin E has excellent anti-aging properties. Shea butter contained in the balm intensively nourishes the skin, and thanks to a large content of vitamins it delays skin ageing processes and protects it from harmful external factors such as frost, sun or wind.

Source: own study.

1.2 Methods

Stability

This test allows you to determine whether a preparation is destabilized e.g. separation into layers under the influence of changing temperature. For this purpose, a centrifuge test and a thermal test are used. The thermal test determines the behavior of samples under the influence of temperature changes. The sample is held in a hothouse (phot) at 40ºC, and then in a refrigerator at 4ºC. This cycle was repeated alternately for 24 hours over a period of 7 days [Sułek et al. 2006].

pH

The measurement was carried out at room temperature using Elmetron pH-meter type CPC-401. The measuring electrode of the pH-meter was placed in the tested sample of cream, then after the measurement stabilized, the pH value was read.

Three measurements were taken for each sample, the arithmetic mean was considered as the final results [Zięba et al. 2015].

Viscosity

In this research work, viscosity measurement was performed on a Brookfield rotational viscometer type RVDV-1+. As the submerged spindle rotates, the viscosity of the samples obtained is measured. The device has seven different spindles depending on the particular measurement ranges. The test was conducted using spindle number 6. Three measurements were made for each sample [Sułek et al. 2006].

Yield stress

Measurements were made using a Brookfield HA DV III Ultra viscosity meter. The test was performed using a paddle spindle at a constant spindle speed of 1rpm. Three measurements were taken for each sample and the results were averaged. The minimum value of shear stress was the flow limit above which the liquid flowed [Klimaszewska et al. 2018].

Transepidermal water loss (TEWL)

TEWL was measured using a Tewameter TM300 MPA probe coupled to a computer. The principle of measurement was to perform six measurements at 10-minute intervals . The test was performed for each sample, on each tested skin area. From the results obtained, the arithmetic mean was calculated for each sample. Then it was interpreted according to the values in the table 3.

Table 3 Interpretation of TEWL values

TEWL [g/h·m²]	Skin characteristic
0-10	Very healthy
10-15	Healthy
15-25	Normal
25-30	In poor condition
>30	In critical condition

Source: [Klimaszewska et al. 2018].

Skin moisturization

The degree of skin moisturizing was measured using a Corneometer CM 825 probe coupled with a computer. The principle of measurement was based on the application of a measuring probe to the skin, the measurement occurred as a result of light pressing the measuring head to the skin on the inside of the forearm. Six measurements were taken on each test area at a time interval of 10 minutes. From the given values, the arithmetic mean was calculated for each sample [Klimaszewska et al. 2018].

2. Results

2.1. Stability

The stability and appearance of the tested formulations is a very important aspect for further research and a criterion for the consumer to choose the product.

Tests carried out on the preparations made according to the prepared formulation as well as on the commercial preparations showed that they were stable and did not deseparation. It can therefore be concluded that the addition of oil to the emulsions does not adversely affect their stability during storage at varying temperatures. Centrifugation test also gave positive results as the formulations did not separate.

2.2. pH

The pH measurement is performed in order to exclude any irritating effect on the skin after the use of a cosmetic product. The value which has the best effect on the skin is between 4.5 and 6, thanks to which the skin becomes a protective barrier and does not lose water from the epidermis, thus looking radiant and moisturized.

The study was conducted to evaluate the effect of oil addition on the pH level of the formulations made. Both the base formulation and commercial products were tested and commercial products were also tested. The results are shown in Fig. 1.

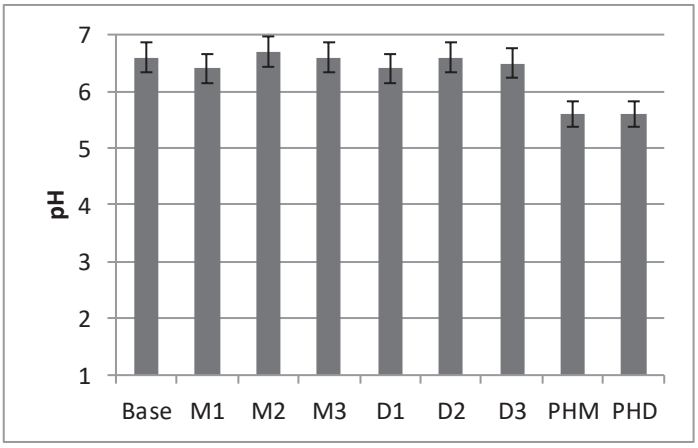

Fig. 1. pH value of emulsions

Source: own study.

The results shown in Fig. 1 indicate that the addition of oils does not have a large effect on the pH of the obtained creams. The values of the parameters range from 6.4 to 6.7. From the presented relationships the highest pH value is characteristic for the preparation containing 2 wt. % of raspberry seed oil (M2) - 6.7. The lowest pH value is characteristic for the preparations containing 1 wt. % of oil each (M1 and D1)-6.4. The pH values of all original preparations were equalized with citric acid water solution to a pH consistent with that of the skin (about 5.5).

2.3. Viscosity

The appropriate value of dynamic viscosity indicates a high content of active ingredients in the product and has an impact on its quality and properties. The correct viscosity of the product facilitates its application and spreading on the skin. The viscosity of the creams was measured on a Brookfield viscometer at 50 RPM. The results obtained are presented in Figure 2.

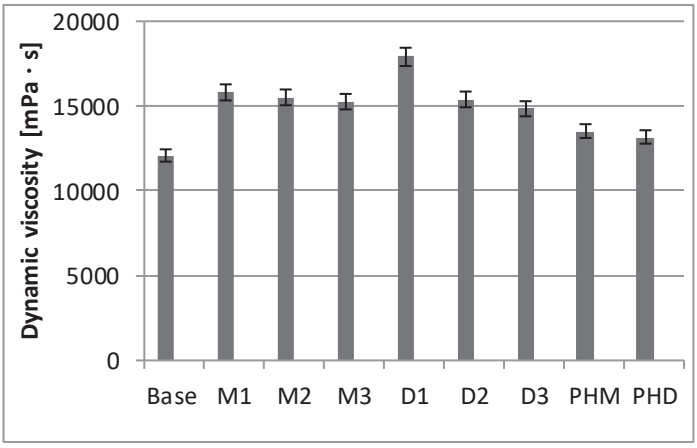

Fig. 2. Dynamic viscosity of emulsions

Source: own study.

From the results presented in Fig. 2 it can be seen that the preparation with the content of 1 wt. % of pumpkin seed oil (D1) has the highest viscosity. It can be seen from the presented relations that the base preparation as well as the commercial preparations show the lowest viscosity.

1.4. Yield stress

The final appearance of a product is influenced by many issues, one of which is the study of the limit of flow of a given emulsion, which verifies the type of

packaging or the way in which the emulsion will be applied to the skin or used by consumers. The measurement results are shown in Fig. 3.

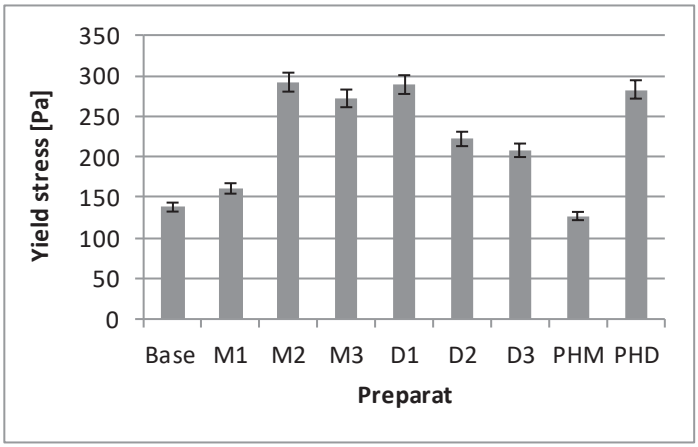

Fig. 3. Yield stress of emulsions

Source: own study.

According to the posted results, it can be seen that as the content of raspberry seed oil increased, the yield stress increased. The highest value of this parameter was observed for the emulsion containing 3 wt. % of raspberry seed oil. A different situation was observed for pumpkin seed oil. With the increase of oil content, the yield stress decreased. The value for the commercial preparation with the content of pumpkin seed oil was comparable for the sample with the content of 1 wt. % of pumpkin seed oil.

1.5. Transepidermal water loss (TEWL)

Transepidermal water loss (TEWL) determines the rate of water loss through the epidermis, and was measured to estimate the skin's ability to retain water. The test was conducted in the natural state, i.e. before using the raspberry seed oil cream and the pumpkin seed oil cream, and after using these two creams. The measurement results are shown in Fig. 4

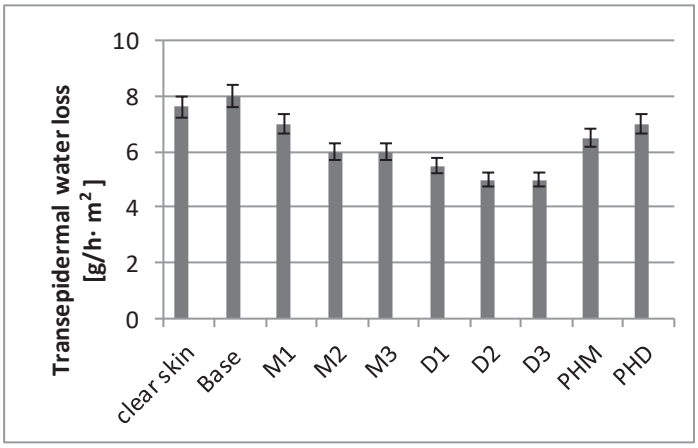

Fig. 4. Transepidermal water loss (TEWL)

Source: own study.

According to the results in Figure 4, it can be observed that as the content of vegetable oils increases, TEWL decreases. This is due to the formation of a lipophilic occlusive film on the epidermal surface, which persists until the emulsion is used. When preparations are used regularly, an occlusive effect of fatty raw materials occurs. The tightness of the occlusive film depends on the amount of lipid components in the cream formulation and their chemical structure. The average TEWL value measured before application of the samples was 7.6 [g/h·m^2].

It can be concluded that the original emulsions produced meet consumer expectations. As a result of application of prototype emulsions occlusive action occurs, which causes protection of proband's skin against excessive transepidermal water loss. It can be deduced from the study that TEWL decreased with the duration of cream application. The value of TEWL decreases, because the merging of irregular cells occurs as a result of application and the protective barrier increases.

1.6. Skin moisturization

The test was performed to assess moisture in the skin measuring the water content of the stratum corneum. The effect is based on electrical conductivity, the more water the skin's stratum corneum contains, the better the current flows, which means a higher level of skin moisturizing. The measurement results are shown in Fig. 5.

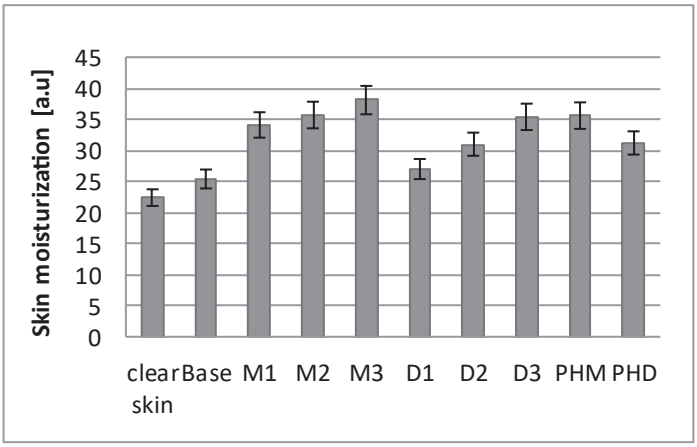

Fig. 5. Skin moisturization

Source: own study.

The average hydration value that was measured to the probands prior to application of the emulsion was 22 IU. When the emulsion without vegetable oils was applied to the application site, the hydration level increased slightly. However, with the increase of the amount of oil in the emulsion, the moisture value increased. The emulsion containing raspberry seed oil (M1, M2, M3) showed the best level of hydration, whereas the emulsion containing pumpkin seed oil (D1, D2, D3) showed a slightly lower level of hydration. The commercial formulation with raspberry seed oil was the most similar to the sample with 2 wt. % raspberry seed oil (M2). The commercial formulation with pumpkin seed oil (PHD) showed skin hydration comparable to the sample with 2 wt. % pumpkin seed oil (D2).

2. Discussion

The aim of this work was to develop an original recipe and to produce skin creams containing raspberry seed oil and pumpkin seed oil. Then the influence of these components on selected physicochemical and functional properties of the obtained preparations was determined.

Finally, a base cream formulation was developed and a base preparation containing neither raspberry seed oil nor pumpkin seed oil was made on its basis. Three creams containing different amounts of raspberry seed oil and pumpkin seed oil, i.e. 1, 2, 3 % by weight, were prepared on the base. The obtained creams were subjected to tests in order to determine selected properties.

For comparison, two commercial preparations were also subjected to the same tests. On the basis of the performed tests it was found that: the prepared formulations are characterized by stability in thermal and centrifugal tests no signs of instability such as delamination or emulsion breaking were observed. Concentration of oils in original preparation of pumpkin seed oil and raspberry seed oil slightly influences the decrease of emulsion viscosity. The obtained viscosity values are comparable to the commercial product.

The pH value of the obtained creams is close to the pH of human skin, and raspberry seed oil and pumpkin seed oil have little effect on this parameter. An increase in the concentration of raspberry seed oil does not affect adhesion, regardless of the oil content - the preparations are well absorbed.

In case of TEWL measurement, it can be stated that with increasing concentration of applied oils, the value of this parameter decreases, which indicates protection of the skin against excessive transepidermal water loss. Skin hydration increases with increasing oil concentration in the emulsion, it was found an increase in the degree of skin hydration after application with preparations containing raspberry seed and pumpkin seed oils in relation to the base.

As the content of pumpkin seed oil increased, the values of the yield stress decreased, while those of the preparations with raspberry seed oil increased, making the preparation a little more difficult to spread. The cream with 2 and 3 wt. % of

pumpkin seed oil showed the best formulation. These preparations spread best on the skin surface.

3. Conclusions

On the basis of the conducted research it can be concluded that the aim of the work was achieved. Raspberry seed oil as well as pumpkin seed oil have beneficial effect on skin condition and can be successfully used in body care emulsions. The satisfactory results of the study may provide a rationale for expanding research into the use of waste raspberry seed oil and pumpkin seed oil as attractive skin care ingredients in other cosmetic forms.

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PROPERTIES OF NATURAL FACE PEELING WITH THE ADDITION OF GRAIN COMPONENTS

KATARZYNA SMOLAREK, KATARZYNA MICHOCKA

[1]*Poznań University Of Economics And Business, Institute of Quality Science*
e-mail: katarzyna.michocka@ue.poznan.pl

Abstract
Conscious face care is an important step in caring for the skin, cleansing it, and exfoliating dead skin. While washing the face should be part of the daily care ritual, exfoliation is done less frequently. Nevertheless, it is a very important aspect of the art of beautification. Peels help to reach the deeper layers of the skin, removing residual impurities, opening and cleansing the pores, and smoothing the complexion. Exfoliating additives are essential in this type of preparation.
The study aimed to analyze the parameters of facial peels, consumer sensory evaluation, and to learn about the preferences of consumers regarding exfoliating products containing some cereals, such as oatmeal, rice, and semolina. Peels made independently from food products and drugstore peels were tested. The scope of the analysis of the parameters included the determination of the pH value of cosmetics, the degree of hydration, the degree of transepidermal water loss (TEWL), viscosity, and the total content of phenolic compounds. The products were also subjected to an organoleptic evaluation and their effect on the skin was analyzed.

Keywords: grain, peeling, natural cosmetics, usefulness properties

Introduction

Body care has been with a man for a long time. Women are trying to learn the secrets of beauty and eternal youth from ancient times. Already in antiquity, the first cosmetics were experimented with, using sand as a scrub or using moisturizing and brightening milk baths, known as one of Cleopatra's ways to dazzle with beauty. Some of these natural preparations are still used today. There are more and more innovative body care products on the market available to everyone. Along with the

expanding offer of cosmetics, the expectations and awareness of consumers are also growing. By purchasing a product, they want not only to beautify their body but also have a positive impact on other aspects, such as health and the environment.

Natural cosmetics market

The global market of natural cosmetics and personal care products continues to grow. It is estimated that the value of this market will grow by approximately $ 20 billion over 10 years (from approximately $ 34.5 billion in 2018 to approximately $ 54.5 billion in 2027), Figure 1. This proves the growing importance of the natural cosmetics market and organic. The consumer becomes more attentive and sensitive to the composition of the product, and also has more and more knowledge about its processing [statista.com/nc]. But not only the content of the cosmetic must be natural but the growing trend of being "eco" also means that the packaging of the cosmetic itself should be biodegradable. That is why more and more companies decide to introduce natural products that are safe both for the skin and for the environment.

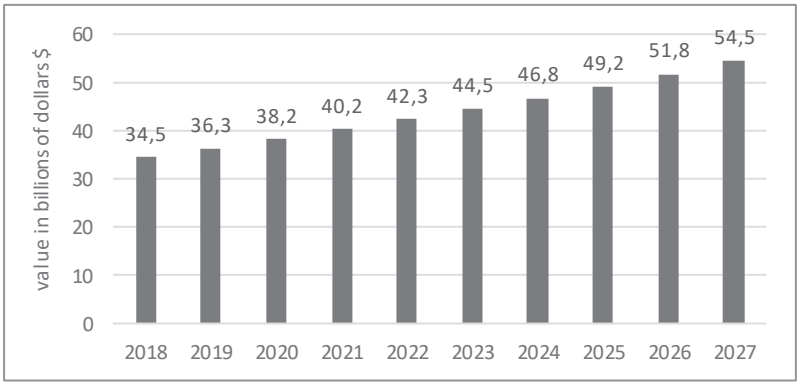

Fig. 1. Estimated value of the global natural cosmetics market in 2018-2027

Source: own study based on www.statista.com/nc.

In 2018, with a result of 38.29%, Europe had the largest share in the global natural cosmetics market. It was influenced, among others, by leading players such as Germany and France, and the constantly growing number of start-ups producing

in this field [grandviewresearch.com]. Taking into account the detailed breakdown by country, the largest natural cosmetics market in the world was characterized by the United States, which in 2018 reached a market value of EUR 4.32 billion. Such a level makes the American market unbeatable. Germany came second because its market in 2018 was worth EUR 1.34 billion, which made it the first in Europe and second in the world in the sale of natural products. Right behind them, in third place with a total of EUR 757 million, is France. Natural and organic products constitute 6.4% of the value of the entire cosmetics market there. According to the source data, sales of natural cosmetics in Europe will increase by an average of 6.3% per year [premiumbeautynews.com]. Due to the growing pro-ecological and pro-health awareness, in the Asia-Pacific region, it is forecast that the average increase in the size of the natural cosmetics industry will amount to 4.42%. It is also caused by the growing number of working generation Y, who by earning money and being more aware of the product, are able to spend more money on natural cosmetics [grandviewresearch.com].

Table 1. Revenues on the cosmetics market in Poland, broken down by product categories (in billions of euros)

Year	Skin care	Color cosmetics	Personal care	Fragrances	Total
2017	0.9	0.5	1.9	0.5	3.7
2018	0.9	0.5	1.9	0.5	3.8
2019	0.9	0.5	2.0	0.6	4.0
2020 *	0.9	0.5	1.9	0.5	3.9
2021 *	1.0	0.5	2.0	0.6	4.1
2022 *	1.1	0.5	2.1	0.6	4.3

**- estimated value*

Source: own study based on [Wspieramyeksport.pl].

The Polish cosmetics market in 2019/2020 reached the value of PLN 11.2 billion (EUR 4 billion) - Table 1. It consists of skin care products, color cosmetics, intimate and personal care products, oral care products, and cosmetics for children. The ecological part accounted for less than 2% of the market value - PLN 193.5 million. However, in the analyzed period, the segment of organic products recorded an increase of 39%, while the value of the entire cosmetics market decreased by 1.4% [forsal.pl]. It is mainly influenced by the trends prevailing in the market. The most important of them is the so-called "green beauty", which focuses on caring for and caring for the environment. Ecological packaging, certified ingredients, a transparent brand, and the smallest possible impact on the natural environment are the basic principles that guide the ever-expanding segment of eco-cosmetics. It is also important that the substances contained in the product are harmless to health and not tested on animals [hurtidetal.pl; wk.pl]. According to research carried out by Nielsen, almost 40% of consumers in Poland pay attention to the product's eco-friendliness and its impact on the environment. With an emphasis on the naturalness of cosmetics, the most frequently chosen groups in this field are cosmetics for children, face care, and toothpaste [Jarosik 2020].

Peeling, called abrasion of the facial skin or its exfoliation, is a cosmetic procedure aimed primarily at improving the appearance of the skin and its rejuvenation. It focuses on removing dead skin, revealing fresher and cleaner skin below the surface. The degree of exfoliation depends on the type of treatment performed, and more precisely on the method and preparation used. For the best results, each peeling should be matched to the individual needs of the skin and be repeated every few days or weeks, depending on its type. Well-chosen peels will clearly cleanse and firm the skin, remove discoloration, and minimize the appearance of open pores and smooth wrinkles [topdoctors.co.uk; organicseries.pl]. An important aspect is also not to use body scrubs interchangeably with face scrubs. Both of these areas require exfoliation, but the product will not perform well in both cases. Body scrubs are usually denser in consistency and have a stronger acid concentration, which can lead to irritation of the facial skin [skincare.com]. The simplest peeling can be done at home using easily available products that everyone has in their kitchen - sugar or coffee.

This type of peel allows you to remove the dead epidermis, while more advanced peels made in beauty salons can also affect the deeper parts - the dermis. In order to distinguish all types of peels, it is necessary to take into account various criteria for their classification, such as the degree of advancement of the treatment, the techniques and preparations used, and the depth of exfoliation.

1. Material and methods

The aim of this study was to evaluate and compare selected performance parameters of facial peeling cosmetic products in which cereals were a characteristic ingredient. For the analysis, two products purchased in a cosmetic drugstore were selected (oat peeling by St. Ives PS, rice peeling by Bania Agafii PB), and three home peelings PO - home oat peeling, PR - home rice peeling, PK - home semolina peeling.

Producer St. Ives (abbreviation: PS) of the oat peeling company declares the following composition - *Aqua, Glycerin, Hydrated Silica, Sodium Methyl 2-Sulfolaurate, Decyl Glucoside, Acrylates Copolymer, Cocamidopropyl Betaine, Acrylates / Palmeth-25 Acrylate Copolymer, Disodium 2-Sulfolaurate, Avena Sativa Straw Extract, Cocamidopropyl PG-Dimonium Chloride Phosphate, Disodium EDTA, Iodopropynyl Butylcarbamate, Juglans Regia Shell Powder, Lactic Acid, Parfum, PEG-4 Dilaurate, PEG-4 Laurate, PEG-4, Phenacrylamide, Polyacrylamide, Propylene Glyclorolide, Propylene Glyclorolide Sodium Hydroxide, Hexyl Cinnamal, CI 77891).*

Composition of prepared cosmetic emulsions rice scrub by Bania Agafii (hereinafter called PB) - *Sodium Chloride, Organic Helianthus Annuus (Sunflower) Seed Oil, Cetearyl Alcohol, Glycerin, Oryza Sativa (Rice) Powder, Cocomidopropyl Betaine, Hydrolyzed Rice Protein, Organic Iris Sibirica Root Oil, Linum Usitatissimum (Linseed), Seed Oil, Parfum.*

The composition of home oat scrub (hereinafter referred to as PO) is presented in table 2.

Table 2. Composition of home oat scrub (hereinafter referred to as PO)

Quantity	Component	Properties and function
40 g	Oatmeal by "Melvit", ground in a mortar	The flakes act as a cleaning agent for dead skin cells. They cleanse the pores, soothe irritations, smooth the skin, and have antioxidant properties.
20 ml	Distilled water	Binding component
10 g	Multiflorous honey	It has moisturizing, bactericidal, and soothing properties for skin irritations.
10 ml	Lemon juice	It has nutritional and detoxifying properties and brightens and evens out skin tone.
10 ml	Jojoba oil from the "Nacomi" company	Moisturizes, regulates the secretion of sebum, has antioxidant properties, and has a regenerating effect.

Source: own study.

The composition of homemade rice peeling (hereinafter referred to as PR) is presented in table 3.

Table 3. Composition of home-made rice peeling (hereinafter referred to as PR)

Quantity	Component	Properties and function
90 g	Rice flour by "Melvit"	Works as an exfoliant. It brightens the skin tone and soothes inflammation.
100 ml	Rice milk by "Sante Organic"	It smoothes the skin, soothes inflammation and irritation, and shows antioxidant properties.
20 g	Multiflorous honey	It has moisturizing, bactericidal, and soothing properties for skin irritations.

Source: own study.

The composition of homemade semolina peeling (hereinafter referred to as PK) is presented in table 4.

Table 4. Composition of home-made semolina peeling (hereinafter referred to as PK)

Quantity	Component	Properties and function
60 g	Semolina by "Janex"	It acts as an abrasive. It has moisturizing and cleansing properties.
90 g	Sour cream 12% by "Piątnica"	Nourishes the skin, cleanses it, and has exfoliating properties.

Source: own study.

1.1 The method of determining the pH of peels

Measurements of the pH of the analyzed peels were made at room temperature with the use of an integrated pH meter ELMETRON CP-511. The principle of operation of the device is based on converting the measured value of the electromotive force of the tested sample into the result from the pH scale. The test was carried out by placing the measuring electrode directly in the test sample, and the results were recorded only when the measuring system was stabilized.

1.2 Examination of the degree of skin hydration

To test the degree of skin hydration, a CM 825 corneometer was used to test the condition of the skin in the stratum corneum. It works by measuring skin hydration by testing its electrical capacity. A high result, given in relative units CU (CU), in the range of 0-130, 1 CU corresponds to 0.02 mg of water per 1 cm^2 of the stratum corneum), which proves good skin hydration [Heinrich et al. 2003]. The research group consisted of one person aged 25 who had normal skin. Peels were applied to the forearm surface by making circular movements to activate the abrasive agent. They were left on the forearm for 10 minutes as a "mask" and then washed off. The corneometer test was performed before applying the peels, immediately after washing off the peels, and 15 minutes, 30 minutes, 45 minutes, and 60 minutes later.

1.3 Assessment of the degree of water loss (TEWL)

The test of transepidermal water loss (TEWL) was carried out using the TM 300 tevameter. The device is equipped with two sensors for measuring the humidity and temperature of the skin. The higher the value of the results obtained, the greater the loss of water. This result indicates a weakened epidermal barrier. TEWL (Trans Epidermal Water Loss) is conventionally expressed in [g/(m^{2}h)]. Typically, for healthy skin, the TEWL value is between 5 and 25 g/m^{2}h [Heinrich et al. 2003]. The determination was performed in the same way as in the case of using the corneometer.

1.4 Determination of dynamic viscosity

The dynamic viscosity of the facial peels was measured using the AMETEK Brookfield DV2T EXTRA rotational viscometer. The spindle type is selected based on the projected viscosity value.. The research used RV7 spindles for semolina peels, oat St. Ives, Bania Agafii rice, and home-made oatmeal and RV5 spindles for home rice peeling. The rotational speed was V = 100 rpm and the measurement time for each sample was 30 s. The tests were carried out at room temperature T = 23.8°C.

1.5 Determination of the total content of phenolic compounds

The spectrophotometric method was used to conduct the research, based on the quantitative measurement of the light reflected or transmitted by the tested sample. Metertech SP-8001 spectrophotometer was used in the study. The tests were performed with the Folin-Ciocalteu reagent, using gallic acid as the reference. The absorbance was measured at a wavelength of λmax = 765 nm. This is the length at which the end product formed in the oxidation process has the maximum absorption.

1.6 Consumer sensory analysis

The research consisted in assessing the feelings of consumers after the exfoliating treatment with the use of standardized verification principles. Peelings performed too often may cause irritation, so they are performed once a week, which extended

the analysis time to 5 weeks. The testers were a group of 10 women between the ages of 20 and 45. The respondents declared the type of combination skin, as oily, dry, acne-prone, sensitive, and mature. The research was conducted at home. A five-level scale was used to evaluate the peels (1-very bad, 2-bad, 3-satisfactory, 4-good, 5-very good) allowing for a point-based evaluation of the peels in terms of qualitative parameters, such as consistency, adhesion, spreading, smoothing, ease removal after the treatment, the effect of the exfoliating agent on the degree of cleansing the epidermis, the quality of the skin after the treatment, the smell, the general evaluation of the preparation and the general evaluation of the preparation's performance. The questionnaire was accompanied by a table prepared on the basis of [Sułek, Małysa and Pytlas 2006].

1.7 Consumer survey research

The aim of the research was to understand the preferences of consumers regarding the use of facial scrubs. An online questionnaire was used as a research tool. The survey covered the territory of Poland. The author's questionnaire was divided into two parts, in which the first concerning general information related to the use of natural cosmetic products, while the second, more extensive, related to the use of facial scrubs. 165 people took part in the study, who took part in study in the age range from 18 to over 45 years. The most numerous group was constituted by respondents aged up to 25, who provided nearly 68% of all responses. 86% of the respondents are women.

2. Results

2.1 Results of peeling pH determination

Human skin may have a different pH, but the most preferred pH is 4.5-6, which is slightly acidic. In order not to harm it and not disturb the natural pH, beware of highly alkaline products that have a strong drying effect (pH> 8). A neutral reaction

(pH = 7) is not harmful to human skin. Even if the skin's pH is slightly raised, it will revert to its natural pH over time. Among the peels tested, the lowest pH value was shown by semolina peeling - 4.63. The result may be dictated by the presence of sour cream in the composition. The highest result was obtained by the purchased oatmeal peeling from St. Ives - 6.71. The pH level is close to neutral. The differences in values are small between the other three peels. Each of the tested cosmetics is more or less acidic, so in terms of pH, all of the tested products are suitable for an exfoliating treatment on the face.

2.2 The degree of skin hydration

According to the study, the best skin hydration is provided by the Bania Agafii rice scrub. Measurement immediately after washing off the peel showed almost twice the value that of all home peelings. Within an hour, skin hydration decreased by 20 units, still maintaining the highest parameters. Such high indexes may be influenced by the ingredients present in the product, such as sunflower oil, which is high in composition, and linseed oil, leaving an occlusive layer on the skin, inhibiting water loss and thus indirectly moisturizing. This is probably due to the high content of glycerin and substances such as lactic acid or propylene glycol, which have a moisturizing effect on the skin, or, as in the case of glycol, create a protective film. Homemade scrubs show a slight moisturizing effect, in particular semolina peeling, in which the amount of hydration immediately after washing was lower than before its application. It can therefore be concluded that this peeling had a completely opposite effect than the intended one. A possible reason may be too few moisturizing agents in the composition because only semolina exhibits them. Homemade oat and rice scrubs moisturize the skin at an almost identical level. Considering the parameters before application and "immediately after", this is not a high level, as the difference in moisture was slightly more than two units in both cases. Within an hour of washing off, the parameters of the rice peel dropped by more units compared to the moisture level specified for the oat peel. It could have been influenced by the jojoba oil used in oat scrub, which, apart from the honey present in both peels, also has moisturizing properties.

Table 5. The degree of skin hydration

	Before applying [CU]	After application [CU]	15 min [CU]	30 min [CU]	45 min [CU]	60 min [CU]
PO	49.0	51.4	49.9	48.6	47.0	45.8
PR	49.1	51.2	45.7	39.4	38.2	36.7
PK	49.1	45.2	31.9	31.7	31.4	30.9
PB	49.2	99.4	69.3	76.7	73.7	70.8
PS	49.1	85.7	63.1	58.1	55.2	51.4

Source: own study.

Homemade oat and rice scrubs moisturize the skin at an almost identical level. Considering the parameters before application and "immediately after", this is not a high level, as the difference in moisture was slightly more than two units in both cases. Within an hour of washing off, the parameters of the rice peel dropped by more units compared to the moisture level specified for the oat peel. It could have been influenced by the jojoba oil used in oat scrub, which, apart from the honey present in both peels, also has moisturizing properties.

2.3 Water Loss Rate (TEWL)

The lowest level of water loss (TEWL) immediately after washing was obtained from the Bania Agafii rice scrub. As in the case of skin hydration, it is influenced by the moisturizing substances contained in the composition and inhibiting water loss from the epidermis. The difference between the initial TEWL value after washing and one hour after it is 8.5 g/hm^2, which is the highest among the compared samples. St. Ives, homemade rice, and homemade semolina show similar levels of TEWL. The highest result, exceeding the aforementioned peelings at least twice, is the home oat scrub. Its use resulted in a large increase in the height of TEWL immediately after washing compared to the size before application. Initially, its use resulted in lower than original results, but after 45 minutes the water loss began to increase again. In the remaining analyzed cosmetics, the value of the TEWL coefficient increased with the increase of time. Finally, after the application of each test product, a similar

TEWL value was obtained and all results, except for semolina peeling, exceed the level of water loss before application. However, it should be taken into account that cosmetics such as peels are not aimed at long-term moisturizing and stopping epidermal water loss. In this case, most peels have a lower degree of water loss than before their application, which means that they have a beneficial effect on the skin.

Table 6. Water Loss Rate (TEWL)

	Before applying [g/hm^2]	After application [g/hm^2]	15 min [g/hm^2]	30 min [g/hm^2]	45 min [g/hm^2]	60 min [g/hm^2]
PO	10.2	17.1	12.7	12.3	13.5	14.0
PR	10.1	7.4	8.4	10.5	11.5	13.1
PK	10.2	6.4	8.4	9.2	9.7	10.2
PB	10.0	2.9	3.3	7.9	9	11.4
PS	10.1	5.4	6.4	7.3	10.3	12.1

Source: own study.

2.4 Results of viscosity testing of selected peels

Depending on their type, face scrubs have different viscosities. In the case of granular peelings subjected to the test, these are cosmetics similar to the gel or cream form with various types of abrasives. It is important that the viscosity is not too low as this may cause the peeling to run off the face during the treatment. It is also not advisable to have a too high viscosity of the product due to the heavy spreading of the abrasive material on the skin and the possibility of irritation at the moment of high friction. The Bania Agafii peeling has the highest viscosity. The high result may be due to the main ingredients of the product, as it contains a large amount of salt and oil. If the cosmetic is static for longer, it delaminates and should be mixed before applying it to the face. To the touch, it creates the most sticky and greasy feeling of all tested peelings. The porridge peeling is characterized by a slightly lower value, in which the recipe consists only of semolina and sour cream. The cream used was thick which may be the reason for the high viscosity of the final product. Homemade rice peeling has by far the lowest result. Its viscosity is about 7 times lower than that

of other peels. The main ingredients are milk and rice flour that make up the slurry. To increase the peeling viscosity, more rice flour should be added. Peels may have different viscosities, and so, according to the research carried out by Małysa and Witkowska, the viscosity of the tested granular peels is about 9.000 mPa * s and may increase with an increase in the amount of abrasive material. In addition, Aglawe et al. have developed a herbal facial scrub with a viscosity of 145.80 mPa*s with a gel-like consistency, therefore even the lowest viscosity value can be considered sufficient for a face scrub [Aglawe et al. 2019; Małysa & Witkowska 2015].

Table 7. Viscosity of the tested peels

Peeling	The size of the spindle	Viscosity [mPa*s]	Measurement error [mPa*s]
PO	7	16780	400
PR	5	2360	40
PK	7	16920	400
PB	7	17080	400
PS	7	15960	400

Source: own study.

2.5 Results of the study of the total content of phenolic compounds

Phenolic compounds are found in many plants and have a number of positive features, such as antibacterial, anti-inflammatory, and antioxidant properties. Due to the high content of polyphenols, plant extracts are readily used in cosmetology and medicine, as they prevent various diseases related to oxidative stress [Dai & Mumper 2010]. For oat flakes and rice flour, it was 109.855 mg/l each. On the other hand, semolina was characterized by a slightly lower content of phenolic compounds - 92.892 mg/l. The content of polyphenols may be influenced, among others, by the type and temperature of the solvent used for extraction, the test method, and, in the case of rice, its type [Pieszko & Zaremba 2013].

2.6 Consumer sensory analysis results

Commercial oat scrub from St. Ives was rated the highest in terms of its spreadability on the skin (5.0) and consistency (4.6). It obtained the maximum spreadability score, so it can be concluded that it turned out to be the product that best meets the needs of the respondent's expectations regarding the application of facial scrubs. The worst result was the effect of the exfoliating agent on the degree of skin cleansing (3.9). This could be due to, inter alia, the small dimensions of the abrasive material. Taking into account the fact that peels were assessed, one of the most important tasks of which is to clean the skin of the face, this criterion is quite an important aspect for the potential choice of a product in the future. In the additional question regarding the reduction of the visibility of pores, 60% of the respondents gave a positive answer.

2.7 The results of the sensory analysis of the tested peels

By analyzing and comparing the results of all five peels, it can be stated that St. Ives (4.26). It was largely due to its consistency, adhesion, spreading, and the quality of the skin after the treatment, which were rated the highest by consumers among all the criteria. The moisturizing glycerin and hydrated silica in the composition, increasing the adhesion of cosmetics and facilitating distribution, could have subconsciously influenced the choice of testers. The consistency of the peeling was smooth, with hardly perceptible oat particles, which could also make it easy and pleasant to spread on the skin. In the category of skin smoothing and fragrance, the testers rated the Bania Agafii rice peeling the highest. In the context of smoothing, the oils visible in the composition and a large amount of salt as an abrasive could have the greatest impact. In terms of smell, no aromatic additives were used in the preparation of home peelings. They had their own natural smell, which could have contributed to their low scores in this criterion. Among all the peels tested, the Bania Agafii product had the most perceptible smell, therefore it can be concluded that olfactory sensations are also an important issue when choosing a peel for some consumers. Homemade oat scrub has been selected as the

best type of exfoliant for the degree of cleansing of the skin. The feeling of better cleaning could be caused by the different sizes of the abrasive in the product. The oat flakes were ground before being used in peeling, however, the consistency of the particles obtained was not homogeneous or smooth. Due to the different sizes of the abrasive particles, the peeling could better clean the skin of the people taking part in the study. The semolina peeling turned out to be the easiest to wash off. Compared to other cosmetics subject to the study, it was distinguished by the smallest number of ingredients, which, in addition, were very easy to rinse off with running water, and did not contain any oils. Unfortunately, when averaging the results, it was the worst compared to other peels (3.58). Perhaps it would be worth improving its composition with additional substances that could positively affect the properties and visibility among consumers.

The testers were also asked about the willingness to buy or prepare any of the peels at home, as well as about the choice of the least attractive product among the respondents. Despite the high scores obtained immediately after the exfoliating treatment performed by the Bania Agafii drugstore rice scrub, 80% of respondents said that they would not buy this product again. It is mainly caused by the deterioration of the skin condition a few days after peeling. The composition of the peeling, which contained a lot of oils and salt as an abrasive, may be responsible to the greatest extent. It was indicated due to the quality of the facial skin after application.

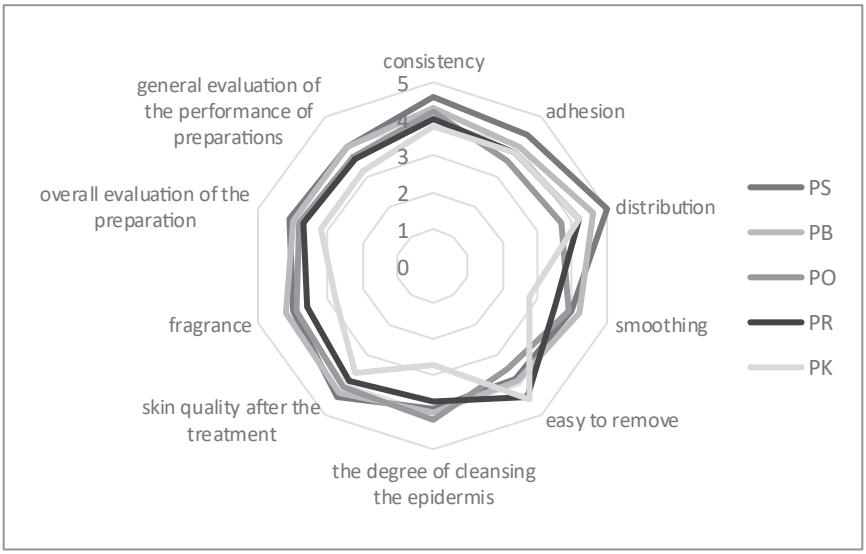

Fig 2. Sensory evaluation of tested preparations

Source: own study.

2.8 Consumer research survey results

In the first stage of research on natural cosmetics, the respondents were asked whether they pay attention to the naturalness or organic nature of the cosmetics used, the vast majority of 73% answered in the affirmative. This is a high result, in line with the current, constantly growing market trend for natural cosmetics, in which an increasing number of people have knowledge in the field of conscious care. It is also related to the market trend of being "eco" and returning to naturalness, where the consumer expects from the producer not only natural ingredients contained in the product, but also their sustainable sourcing or minimizing packaging waste. According to the research conducted by the Statista portal, the main reasons for the use of natural cosmetics by women in Poland in 2019 were a concern for health (approx. 75% of responses) and the environment (approx. 50% of responses) [statista.com/kn].

Among 74% of respondents who practice the use of facial scrubs, slightly over 36% apply them once a week, 25.4% several times a week, and about 22% several

times a month. There is no clear-cut and specific rule regarding the frequency of using facial scrubs, as the use should depend on the condition of the skin and its needs. However, it is not advisable to use peels daily because of the possibility of disturbing the skin's hydrolipid barrier, which is a protective barrier. Frequent use of peels increases the likelihood of its destruction, which may result in unpleasant effects such as dry skin being prone to irritation. The survey results show that only a small percentage of people perform an exfoliating treatment every day (3%). However, it should also be borne in mind that such a procedure should not be carried out too rarely. A properly selected and performed peeling helps the skin to get rid of the dead epidermis with all impurities and forces it to self-regenerate by damaging it on a micro-scale. Systematic use of the exfoliating treatment allows you to improve the skin tone, and its general condition and lighten discoloration. The complexion becomes visibly healthier.

Slightly over 68% of respondents who pay attention to the naturalness of a cosmetic recognize it by analyzing the composition, and 35% trust the manufacturer's assurance on the label. Slightly less, i.e. 32.5%, check whether the product has certified natural or organic, and almost 17% use the available composition analyzers. The highest percentage of received responses confirms the increase in consumer knowledge in the area of ingredients of cosmetic products. Based on the analysis of the composition of the preparation, the consumer is able to determine whether it contains natural and harmless substances.

The most frequently used type of natural cosmetics by respondents are face care products - 52.5%. Hair care products, followed by body care products (13.3%), are in second place with a result of 31.7%. The use of organic or natural makeup products was the least frequently chosen answer by the respondents - 2.5%.

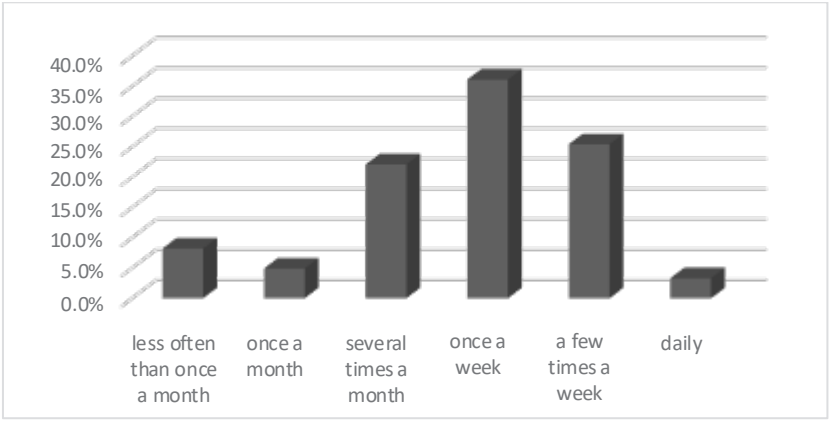

Fig 3. Sensory evaluation of tested preparations

Source: own study.

When buying facial scrubs, respondents most often look at the product composition (64%), price (54%), and the opinion of others (51%). The brand of the cosmetic (39%) and recommendations about it (40%) are also often taken into account when making the purchasing decision of the respondents. The advertising (0.8%) and the graphic design of the product (3.3%) were definitely the least important for users. On the basis of the obtained results, it can be concluded that they coincide with the current trend of increasing cosmetic awareness. Customers stop relying on manufacturers' assurances regarding the properties of the cosmetic and decide to conduct a composition analysis on their own. For less experienced users, internet analyzers and applications that are able to describe and interpret cosmetic substrates in depth are also of help. Some of them additionally provide information on product testing on animals and the possibility of issuing opinions on the products used. Reading the label becomes easier and the consumer can avoid a product with unwanted ingredients. The composition of the peel is crucial because the undesirable substances present in the cosmetics may lead to irritation or serious skin changes. By performing the peeling, we interfere with the skin structure, so its composition should be carefully selected according to the needs and type of skin.

The consumer who purchases the peeling wants it to be tested in terms of its operation and possible effects. Approximately 51% of respondents rely on the opinion of others to make a purchase decision. The development of technology and digitization makes it possible to obtain reviews not only from friends or family but also from the wider community. There are many blogs on the subject of care, as well as groups and cosmetic fan pages, where it is possible to share personal feelings related to the products used. In order to obtain qualitative information, consumers more and more often pay attention to the opinions of people with higher cosmetic or medical education. At a time when celebrities promote cosmetic brands for a fee, consumers seem to rely more on the subjective opinion of other customers and the recommendations of competent, educated people than on advertising financed by the manufacturer.

According to the respondents, the graphic design becomes insignificant when it comes to the purchase of the peeling, however, the first visual impression that the cosmetic makes on the consumer may be an important aspect. The potential customer first notices the packaging graphics and although graphic variations are not the decisive purchasing factor, attracting the consumer's attention may increase the likelihood of their noticing and possible purchase.

The average amount that respondents most often spend on the purchase of facial scrubs is up to PLN 50 (77%). About 19% spend an average of PLN 51 to PLN 100, and the remaining 4% spend up to PLN 200 on peels. Depending on the type of cosmetic, the price of peelings varies greatly. The more expensive version is peels in the dermo-cosmetics category, which contain higher concentrations of active ingredients than drugstore cosmetics. In addition, the price of the product is influenced by many factors, ranging from its composition, and packaging, to the types of production, the tests carried out and the margin imposed by the manufacturer.

The respondents most often purchase face scrubs in beauty stores (84%) and online (44%). Shopping at stationary beauty stores offers customers the opportunity to test the product before purchasing it by providing free samples and testers. This is undoubtedly one of the most important arguments in favor of shopping in traditional stores. The consumer can see the consistency of the cosmetic, its fragrance, or color, which stimulates its senses. Producers use the so-called sensory marketing to

encourage the customer to buy by evoking positive emotions. It is also possible that the high percentage of consumers who use drugstores is caused by their habituation to conventional forms of purchase. Increasing digitization is having a positive effect on e-commerce.

Online stores have greatly increased in popularity during the COVID-19 pandemic, during which, to be cautious and minimize the risk of contamination, a large number of consumers have opted for online shopping. Additionally, an annual increase in the importance of online sales of cosmetic products in Poland is forecast [pmr.com; pomocamyeksport.pl]. For the consumer, it means convenience, time savings, lower purchase costs, and an extensive range of cosmetics that may not be included in the assortment of brick-and-mortar stores, as well as the possibility of comparing them. For an entrepreneur, e-commerce, compared to stationary commerce, means lower maintenance costs caused, among others, by resigning from renting the premises, which translates into lower retail prices. Through Internet channels, it is also possible to reach a wider group of buyers than in the case of a stationary store. Purchasing products in a pharmacy (12%) or a supermarket (4%) turned out to be less popular among the respondents. Approximately 7% resign from buying ready-made peelings in the available sales channels, focusing on self-preparation of these cosmetics in the privacy of the home. Pharmacy products are usually more expensive than drugstore or online cosmetics, as a result of which the sales channel may not be so widespread and recognized among consumers. On the other hand, supermarkets are not specialized in the field of cosmetics, and as a result, they may not be reliable enough sources for purchasing personal care products for the customer.

Using a face scrub, the respondents mainly expect the exfoliation of dead epidermis and stimulation of the skin to regenerate (approx. 83%), as well as removing impurities, opening and cleansing the pores (73%). Fewer people require skin smoothing and firming from this treatment (approx. 53%). Improving skin tone (31%), better absorption of nutrients and skin hydration (23%), and reduction of fine lines (9%) are the least desired effects by respondents in peeling treatments.

One in three people shows average satisfaction with the results of peeling, half of the respondents are satisfied with them, and about 17% are very satisfied. The

effects are not satisfactory only for 3% of respondents. Among the respondents who are very satisfied with the action, it can be noticed that more than half use products containing acids (55%). Slightly less, because 40%, purchases clay peelings. The leading brand among the most satisfied respondents is The Ordinary with 45% of the votes. Brands such as Bielenda and Tołpa also appeared in numerous responses. Interestingly, among dissatisfied people, acid peels are also the most common answer (75%), and brands that do not meet consumer expectations include Garnier, Ziaja, or Biotaniqe. In the case of acid peels, dissatisfaction may result from the wrong selection of the type or concentration of the active substance contained in the product. Not all cosmetics work for everyone to the same extent.

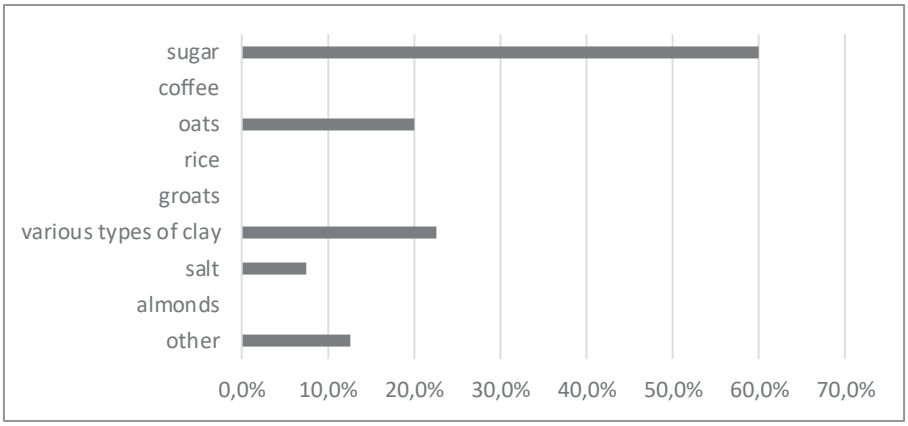

Fig 4. Sensory evaluation of tested preparations

Source: own study.

Approximately 33% of respondents when asked about self-preparation of home peelings answered positively. The most frequently used ingredients turned out to be coffee (90%) and sugar (60%). They are one of the most common substances that can be used to perform peeling. Easy to find in any kitchen, with antibacterial and antioxidant properties. Clay (22.5%) and oatmeal (20%) are less frequently used by the respondents, but they also have a positive effect on the skin. Like coffee, oatmeal has antioxidant properties, additionally soothing irritation. Clay, depending on its

type, is antibacterial and cleansing well (green clay), they help soothe inflammation and soothe the skin (white clay). None of the respondents use almonds, groats, or rice when preparing home peeling (Fig. 4). This may be due to the ignorance of the positive effects of these products on the skin, being used to other ingredients, or being allergic to any of them, or the lack of availability. Other ingredients that consumers use to prepare the scrub are honey, aloe, and oil or olive oil.

3. Conclusions

The work focuses on face scrubs, which contain semolina, oatmeal, and rice. Two commercial peelings were used for the research: oatmeal from St. Ives and rice by Bania Agafii, as well as three, prepared independently, in which the main grinding ingredients were ground oat flakes, rice flour, and semolina. Testing the pH of cosmetics is quite important for the safety of using the products. The pH of all tested peels ranged between 5.08-6.71, so the preparations were adapted to the care of the facial skin. Self-made products gave almost two times lower levels of hydration, on average around 50CU. Drugstore peels provided better hydration than peels made by yourself. It can be concluded that this is due to the significantly smaller number of moisturizing ingredients in the formula of a handmade product. In order for home scrubs to show a similar level of hydration, they would need to be added with more moisturizing ingredients or enriched with additional ones with better properties. The highest degree of TEWL transepidermal water loss was recorded for the prepared semolina peeling. It was at least twice as high as read for other products. In this case, in order to minimize the loss of water from the epidermis and moisturize the skin, additional serum or cream should be applied to the face. The primary task of peeling is cleansing rather than long-lasting hydration, yet it should not contribute to any faster loss of water from the epidermis. In the case of semolina peeling, it would be worth supplementing the composition with more substances that have moisturizing effects. The viscosity of cosmetics is also quite an important aspect of their application. The desired value mainly differs with the type of substance. In the case of face scrubs, it must not be too low, because there is a high risk that the product will run over the face

during application, making the procedure much more difficult. Too high viscosity will cause heavy spreading of the cosmetic on the face, resulting in irritation. Among the peels tested, the home rice peel clearly had the lowest viscosity - 2360 mPa*s. It turned out to be a value that is sufficient to prevent the product from dripping off the face and creating discomfort during the procedure. Prepared oat peeling, semolina, and purchased Bania Agafii rice peels and St. Ives has an average viscosity of around 16.600 mPa*s. These are denser peels, but not so much as to irritate the skin and cause problems when applying the product to the face. The overall content of phenolic compounds in all tested products was at a very similar level. Thiranusornkij et. all [2018] and its group tested black rice flour for its polyphenol content and its potential use as an alternative to a gluten-free bread ingredient. Unfortunately, due to the use of various solvents during extraction and different product characteristics, it is impossible to compare the test results. Taking into account oatmeal, the influence of oat soaking and sprouting on phenolic compounds was investigated. The results showed that the stages and time of softening and germination had an influence on the content of polyphenols and the antioxidant activity. However, there are no studies in the literature that fully correspond to the test conditions, which also makes it impossible to compare the obtained result with other results known from the literature [Xu et al. 2009]. The situation is similar in the case of semolina, in which the content of phenolic compounds was 92.892 mg/l. In the literature, you can only find research on semolina made from durum wheat, while semolina comes from common wheat. According to the consumer sensory assessment, the drugstore oatmeal peeling by St. Ives turned out to be the best of the five tested peels. According to the received responses, it has the consistency and adhesion of the product most desired by consumers, additionally, it has the best effect on the quality of the skin after the treatment. Of those evaluated, 60% would choose to buy it and reuse it. From the analysis of the conducted research, it can be concluded that the prepared cosmetics did not have enough moisturizing agents and that their compositions should be enriched with additional substances to improve the overall quality of the peeling. They did not exert a sensational product on the testers, but they were also not considered to be the worst performing their task. Surveys on consumer preferences in the facial peelings market

have shown that respondents pay more attention to the natural or organic nature of the cosmetics used. Most often, they rely on their knowledge, analyzing the recipe themselves, or on the manufacturer's assurances on the label. When purchasing a product, the respondents pay the most attention to the composition when purchasing. Slightly less important, but still very important for them is the opinion of others and the price of peels. They mainly use mechanical (granular) peels and, less frequently, chemical (acidic) peels, the main ingredients of which are mainly acids and various types of clays. Approximately 67% of respondents prepare home peels, usually using coffee and sugar. The conducted research made it possible to notice the differences between the parameters of facial peelings and their operation, as well as to learn about the preferences of consumers regarding these products. Despite the superiority in the consumer assessment of one of the drugstore peels over the peels prepared by oneself, it can be concluded that by enriching the composition of home cosmetics, they could enjoy a comparable assessment by consumers. Knowing exactly the quantity and quality of ingredients in home scrubs, you might risk saying that they pose a lower risk of side effects.

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MODERN ANTHROPOMETRIC TOOLS USED IN THE QUALITY ASSESSMENT OF THE FOOTWEAR FITTING

PIOTROWSKA KATARZYNA[1], CHOCHÓŁ ANDRZEJ[2], GAJEWSKI ROBERT[3]

[1]*Lukasiewicz Research Network Łódź Institute of Technology,*
e-mail: katarzyna.piotrowska@lit.lukasiewicz.gov.pl
[2]*Departament of Metrology and Instrumental Analysis, Institute of Quality and Product Management Sciences, College of Management Sciences and Quality, Cracow University of Economics,*
e-mail: chochola@uek.krakow.pl
[3]*Lukasiewicz Research Network Łódź Institute of Technology,*
e-mail: robert.gajewski@lit.lukasiewicz.gov.pl

Abstract
Footwear is a group of products that is diversified in terms of construction and materials. The production process requires theoretical and practical knowledge in the fields of anthropology, materials and commodity science, footwear construction and technology. It is also essential to be familiar with the current fashion trends. The multitude of activities performed at the stage of footwear design before prototyping the models and the final product shows that the quality of the footwear is dependent on many factors.
One of the most important factors determining the quality of footwear is fitting. The fitting of the footwear to the foot depends on the footwear's interior parameters, which is determined by the dimensions and shape of the last. The sizing of the last is based on knowledge of the anthropometric parameters of the consumer's feet (in the case of custom made shoes) or the consumer population (in the case of mass-produced shoes). The anthropometric measurement techniques used so far were based on manual measurements, with a high risk of making a mistake. Currently, it is becoming more and more common to use 3D scanners that enable quick and precise measurements.
The article discusses the directions and perspectives of development of the methods of anthropometric measurements.
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Keywords: anthropometry, 3D scanner, footwear, quality, management

1. Introduction

Footwear is a basic need product. Archaeological data indicates that footwear was used in the late Pleistocene [Trinkaus & Shang 2008; Buldt & Menz 2018; Franklin et al. 2015]. Traces of a kind of soft footwear were found in Cussac Cave (France) [Ledox at al. 2021]. The original function of the footwear was not only covering the foot but also its protection against the harmful effects of weather conditions or injuries [Buldt & Menz 2018; Franklin et al. 2015]. Over time, the basic functions have been replaced by aesthetic and fashion requirements, which relegates the fit of the footwear to the foot to the background.

Consumers are increasingly aware of their needs. They expect not only fashionable footwear [Xiong et al. 2010] but also compatible with their foot dimensions (it means - fitted). Fit means *"how footwear can accommodate the morphology of the foot"* [Goonnetillekee & Luximon 2000; Buldt & Menz 2018]. The process of fitting footwear is based on an attempt to place the shape of the foot of an irregular shape into a block of the foot having a standardized, more regular shape [Goonelilleke 2001]. For manufacturers of mass produced footwear, the most important information is the data from anthropometric measurements of a representative population. Nowadays, the footwear market is dominated by mass production, which is dedicated to the largest possible population of consumers, and not to one specific user. For manufacturers of serial footwear, customization of footwear in terms of dimensions is something unattainable. Not only for economic reasons, but also due to the lack of access to current data from anthropometric measurements. Footwear manufacturers rely on data on the average dimensions of feet in a given population, which have not been updated for years.

Anthropometric methods of measuring feet were developed already in the nineteenth century. Over the years, the method of measuring the irregular solid of the foot has been standardized. The number of measurable parameters allows for an almost perfect representation of the foot body [Gajewski 2006]. However, the process of obtaining data using traditional (manual) methods is long and burdened with a high risk of error.

In Poland, last population measurements (in adults and children) were carried by prof. Łuba in the years 1956-80 [Łuba et al. 2015; Skrzyńska et al. 2012]. The awareness of the phenomenon of the secular trend in the foot dimensions leads to a hypothesis that contemporary footwear designed on the basis of data from the 1970s and 1980s is not adapted to the foot dimensions of today's population - especially in children [Skrzyńska et al. 2012].

The phenomenon of the secular trend in the children's feet is confirmed by the research of the Institute of Leather Industry in Kraków [Skrzyńska et al. 2012]. The literature shows that there is data confirming that nearly 66% of the adult population wear footwear that is not adjusted to the foot size, mainly in width parameter [Chantelau & Gede 2002].

Adjusting the footwear to the three-dimensional shape of the foot is a difficult task. The main problem is the morphological variation of the feet in the population, which is not reflected in the last shape. Usually, manufacturers of serial footwear (mass produced) rely on several lasts as the starting block for footwear design [Buldt & Menz 2018; Chantelau & Gede 2002].

Another aspect is the process of shoe selection by the final customer. It is made on the basis of the subjective feeling of comfort while fitting, but also on the basis of qualitative factors, such as the set of materials used and compliance with fashion trends [Au & Goonetilleke 2007; Buldt & Menz 2018].

The comfort of wearing shoes is not synonymous with its adjusting to the dimensions of the foot (fitting). The compatibility of the internal dimensions of the footwear with the dimensions of the foot is only one of the factors of wearing comfort.

The subjective feeling of footwear comfort is often influenced by the material from which the footwear is made (e.g. the use of an insole made of an EVA foam element with low hardness in footwear intensifies the so-called feeling of comfort and softness under the feet). Aesthetic considerations and the fashion aspect are particularly important for women who often choose high-heeled and narrow-heeled shoes. High-heeled footwear is a kind of canon of women's fashion. Unfortunately, it is harmful footwear, whose dimensions, especially in the forefoot, are significantly narrowed. High-heeled footwear can cause deformities in the feet (forefoot overload

syndrome, hallux valgus, hammer toes) [Snow & Williams, 1994]. There are also studies on the harmfulness of high-heeled footwear on the health of the user – constantly raising the heel a few centimeters above the ground forces a change in the position of the center of gravity of the body (called COP) [Ko & Lee 2013]. This, in turn, can cause not only muscle contractures (e.g. abdominal calf) but also back pain and migraines [Cowley et al. 2009]. High-heeled footwear is one of the classic examples of fashionable footwear – not matched by its shape and internal dimensions to the dimensions of the feet. The only dimension that compatibile with the anatomy of the foot is foot length dimension.

Most of the footwear produced occurs in the G fit (medium fit). In the population, however, we have users with fit above G (wide feet) and also with slimmer feet, where fit is below G. Research conducted by IPS in the years 2007-2013 showed that in children aged 1-15 years in one length number there are as many as 4 fits [Skrzyńska et al. 2012].

A similar study was made on a group of 32 women who wore size 37 shoes. In the study population, differences were noted not only in the width of the feet, but also in the proportion of the length of the toes in relation to the length of the forefoot [Skrzyńska et al. 2007].

However, the differentiation of foot morphology in the Polish population is not reflected in the diversity of lasts. These, as a starting element used to design footwear, differ mainly in the shape of the forefoot, which determines the final shape of the footwear.

There are many studies which show various aspects of correct fitting of footwear to the foot. They are mostly based on the length of the foot and the forefoot width, and they show that nearly 72% of respondents wear incorrectly fitted shoes. Including the gender criterion, women usually wear footwear that is less fitting to the feet than men [Castro et al. 2010; Buldt & Menz 2018]. Dobson, in his research with the use of a 3D scanner, showed that among the respondents the degree of footwear matching to the foot length is correct, while most of the study participants wear footwear too narrow in relation to the foot dimensions [Buldt & Menz 2018; Dobson et al. 2018]. Improper fitting shoes may cause foot pain and deformation of the big toes

and smaller toes. This indirectly affects the deterioration of the quality of life [Burns et al. 2002; Buldt & Menz 2018].

There are many devices that allow you to measure the length and width of the foot. Some even make it possible to compare the dimensions of the feet with the dimensions of the inside of the footwear with feedback on the need to replace the footwear with larger ones. This allows you to obtain information about the degree of fit of the footwear to the foot at the time of purchase. An example of such a device is the Clevermess measure [clevermess.pl]. This device allows not only to measure the foot (foot length and forefoot width) but also to measure the inside of the footwear (the inner length of the footwear and the width of the forefoot). After collecting the data, the device displays information on the footwear fitting to the foot. It is a kind of information about whether the shoe is too long / too short or too wide / too narrow in relation to the foot. It is a device especially dedicated to Parents. It is necessary to inform parents about the need to replace shoes with new, larger ones.

In recent years, 3D scanners have also gained popularity. Popular ”*e-obuwie scanners”* which are located in malls in big cities, allow to obtain a 3D scan of the foot and choose the right footwear models from the shop assortment. However, this type of scanners are used more for marketing than scientific purposes.

Nowadays, in the era of digital transformation, the traditional tools are being replaced in favour of modern methods of foot measurement using 3D scanning techniques. These methods are already very popularized, they are also used in the selection of personal protective equipment [Hrynyk et al. 2016].

A 3D scanner is a device that creates a 3D model based on a physical object (in this case a foot), generating a file in the form of a point cloud (most often in STL format). 3D scanning allows you to meticulously collect foot measurements in a much shorter time, with the possibility of eliminating the human error factor. This advanced tool used in anthropometry enables the registration of the foot geometry without the use of markers.

2. Material and methods

The paper shows the methods of performing anthropometric tests using traditional tools and 3D scanners (visible light and laser). The range of measurements that can be obtained in all techniques is discussed. Each time the data from the scanner were combined with anthropometric measurements obtained using traditional methods.

A comparison was made of the traditional method of anthropometric measurements and 3D scanning of the foot in terms of the time of the test and the amount of data obtained, or the accuracy of the mapping.

2.1. Traditional anthropometric method

Anthropometric studies of the lower extremities are based on two basic methods [Rajchel-Chyla 2020]:

- measurements in vivo (taking measurements directly on the foot),
- obtaining an image of the foot using a plantograph or a podoscope with a camera or a 2d / 3d scanner.

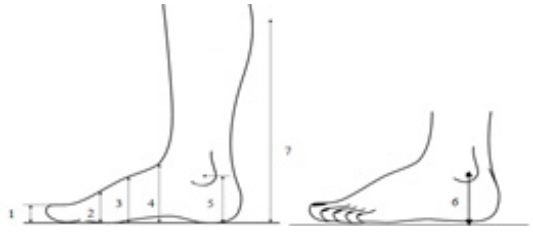
Measurements made on the foot with the use of simple tools such as a spreading caliper, measuring tape or an altimeter.

During the examination, the patient stands in a upright position, evenly overloading both feet. Height, width and length measurements of the foot and calf are made as well as girth. The figures 1 and 2 show where the measurements are taken on the foot.

Fig.1 . Lenght, width and girth measurement

		
Foot lenght	Forefoot width Heel width	1. Forefoot girth 2. Instep girth 3. Long heel girth 4. Ankle girth 5. Minimum calf girth 6. Maximum calf girth

Fig.2 Height and girth measurement



Wysokość:
1. Toe end height
2. 1st metatarsal head height
3. Forefoot height
4. Instep height
5. Inner ankle height
6. Outer ankle height
7. „Maximum girth calf" height

Source: Łukasiewicz-ŁIT.

The next stage of research is to make static and dynamic plantograms using a plantograph. The resulting footprints are then analyzed using some indicators and angles on the print. In order to make measurements on the plantogram, a ruler, a caliper and a protractor are used. Figure 3 shows the plantogram with the outline of the foot marked and the basic indicators plotted:

- alpha angle (toe angle),
- beta angle (angle of the fifth finger),
- Clarke's angle (basic indicator of the assessment of the longitudinal arch),
- heel width and forefoot width.

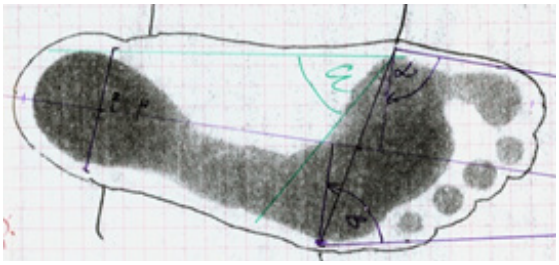


Fig.3 . The plantogram of a feet

Source: own study.

The accuracy of the obtained measurements is negatively affected by the human factor and the high risk of making a mistake (error). In addition, the time of taking measurements using traditional methods extended by the analysis of data from foot plantograms is long and reaches up to 30 minutes depending on the number of parameters collected.

2.2. Visual light 3D scanner

The test using a visible light scanner consists of two stages. The first step is to make a foot negative in a special foam. The scanner then takes a picture of the dorsal side of the patient's foot. After removing the foot from the foam, the scanner takes a picture of the negative of the foot. The images are then put together using software.

Figure 4 shows the procedure for performing a foot scan using a visible light scanner. The scan time is about 10 minutes.

The measurement of a foot can only be performed in two dimensions. It is possible to combine any points selected on the scan, but the measurement is performed only in one plane (in classical anthropometric methods, points on different planes are combined).

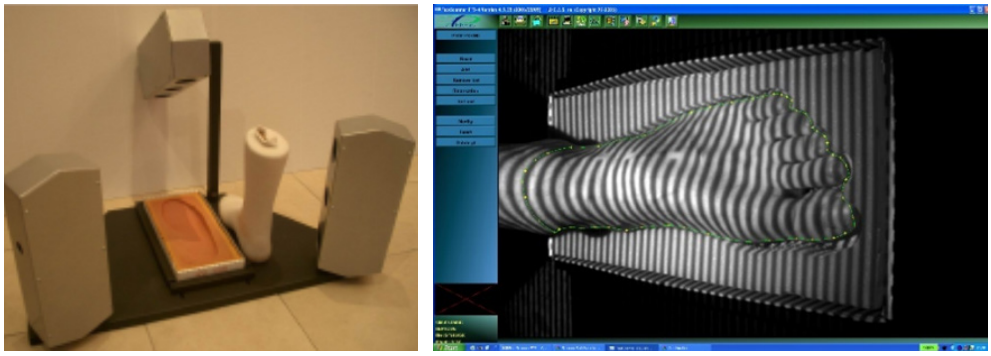


Fig.4 . Test stand for FTS 4 scanner, IDEAS company

Source: Łukasiewicz-LIT.

2.3. Laser 3D scanner

The most advanced achievement of the 3D scanning technique is the use of a laser beam. Obtaining an image using this type of scanner takes a short time – about half a minute. The possible elimination of artifacts and the need to re-perform the scan extend the entire process accordingly.

As a result of the study, we obtain over 40 parameters measured automatically by the computer's algorithm.

3. Results

3.1. Comparison of anthropometric research methods

Methods of anthropometric testing of the feet are different. While classical methods are time-consuming, they have no limitations – we are able to take measurements in all conditions, also in field conditions. An additional advantage is the ability to measure any dimension in any plane. The disadvantage of these studies is their time-consuming and difficult possibility of digitizing the results, which in the case of population studies is of great importance.

Therefore, 3D scanners are becoming an advantage in modern anthropology.

The anthropologist's experience shows that the average time to make measurements using traditional tools is about 10 minutes. In this way of measuring, using plantograms we also receive about 9 anthropometric measurements and footprints. Then, entering the data into the computer database is needed. In the case of children, the examination time is very often extended. Moreover, in case of high mobility children, it is not possible to take all anthropometric measurements.

The high-tech 3D scanners can be used to scan not only the foot's sole, but also the body of the foot in about 17 sec per 1 foot (according to the manufacturer's data from the company KOORDYNACJA). Scan needs to be checked to eliminate artefacts and evaluate the correctness of measurements which were obtained by the scanner algorithms. The 3D scanner software makes it possible to correct the position of some anthropometric points, but it is associated with the laboriousness greater than in traditional methods. The test report is generated automatically, so there is no need to enter data into the computer database. The total duration of the study test from the 3D study (when trying to repeat the scan and analysis of measurements) takes 7-8 minutes (the need to repeat the scanning procedure and manual correction of measurements).

Table 1 shows the advantages and disadvantages of the anthropometric research method.

Table 1. Advantages and disadvantages of traditional method of measurements, compares with hi-tech 2d and 3d scanners

	Traditional method with footprint making	**3D scans (visual light)**	**3D scans (laser beam)**
Time of measurement	10 minutes	10 minutes	7-8 minutes
Number of parameterts obtained	9 basic parameters (it is possible to increase the number of measurements)	It depends. We can take a measure only in one plane but we can also measure the calf	About 4 We can't measure the calf
Measurement in static conditions	YES (static plantogram)	YES	YES
Measurement in dynamic conditions	YES (dynamic plantogram)	NO	NO
Limitations	NO Only limitation is the anatomy of the foot	Measurements of the foot sole only From the photo of the foot negative from the foam	NO
The possibility of archiving data in a digitized form	NO Only for entering data to the computer databas. Plantograms are only 2D images of the foot	YES	YES Archiving in .stl i .scm .jpg
Disadvantages	- Long measurement time - Measurement error (human factor) - no information about the shape of the foot, we only get a numerical result (in 2D)	- Scanning requires a fully darkened room - Inability to conduct outdoor research without access to electricity	- Inability to conduct outdoor research without access to electricity - - High price of the scanner - in the case of some feet (deformed, children's), it is often necessary to correct manually measurement the foot shape, which, due to the inability to sense the individual places of the foot organoleptically, increases the risk of erroneous measurements - working in a room that is too bright is impossible

	Traditional method with footprint making	3D scans (visual light)	3D scans (laser beam)
	-Possibility to perform tests in all conditions (including field conditions)		- Short time of measurement; - Elimination of the human factor in measurement errors; - Ability to work with a foot scan in a 3D environment (modification and creation of an individual last, printing on a 3D printer) - Does not require a complete darkening of the room - the possibility of obtaining the shape of the foot, e.g. a cross-section in a given place.

Source: own study.

3.2. Comparison of the 3D scanners

3D scanners transfer a two or three-dimensional image of the foot sole to the computer where specialized software measures the feet and analyses the plantar side of the foot. It is necessary not only for measurement but also (what is more important) for correct fit of the appropriate insoles. Images of the foot obtained from the scanner are the base for the design and production of insoles, using e.g. CNC method or a 3D printing method.

The diversity of scanners translates into a heterogeneity of images that we are given while scanning the feet, and thus - different foot measurement algorithms. The method of measuring the scanned foot solid depends on the computer program that supports the given 3D scanner. Below we present the different types of 3D scanners.

The presented scanners allow to obtain an image of the foot body in 3D in various ways: using visible light or laser beam. Scanners based on laser light technology, although more expensive, are currently the most popular. The image obtained with their help is characterized by higher resolution. At the beginning of the twenty-first century, a popular and much cheaper alternative were scanners using a beam of

visible light. The resulting image was one much less accurate. Figure 5 shows the different images obtained with different 3D scanners.

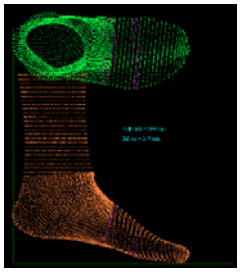
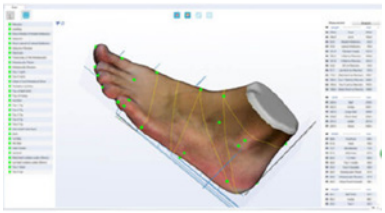
	
Footscanner FTS-4, IDEAS company	3D LASER FULL FOOT SCANER (VUPD-S), KOORDYNACJA company
Visual light used. Measurement accuracy: > 0,5mm Software: easy to use, allows you to take measurements between any 2 points lying on one plane	Laser beam used Measurement accuracy: 0,5mm Software: intuitive, easy to use, enables automatic diagnostics of longitudinal arch, toe deformities and heel angle

Fig. 5. Types of images obtained with different 3D scanners

Source: [KOORDYNACJA, IDEAS, materiały własne Łukasiewicz-ŁIT].

The obtained images differ significantly in the degree of accuracy of reproduction of the foot solid and resolution. In the case of scanners using a laser beam of visible light, the obtained image has a low resolution, the solid of the foot is not continous (we can see the lines or points). In addition, the scan time itself is long and multi-stage.

Measurements carried out at IPS Kraków (now: Łukasiewicz-ŁIT) with the use of a scanner showed large differences compared to the measurement performed using the traditional method. The degree of complexity of obtaining the image meant that in the length dimension the average difference between the obtained dimensions was 8.3mm [Gajewski 2006].

The image obtained from a scanner using laser light technology is much more accurate. The resulting solid is continous and allows you to perform more than 30 measurements based on the designed algorithm. The process of obtaining measurements

is fast and ranges from a few to several dozen seconds. The discrepancy in the results of anthropometric measurements is undoubtedly influenced by the use of an appropriate measurement method.

In table 2, there is shown the comparison of different techniques of foot measurement and anthropometric parameters which we received.

Table 2. Anthropometric parameters from different techniques of foot measurement

Parameter	foot measurement *in vivo*	plantogram	3D Scanner (visual light)	3D scanner (laser beam)
Foot length	Yes	Yes	Yes	Yes
Forefoot width	Yes	Yes	Yes	Yes
Ball girth	Yes	No	No	Yes
Instep girth	Yes	No	No	Yes
Heel girth	Yes	No	No	Yes
1st toe height	Yes	No	No	Yes
Ankle height	Yes	No	No	Yes
Clarke's Angle	No	No	No	No
Alfa angle	No	Yes	No	Yes
Beta angkle	No	Yes	No	Yes
Gamma angle	No	Yes	No	Yes
Varus/valgus angle	Yes	No	No	Yes
others	All kind of measurements are possible	All kind of measurements are possible as well as angles indicates	All kind of measurements are possible but the measure points have to be in one plane	The algorithm selects about 30 points and performs 43 measurements as a standard

** Based on Laser Full Foot 3DScaner, KOORDYNACJA company.*

The development of anthropometric tools simplify the method of measurements (increasing the precision of measurements, reducing duration of measurement and eliminating human mistakes). It is necessary to study the comparative analysis of the manual measurements and the 3D scanner measurements.

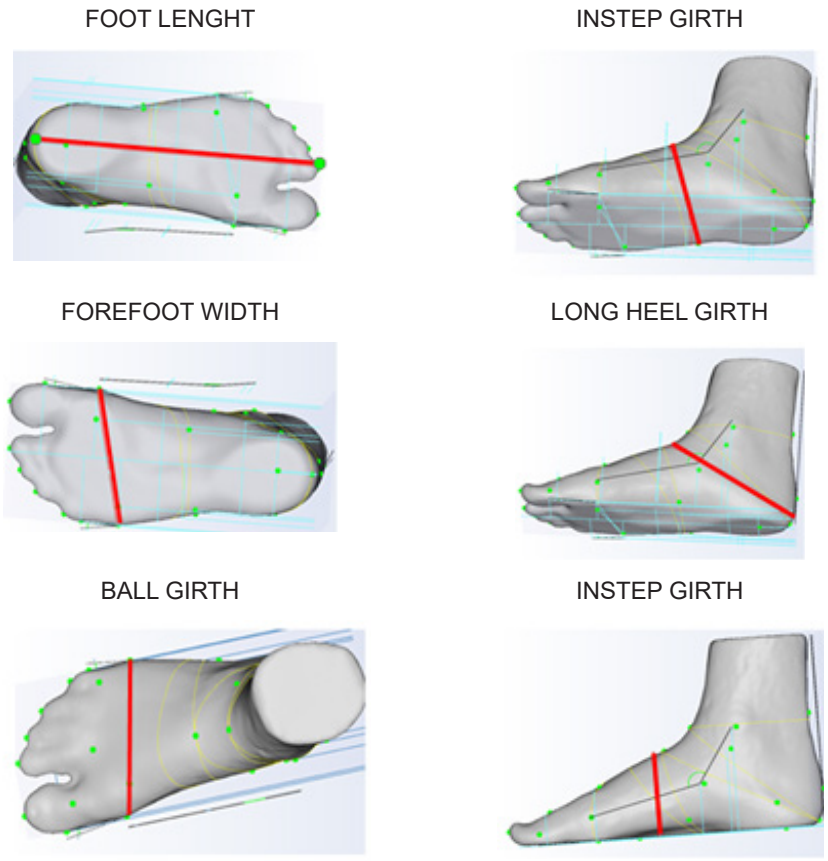


Fig.6. A method pf measuring anthropometric parameters by a 3D scanner

Research was carried out in a population of 500 people, aged 15-70. The study shows that the scanner's algorithm works properly in case of measuring slim feet without fat pads. In the case of an „untypical" foot, such as a foot with greater fat pads, the risk of a wrong detection of the anthropometric point is greater.

Figure 7 shows the way of measuring the parameter called „long heel girth", on the foot at 2 and 7 years of age. In the case of younger children, adiposis of children's feet causes wrong detection of anthropometric points. In this case, there is a manual correction in the computer program needed.

2 years old
INCORRECT

7 years old
CORRECT

Fig. 7 Incorrected measure (long heel girth) in 2 years old girl

Source: [materiały własne Łukasiewicz-ŁIT].

A study of 461 children aged 6-10 revealed that despite using various techniques of anthropometric measurement does not affect the quality of obtained results. Moreover, the results are similar and practically and any measurement method does not affect the shape of the last/interior of the footwear [Piotrowska et al. 2021a]. Similar results were obtained when analysing the population of 50 adults aged 15-70 years [Piotrowska et al. 2021b]. However, in both studies, in some cases there was necessary a manual intervention in case of 3D scanners.

4. Discussion

Over recent years, 3D scanning and visualisation technology has been developing intensively. These tools are very useful in creating algorithms for adjusting objects (e.g. lasts, shoes) to the obtained 3D scans, including feet [Witana et al. 2004]. 3D Scanning and 3d printing techniques are used in producing customized/ personalized footwear. The mass production requires creating footwear on the last which has an average dimensions which will fit the feet of the largest group of users in the population.

The effect of 3D technology is the development of new anthropological methods. Modern tools enable faster and more accurate acquisition of the data necessary to

monitor the population in terms of the dynamics of changes in body dimensions. This information is crucial in the design of products such as footwear, clothing, personal protective equipment and even hearing aids [Hrynyk et al. 2016; Fu & Luximon 2022]. Thanks to modern methods, easier and more universal digitization of research results is possible. It not only offers an opportunity to archive data, but also is the starting point in the product customization (personalization) process.

The modern consumer is aware of his needs and requires the greatest possible personalization of products while maintaining the highest quality and the lowest possible price [Zhang et al. 2011].

In the case of footwear, the greatest possible fitting /adjusting the dimensions of footwear (and last) to the foot dimensions is necessary. Not only from the customer's needs point of view but also because of the safety aspects of using products.

The 3D scanning technology using a laser light beam offers a great possibilities. High accuracy of reproduction of the foot solid translates into accuracy and precision of measurement. However, it is necessary to modify the existing algorithms for performing foot measurements, which give some errors in data. It is very often in case if more fatty children's feet.

5. Conclusions

In modern anthropology, advanced measuring methods of human feet have already been implemented. They enable proper management of footwear production technology and thus increase the quality of the final product. 3D scanning is undoubtedly the future of this discipline of knowledge. The development of scanning technology may make it possible in the future to perform dynamic scans, thanks to which it will be possible to assess the variability of foot dimensions while walking.

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APPLICATION OF LEVAN-RICH DIGESTATE EXTRACT IN THE PRODUCTION OF BODY CARE LOTIONS

ARTUR SEWERYN[1], TOMASZ WASILEWSKI[2], NATALIA KOROLSKA[*3]

[1] *Department of Industrial Chemistry, Faculty of Chemical Engineering and Commodity Science, University of Technology and Humanities in Radom; ONLYBIO.life S.A., ul. Jakóba Hechlińskiego 6, 85-825 Bydgoszcz, Poland,*
e-mail: a.seweryn@uthrad.pl
[2] *Department of Industrial Chemistry, Faculty of Chemical Engineering and Commodity Science, University of Technology and Humanities in Radom; ONLYBIO.life S.A., ul. Jakóba Hechlińskiego 6, 85-825 Bydgoszcz, Poland,*
e-mail: tomasz.wasilewski@uthrad.pl
[3] *Department of Industrial Chemistry, Faculty of Chemical Engineering and Commodity Science, University of Technology and Humanities in Radom,*
[*] e-mail: nataliakorolska98@gmail.com

Abstract
The study presented in this paper was aimed to evaluate the applicability of levan-rich digestate extract in body care lotions. It was presumed that the introduction of this type of extract would produce a body lotions with beneficial properties.
It was found that the introduction of a levan-rich digestate extract into body lotion prototypes resulted in lower viscosity values. Colorimetric analysis indicated that the addition of the plant raw material influenced the color change of the samples. The determined values of transepidermal water loss (TEWL) and skin hydration after its application indicated a significant improvement of skin barrier function.

Keywords: body care lotions, digestate extract, viscosity, hydration, TEWL

Introduction

Recently, the activities of companies in the field of cosmetics production focuses mainly on implementation of sustainable growth solutions for production and consumption. Consumers' concerns regarding cosmetics safety, chemical ingredients and toxic substances exposure, influence of packaging from the cosmetics industry on environment and problem with their disposal pose a great challenge for the cosmetics industry. This topic is receiving increasing attention. Creating postulates of sustainable development in the production of cosmetics has thus become an answer of producers for the consumers' concerns regarding cosmetics in terms of their use and environmental impact. By definition, activities leading to obtaining a sustainable cosmetic product should include all product life cycle phases. In reality, however, in many studies on the topic, the cosmetic product planning and production are indicated as key phases for its sustainability. Studies in this area take into account mostly use of raw materials of natural origin for cosmetics production. Choice of proper raw materials of natural origin may be a big challenge due to reported problems, such as: low yield, instability, aesthetic restrictions or safety of use. Maintaining a proper, expected by consumer quality of the cosmetic is an important aspect [Amberg & Fogarassy 2019; Bom et al. 2019; Kolling et al. 2022]. Emerging problems are a driving force for a growing number of scientific papers regarding cosmetics based on natural raw materials [Costa et al. 2021; Fresneda et al. 2020; Luengo et al. 2021]. They concern use of plant extracts [Bujak et al. 2021; Bujak et al. 2022] or surfactants of natural origin [Seweryn & Bujak 2018]. An important trend of research is the topic of raw materials of biotechnological origin in cosmetics. Particularly interesting seems to be use of biosurfactants [Vecino et al. 2017] and biopolymers [Aranaz et al. 2018; Gilbert et al. 2013], which, according to the source data, are completely safe for consumers and environmentally-friendly.

A relatively new trend of research is assessment of possibility of application of extracts of digestates obtained via biotechnological processes from the vegetable matter, which represents waste from other production processes. It is important that the extracts of digestate constitute a mixture of various chemical compounds with

known biological and cosmetological effects, e.g.: mineral salts, proteins or fatty acids. By choosing proper process conditions and bacteria species, it is possible to obtain a raw material with ingredients suited to particular cosmetic applications [Konkol et al. 2019; Sivamaruthi et al. 2018] . For example, use of *Bacillus subtilis* bacteria allows for obtaining raw material with a significant share of surfactin [Lewińska et al. 2022] or levan [Domżał-Kędzia et al. 2019]. These ingredients have a large application potential in cosmetics. Surfactin, as a biosurfactant, shows surface activity, has low irritating potential, is non-toxic and fully biodegradable [Fei et al. 2020]. Whereas levan as a biopolymer - fructose derivative has antioxidant and moisturizing properties, and is non-toxic for human cells [Domżał-Kędzia et al. 2019]. As a polymer it can also decrease irritating properties of washing cosmetics based on surfactants [Wasilewski et al. 2022; Seweryn 2018]. Despite proven properties of levan, beneficial from the point of view of application in cosmetics, there is no information on how the use of levan rich in digestate extract will translate into quality parameters of finished cosmetic products. For this reason, the Authors of the study attempted to use of levan rich in digestate extract in body balms. The aim of the study was showing possibilities of use of this type of raw material of biotechnological origin in emulsion cosmetics and assessment of the influence of concentration of this ingredient on basic quality parameters developed based on the original recipes of the prototypes of the products. 4 samples of body care lotions were prepared, and the maximum concentration of the extract of digestate used in prototypes was 10 wt.%. It was assumed that addition of this type of extract will allow for obtaining body lotions with favourable functional and skincare properties. The reference sample in the research was the cosmetic's prototype without the addition of the extract of digestate. Viscosity and colour of balm prototypes were evaluated, as well as transepidermal water loss (TEWL) after their application on skin.

1. Material and methods

1.1. Materials

The body care lotions were made with raw materials of plant origin and approved for the production of natural cosmetics: Cetearyl Olivate/ Sorbitan Olivate (trade name: Olivem 1000, supplier: B&T), Glyceryl Stearate (trade name: Tegin Pellets, supplier: Evonic), Cetearyl Alcohol (trade name: Sabowax AO, supplier: SABO S.p.A), Capric/Caprilic Triglicerides (trade name: Crodamol GTCC, supplier: Croda), Argania Spinosa Oil (trade name: olej arganowy kosmetyczny, supplier: PPH Standard), Glycerin (trade name: Gliceryna roślinna farmaceutyczna, supplier: Brentag), Tocopheryl Acetate (trade name: Octan tokoferolu, supplier: PPH Standard), Sodium Benzoate and Potassium Sorbate as preservatives (trade name: KEM BS, supplier: Akema Fine Chemicals, Italy), *Bacillus Subtilis* Ferment Extract, Propanediol, Pentylene Glycol, Levan (trade name: InbioLev, supplier: InventionBio), Lactic Acid (trade name: kwas mlekowy, supplier: POCH Poland), distilled water.

1.1.1. Development of formulations and technologies to obtain body lotion containing digestate extract

A model body care lotions were prepared. All the components used were in line with EcoCert and COSMOS requirements. The formulations are shown in Table 1.

Table 1. Model formulations of body care lotion containing digestate extract.

	Name according to INCI [1]	BL_0	BL_1	BL_2	BL_3	BL_4
1	Capric/CaprylicTriglycerides	7.0				
2	Argania Spinosa Kernel Oil	3.0				
3	Cetearyl Olivate / Sorbitan Olivate	3.0				
4	Glyceryl Stearate	2.0				
5	Cetearyl Alcohol	1.5				

	Name according to INCI [1]	BL_0	BL_1	BL_2	BL_3	BL_4
6	Tocopheryl Acetate	0.1				
7	*Bacillus* Ferment Extract, Propanediol, Pentylene Glycol, Levan	0	2.5	5.0	7.5	10.0
8	Glycerin	2.0				
9	Sodium Benzoate, Potassium Sorbate	0.5				
10	Aqua	to 100				
11	Lactic Acid	do pH 5.5				

[1] *INCI= International Nomenclature of Cosmetic Ingredients.*

Source: own study.

The components of the hydrophobic phase (items 1 to 6) and the hydrophilic phase (items 8, 10) were placed in separate beakers, heated to a temperature of 75 ^{O}C and thoroughly mixed. The phases were then combined and stirred until cooled to room temperature. After cooling, the preservative (item 9) was added to the body lotion and mixed thoroughly. The pH of the formulation was adjusted (item 11). In the last step of the extract was added to each portion body lotion and mixed thoroughly.

1.2. Methods

1.2.1. Stability

The stability of the body lotions was assessed visually and by stress testing. The visual evaluation of body lotions was performed by evaluating their appearance, consistency, homogeneity, stability, or signs of instability such as: separation, coalescence, etc. Resistance to microorganisms was also checked by observing the appearance of mould or other symptoms of microbiological contamination present in the preparation. Visual evaluation of prepared emulsions was performed immediately after their preparation and also after a specified time (after 1, 7 and 14 days).

The centrifugal test was performed using a centrifuge type Rotofix 32A (producer Hitch), under the conditions of rotational speed equal to 3000 rpm. The thermal test

was carried out by subjecting the preparations alternating to low (t = 4°C, the cooler Amica) and high (t = 40°C incubator ST-1 by Pol-Eko Aparatura) temperatures for a period of 14 days. The observation of the preparations was carried out every 24 hours. The prototypes were visually evaluated after testing.

1.2.2. Viscosity

Viscosity measurements were conducted using a Brookfield RV DVIII viscometer. The measurements were performed at the rotational speeds of 1, 10, 50, rpm and at a temperature of 25°C was used. Every measurement was performed five times. The results shown in the graphs are averaged values.

1.2.3. Determination of the Color Parameters

Samples of cosmetics with digestate extracts were tested at room temperature, 48 h after their preparation. A CHROMA METER CR-400 (Konica Minolta, Sensing Inc., Japan) was used to evaluate the color parameters (CIELAB coordinates). The CIELAB system was defined by the International Commission on Illumination in 1978. It is based on three color attributes: L*, a*, b*, where L* is a brightness variable proportional to the value in the Munsell system, and a* and b* are chromatic coordinates. The a* and b* coordinates indicate positions on the red/green and yellow/blue axes, respectively (+a = red, −a = green; +b = yellow, −b = blue).

General color difference ($\Delta E_{\text{cosmetic with digestate extract / base cosmetic}}$) was calculated according to the following formula:

$$\Delta E_{\text{cosmetic with digestate extract / base cosmetic}} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1.1)$$

where: where: ΔL*, Δa*, and Δb* are the mathematical differences between cosmetic with extracts L*, a*, b* and base cosmetic L*, a*, b* values [Wan et al. 2019; Mokrzycki & Tatol 2011].

1.2.4. Skin moisturisation after application of the prototype cosmetic

The skin moisturising effect triggered by the analyzed samples was evaluated on the basis of a specially designed original methodology [Ziemlewska et al. 2021; Seweryn & Bujak 2018]. Methodology was designed according to the recommendations of the apparatus producer (Courage-Khazaka). The tests were conducted using a Corneometer CM 825 probe from Courage-Khazaka (Köln, Germany) connected to a Cutometer MPA 580 adapter. Testing was carried out at 30, 60, 120 and 180 minutes after application. It is assumed that: moisturising effect (expressed as a percentage relative to baseline) is the amount of increase in skin hydration at time t after application of the product, expressed as a percentage.

1.2.5. Assessment of transepidermal water loss (TEWL)

Transepidermal water loss triggered by the analyzed samples was evaluated on the basis of a specially designed original methodology [Wasilewski et al. 2016]. Methodology was designed according to the recommendations of the apparatus producer (Courage-Khazaka). The tests were conducted using a Tewameter TM 300 probe from Courage-Khazaka (Köln, Germany) connected to a Cutometer MPA 580 adapter. Testing was carried out at 30, 60, 120 and 180 minutes after application. The TEWL value has been given in the unit $g/h/m^2$.

2. Results and Discussion

2.1. Stability

Stability is an elementary condition, which should be met by the cosmetics in the form of an emulsion [Zieliński 2006]. The evaluation of the stability of emulsions consisted in carrying out two types of tests: to the action of centrifugal force and thermal. All the lotions passed the centrifugal and thermal tests. On this basis, the original body care lotion were qualified for further tests. No symptoms of emulsion unstable were observed in the visual assessment.

2.2. Viscosity

Viscosity is a very important parameter for the quality assessment of emulsion cosmetics [Kwak et al. 2015; Bujak et al. 2021]. In the case of body care lotions it determines their properties, e.g.: absorption, spreadability on the surface of the body and ease of dispensing from the package. Figure 1 presents the results of viscosity measurements performed for body lotions prototypes containing digestate extract.

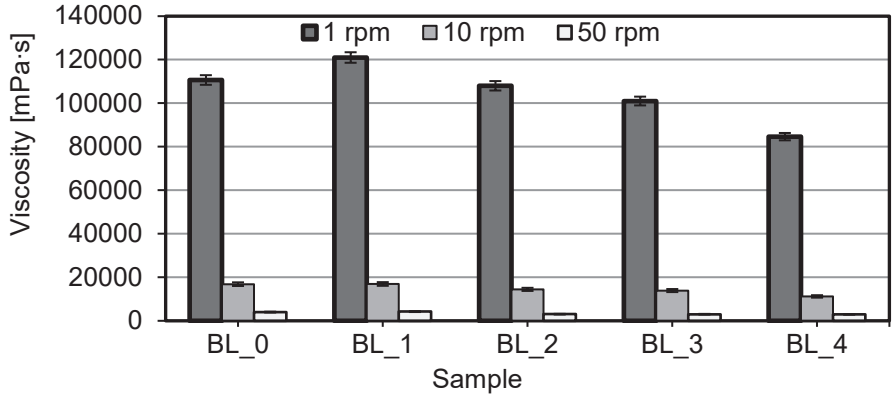

Fig. 1. Viscosity for the body care lotions containing digestate extract

Source: own study.

The obtained results of dynamic viscosity for the body lotions prototypes based on the extract of digestate indicate that with the increase of the spindle speed value and the increase of the concentration of the digestate extract, the dynamic viscosity decrease was observed in the samples. The most significant, as much as almost 10-fold is the viscosity decrease at spindle speed 10 rpm as compared to spindle speed 1 rpm. So big decreases of viscosity under the influence of the rotating spindle indicate the susceptibility of produced emulsions to destruction under the influence of shear forces. It has an impact on dosing of the product from packaging. At the moment of product application from the tube, under compression of the packaging surface, the decrease of viscosity will occur, guaranteeing free flow of the product from the tube. In case of the analysed prototypes of products, all of them tend to show

a rapid viscosity decrease under the influence of shear forces. Thus, it can be assumed that these balms will be easy to apply to skin and distribute on its surface [Brummer & Godersky 1999; Khan et al. 2011]. Analysing the influence of the concentration of the extract, a significant decrease of the determined parameter with the increase of the concentration of the extract is observed. At a speed of 1 rpm, the value of dynamic viscosity of the C_4 composition with the highest analysed concentration of the digestate extract, as compared with the reference sample, decreases by almost 30000 mPa·s. However, the obtained viscosity values for the cosmetics prototypes are still acceptable for the body care lotions. Analysing the viscosity value at higher speeds, it was also observed that the determined parameter decreases with the increase of the extract concentration in the sample. These decreases are not so sudden, as in case of values obtained at the speed of 1 rpm. As shown in the study, the concentration of the extract used for producing prototypes of the product in the form of emulsion affects their viscosity, and therefore their consistency, which is assessed in the products by consumers. This parameter influences sensory parameters of the assessed body lotions [Moravkova & Filip 2016].

2.3. Colorimetric evaluation

Plant extracts rich in bioactive substances, which additionally have the ability to impart color, can be a valuable raw material for the cosmetics industry [Wan et al. 2019]. Results related to the marked and calculated color parameters for model body lotions are presented in Table 2.

Table 2. Color parameters for cosmetic (body lotion).

	L*	a*	b*	$\Delta E_{\text{cosmetic with digestate extract / base cosmetic}}$
BL_0	63.46	−1.44	1.70	--------
BL_1	62.52	−1.19	1.86	1.00
BL_2	62.45	−1.08	2.71	1.47
BL_3	62.35	−1.30	2.95	1.68
BL_4	62.14	−1.20	3.85	2.53

Source: own study.

It was found that the addition of a digestate extract did not significantly modify the appearance of the body care lotion prototypes. This is confirmed by the relatively low values of the $\Delta_{\text{Ecosmetics with digestate/base cosmetic}}$. The values of $\Delta_{\text{Ecosmetics with digestate/base cosmetic}}$ are in the range 1.00–2.53. This means that the difference in color is only noticeable for an experienced observer [Wan et al. 2019; Mokrzycki & Tatol 2011]

2.4. Moisturising effect

The post-ferment extract introduced in body lotions contains large amounts of levan, minerals, flavanoids, polyphenols or amino acids or proteins [Wsilewski et al. 2022; Domżał-Kędzia et al. 2019] . These ingredients due to the presence of hydroxyl groups in the molecules, may form hydrogen bonds with water and hold moisture in the skin. It impacts not only the skin moisture level. Moreover may lower the amount of water that evaporates of epidermis (transepidermal water loss, TEWL) [Bonté 2011]. Figure 1 presents the results of viscosity measurements performed for body care lotions prototypes containing digestate extract. Figure 2 and Figure 3 presents the results of moisturising the skin measurements and TEWL measurements performed for prototypes body care lotion containing digestate extract.

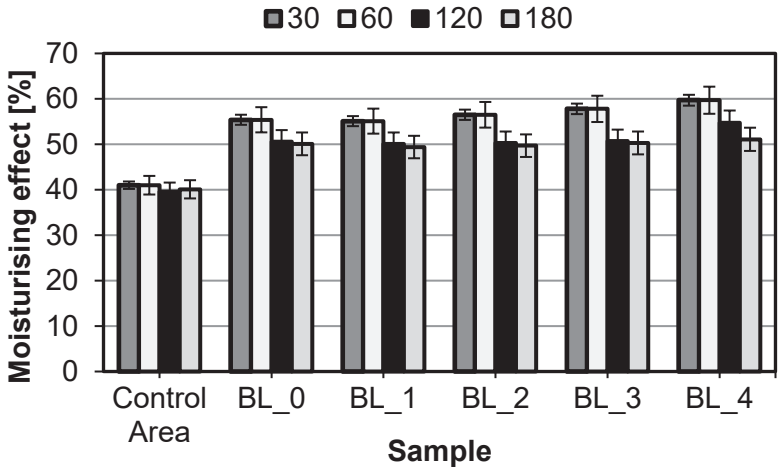

Fig. 2. Influence of prototypes body care lotion containing digestate extract on skin hydration

Source: own study.

The application of the analyzed cosmetics on the skin causes a significant increase in skin moisture level. A total of 60 min after cosmetic application, all analysed compositions body lotion showed the strong moisturizing properties. In relation to the control field (without body lotion application), a rise in the analysed parameter by over 10 units was noted. A total of 180 min after application of the analyzed compositions on the skin not significant decrease in skin moisture was noted, but the observed values were significantly different from the control area. The skin moisture level observed for of all analysed body lotions was about 20% higher than for the control area. The concentration of the extract was not shown to have an effect on the moisturising properties of the studied emulsion cosmetics.

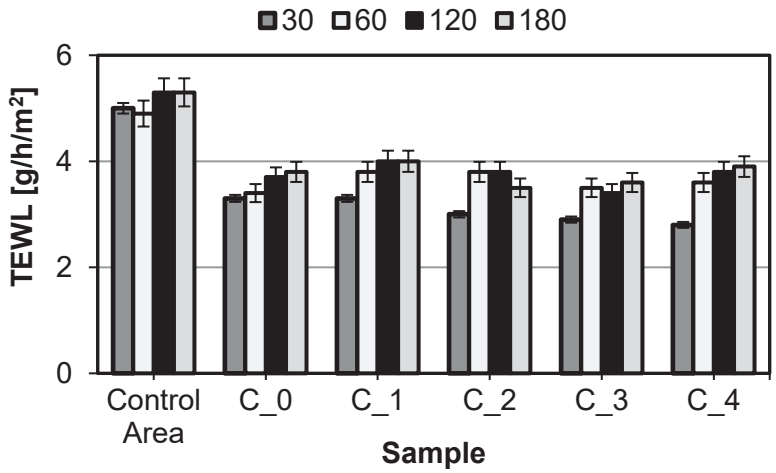

Fig. 2. Influence of prototypes body care lotion containing digestate extract on TEWL

Source: own study.

In measuring TEWL (Figure 3), the same correlation was obtained as for skin hydration (Figure 2).The strongest properties related to TEWL decrease were observed for prototypes body care lotion containing digestate extract. TEWL value 30 min, 60 min, 120 min and 180 min after application of cosmetics was lower in relation to the control area field by about 40%, 27%, 26% and 26%, respectively. The addition

of post-fermentation extract had little effect on the TEWL value of the body lotion prototypes analysed in the study. The study did not show any influence of the extract concentration on the tested parameter. The results obtained indicate that the cosmetic prototypes analysed provide good skin moisturisation. In addition, they are effective in protecting against excessive water loss.

3. Conclusions

This article analyses the possibility of producing body care lotions through the application of digestate extract. The studies reported in this article show that the substitution of aqua with a raw material of natural origin leads to a obtain stable compositions. The obtained viscosity measurement results indicate that the addition of the digestate extract slightly decreases the evaluated parameter. The observed significant decrease in viscosity with an increase in the rotational speed of the measuring spindle for all the analysed formulations confirms that the prototypes have positive application characteristics, will easily dose from the package and will spread on the skin surface. The calculated $\Delta E_{\text{cosmetics with digestate/base cosmetic}}$ values proves that the color difference is only slightly discernible, only by an experienced observer. The obtained results for cosmetic prototypes indicate that they have a moisturising effect. In addition, they are effective in protecting against excessive water loss from the epidermis. As shown by the analysis, the application of the digestate extract makes it possible to obtain body care lotions with a high level a protective effect and appropriate functional properties.

4. Acknowledgements

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UNIVERSITY STUDENTS 'INTEREST IN PURCHASING ISOTONIC BEER

MICHAŁ ŚWITALSKI[1], AGNIESZKA RYBOWSKA[2]

[1]*Faculty of Management and Quality Science, Gdynia Maritime University,*
e-mail: michal.switalski@sd.umg.edu.pl
[2] *Faculty of Management and Quality Science, Gdynia Maritime University,*
e-mail: a.rybowska@wznj.umg.edu.pl

Abstract
The contemporary beer market in Poland is extremely modern, innovative and competitive. Breweries compete for potential customers not only through the high quality of alcoholic beverages, but also through a unique, innovative product offer. An example of such an action is an attempt to introduce isotonic beers to the market.
The aim of the study was to identify students' interest in purchasing isotonic beer and to determine their awareness of beer osmolality, with particular emphasis on gender, year of study and physical activity of the respondents. The objective was accomplished by conducting a study that employed an online survey method. The study group consisted of 162 students aged 18-28. They were full-time and part-time students of Tri-City universities.
The research results show a potential chance to increase sales of isotonic beer on the beer market. The vast majority of the surveyed students declared occasional or regular physical activity, and almost half of them were interested in the occasional or regular purchase of isotonic beer. Nevertheless, awareness of the osmolality of conventional beer varies among respondents, which shows the need to educate and make young consumers aware of it.
The presented results may constitute valuable knowledge for breweries and thus suggest the direction of research aimed at introducing a wider offer of isotonic beers, as well as the direction of conducting marketing activities.

Keywords: isotonic beer, university students, functional beverages, osmolality

Introduction

Despite the fact that beer is a drink known for millennia, the modern beer market is extremely modern, innovative and competitive. Only in 2021, 38 new breweries started operating, and the plants offered consumers 2.368 new beer premieres. Such a wide selection on the market creates the need to compete for potential customers not only through the good quality of alcoholic beverages produced, but also through attempts to stand out on the market. Such activities include, for example cooperation with foreign breweries, offering barrel-aged beers, introducing specific hops into the recipe, or extreme additives such as e.g. oscypek, tobacco or mussels [Groń & Papińska 2022]. Selected breweries decide to give the beer additional functional properties. An example of this activity is several attempts to introduce isotonic beers to the market, e.g. Power Ale isotonic beer from Browar BK or a series of Birell beers from Carlsberg Polska. The beer with isotonic properties currently available on Polish market is Zero to Hero from the Inne Beczki brewery. The failure of selected brands in keeping isotonic beer on the market may result from the lack of interest in this product by consumers. As Waliczek [2015] points out, it is the consumer who plays a fundamental role in each of the stages of product design and implementation and decides about the acceptance of a given product on the market. Babicz-Zielińska [2011] states that the key to the acceptance of functional food is the belief in a positive impact on human health. As Luboińska research results [2018] shows, also university students students pay great attention to the on the effects of the functional product on their bodies.

Young people, including university students could be a potential group that may be interested in purchasing innovative beers with functional properties. As researchers mention, students and young people are characterized not only by a high frequency of beer consumption [Jąder 2013], but also by eager search for new products that meet their expectations [Płaziak & Szymańska 2014].

Therefore, it is necessary to conduct research on the interest in isotonic beer by students as a potential group of consumers, representing an opportunity for increased sales and thus a competitive advantage of breweries.

The interest in the above subject is the result of previous research [Świtalski & Rybowska, 2021a], which showed that nearly 78% of surveyed students were interested in purchasing isotonic drinks based on natural ingredients and colourants. Such an offer of a drink may be beer, which is produced from natural ingredients (water, malt, hops and yeast) and thus may be a response to the expectations of young adults.

The above topics constitute a research gap. Polish youth and students have been assessed many times in terms of their awareness, attitudes and preferences regarding functional drinks, especially energy drinks. However, the subject of Polish students' interest in purchasing isotonic beer has not been discussed in previous research and scientific articles.

1. Isotonic beverages - product characteristics

Isotonic drinks belong to the group of functional drinks. The ingredients of conventional isotonic drinks are water, carbohydrates (including glucose, maltose, maltodextrin), sodium, potassium, magnesium, chlorine and vitamins [Pivnenko et al. 2018; Stasiuk & Przybyłowski 2017; Świtalski et al. 2020]. Their primary purpose is to replace fluid, electrolytes and glucose in the form of glycogen lost due to physical activity [Stasiuk & Przybyłowski 2017; Styburski et al. 2020].

The basic parameter that characterizes isotonic drinks is osmolality. According to the definition proposed by Pivnenko [2018], the osmolality coefficient is the sum of all kinetically active particles, such as cations, anions and non-electrolytes, diluted in 1 kg of solvent (water). These molecules regulate the osmosis process and thus determine the degree and speed of absorption of aqueous solutions by the intestines [Mettler et al. 2006; Pivnenko et al. 2018]. The ingredients that influence the osmolality of beverages are mainly carbohydrates and minerals.

As EFSA (European Food Safety Authority) points out, the osmolality inherent in isotonic drinks is considered to be an osmolality in the range of 300 (+/- 10%) mOsm / l kg of solvent (water) [EFSA 2011]. This value is close to the osmotic pressure of human blood, thus it ensures relatively fast absorption of water and ions of minerals [Stasiuk & Przybyłowski 2017].

The target group of sports drinks consumers are athletes and physically active people. The consumption of these beverages is justified for people undertaking physical exercise lasting more than 60 minutes [Styburski et al. 2020]. Their unjustified consumption may result in a greater supply of sodium chloride and simple sugars, which are in excess in the diet of the majority of the population in Poland [Świtalski & Rybowska 2021b].

2. Isotonicity of beer

Due to the fact that students are focused on the effects that a functional product benefits, it is necessary to take care of the appropriate quality and isotonicity of functional drinks. As Barska [2013] recognizes, quality is one of the 5 most important factors for young adults. The technology for creating qualitative isotonic beer may differ from that used for conventional sports drinks.

2.1. The influence of alcohol on the isotonicity of beer

Commonly consumed beers with an alcohol content of around 4 - 6% have osmolality values much higher than the EFSA assumptions. It has been shown, inter alia, in the studies by Tarancon and Lachenmeier [2015], in which the osmolality of beers was about 709 - 1391 mOsm / kg. For strong beers, these values even exceeded 1600 mOsm / kg. These values largely resulted from the alcohol content in the beverages. Alcohol belongs to the so-called ineffective osmoles. This compound easily penetrates the semipermeable membranes and does not affect the osmosis phenomena like the aforementioned carbohydrates or minerals which do not or poorly penetrate the semipermeable membranes. Ineffective osmoles presence in a solution (drink) may, however, increase the determined osmolality compared to the effective osmolality [Olędzka-Oręziak et al. 2017].

It is essential, due to the disturbance of the osmolality measurement, that isotonic beers should be alcohol-free or low-alcoholic. An additional argument in favor of creating non-alcoholic isotonic beers is the diuretic effect of alcohol on the human body. It is assumed that beverages with an alcohol content > 2% show a diuretic

effect and a very weak hydration [Urdampilleta et al. 2015; Frączek et al. 2019]. Consuming beer gives a negative fluid balance (1l of standard beer causes a loss of about 1.4 l of fluid) [Mizera 2017], which, after exercise, may lead to an increase in dehydration and even reduce the level of fluid in the intracellular space [Frączek et al. 2019; Friedrich 2020]. Among other unfavorable effects of consuming higher doses of alcohol, disturbances in regeneration of damaged muscles of an athlete caused by a negative influence on immunoendocrine functions, blood flow and protein synthesis are highlighted [Barnes 2014].

2.2. An example of isotonic beer technology

Key aspect in the production of isotonic beer is to design a beer recipe which provide the appropriate content of individual beer components: alcohol, carbohydrates and minerals. It is important to pay attention to factors such as the quality parameters of the malt (including extract, moisture content and diastatic power), mineral composition and planned modification of the water composition (addition of individual minerals depending on the beer style), mashing scheme (enabling starch gelatinization and activity of individual enzymes), the conditions and time of fermentation, and the selection of an appropriate yeast strain.

An example of the isotonic beer production process was presented by De Fusco et al. [2019]. Its stages are shown in Fig. 1.

In the process proposed by De Fusco et al. single-temperature mashing was used (70°C). Keeping the mash at this temperature allowed for the creation of optimal conditions for the action of α-amylase. This enzyme, responsible for breaking the internal bonds of the starch chain, allowed to decompose the starch present in the mash into linear and branched dextrins belonging to sugars not fermented by yeast. Although a certain amount of fermentable sugars is formed at this temperature, it is much lower than in the case of optimal conditions for the action of β-amylase [Hu et al. 2014]. Thus, the mashing method used in the research allowed to obtain a wort with a lower degree of attenuation, which reduced the alcohol content in the final product. Maintaining a low level of alcohol in beer also resulted from the use of

the intermittent fermentation. Centrifugation was used to premature removal of the yeast, and the fermentation time was 2 days instead of the standard 7 days.

To ensure the proper amount of minerals and to comply with the standards for sports drinks sodium chloride and potassium phosphate were added to the green beer before the maturation stage. Then the beer was pasteurized and carbonated [De Fusco et al. 2019].

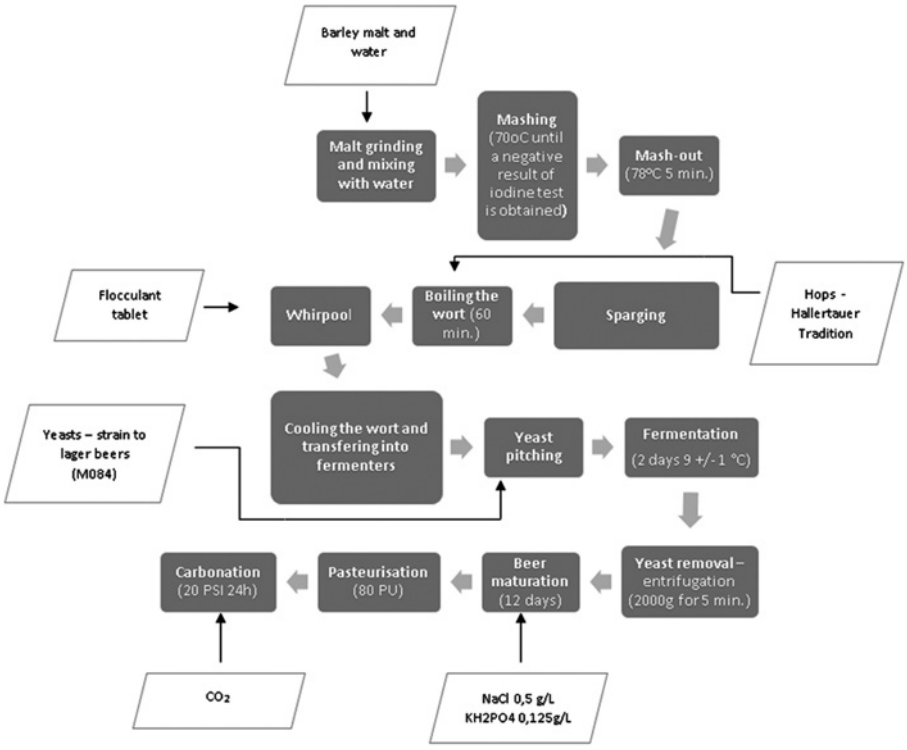

Fig. 1. The process of producing isotonic beer

Source: Source: own study based on [De Fusco et al. 2019].

The presented process made it possible to obtain low-alcohol (0.26% alcohol), isotonic beer (osmolality was 282 +/- 3 mOsm kg -1) with the content of minerals comparable to sports drinks, pH value close to 5 and sensory quality similar to conventional beer.

3. Aim of the study and research methodology

The above chapters organize information on the characteristics necessary to create isotonic beer and show the possibility of its creation (even in small breweries). However, before such beer is introduced to the market, it is necessary to examine interest in purchasing this type of product by selected groups of consumers.

The aim of the study was to identify students' interest in purchasing isotonic beer and to determine their awareness of beer osmolality, with particular emphasis on gender, year of study and physical activity of the respondents.

The objective was accomplished by conducting a study that employed an online survey method. The questionnaire examined the interest in purchasing isotonic beer and the respondents' awareness of the isotonicity of beer.

The study group consisted of 162 students aged 18-28 (the average age of the respondents was 23). Full-time and part-time students of Tri-City universities (Gdańsk University of Technology, Gdynia Maritime University, Medical University of Gdansk, University of Physical Education and Sport in Gdańsk, Gdańsk School of Banking and the University of Social Sciences and Humanities in Sopot) were surveyed. The group consisted of 65.43% women and 34.57% men attending first-cycle (60.55%) and second-cycle (39.45%) studies.

The surveyed respondents showed diversified physical activity, which is presented in Table 1.

Table 1. Respondents' physical activity

Declared physical activity	Percentage of respondents
Yes, I do sports regularly:	37.04
• Workouts lasting less than 60 minutes • Workouts lasting 60 minutes and longer	10.49 26.55
I do physical activity occasionally	46.91
I don't do sports	16.05

Source: own study.

Over 80% of them declared that they are physically active. The most numerous group were people who occasionally decided to exercise. More than 1/3 of the respondents declared regular participation in trainings, and 1/4 attended trainings lasting over 60 minutes. The above-mentioned data on the respondents' physical activity justify the choice of students as potential consumers of isotonic beer.

Statistical analysis was performed in the STATISTICA program. Statistical relationships were determined with the use of a non-parametric measure - the Spearman rank-order correlation coefficient. Correlations at the value of $p \leq 0.05$ were considered statistically significant. To interpret the correlation coefficients convention proposed by Guilford were used.

4. Results

The results of the research concerning the assessment of the respondents' awareness of the isotonic nature of beer showed that the respondents were highly aware of the isotonicity of beer (Table 2).

Table 2. The respondents' awareness of the isotonicity of beer (%)

Attitude regarding the statement "Beer is an isotonic drink"	Total	Women	Men	First-cycle students	Second-cycle students
Strongly disagree	22.84	22.60	23.21	20.22	26.03
Disagree	31.48	35.85	23.21	28.09	35.62
I neither agree nor disagree	32.72	33.02	32.14	38.20	26.03
I agree	10.49	6.60	17.86	11.24	9.59
I strongly agree	2.47	1.89	3.57	2.25	2.74

Source: own study.

Most of the respondents (over 53%) did not agree with the statement that beer is an isotonic drink. Respondents answered the question correctly. Most of the beers available on the market are hypertonic drinks, and only a few non-alcoholic beers can have the osmolality appropriate for isotonic drinks. Similarly high awareness of the definition of an isotonic drink was also demonstrated in studies on the group of physically active adolescents (Joachimiak & Szołtysek 2013) and young adults (Przeor et al. 2016). At the same time, 1/3 of the respondents could not clearly answer the question about the isotonicity of beer. This may be due to the presence of false information about the isotonic properties of the drink on selected popular websites. A greater percentage of people considering beer as an isotonic drink occurred in the group of men, which may be due to the attempt to justify the consumption of this drink with health issues. Both more women and second-cycle students disagreed with the statement (Table 2).

Another question asked to the respondents made it possible to determine their interest in purchasing isotonic beer. The individual response rates are presented in Table 3.

Tabela 3. The respondents' interest in purchasing isotonic beer, considering differences in gender and year of study (%)

Declaration of purchase isotonic beer	Total	Women	Men	First-cycle students	Second-cycle students
Yes, I am interested in purchasing regularly	8.43	6.38	11.11	2.13	16.67
Yes, I am interested in occasional purchase	44.58	44.68	44.44	51.06	36.11
No, I'm not interested in purchase	46.99	48.94	44.44	46.81	47.22

Source: own study.

More than half of the respondents were interested in buying isotonic beer. However, the vast majority of them only occasionally declared willingness to buy such a drink. Almost half of the respondents (47%) were not interested in choosing this type of drink for sportsmen. More interest in buying isotonic beer was seen in men than in women group. A higher percentage of people declaring buying isotonic beer regularly was observed in the group of students 4-5 years of study compared to the group of first-cycle students (Table 3).

Due to the varied declared physical activity of the respondents, the responses regarding the interest in purchasing isotonic beer were analysed taking into account these data. The responses by each group are presented in Table 4.

Table 4. The respondents' interest in purchasing isotonic beer, considering differences in physical activity (%)

Declaration of purchase isotonic beer	Total	People who do not do sports	Occasional exercisers	Regular sportsmen
Yes, I am interested in purchasing regularly	8.43	0.00	5.41	14.71
Yes, I am interested in the occasional purchase	44.58	33.33	54.05	38.24
No, I'm not interested	46.99	66.67	40.54	47.06

Source: own study.

The most numerous group that was not interested in buying isotonic beer were people not practicing sports. In this group, none of the respondents was interested in purchasing this drink regularly. Among occasional exercisers, the highest percentage declared that they were interested in the occasional purchase of isotonic beer. In the group of regularly exercising, the highest percentage of people interested in purchasing this type of drink for sportsmen regularly was observed, however, it was only nearly 15% (Table 4).

The significance of the relationship between responses regarding physical activity and the declared frequency of purchase were examined. The results of the calculations showed that the correlation of the Spearman 's rank order between the declared physical activity and the declared interest in buying beer with isotonic properties was slight (R Spearman = 0.11) and statistically insignificant (significance level $\alpha = 0.05$). There was also no statistically significant correlation between the declared frequency of purchasing isotonic beer and the duration of training.

Such a low correlation between the regularity of practicing sports and the declared interest in consuming isotonic beer may result from the low interest in consuming isotonic drinks by university students. In the studies by Przeor et al. [2016] showed that as many as 94% of young adults (age 18-35) habitually consumed water during physical exertion, and only about 2% consumed isotonic drinks. Therefore, such a drink designed as isotonic beer could even encourage active people to consume it. As Overman [1991] observed, there is higher consumption of conventional beer among students practicing sports.

The above low interest in isotonic beer may be also due to low awareness of the respondents about the existence of such a product as an alternative to conventional isotonic drinks. Therefore, it seems necessary to carry out appropriate marketing campaigns and actions shaping the awareness of the consumer so that he is oriented in the functional products offered by breweries. However, as the results of the analysis were statistically insignificant, it would be justified to conduct research on a larger group of respondents before specific action taken by the producers.

5. Conclusions

The research results show a potential chance to increase the market share of isotonic beer. The potential target audience of isotonic beer are men, second-cycle students and people who exercise regularly. Such action should, however, be preceded by wider research on a larger group of respondents, taking into account the characteristics of isotonic beer expected by consumers. It is necessary to educate young adults about the existence of the product and the possibility of its consumption during or after physical activity. The presented results may constitute valuable knowledge for breweries and thus suggest the direction of research aimed at introducing a wider offer of isotonic beers, as well as the direction of conducting marketing activities.

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PROPERTIES AND APPLICATION CAPABILITIES OF OTILIONIUM BROMIDE

JOANNA ANTOS[1], DARIA WIECZOREK[1], YING-LIEN CHEN[2], TANG-LONG SHEN[2]

[1] *Katedra Technologii i Analizy Instrumentalnej, Instytut Nauk o Jakości, Uniwersytet Ekonomiczny w Poznaniu,*
e-mail: antosjoanna96@gmail.com,
[2] *Department of Plant Pathology and Microbiology, National Taiwan University, Taipei, Taiwan*

Abstract
Otilionium bromide (OB) is a compound which is known in pharmaceutical industry. It is used as a gastrointestinal spasmolytic agent by patients with irritable bowel syndrome. Around 10-20% of the population in Europe struggle with this type of disorder and approximately 50% of the population is not diagnosed. This compound affects the contractility of smooth muscle cells in the colon, as well as mobility in the large intestine. It is important to know the exact mechanism of action of otilionium bromide. This compound is effective and relieves pain in all types of irritable bowel syndrome and at the same time it is safe for nervous system.

Keywords: otilionium bromide, irritable bowel syndrome, cationic surfactants, drugs

Introduction

Otilionium bromide (chemical name: diethylmethyl (2-(4-(2-octyloxybenzamido)benzoyloxy)-ethyl) ammonium bromide) also called in short OB was discovered by Menarini Research SpA and it is on the market for over thirty years. This compound is known in over 40 countries in all Europe, Asia, America and also Africa and Middle East.

Otilionium bromide is sold as pharmaceutical:

- alone under several names, such as: Doralin, Spasmomen (in Italy, Belgium, Hong Kong), Spasen (Italy) and Spasmoctyl (Spain),
- in combination with diazepam (in two different dosages: 40 mg of OB mixed with 2 mg of diazepam or 20 mg of OB mixed with 2 mg of diazepam) under several names, such as: Spasen Somatico (Italy), Spasmomen Somatico (Italy) [Mannucci et al. 1991].

Otilionium bromide is a quaternary ammonium salt, considers a musculotropic spasmolytic drug and is known by its gastrointestinal spasmolytic properties. Mean application of otilionium bromide is for dealing with irritable bowel syndrome, also known as IBS. This drug reduces abdominal pain and discomfort caused by abdominal diseases [Evangelista et al. 1998; Evangelista 1999].

Irritable bowel syndrome is a disease with chronic, relapsing bowel disorder with cyclic periods with inconvenient symptoms which leads to short or long treatments [Chey at al. 2004]. It causes abdominal pain and it changes in bowel habit (changed stool frequency, stool form, bloating, passage of mucus, abdominal distension) or abdominal distention which are the most distressing symptoms when it comes to forcing patients to search for medical care. Occurrence of patients with irritable bowel syndrome is estimated up to 11.5% of the general population in Europe [Hungin et al. 2003; Czimmer et al. 2001] or even more, because between 10-20% of western population. Those estimations are correct only for people with diagnosed disease. About 50% of patients are still undiagnosed [Hungin et al. 2003; Lovell & Ford 2012]. Women are most commonly diagnosed with IBS and it also is diagnosed for people under 50 years old. Moreover economic status also affecting the possibility of the disease. Statistically people who have higher income are less prone to irritable bowel syndrome. However, it should be emphasized that these are only statistics and people of all ages and gender can be diagnosed with irritable bowel syndrome. Irritable bowel syndrome like any other disease can affect patients physically, but also psychologically, socially and strongly economically (costs of doctors, drugs, psychologist, diet) [Agarwal & Spiegel, 2011; Spinelli 2007]. Furthermore, there is no optimal irritable bowel syndrome pharmacological treatment (which will work

for everyone), duration of treatment, most useful medicine and even if the treatment is promising the disease can return and the next treatment will be needed. Most often the treatment involves diagnosis, explanation of how to reduce the symptoms, reassurance, then it's time to change a lifestyle (fiber enriched diet), addition of antispasmodic and antipsychotics drugs [Bucci et al. 1991; Clavé & Tack 2017]. For people with IBS it is important to reduce stress. Managing IBS symptoms includes: education, eating smaller meals, a good amount of sleep, breathing exercises, yoga, meditation, using probiotics, taking part in IBS support group and exercising [Qin et al. 2014]. When it comes to diet patient should eat more fiber which they can found in beans, oat products, vegetables and fruits. They should avoid gluten, drink at least 2 litre of milk, limit coffee, alcohol, eat regularly, try the low FODMAP diet (Fermentable Oligo Di Monosaccharides and Polyols diet) [Cozma-Petruţ et al. 2017].

The main aim of the review was to summarise current knowledge of otilionium bromide and IBS through an analysis of treatments with OB.

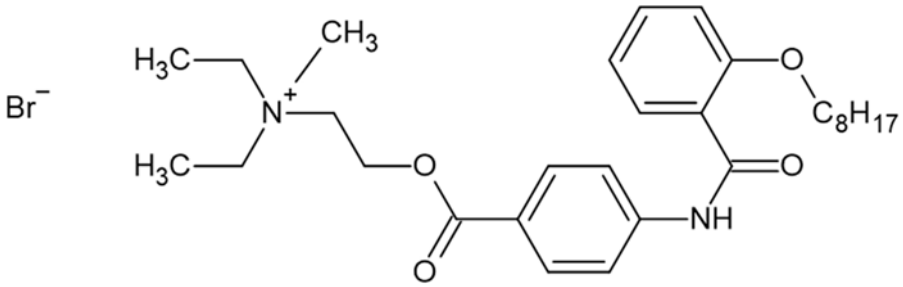

Fig. 1. Structural formula of otilionium bromide

Source: own study.

1. Activity and mechanism of action

Otilionium bromide accumulates in the small bowel and colon and is not absorbed systemically. Otilionium bromide concentrates in large bowel and works locally. When the drug is orally applied it is devoid of both: peripheral and central side

effects (it was confirmed during in vitro and clinical studies, which shown that OB is efficiently absorbed to large bowel walls and was weakly absorbed systemically). Concentration of therapeutic dosage of this compound in small, large bowel and colonic smooth muscle should be around 10 µmol/l. The concentration in plasma is estimated as 1000 times lower, so OB is curing locally and should not cause serious side effects. This low systemic absorption in plasma results from positive polar head of OB molecule [Shrivastava & Mittal 2021]. Out of 97,8% ingested otilionium bromide is excreted in the form of feces (according to the experiments on rats) and less than 1% is excreted with urine. Absorption of otilionium bromide and presence of otilionium bromide in drugs can be determine by analytical techniques such as first-derivative spectroscopy, spectrophotometry, HPLC, LC MS/MS and capillary zone electrophoresis [Santoni et al. 1991; Shin et al. 2008; Lindqvist et al. 2000; Rychter et al. 2014; Evangelista et al. 2018].

Otilionium bromide inhibits mobility patterns of human colonic (in vitro), contractility which are caused by pre-synaptic action or post-synaptic action. Furthermore, these effects result from a complex interaction between OB and the cellular targets [Evangelista et al. 2018].

The main activity of OB (with oral dose of 40-240 mg) is mediated by the inhibition of calcium ion flux from intraand extracellular sites in colonic smooth muscles (mostly entry of a Ca^{2+} block through its L-type channels). Otilionium bromide is an T-type and L-type calcium channel blocker. It associated with NK2 T-type and L-type channels and inhibits it what was shown by using the patch-clamp technique [Martin et al. 2004; Strege et al. 2004]. L-type calcium channels depends on the voltage, depolarization of the membrane potential allows to open the channel. This depolarization is generated by ICC (interstitial cells of Cajal) and its transported through ICC to SMC (smooth muscle cells) [Gibbons et al. 2009; Strege et al. 2009; Strege et al. 2010]. KCl-induced calcium transients in isolated human colon smooth muscle cells were also inhibited concentration of otilionium bromide. Inhibition of Ca^{2+} channels may cause the inhibition of the spontaneous motility. The compound inhibits contractions caused by acetylcholine (Ach), serotonin, tachykinins, substance P (SP), barium chloride and histamine Moreover otilionium bromide shows

an affinity for muscarinic receptors (M1, M2, M4, M5, PAF) [Evangelista 1999; Gandía et al. 1996].

The stability tests presented in the Zhao Y. et al. study shown that disposition of otilionium bromide is limited. In plasma it degraded quickly and easily hydrolysed to two different forms. The stability of otilionium bromide medicine can be improve by adding hydrochloric acid, but it could caused interferences which do not solve the stability problem [Zhao et al. 2010].

2. Results of treatments with otilionium bromide

Few effectivity treatments with otilionium bromide and placebo drug took place all around the world. Few of them are shown in Table 1. In every of these clinical treatments there were similar criteria who should or should not to be involved in the experiment. According to these criteria patients should be above 18 years old, should not have serious disease (when it comes to people above 50 years old), have a positive IBS diagnosis. People of all ages, ganders, location, lifestyle (smokers, different diet) participated in the experiments.

Table 1. Effects of treatments with OB

Population	Treatment	Results	Reference
-160 patients- OB (males-49; females 111), -165 patients- placebo (males- 51; females- 114)	After 2-week treatment with placebo, 325 patients were divided. Dosage: First group: 40 mg OB t.d.s Second group: placebo Treatment duration: 15 weeks	Both groups: significant reduction in abdominal pain.	[Battaglia et al. 1998]
-157 patients- OB (males-49; females 108), -160 patients- placebo (males- 50; females- 110)	After 2-week treatment with placebo, 317 patients were divided. Dosage: First group: 40 mg OB t.d.s Second group: placebo Treatment duration: 15 weeks	Both groups: significant reduction in abdominal pain.	[Glende et al. 2002]

Population	Treatment	Results	Reference
-179 patients- OB, -177 patients- placebo	Dosage: First group: 40 mg OB t.d.s Second group: placebo Treatment duration: 15 weeks + 10 additional weeks	OB patients: significant reduction in abdominal pain	[Clavé et al. 2011]
-88 patients- OB -96 patients- placebo	First group: 40 mg OB t.d.s Second group: placebo Treatment duration: 15 weeks	OB patients: significant reduction in abdominal pain	[Menarini IFR 2012]
-10 patients with IBS -10 healthy patients	Dosage: 80 mg OB, 4 times daily Treatment duration: 5-7 days	Significant reduction of abdominal pain	[Narducci et al. 1986]

Source: own study.

After two weeks pre-treatment with placebo patients with small, medium or large irritable bowel syndrome symptoms were divided to two separate groups. One of them got 40 mg of OB and the other placebo drug 3 times everyday before meals in dosage shown in Table 1.

Improvement or deterioration was noted by patients in special diaries (Criteria form Glende study is shown in Table 2. For the other studies criteria were similar and because of that doesn't need to be quoted). There were several pain and bowel habit criteria but main score was calculated as the result of equation: abdominal pain score x episodes of pain score.

These results were noted by patients and checked by doctors during check-up visits after 5, 10 and 15 weeks of treatment. Patients were clinical examined before the treatment. During check-up visits doctors apart from checking the scores in diaries- counted unused drugs and give new ones, clinical examination was repeated. Patients also took place in laboratory test before and after the 15 weeks of treatment [Glende et al. 2002].

These large clinical trials have shown that the treatments with otilionium bromide is safe, effective and can be commonly used for patients with irritable bowel syndrome. Furthermore it has shown that otilionium bromide reduces abdominal pain, bloating and relieving discomfort better than the treatment with placebo drug.

Otilionium bromide have the ability to inhibit contractility of human sigmoid (in vitro and in vivo). In the trials discussed by Clavé, Battaglia, Glende and Menarini IFR after 10 weeks of treating there is an improvement in treatment and it is stabile and maximal till the end of treatment (around 15 week) [Clavé & Tack 2017].

Table 2. Diaries criteria

Criteria	Score
The intensity of abdominal pain	- Absent - mild to moderate - severe - very severe
The frequency of abdominal pain episodes	- No episodes - 1-3 episodes - 4-7 episodes - 8 or more episodes
Intestinal habits	- regular - constripation - diarrhoea - alternting
The average daily number of evacuations	- 1 or less - 2 - 3-4 - 5 or more
The days without evacuation during the week	- 0-1 - 2-3 - 4-5 - 6-7
Mucus in the stool, difficulty of evacuation	- Never - Sometimes - Frequently - Constanly
The consistency of stools	- Absence of soft/hard stools - Moderately soft/hard - Markedly soft/hard - Watery/very hard and fragmented stools

Source: [Glende et al. 2002].

3. Discussion and conclusions

Irritable bowel syndrome is a common gastrointestinal disease which affecting large intestine. In IBS treatment antispasmodics are used [Zhou et al. 2020]. The present work collect and confirms data that antispasmodic named otilionium bromide (FDA-affirmed) is an effective and well tolerated drug which relieves pain and improve other symptoms in all types of irritable bowel syndrome.

The mechanism of action is briefly discussed in one chapter in this study. The best activity of a drug is with concentration 1-10 μM. The most common dosage of OB is 40 mg. OB inhibit Ca^{2+} through Ca^{2+} T- and L-type channels. However, symptoms of IBS in up to half IBS patients come back. Because of that, cyclic treatment for this disease is needed.

To improve quality of life for people with IBS it is important to constantly take care of oneself by participating in treatments, following a diet, taking care of physical activity and managing stress through yoga, meditation sessions or a support group. It is essential to continue to learn more about the disease and look for newer and newer solutions, treatments. At the same time, patients and the public need to be educated. This may help diagnose more people who is struggling with IBS.

Determination of OB can by analysed by different analytical methods (mostly chromatography and spectrophotometry methods) in biological samples as plasma and in pharmaceutical formulations but this area of analysis is in need to be evaluated (with less toxic chemicals and solvents, faster determination of the analyte, or more sensitivity).

Cationic surfactants as OB have antifungal properties. The growing resistance of microorganisms to biocidal compounds indicates the need to search for new, more resistant compounds. Modification of the well known otilionium bromide may give it a new application in human treatment.

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KRAFFT TEMPERATURE IN AQUEOUS SOLUTIONS OF NONIONIC SUGAR-BASED SURFACTANTS

RYSZARD ZIELIŃSKI

Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economic and Business, Poland
e-mail: ryszard.zielinski2022@gmail.com

Abstract
Surface active agents (surfactants) are chemical structures consisting of two main parts: a polar head group and a nonpolar hydrophobic chain called as the surfactant's tail. One of the most important parameters characterizing a practical suitability of surfactants in aqueous solutions is the Krafft temperature. This is the temperature (or more precisely, the narrow range of temperatures) above which the solubility of a given surfactant in water increases rapidly. The knowledge of the Krafft temperature of any surfactant is required to design a composition of new domestic detergents, shampoos, and cosmetic products of high quality in which a given surfactant can be used an active ingredient.
In this work we report results of our study on the relationship between the Krafft temperature value in aqueous solutions of sugar-based nonionic surfactants and their molecular structure. We propose a novel set of 35 group contributions that can be applied for calculation the Krafft temperature of sugar-based nonionic surfactants in aqueous solutions. Using them, the Krafft temperature values for aqueous solutions of 56 sugar-based nonionic surfactants were calculated and the estimated values obtained in this way were compared with experimental ones. We have shown that the newly developed set of numerical values structural group contributions of the surfactants allows correct estimation of the Krafft temperature value for various types of nonionic sugar-based surfactants in aqueous solutions with the maximum error 5.3^{o}C and the mean square error 2.9^{o}C.

Keywords: Krafft temperature, sugar-based surfactants, nonionic surfactants

Introduction

Surface active agents (surfactants) represent a huge group of various chemical structures consisting of two main parts: a polar part of the molecule (frequently called as the surfactant's polar head) and a nonpolar part of the molecule consisting of the hydrophobic chain (called as the surfactant's tail). Both main parts of the surfactant structure can be linked directly or by means of some connecting group known as the spacer. Depending on the dissociation ability of the molecules in aqueous solutions the surfactants are usually divided into two main groups: ionics (including anionics, cationics, zwitteionics, catanionis and mesoionics) and nonionics [Zieliński 2021].

In dilute aqueous solutions of surfactants their molecules can exist in the monomeric form while above a certain threshold concentration (called the critical micelle concentration or CMC) they can form micellar aggregates being in equilibrium with the surfactant monomers. The numerical value of the CMC depends mainly on surfactant structure and temperature.

One of the most important parameters characterizing a practical suitability of surfactants in aqueous solutions is the Krafft temperature. This is the temperature (or more precisely, the narrow range of temperatures) above which the solubility of a given surfactant in water increases rapidly. The knowledge of the numerical nalue of the Krafft temperature of any surfactant is required to design a composition of new domestic detergents, shampoos, and cosmetic products of high quality in which a given surfactant can be used an active ingredient.

For a long time the existence of the Krafft temperature (or Krafft point) was described as a phenomenon characteristic only to ionic surfactants. Such statements relating the Krafft point phenomena to only aqueous solutions of ionic surfactants can be found in some popular textbooks on surfactants [Holmberg et al. 2003; Myers 2006; Rosen & Kunjappu 2012]. Recently, it was reported that in aqueous solutions of some nonionic surfactants a similar phenomenon can be observed, especially when the polar head groups of the nonionic surfactants are based on carbohydrates.

Figure 1 shows a simplified phase diagram of the two-component system consisting of surfactant and water. As can be seen in Figure 1, a typical phase diagram

drawn for surfactant–water mixtures consists usually of three equilibrium curves. The first one (A-K) located at low temperature range describes the equilibrium between surfactants molecules being in the solid form and those in the monomeric state in aqueous solution. The second one (K-B) located at higher temperature range corresponds to the equilibrium between surfactant in the monomeric and the micellar form. Finally, the third line (K-C) located at high surfactant concentrations described the equilibrium between surfactants molecules being in the solid form and those in the micellar form in aqueous solutions. All these three curves have a one common point called the Krafft point described for given surfactant by the characteristic CMC value and the Krafft temperature.

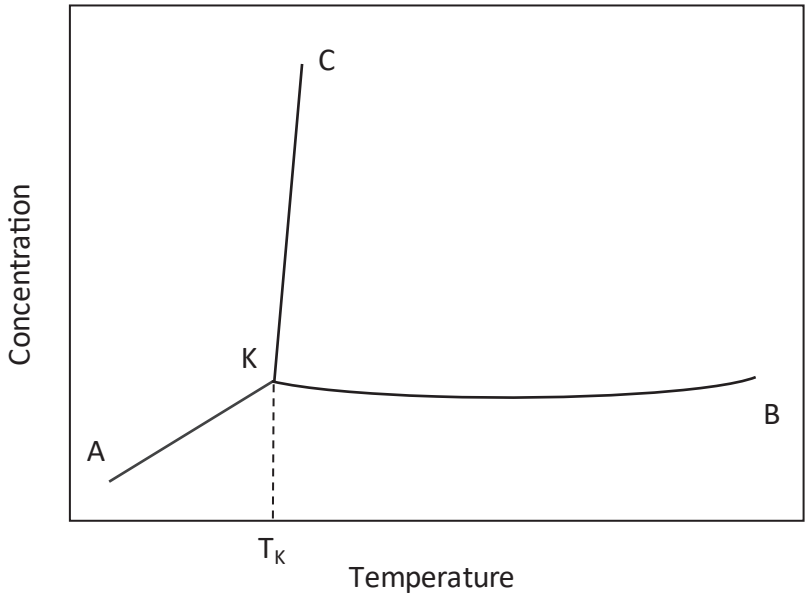

Fig. 1. Simplified phase diagram for surfactant-water system

Source: this research.

The numerical value of the Krafft temperature is best determined by locating the abrupt change in slope of a graph of the logarithm of the surfactant solubility in water plotted against temperature (T) or 1/T. Sometimes the Krafft temperature

has been also defined as the knee in the melting curve of the surfactant in the presence of water in the phase diagram. According to Shinoda [Shinoda 1981] it corresponds to a kind of triple point with coexistence of surfactant molecules forming a molecular solution, a micellar solution and a solid phase. In literature the Krafft temperature (T_K) is known also as Krafft point (KP) or critical micelle temperature (CMT). It is one of the most important experimentally available parameters characterizing a practical suitability of surfactants in aqueous solutions. As can be seen in Figure 1, the value of T_K indicates the temperature (or more precisely, the narrow range of temperatures) above which the solubility of surfactant molecules in water increases very rapidly.

Dissolution of surfactants in water causes a reduction of the surface tension of the resulting solutions. It should be noted, however, that in practice the term "surfactant" usually refers to any agent that lowers the surface tension of a liquid. It was shown [Gaudin et al. 2016] that for sugar-based surfactants the surface tension observed at the CMC increases with the total number of atoms includes in the polar head group of the surfactant molecule. They found that in general at CMC nonionic surfactants with higher number of sugar residues in the molecule exhibit higher surface tensions. For several series of ionic surfactants it was found [Gu & Sjöblom 1992] that there is a linear relationship between the Krafft point and the logarithm of CMC. These relationships have a negative slope for various homologue series of ionic surfactants with the same kind of counter ion. On the other hand, for some homologues of nonionic surfactants, a comparable linearity is also observed but there surfactants exhibit a positive slope. It was suggested that this observation illustrates the subtle balance between attraction and repulsion forces in aqueous surfactant solutions, accountable both for phase separation and micelle formation.

Depending on surfactant concentration their aqueous solutions of can exhibit good surface properties such as: wetting, foaming, detergency, emulsification, washing, solubilisation or dispersion ability [Birdi 2009; Holmberg et al. 2003; Myers 2006; Rosen & Kunjappu 2012; Tadros 2005; Zieliński 2021]. Some of those properties of aqueous solutions, such as washing properties, solubilisation power or emulsification ability are observed only at concentrations exceeding the CMC values.

They are utilized in a number of commercially available products such as high quality domestic detergents, dish washes, hair shampoos, and various cosmetic products [Miyake & Yamashita 2017; Przondo 2010; Zieliński 2021]. All these properties depend on the solubility of surfactant molecules in aqueous solutions, this in turn depends mainly on temperature.

For decades a determination of the numerical value of the Krafft temperature was used as the most popular means of quantifying the tendency of ionic surfactants to precipitate. For this reason the knowledge of the Krafft temperature of any surfactant is required to design a composition of novel domestic detergents, shampoos, and other cosmetic products in which a given surfactant is proposed to be used as an active ingredient. We have to note that at temperatures lower than the value of the Krafft temperature any surfactant is simply insoluble in water, so from a practical point of view such a surfactant is usually useless or some additional ingredients should be used in the composition of the designed product to avoid a precipitation of such a partly insoluble surfactant.

In literature one can find only few experimental data on the Krafft temperature of sugar-based nonionic surfactants in aqueous solutions. Figure 2 shows the experimental data of the Krafft point determined for aqueous solutions of few sugar-based nonionic surfactants plotted as a function of the number of carbon atoms in the alkyl chain of the surfactants. As can be seen in Figure 2 the experimental points plotted as a function of the alkyl chain length for each homologue series of sugar-based surfactants can be represented as a straight line. In each case the slope of the straight lines drawn through the corresponding experimental points is positive and can be regarded as being approximately independent of the type of the polar head group present in a tested surfactant series. This finding suggests that it is possible to find the numerical value of the corresponding group contributions of any structural element of sugar-based surfactants and use them for prediction of the Krafft temperature for various structures.

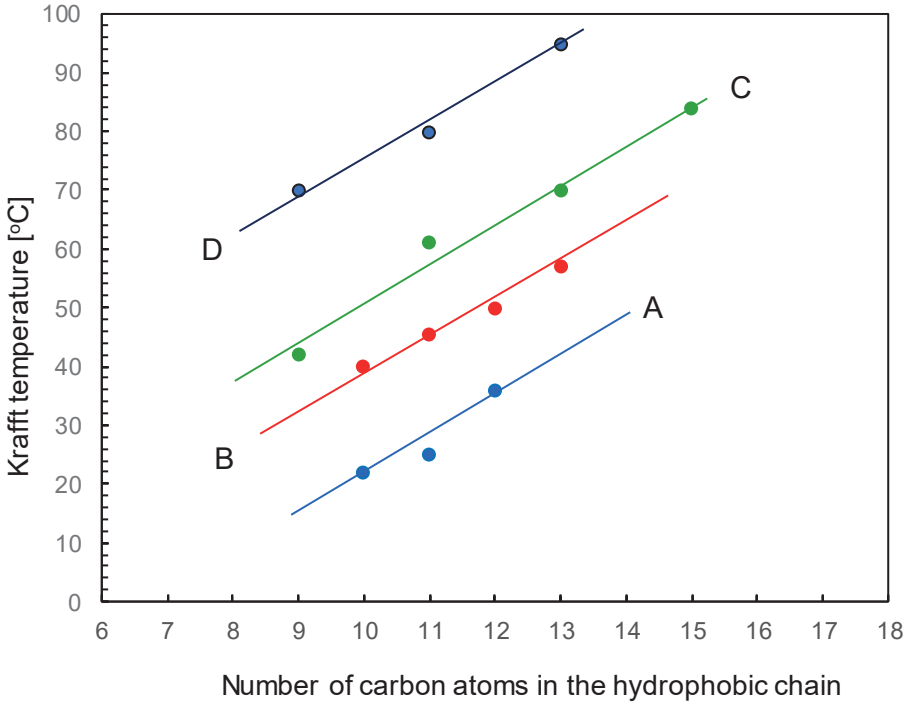

Fig. 2. Effect of alkyl chain length on the Krafft temperature value in water for several homologous series of sugar-based nonionic surfactants

Symbols: A – alkyl-β-glucosides [Hato 2001; Nilsson et al. 1998]), B – N-alkyl-N-methylglucamides [Gaudin 2016; Zhu et al. 1999], C – N-alkyl-N-methylactonamides [Kjellin et al.2001], D – 6-deoxy-(alkanamido)-methyl-α-D-glucosides [Salman et al. 2014]

Source: this research.

It is interesting to note that in literature on anionic surfactants one can find some reports indicating that the following changes in the structure of these group of surfactant molecules lead to Krafft temperature reduction:

- introduction of methyl groups of the hydrophobic chain of the surfactant,
- increase in the number of branches of the hydrophobic chain of the surfactant,
- introduction of double bonds in the hydrophobic chain of the surfactant,
- introduction of a polar spacer (eg oxyethylene group) between the hydrophobic chain and the ionic polar head of the surfactant molecule,

– introduction of to the surfactant structure the counterions of a smaller size.

It seems reasonable that at least some of these observations should also hold for aqueous solutions of sugar-based nonionic surfactants.

Continuing our research on Krafft temperature in aqueous solutions of ionic surfactants [Zieliński 2020], in this work we report results of our study on the relationship between experimental Krafft temperature values and chemical structures of various nonionic sugar-based surfactants in aqueous solutions. The aim of this research is to develop a set of numerical values of group contributions attributed to various structural elements of these groups of surfactants that can be used for prediction the numerical values of the Krafft temperature in aqueous solutions.

1. Material and methods

We have studied a relationship between Krafft temperature and chemical structure of various sugar-based nonionic surfactants including glucopyranosides, glucofuranosides, galactopyranosides, methylglucopyranosides, maltosides, cellobiosides, lactosides, glucamines, glucamides, methylglucamides, lactobionamides, glucose esters, methylglucoside esters, glucuronides and galacturonides.

In our study we have assumed that the observed Krafft temperature of the surfactants can be represented as a simple sum of group contributions attributed to the structural elements forming a single surfactant molecule. In order to derive the numerical values of the group increments for some structural elements to calculate the Krafft point values for aqueous solutions of sugar-based nonionic surfactants we have assumed a simple linear form of the regression equation without any constant value of our model. We have computed the numerical values of the corresponding regression coefficients by means of the multilinear least squares method using Solver macro implemented in the Microsoft Excel 2019 spreadsheet.

2. Results

In this work we propose 35 basic structural group types to describe structures of various nonionic sugar-based surfactants in order to calculate the Krafft temperature value of these surfactants in aqueous solutions. Results of our computations are listed in Table 1.

Table 1. Values of group increments for some structural elements to calculate the Krafft temperature of the aqueous solutions of sugar-based surfactants

Structural element	T_K [°C]
$-CH_3$	-16.231
$-CH_2-$	6.312
-CH<	3.470
-OH	26.548
$-OCH_2CH_2-$	-9.493
-COO-	-54.090
-CONH-	-13.848
$-CON(CH_3)-$	-26.510
-NH-	3.835
>C(ar)-	-3.150
$>C(ar)–CH_2-$	-15.804
$-N(ar)-CH_2-$	2.966
-N(ar)=	3.334
α-branching near -CONH- group	20.631
β-branching	39.470
α-D-glucopyranoside group	9.961
β-D-glucopyranoside group	-12.252
β-D-glucofuranoside group	0.109
β-D-glucofuranosiduro-6,3-lactone	12.419
α-D-galactopyranoside group	29.108
β-D-galactopyranoside group	-2.373
β-D-cellobioside group	-10.207
β-D-maltoside group	-35.640
β-D-lactoside group	19.795
1-sorbityl group	-21.555

Structural element	T_K [°C]
1-deoxy-β-D-glucose group	24.673
6-deoxy-D-glucose group	25.702
6-deoxy-D-maltose group	44.199
6-deoxy-methyl-α-D-glucoside group	48.378
N-gluconamide group	41.161
N-maltobionamide group	-19.830
N-lactobionamide group	11.045
N-methyl-N-gluconamide group	-43.953
(methyl-α-D-glucosid)uronate group	22.886
(methyl-β-D-galactosid)uronate group	57.135

Note: (ar) – indicates C or N atom in the aromatic ring

Source: this research.

The numerical values of structural group contributions listed in Table 1 were computed on the basis of experimental data for 56 nonionic sugar-based surfactants published in the literature by various research groups. As can be seen some of our group contributions to the Krafft temperature listed in Table 2 can be compared to some values published in literature. Our value of 6.312 for methylene group can be compared to the value of 6.114 reported by Chanachichalermwong [2018], while the group contribution of -9.493 found for oxyethylene group is close to the value of -9.467 obtained by Chanachichalerwong [2018] and that of -9.0 published by Gu and Sjöblon [1991] for a set of anionic surfactants.

3. Discussion

The practical application of the method proposed in this work can be illustrated by the numerical example shown in details for methyl-6-deoxy-(dodecanamido)-α-D-glucoside ($C_{11}H_{25}$-CONH-CH_2-$C_5H_5O(OH)_3(OCH_3)$):

T_K = 1 CH_3 + 10 CH_2 + 1 -CONH- + 1 (6-deoxy-methyl-α-D-glucoside group).

$T_K = 1 \cdot (-16.231) + 10 \cdot (6.312) + 1 \cdot (-13.848) + 1 \cdot (48.378)$.

T_K (calc.) = 81.4°C. Experimental value T_K = 80.0°C [Salman 2013].

From the data given in Table 1 it is clear that the increase in the length of the surfactant hydrophobic moiety causes the increase in the Krafft temperature value. One can also conclude that the Krafft temperature for α-glucosides should be much higher than that for the corresponding β-glucosides.

Table 2 contains a list of experimental values of Krafft temperatures published in literature and those computed using the values of our group contributions collected in Table 1 for 56 nonionic sugar-based surfactants in aqueous solutions.

Table 2. Experimental and computed values of the Krafft temperature [°C] in aqueous solutions for 56 nonionic sugar-based surfactants. $\Delta = T_K(\text{comp.}) - T_K(\text{exp.})$

Sugar-based surfactant	T_K (exp.)	T_K (comp.)	Δ	Ref
octyl-α-D-glucopyranoside	38	37.9	-0.1	A
nonyl-α-D-glucopyranoside	46	44.2	-1.8	B
undecyl-α-D-glucopyranoside	55	56.9	1.9	B
(2-ethyl)hexyl-α-D-glucopyranoside	52	52.0	0.0	A
nonyl-β-D-glucopyranoside	23	22.0	-1.0	B
decyl-β-D-glucopyranoside	26	28.3	2.3	C
undecyl-β-D-glucopyranoside	36	34.6	-1.4	B
dodecyl-β-D-glucopyranoside	38	41.0	3.0	D
tetradecyl-triazole-CH_2-β-D-glucopyranoside	42	40.4	-1.6	E
hexadecyl-triazole-CH_2-β-D-glucopyranoside	53	53.0	0.0	E
octadecyl-triazole-CH_2-β-D-glucopyranoside	64	65.6	1.6	E
hexadecyl-tri(oxyethylene)-β-D-glucopyranoside	43	37.7	-5.3	F
octadecyl-tri(oxyethylene)-β-D-glucopyranoside	48	50.3	2.3	F
dodecyl-β-D-glucofuranoside	55	53.3	-1.7	G
decyl-β-D-glucofuranosiduro-6,3-lactone	53	53.0	0.0	G
undecyl-α-D-galactopyranoside	76	76.0	0.0	H
octyl-β-D-galactopyranoside	29	25.6	-3.4	I
undecyl-β-D-galactopyranoside	46	44.5	-1.5	H
dodecyl-β-D-cellobioside	43	43.0	0.0	J
tetradecyl-β-D-maltoside	32	30.2	-1.8	K
hexadecyl-β-D-maltoside	41	42.8	1.8	L
dodecyl-β-D-lactoside	73	73.0	0.0	J

Sugar-based surfactant	T_K (exp.)	T_K (comp.)	Δ	Ref
N-octanoyl-1-β-D-glucamide	30	32.5	2.5	M
N-undecanoyl-N-methyl-D-glucamide	40	38.7	-1.3	N
N-dodecanoyl-N-methyl-D-glucamide	45.3	45.1	-0.2	N
N-tridecanoyl-N-methyl-D-glucamide	50	51.4	1.4	N
N-tetradecanoyl-N-methyl-D-glucamide	57	57.7	0.7	O
N-pentadecanoyl-N-methyl-D-glucamide	67	64.0	-3.0	O
N-undecyl-4-hydroxy-D-glucamide	37	35.2	-1.8	P
N-dodecyl-5-hydroxy-D-glucamide	41	41.5	0.5	P
N-dodecyl-N-methyl-D-glucamide	45	46.3	1.3	P
D-glucose 6-dodecanoate	20	18.5	-1.5	Q
D-maltose 6-dodecanoate	37	37.0	0.0	R
6-deoxy-(octanamido)-D-glucose	32	33.5	1.5	M
N-octyl-D-gluconamide	69	69.1	0.1	S
N-nonyl-D-gluconamide	75	75.4	0.4	S
N-decyl-D-gluconamide	84	81.7	-2.3	S
N-undecyl-D-gluconamide	87	88.1	1.1	S
N-dodecyl-D-gluconamide	95	94.4	-0.6	S
N-methyl-N-tetradecyl-D-gluconamide	20	21.9	1.9	T
N-methyl-N-octadecyl-D-gluconamide	49	47.1	-1.9	T
N-tetradecyl-D-maltobionamide	46	46.0	0.0	S
N-nonyl-D-lactobionamide	42	45.3	3.3	S
N-undecyl-D-lactobionamide	61	57.9	-3.1	S
N-tridecyl-D-lactobionamide	70	70.6	0.6	S
N-pentadecyl-D-lactobionamide	84	83.2	-0.8	S
6-deoxy-(decanamido)-methyl-α-D-glucoside	70	68.8	-1.2	U
6-deoxy-(dodecanamido)-methyl-α-D-glucoside	80	81.4	1.4	U
6-deoxy-(tetradecanamido)-methyl-α-D-glucoside	95	94.0	-1.0	U
6-deoxy-(2-ethyl-hexanamido)-methyl-α-D-glucoside	55	51.4	-3.6	U
6-deoxy-(2-butyl-octanamido)-methyl-α-D-glucoside	75	76.7	1.7	U
6-deoxy-(2-hexyl-decanamido)-methyl-α-D-glucoside	100	101.9	1.9	U
6-decanoyl-methyl-α-D-glucoside	26	28.6	2.6	I

Sugar-based surfactant	T_K (exp.)	T_K (comp.)	Δ	Ref
6-dodecanoyl-methyl-α-D-glucoside	43	41.2	-1.8	I
dodecyl (methyl-α-D-glucosid)uronate	22	22.0	0.0	I
octyl (methyl-β-D-galactosid)uronate	31	31.0	0.0	I

Experimental data: A – Nilsson et al. 1998; B – Hato 2001; C – Salkar et al. 2004; D – Gaudin et al. 2019; E – Sani et al. 2012; F – Moore et al. 2018; G – Raaijmakers 1993; H – Sun et al. 2009; I – Lu 2016; J – Rosevear et al. 1980; K – Ericsson et al. 2005; L – Hansson 2001; M – Lu 2015; N – Zhu et al. 1999; O – Gaudin 2016; P – Vermeer & Harichian 1998; Q – Söderberg et al. 1995; R – Kjellin et al. 2001; S – Vermeer 1997; T – Burczyk et al. 2001; U– Salman et al. 2014

Source: this research.

Figure 3 presents the comparison of the experimental and calculated values of the Krafft temperature for 56 nonionic sugar-based surfactants.

One can observe a very good linear correlation ($r^2 = 0.9922$) between computed and experimental values of the Krafft temperature for the tested set of surfactants. Such a good linear correlation allows for effective prediction of the Krafft temperature values for aqueous solutions of various groups of nonionic sugar-based surfactants. It was found that the maximum error of estimating the Krafft temperature using the values of group contributions listed in Table 1 is 5.3°C, and the mean square error is 2.9°C.

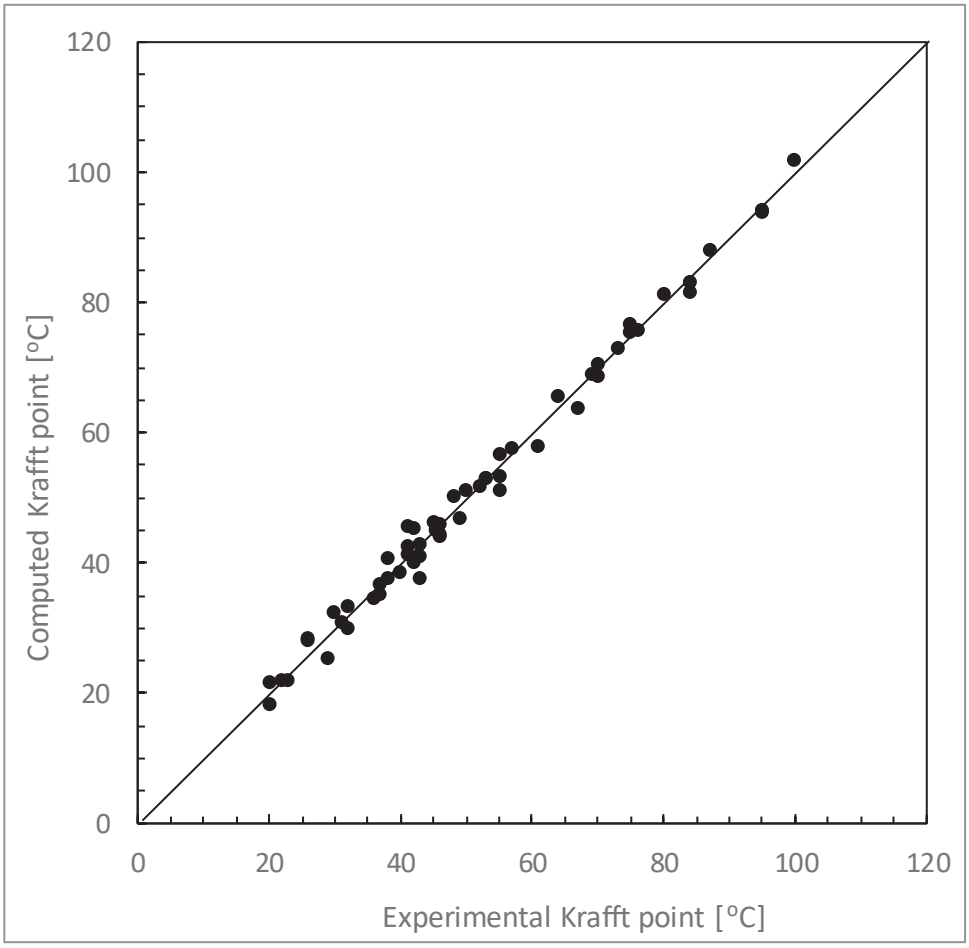

Fig. 3. Comparison of computed and experimental values of the Krafft temperature for 56 sugar-based nonionic surfactants in aqueous solutions

Source: this research.

Therefore, the newly developed set of 35 group increments listed in Table 1 can be used for fast and reasonable good estimation of the Krafft temperature values for various structures of sugar-based nonionic surfactants in aqueous solutions.

4. Conclusions

In this work we report results of our investigation on the Krafft temperature of sugar-based nonionic surfactants. Here, we present a set of group contributions consisting of 35 group increments for calculation the value of Krafft temperature in aqueous solutions of sugar-based nonionic surfactants including glucopyranosides, glucofuranosides, methylglucopyranosides, maltosides, cellobiosides, lactosides, glucamines, glucamides, methylglucamides, maltobionamides, lactobionamides, glucose esters, methylglucopiranoside esters, glucuronides and galacturonides. We have tested these group contributions and compared the computed values to available in literature experimental values of the Krafft temperature for 56 nonionic sugar-based surfactants in aqueous solutions. It was demonstrated that the proposed set of numerical values of the group contributions correctly predicts values of the Krafft temperature with the maximum error 5.3°C and the means square error 2.9°C for various types of nonionic sugar-based surfactants in aqueous solutions.

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APPLICATION OF STRAWBERRY SEED EXTRACT OBTAINED UNDER SUPERCRITICAL CARBON DIOXIDE CONDITIONS AS A COMPONENT OF EMULSION HAIR CONDITIONER FORMULATIONS

MAŁGORZATA ZIĘBA*, JOANNA TUSZYŃSKA

Department of Industrial Chemistry, Faculty of Chemical Engineering and Commodity Science, University of Technology and Humanities in Radom, 26-600 Radom,Chrobrego 27, POLAND,
*e-mail: m.zieba@uthrad.pl

Abstract
In this study an attempt was made to use strawberry seed extract obtained under supercritical carbon dioxide conditions (Fragaria Ananassa (Strawberry) Seed CO_2 Extract) as a component of hair conditioner formulations in the form of emulsion. The effect of extract concentration on selected physicochemical properties of produced hair conditioner prototypes was evaluated. The obtained results were compared to the emulsion with no extract added and to the reference commercial product.
Homogeneity profiles of prepared hair conditioners confirmed their stability over time. It was shown that an increase in extract concentration results in a decrease in dynamic viscosity values of cosmetic emulsion prototypes. In case of measurements of adhesion force and hardness of hair conditioners also a decrease in values of measured parameters was observed as a function of the extract percentage in formulation. It was shown that introduction of Fragaria Ananassa (Strawberry) Seed CO_2 Extract to the conditioner composition did not change the degree of whiteness of developed cosmetics. The addition of Strawberry Seed Extract obtained under supercritical CO_2 conditions, on the other hand, slightly enhances green and yellow colour of emulsions.
On the basis of the obtained results it was stated that Fragaria Ananassa (Strawberry) Seed CO_2 Extract exerts significant influence on physicochemical and functional properties of cosmetic emulsions. Proper selection of the extract concentration allows to obtain a product with high utility values.

Keywords: plant extracts, cosmetic emulsions, hair conditioners

Introduction

Hair conditioners are the group of cosmetics designed for one-time hair care treatments. These cosmetics are most often produced in the form of emulsions, foams and oils. As active components, hair conditioners usually contain ingredients, which are the product of heavy chemical synthesis (e.g. silicones, cationic surfactants, protein hydrolysates) [Ajayi et al. 2021; Alessandrini & Piraccini 2016; Drechsel et al. 2016; Fernández-Peña & Guzmán 2020; Towle et al. 2019; Zięba et al. 2017]. These ingredients, due to the solvents used in the process, high level of processing and insufficient purification, may generate skin irritations [Ananthapadmanabhan 2017; Seweryn 2018; Zięba, Seweryn et al. 2019]. Therefore, in recent years there has been a trend of replacing synthetic cosmetic raw materials with plant derivatives. Commonly used plant derivatives in cosmetics are extracts [Bujak et al. 2021; Díaz-Reinoso et al. 2006; Raczyk et al. 2021, Zięba et al. 2016]. Recently, there has been growing interest in obtaining plant extracts using supercritical carbon dioxide. This interest is dictated by many advantages of the applied method: products are characterized by high microbiological purity, extracts can be stored for a long time without degradation process, the process is carried out at relatively low temperature (up to 55°C), under conditions of compressed (about 300 bar) carbon dioxide, which after the process is completely removed from the extract. Thus, a product of high purity and stability is obtained, and what is most important for cosmetic raw materials - without degradation of valuable active substances [Bulley et al. 1984; Díaz-Reinoso et al. 2006; Mira et al. 1999; Rój et al. 2016].

Considering the availability of plants obtained from indigenous crops, strawberry seems to be an interesting object of research on potential application in cosmetics is [Hong et al. 2019; Karlińska et al. 2021].

Raczyk et al. [Raczyk et al. 2021] have evaluated the quality of cold-pressed berry seed oils e.g. strawberry. As a result of their research (acid and peroxide values, fatty acid profiles) it was confirmed that seed oils obtained by applied method can be valuable raw materials for cosmetic industry mainly due to high content of polyunsaturated fatty acids and bioactive compounds. The authors suggest to use cold-pressed berry seed oils as components in skin and hair care products.

In turn Markiewicz et al. [Markiewicz et al. 2019] used strawberry hydrolysate enriched with L-ascorbic acid using microneedle mesotherapy. According to the researchers microneedling with strawberry hydrolysate improves skin tone, hydratation, firmness and decreases the visibility of hyperpigmentation.

In publications Gasparrini et al. [Gasparrini et al. 2015; Gasparrini et al. 2017] indicate that by enriching a cosmetic preparation with strawberry extract it is possible to obtain prevention of UVA exposure-induced inflammation, and the extract itself shows high antioxidant capacity, as well as an important anthocyanin and vitamin content.

Also Sikora et al. [Sikora et al. 2015] investigated the possibility of using strawberry seed extract obtained under supercritical carbon dioxide conditions as an ingredient of shower/bath products. They evaluated both the properties of the extract and prototypes of cosmetics. They noted a very high content of unsaturated fatty acids in extract, which are key to maintaining the right level of skin hydration. These assumptions were confirmed by their studies on skin moisturization, which indicated an increase in measured parameter after using a cosmetic with strawberry extract. In addition, the formulation with Fragaria Ananassa Strawberry Seed CO_2 Extract did not cause any negative changes in foaming properties or viscosity of the developed products.

Based on a thorough analysis of the current literature, the aim of the study was formulated. The aim of this work was to develop formulations of emulsion hair conditioners with Fragaria Ananassa (Strawberry) Seed CO_2 Extract and to determine the effect of extract concentration on selected physicochemical and functional properties of the produced cosmetic prototypes.

1. Material and methods

1.1. Raw materials

The following raw materials have been used for the production of rinse-off hair conditioners (using INCI): Ceteareth-20 (Eumulgin B2, BASF, Poland), Cetearyl Alcohol (Lanette O, BASF, Poland), Ethylhexyl Hydroxystearate (Crodamol OHS,

Croda, Poland), Glyceryl Stearate (Cithrol GMS 40 SE, Croda, Poland), Paraffinum Liquidum (Sigma-Aldrich, Poland), Fragaria Ananassa (Strawberry) Seed CO_2 Extract, (Instytut Nowych Syntez Chemicznych, Poland), Dehyton K (Cocamidopropyl Betaine, BASF, Poland), Sodium Benzoate and Potassium Sorbate (KEM BS, Pol Nil S.A., Poland), Citric Acid (HSH Chemie, Poland).

1.2. Recipes

Based on literature data [Ajayi et al. 2021; Alessandrini & Piraccini 2016; Drechsel et al. 2016; Fernández-Peña & Guzmán 2020; Towle et al. 2019] and own experience [Zięba et al. 2017] original recipes of 6 rinse-off hair conditioners in emulsion form were developed. The prototypes of hair cosmetics differed in the percentage of strawberry seed extract obtained under supercritical carbon dioxide conditions, which respectively replaced paraffin oil in the formulation (Table 1).

Table 1. Qualitative and quantitative composition of hair conditioner prototype formulations.

Raw material (according to INCI)	Phase	**Formulation**					
		HC1	HC2	HC3	HC4	HC5	HC6
Ceteareth-20	I	3.0					
Cetearyl Alcohol	I	5.0					
Ethylhexyl Hydroxystearate	I	2.0					
Glyceryl Stearate	I	1.0					
Paraffinum Liquidum	I	**4.0**	**3.5**	**3.0**	**2.0**	**1.0**	**-**
Fragaria Ananassa (Strawberry) Seed CO_2 Extract	I	**-**	**0.5**	**1.0**	**2.0**	**3.0**	**4.0**
Aqua	II	Up to 100					
Cocamidopropyl Betaine	II	2.0					
Sodium Benzoate and Potassium Sorbate		1.0					
Citric Acid		to pH = 5.5					

Source: own study.

Procedure for obtaining

The components of phase I were measured and mixed. The components were stirred until completely dissolved on a magnetic stirrer with simultaneous heating on a water bath to the temperature of about 70 - 80°C. The components of phase II were mixed similarly. Both phases were mixed when equal temperatures were reached. The mixture was stirred for a while on a magnetic stirrer on a water bath, then stirred and cooled simultaneously to about 30°C. Then preparations were homogenised. A preservative was then added and the pH adjusted to 5.5.

Reference trade hair conditioner (THC) containing inter alia: Cocamidopropyl Betaine, Persea Gratissima Oil, Orbignya Oleifera Seed Oil, Quaternium-18 was selected for testing.

1.3. Methods

1.3.1.Stability

In order to verify the stability of hair conditioners, temperature stress tests were applied, which allowed visual assessment of stability of cosmetics stored alternately at elevated (40°C, 1 day) and reduced (5°C, 1 day) temperatures. They were carried out in a incubator type ST-68 and refrigerator (Amica). The test lasted 8 days (4 complete cycles). Additionally, the emulsions were evaluated for their resistance to centrifugal force using centrifuge Rotofix 32 A (Zentrifugen). The test lasted 10 minutes and was carried out at a speed of 1500 rpm.

In addition, in order to identify phenomena that could not be observed visually, samples were analysed using Formulaction Turbiscan Lab Cooler, which allows characterisation of physicochemical processes and phenomena at a very early stage. Cosmetics were stored in incubator at 40°C. The study lasted 21 days and samples were evaluated once a week.

1.3.2. Dynamic viscosity

Dynamic viscosity measurements of emulsions were performed using a Brookfield RVDV-I+. The test was carried out at a temperature of approximately 20°C, with a spindle speed of 10 rpm.

1.3.3. Texture analysis

Texture testing was performed using a Brookfield CT3 texture analyser. A spherical sampler TA43 made of polyamide was used (sampler immersion depth 10 mm at constant head speed 0.1 mm/s). The obtained results were recorded by Texture Pro CT software. In the texture profile analysis (TPA), hardness and adhesion strength were determined. The exact methodology is described in the literature [Zięba, Wieczorek et al. 2019].

1.3.4. Colour assessment

The colour of emulsions was determined using Konica Minolta Chroma-Meter model CR400. For individual cosmetics the measuremente were carried out in the CIE system based on the measurement of three trichromatic components - L* a* b*. The exact methodology was described in the literature [Klimaszewska et al. 2016].

1.3.5. Statistic analysis

The bars in the graphs represent the arithmetic mean values from three independent measurements. Confidence intervals have been defined which represent the measurement error for a confidence level of 0.90. The error values are shown in the graphs and table.

2. Results and discussion

2.1. Stability

Cosmetic stability is the main requirement for cosmetics in emulsion form. Load tests confirmed the stability over time of all tested hair conditioners at both low and high temperatures. Also on the basis of centrifugal tests performed no symptoms of instability of the produced cosmetics and the commercial product were found.

To confirm the preliminary results, an advanced stability analysis method was performed using Turbiscan Lab Cooler. The examples of results are shown in Fig. 1 and Fig. 2.

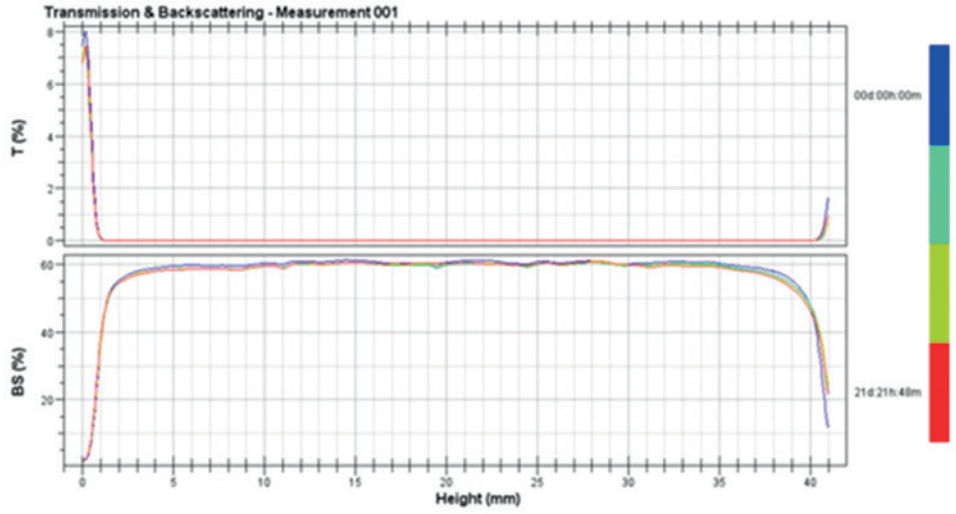

Fig. 1. Dependence of transmittance (T) and back scattering (BS) on sample height for a prototype HC6 cosmetic emulsion stored at 40°C for 21 days (Turbiscan); dark blue line - evaluation of the preparation immediately after application into tubes (time "0"), red line - stability after 21 days

Source: own study.

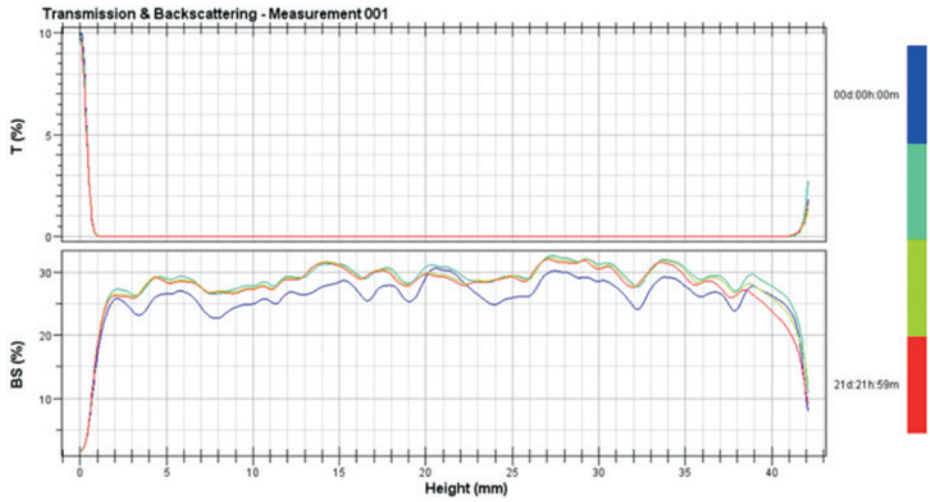

Fig. 2. Dependence of transmittance (T) and back scattering (BS) on sample height for a marketed cosmetic emulsion (THC) stored at 40°C for 21 days (Turbiscan); dark blue line - evaluation of the preparation immediately after application to the tubes (time "0"), red line - stability after 21 days

Source: own study.

The results of the study (Fig. 1) showed that the original hair conditioners were stable when stored in an incubator for 21 days at elevated temperature. However, in the case of marketed product (THC) the results of the dependence of transmittance (T) and scattered light flux (BS) on sample height show the first symptoms of emulsion instability in the form of flocculation or coalescence (Fig. 2).

Krasodomska and Jungnickel [Krasodomska & Jungnickel 2015] studied the stability of o/w emulsions using strawberry, black currant, raspberry and apple seed oils as ingredients. Their results indicated the most favourable stability of emulsions in which seed oils were used at concentrations of 4 and 5%, where the ratio of the oil phase to the water phase was 20:80.

Also in the case of earlier work [Klimaszewska et al. 2016], the results of homogeneity tests on facial masks confirmed the possibility of obtaining stable systems

involving an extract, e.g. from blackberry seeds obtained under supercritical carbon dioxide conditions.

2.2. Dynamic viscosity

Product viscosity is one of the basic physicochemical properties perceived by consumers as an indicator of quality. A high viscosity value is perceived by consumers as a high content of active ingredients in the product. In reality, a high viscosity level can be achieved by introducing, for example, rheology modifiers into the formulation. The results of dynamic viscosity (η) measurements of produced emulsions and market emulsion are presented in Fig.3.

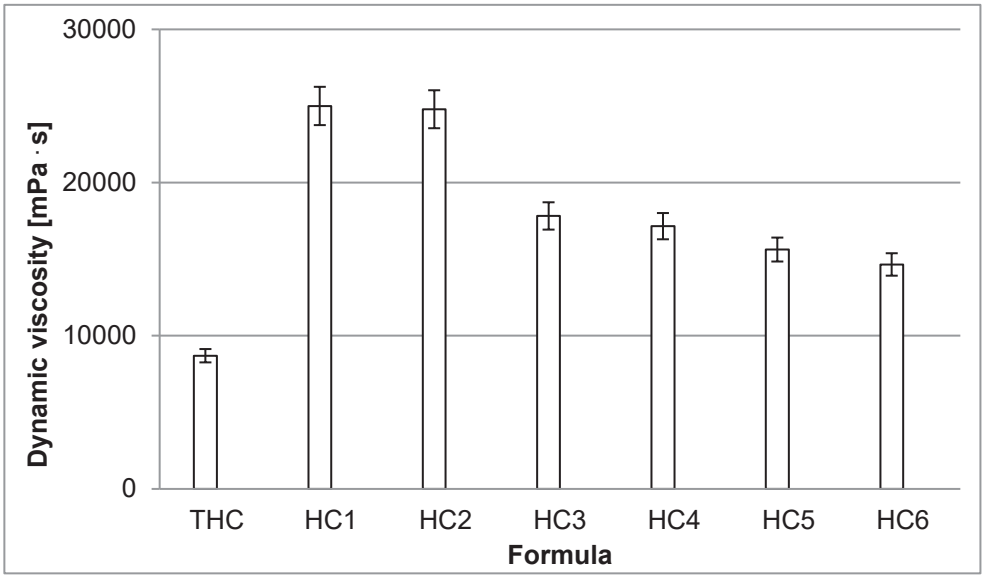

Fig. 3 Dynamic viscosity values for analysed hair conditioners

Source: own study.

Dynamic viscosity of emulsion without Fragaria Ananassa (Strawberry) Seed CO_2 Extract (HC1) was 25000 mPa·s. Introduction of the extract in the lowest concentration of c=1% (HC2 formulation) did not change the measured parameter, however, every further increase in the extract percentage at the cost of lowering paraffin oil content in the formulation caused decrease in η value even by over 40% in comparison with HC1 emulsion. The lowest viscosity was recorded for a commercial hair conditioner (η= 8700 mPa·s).

The work on the use of hydrolysed silk in hair conditioners [Zięba et al. 2017], indicates the viscosity of the obtained emulsions at about 8000 mPa·s, which is lower than that obtained in present work.

Zięba et al. [2016] studied the influence of the type of extract obtained under supercritical carbon dioxide conditions on the viscosity level of the developed cosmetic emulsions. The results of their work show η values ranging from 6000 to 43000 mPa·s.

Other literature data [Klimaszewska et al. 2016] also indicate that replacing hydrophobic emulsion components, e.g. grape seed oil, with blackberry seed extract results in viscosities in the order of 29000 mPa·s, without adversely affecting cosmetic application.

In turn, studies on, e.g. the measurement of dynamic viscosity of emulsion masks with the addition of CO_2 extract of blackberry seeds [Klimaszewska et al. 2016], which rheological properties were regulated with carrageenan gum and xanthan gum give values of the measured parameter at the level above 10000 mPa·s. Thus, they coincide with values obtained for the developed cosmetics.

2.3. Texture analysis

The evaluation of texture of hair conditioners is important for the determination of the proper consistency (hardness) that guarantees easy dosage from the packaging and for the proper adhesion to hair surface. The results of the evaluation of parameters characterizing texture are presented in Fig. 4.

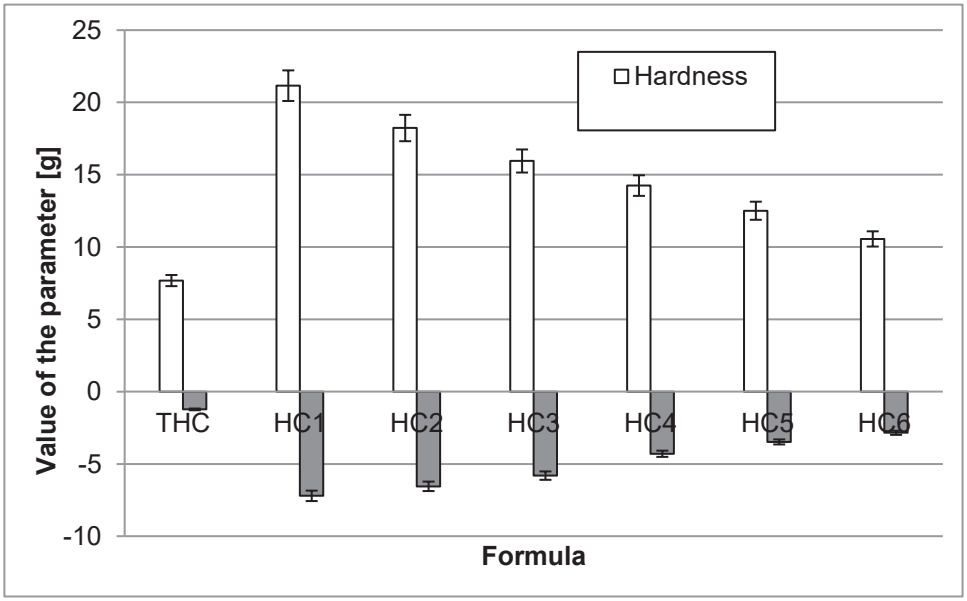

Fig. 4. Hardness and adhesive force values for analysed hair conditioners

Source: own study.

The results of texture measurements (Fig. 4) correlate with the results of viscosity of the developed hair conditioners. The analysis of the obtained results allows formulation of a generalization that the introduction of strawberry seed extract in place of paraffin oil causes a decrease in hardness of the developed emulsions. The highest emulsion hardness (21.16 g) was obtained for base cosmetic containing only paraffin oil (HC1). After the introduction of Fragaria Ananassa (Strawberry) Seed CO_2 Extract the hardness values were in the range from 18.23 g to 10.56 g. Thus, a decrease in the measured quantity was observed with an increase in the proportion of vegetable powder in the formulation, even by ½ compared to the standard. From the point of view of application properties, the results obtained are favourable. Prototypes of hair conditioners are available in the market in jar or squeeze tube packaging. The results of the study indicate that these cosmetics will be easy to dose and apply on hair.

In the case of adhesion, the opposite trend was observed. The value of adhesion force decreases as a function of extract concentration. Values of the measured parameter decrease even 2 times in comparison to the value measured for HC1. However, based on the obtained data, it can be concluded that both spreading and application of the conditioner on hair will be easy for the consumer.

The literature on the subject [Zięba et al. 2017] indicates, in turn, that the introduction of hydrolysed silk into conditioners determines an emulsion hardness of 2.3 to 3.0 g and an adhesion strength in the range of -1.65 to -1.0 g.

Klimaszewska et al. [2016] also obtained trends analogous to those contained in the present work. Increasing the percentage of blackberry extract resulted in lower values of hardness (4.5 g to 5.5 g) and adhesion strength (-1.5 - 1.0 g). Thus, they were significantly lower than those obtained in present work.

2.4. Colour assessment

The use of different extract contents in formulation can cause colour changes of the product. A colorimetric evaluation of made cosmetic emulsions was carried out and the results are presented in Table 2.

Tab. 1. Results of colour evaluation of hair conditioner prototypes.

Formula	Value of the parameter		
	L*	a*	b*
THC	59.16±0.23	-1.37±0.01	-0.10±0.01
HC1	66.43±0.10	-1.48±0.01	1.24±0.01
HC2	66.24±0.12	-1.42±0.02	1.45±0.01
HC3	66.63±0.10	-1.56±0.01	1.53±0.01
HC4	66.44±0.11	-1.71±0.03	2.45±0.01
HC5	66.15±0.20	-1.85±0.01	2.83±0.02
HC6	66.19±0.21	-1.88±0.01	3.70±0.02

Source: own study.

The use of strawberry seed extract in the formula of hair conditioner does not, in principle, cause any change in the value of the L* parameter. The values of the L* parameter are about 66. A lower brightness of the sample was obtained for the commercial product (L*=59.16).

For "a" the values change from -1.48 (for the base emulsion) to -1.88 (for the HC6 mask). In practice, this means that an increase in the concentration of Fragaria Ananassa (Strawberry) Seed CO_2 Extract in the emulsion determined an insignificant increase in green colour intensity, imperceptible to the human eye. The parameter a* for the market conditioner was -1.37.

The parameter "b" took positive values for all prototype masks in the range from 1.45 to 3.7 in relation to the emulsion without added extract (b*=1.24). Thus, it can be concluded that the application of the extract resulted in an increase in yellow colour intensity. For formulation THC the tested parameter was recorded as -0.10.

Work on the addition of blackberry seed extract obtained under supercritical CO_2 conditions to face mask formulations on the change of L*, a*, b* parameters [Klimaszewska et al. 2016]. The researchers found that the introduction of the additive resulted in a yellow-green colour in samples, while an increase in the percentage of the extract resulted in a dominance of the yellow colour and an increase in its saturation.

Bujak et al. [2021] evaluated the colour of emulsions when aqueous-ethanol plant extracts from: *Gomphrena globasa* L. (GGE), *Clitoria ternatea* L. (KTE), *Carthamus tinctorius* L. (CTE), *Punica granatum* L. (PGE), *Papaver rhoeas* L. (PRE). The introduction of plant extracts significantly affected the parameters a* (from -1.06 for the base formulation to 6.23 for the emulsion with KTE) and parameter b* (from 1.43 for the base formulation to 18.92 for the emulsion with *Clitoria ternatea* L.). The degree of whiteness of the samples also changed. For example, after the introduction of *Clitoria ternatea* L. into the base emulsion, the L* value decreased from L* = 91.40 to L* = 68.19, i.e. by 25% relative to the standard.

Also plant raw materials in powder form, introduced into the emulsion can cause changes in its colour. In the study by Klimaszewska et al. [2021] confirmed the effect of the addition of powder obtained from *Lonicera Caerulea* Fruit on all measured

parameters. Based on the results obtained, it was found that the introduction of the powder from Kamchatka berry to the emulsion results in giving the samples a yellow-red colour. In addition, a dominance of the red colour was observed as well as an increase in its saturation and hue.

3. Conclusions

The aim of the article was to develop formulas of emulsion hair conditioners with Fragaria Ananassa (Strawberry) Seed CO_2 Extract and to determine the effect of the extract concentration on physicochemical and functional properties of the produced prototypes.

The following tests, which are the criteria of quality assessment of hair conditioners, were performed: stability of product, dynamic viscosity, texture analysis, colour evaluation of cosmetics.

Based on the laboratory results, the fallowing conclusions can be drawn:

- the developed prototype formulations were stable and showed a more favourable form stability compared to the commercial product;
- dynamic viscosity of cosmetics was in the range from 25000 to 14600 mPa·s. It was found that the substitution of paraffin oil in the formulation by Fragaria Ananassa (Strawberry) Seed CO_2 Extract resulted in a decrease of η value. A commercial cosmetic showed dynamic viscosity of 8700 mPa·s;
- values of hardness of prepared emulsions decreased as a function of increasing extract concentration in formula. The tested parameter was in the range from 10.5 to 21.0 g. Adhesion force varied similarly to hardness. It was estimated in the range from -7.2 to -2.8 g. The results obtained for the market hair conditioner were within the ranges of values determined for the original emulsions. The results of hardness and adhesion force were coherent with the results obtained in dynamic viscosity tests;
- conditioner containing only paraffin oil showed the highest degree of whiteness. With the substitution of paraffin oil by strawberry extract changes of L* parameter were insignificant. Substitution of paraffin oil with Fragaria

Ananassa (Strawberry) Seed CO_2 Extract in the developed emulsions caused green-yellow colour of hair conditioners.

The results of the research presented in this work may serve as a basis for further research and attempts to modify hair conditioner formulations in order to obtain the most beneficial functional properties, especially when it is necessary to develop a product with strictly specified parameters.

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THE FEATURES DETERMINING THE DERMOCOSMETICS' QUALITY

PAULINA MALINOWSKA[1], HENRYK SZYMUSIAK[2]

[1] *Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economics and Business,*
e-mail: paulina.malinowska@ue.poznan.pl
[2] *Department of Technology and Instrumental Analysis, Institute of Quality Science, Poznan University of Economics and Business,*
e-mail: henryk.szymusiak@ue.poznan.pl

Abstract
The aim of the study was to identify the features determining the quality of dermocosmetics. It was conducted on the basis of the survey with consumers and cosmetic sector experts. As a result, the main features determining the quality of dermocosmetics according to consumers and experts were identify, such as effectiveness in skin problem care, safety for health, no adverse skin reactions after using the product, lack of potential allergens, caring properties and the content of highly advanced active ingredients.

Keywords: quality, dermocosmetics, dermocosmetics' market

Introduction

According to PN-EN ISO 9000:2015-10, quality is the degree to which a collection of inherent object features meets the requirements [PN-EN ISO 9000:2015-10]. In commodity science, the concept of product quality has transformed over the years. It was initially treated as compliance with technical conditions, then fitness for use – value in use, user suitability, and finally, the ability to satisfy user-consumer needs and expectations [Karpiel & Skrzypek 2000].

Karpiel and Skrzypek [2000] broke down product quality attributes into several subgroups:

- technical (technical parameters of the product structure and technology),
- utility (functionality, convenience, safety of use, reliability of the product),
- aesthetics (external appearance and how meticulously the product is finished),
- economical (cost of acquisition, installation, operation, etc.),
- ergonomic (the degree the product is adjusted to the anatomical, physiological and psychological characteristics of its users),
- ecological (the interaction between the product and the environment, i.e., consumption and disposal of products),
- logistics (optimal flows of goods, raw materials, and materials as well as any related information).

Quality attributes apply to all products, including dermocosmetics studied in this paper. Dermocosmetics are cosmetics intended to care for specific skin problems, distributed mainly in pharmacies and selected drugstore chains. Dermocosmetics are used as adjuncts to pharmacological and light therapies for skin problem. Dermocosmetics may minimize the side effects of some medications such as skin irritation. Furthermore, dermocosmetics may provide a synergistic effect of improving the efficacy of other treatments [Araviiskaia & Dreno 2016; Goh et al. 2016].

The dermocosmetics' market is extremely profitable though in recent years it has begun to economise. Its growth in quantity terms is still observed, but it is no longer so impressive in terms of value, given that there are more and more brands available at affordable prices. For this reason, dermocosmetic companies continually compete for customers, trying to cater for their changing needs and to be one step ahead of their expectations. The dermocosmetic products bought by today's customers are different from the ones sought only a few years ago. The contemporary dermocosmetics industry promptly reacts to the evolving market requirements, also envisaging a number of changes that are likely to take place in the coming years [Frąckowiak 2015].

Both dermocosmetics and cosmetics embrace the following types of features:

- technical (physicochemical parameters of the product such as viscosity, density, pH, and chemical parameters such as preservative content),
- utility (comfort of use, safety of use, or durability of the product determined by its expiration date),
- aesthetics (shape and color of the packaging, external appearance of the product adequate to its function or its sensory qualities, e.g., smell, color),
- economical (the product price adequate to its properties and functions, and product efficiency adequate to its price),
- ergonomic (convenient package shape or functional package closures),
- ecological (microplastics replaced by natural polymers, biodegradable ingredients, recyclable packaging of cosmetic products, ecological labels),
- logistics (packaging of the product that facilitates the packing and transporting processes, e.g., flat bottoms in face cream containers, cuboid cartons for soap bars) [Wolniak & Moskaluk-Grochowicz 2015].

This paper presents the survey results regarding the features that decide on the dermocosmetics quality; the survey was conducted among consumers (purchasers of dermocosmetics) and experts employed in the cosmetics industry (mainly representatives of producers). Even though since 2016 dermocosmetics have also been distributed beyond pharmacies, consumers still associate this product group mainly with pharmacies and specialized effects. Therefore, studying the quality characteristics of this product group becomes even more vital. The consumer's and manufacturer's perspective on the characteristics that define dermocosmetics quality is rooted in various expectations of the product. The former wants the product to satisfy all their functional (comfort of use, reliability, cost-effectiveness) and non-functional needs (image building, aesthetics). In turn, manufacturers expect the product to be competitive and profitable.

1. Material and methods

Face-to-face questionnaire interviews were conducted with consumers who declared they regularly purchased dermocosmetics and experts from the cosmetics industry. Five hundred fifty-three female respondents from the Wielkopolska province and fifty-eight experts working in various departments of cosmetic companies were asked to indicate the features determining the dermocosmetics quality. The respondents were selected using a non-random, purposive sampling method, as the study results indicate high participation of women in making purchase decisions [Kieżel & Smyczek 2012], both for cosmetics [Jurowczyk 2013], and dermocosmetics [TNS OBOP 2012]. Experts, also selected through the non-random purposive selection method, were, on the other hand, characterized by different lengths of experience in the industry; they worked in the departments of research and development or technology, quality or legal regulations, and marketing or trade marketing in Polish and foreign enterprises.

Consumers, as well as the experts, evaluated the importance of thirteen features that determine the dermocosmetics quality, such as a brand, price, safety for health, lack of adverse skin reactions after product application, highly advanced active ingredients, natural ingredients, absence of potential allergens, such as fragrances, preservatives, alcohol, dyes, coherence between actual care properties of dermocosmetics and those declared by the manufacturer on the packaging, effectiveness in problem skincare, usability/sensory properties, packaging functionality, recommendations of dermatologists and/or research institutes as well as quality and/or environmental certificates.

Spearman rank order correlation, Mann-Whitney U test, and Kruskal-Wallis test were performed to identify statistically significant relationships.

2. Results and disscusion

The results of survey are presented in table 1. According to the consumers, the most important features determining the dermocosmetics quality cover the lack of undesirable skin reactions after product application, effectiveness in problem skin

care, safety for health, lack of potential allergens, e.g., fragrances, alcohol, dyes, the content of highly advanced active ingredients and care properties of dermocosmetics. Features such as the absence of adverse skin reactions after product application and the absence of potential allergens are essential given the purpose of dermocosmetics for sensitive and allergic skin. Persons with the most delicate skin purchase products from these product groups; hence they expect effectiveness in caring for troubled skin without the risk of irritation. This is related to safety for health and a fundamental quality characteristic for dermocosmetics consumers in the broadest sense. According to Regulation No. 1223/2009/EC and its subsequent amendments, each cosmetic product made available on the market should be safe for human health under normal or foreseeable conditions of use.

Table 1. The features determining the dermocosmetics' quality in the opinion of consumers and experts

Feature	Consumers' opinion	Experts' opinion	Results of U Mann-Whitney test
Brand	3.63 ± 1.13	3.41 ± 1.20	Z = -1.261; p = 0.207
Price	3.67 ± 1.15	3.24 ± 1.14	Z = -2.590; p = 0.010
Safety for health	4.34 ± 0.90	4.24 ± 1.08	Z = -0.483; p = 0.629
Lack of adverse skin reactions after product application	4.46 ± 0.79	4.09 ± 1.17	Z = -2.082; p = 0.037
Highly advanced active ingredients	4.22 ± 0.86	3.90 ± 1.02	Z = -2.237; p = 0.025
Natural ingredients	4.09 ± 0.94	3.33 ± 1.15	Z = -4.732; $p < 0.001$
Absence of potential allergens , such as fragrances, preservatives, alcohol, dyes	4.23 ± 0.91	3.93 ± 1.12	Z = -1.744; p = 0.081
Care properties of dermocosmetics	4.22 ± 0.88	4.19 ± 1.00	Z = 0.121; p = 0.904
Effectiveness in problem skincare	4.34 ± 0.85	4.45 ± 0.78	Z = 0.690; p = 0.490
Usability/sensory properties	3.79 ± 0.97	3.12 ± 0.90	Z = -4.824; $p < 0.001$

Feature	Consumers' opinion	Experts' opinion	Results of U Mann-Whitney test
Packaging functionality	3,32 ± 1,08	2,57 ± 0,98	Z = -4,776; *p < 0,001*
Recommendations of dermatologists and/or research institutes	3,52 ± 1,06	3,81 ± 1,02	Z = 2,022; *p* = 0,043
Quality and/or environmental certificates	3,44 ± 1,13	3,60 ± 1,08	Z = 1,095; *p* = 0,273

Explanations: scale 1–5, where 1 means the less important feature, 5 means the most important feature;

p – significance level for the test value; Z – value of the test

Source: [Malinowska 2020].

The absence of adverse skin reactions after product application as a quality-defining characteristic was more critical for female consumers over 40 than for younger consumers. Consumers perceive safety as a feature associated with a lower risk of adverse skin reactions. Safety for health significantly less determined the dermocosmetics' quality according to female consumers aged 20-29 than in the other groups. Other quality characteristics, such as efficacy in the care of problem skin, the content of highly advanced active ingredients, and care properties of dermocosmetics, are also closely interrelated. Manufacturers of dermocosmetics put a lot of effort into preparing appropriate information materials on websites or leaflets describing comprehensive care properties of the products they offer, tests, advanced active ingredients, or formulas. This impacts the opinions of consumers, who mainly expect better cosmetic effects after using the products with higher concentrations of active ingredients acting on a specific skin problem.

The conducted study proved that efficacy in problem skin care was of lower significance for consumers with basic vocational and secondary education in determining the quality than in the groups of respondents with basic and higher education. In contrast, the content of highly advanced active ingredients became more critical as a quality-defining characteristic as the income of female consumers increased. The care properties of dermocosmetics were less critical to consumers aged 15-19

than to other groups, while with increasing income and better financial situation, respondents increasingly associated this feature with the dermocosmetics quality.

According to the consumers surveyed, the price determines the quality of dermocosmetics to a lesser extent than such features as safety for health, absence of adverse skin reactions, the content of highly advanced active and natural ingredients, absence of allergens, care properties, effectiveness or usability properties. In turn, the price determines quality more than a brand, packaging functionality, institute recommendations, or quality certifications. Consumers with primary and vocational education associate the price with the quality of the dermocosmetics to a greater extent than respondents with secondary and higher education. There are growing views in the literature that the phenomenon of inferring quality based on price is less common than one might think [Boyle & Lathrop 2009]. This is because the perception of quality also depends on several factors beyond the price – the product's appearance, other people's opinions about it, the brand, and the point of sale [East et al. 2015]. The research suggests that the importance of price as a quality indicator depends on which product elements a customer values [Brucks, Zeithaml & Naylor 2000]. The price promises reliability, fulfillment, and satisfaction to the consumer [Przybylska 2010].

According to the respondents, the brand determines the dermocosmetics quality also to a lesser extent than such features as safety for health, lack of adverse skin reactions after product application, highly advanced active ingredients, natural ingredients, lack of potential allergens, care properties of dermocosmetics, effectiveness in problem skin care, utility/sensory properties and price. The brand determines the dermocosmetics quality more than the packaging functionality, recommendations from dermatologists and/or research institutes, and quality and/or environmental certificates. The literature describes the brand as a synonym of a high-quality product – it is associated with utility features or symbolics of a given product. They say there is a close relationship between quality and brand. It is worth noting that perceived quality does not always have an objective basis, and actual quality often differs from the perceived one [Przybylska 2010]. Female consumers aged 15-19 ascribed the greatest importance to the brand being an attribute that defines the dermocosmetics

quality, while respondents aged 20-29 ascribed the least importance to this feature. Associating the dermocosmetics brand with its quality decreased as the educational level of the female consumers surveyed increased.

The least important quality features are recommendations from dermatologists and/or research institutes, quality and/or ecological certificates and the packaging functionality.

According to experts, the most important features of dermocosmetics are effectiveness in problem skin care, safety for health, care properties of dermocosmetics, lack of adverse skin reactions after product application, lack of potential allergens and content of highly advanced active ingredients. Less important factors are recommendations from dermatologists and/or research institutes as well as quality and/or organic certifications. Brand name, natural ingredient content, price, sensory properties, and packaging functionality are considered the least important factors.

Expert opinions differed when it comes to the importance of the various characteristics that define the dermocosmetics' quality depending on their seniority in the industry, department, size, and type of company they worked for. Marketing and trade marketing professionals assigned significantly higher ratings to safety for health and efficacy in problem skincare compared to experts in R&D and technology, and quality and regulatory departments. In expert opinions coming from foreign enterprises, such features as lack of adverse skin reactions after product application, highly advanced active ingredients, natural ingredients, lack of potential allergens and care properties of dermocosmetics, play a greater role in determining the quality of dermocosmetics than for specialists from Polish companies. In contrast, groups of respondents who work in large and medium-sized enterprises rated the role of this feature higher than those working in small and micro enterprises.

The Mann-Whitney U test was used to compare the opinions of experts and consumers on the features that determine the dermocosmetics' quality (table 1). Opinions on seven of the thirteen characteristics defining the dermocosmetics quality were statistically significantly different between the experts and consumers surveyed. Consumers rated the importance of features such as price, no adverse skin reactions after product application, content of highly advanced active ingredients,

content of natural ingredients, usability/sensory properties and packaging functionality higher than the experts. The experts, on the other hand, found the recommendations by dermatologists and/or research institutes to be a more essential quality feature of dermocosmetics. Experts and consumers were similar in their evaluation of the following features: brand, safety for health, absence of potential allergens, care properties of dermocosmetics, and effectiveness in the care of problem skin, as well as quality and/or ecological certificates.

3. Conclusions

According to the consumers, features that determine the dermocosmetics' quality, such as lack of adverse skin reactions after product application, effectiveness in troubled skin care, safety for health, lack of potential allergens or the content of highly advanced active ingredients, emphasized by the company in its marketing communications and at the same time being the actual features of the offered dermocosmetics, are the key to effective competition in the dermocosmetics' market. Enterprises should develop dermocosmetics that minimize the risk of skin allergies, preferably free of allergens while containing effective active ingredients. "Specialized" communication and the "medical environment" of dermocosmetics will not help an enterprise make better profits, if the products they offer are not effective in solving skin problems, and the actual skincare properties are not coherent with the ones claimed. Furthermore, the studies have shown that consumers do not associate recommendations from dermatologists or research institutes with product quality. Manufacturers who offer dermocosmetics should, therefore, pay attention to this fact, as opinion-forming or clinical studies in medical centers definitely increase the enterprises' costs related to formulation and development.

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CECHY OKREŚLAJĄCE JAKOŚĆ PRODUKTÓW DERMOKOSMETYCZNYCH

Streszczenie
Celem pracy była identyfikacja cech określających jakość dermokosmetyków. Przeprowadzono ją na podstawie wywiadów indywidualnych z konsumentami oraz ekspertami zatrudnionymi w branży kosmetycznej. W rezultacie zidentyfikowano główne cechy określające jakość dermokosmetyków według konsumentów i ekspertów, takie jak skuteczność w pielęgnacji skóry problemowej, bezpieczeństwo dla zdrowia, brak niepożądanych reakcji skóry po zastosowaniu produktu, brak potencjalnych alergenów, właściwości pielęgnacyjne dermokosmetyku oraz zawartość wysoce zaawansowanych składników aktywnych.

Słowa kluczowe: cecha jakościowa, dermokosmetyk, rynek dermokosmetyczny

WPŁYW NATURALNYCH MODYFIKATORÓW LEPKOŚCI NA PARAMETRY UŻYTKOWE HYDROŻELOWYCH BAZ KOSMETYCZNYCH

MAGDALENA WASYLUK, ANITA BOCHO-JANISZEWSKA, PAULINA JABŁOŃSKA

Katedra Chemii Przemysłowej, Wydział Inżynierii Chemicznej i Towaroznawstwa, Uniwersytet Technologiczno-Humanistyczny w Radomiu,
e-mail: m.wasyluk@uthrad.pl

Streszczenie
Opracowano i sporządzono hydrożelowe bazy kosmetyczne z zawartością gum pochodzenia naturalnego. Oceniono wpływ różnych stosunków wagowych gumy guar do gumy ksantanowej (1:0; 0:1; 0,5:0,5; 0,3:0,7; 0,7:0,3 % wag.) na parametry użytkowe baz kosmetycznych. Wykonano badanie lepkości dynamicznej, tekstury, pomiary korneometryczne i tewametryczne oraz dokonano analizy sensorycznej.
Stwierdzono, iż istnieje możliwość wytworzenia hydrożelowych baz kosmetycznych o pożądanych właściwościach aplikacyjnych (sensoryka, tekstura) i kosmetycznych (podwyższenie nawilżenia skóry i obniżenie przeznaskórkowej utraty wody (TEWL).
Sporządzone bazy mogą służyć jako medium dla składników aktywnych rozpuszczalnych w wodzie. Także mogą stanowić gotowy produkt pielęgnacyjny.

Słowa kluczowe: hydrożelowe bazy kosmetyczne, guma guar, guma ksantanowa, modyfikatory lepkości

Wprowadzenie

W ostatnich latach na rynku kosmetycznym obserwuje się dwa skrajne trendy, tj. kosmetyki z bardzo wysoką zawartością wody i produkty bezwodne lub z minimalną ilością wody. Kosmetyki wodne są szczególnie popularne na rynku azjatyckim szczególnie w Korei Południowej skąd pochodzi, tzw. trend K-Beauty. Trend ten nazywany inaczej Korean Beauty czy Korean Care jest popularny także na rynku

europejskim. Koreańska filozofia dbania o skórę propaguje wieloetapową pielęgnację, w której stosuje się m.in. produkty z wysoką zawartością wody. Są to produkty handlowe nazywane esencjami, galaretkami oraz maski w płachcie i hydrożelowe płatki pod oczy. Produkty pielęgnacyjne bazujące na dużej zawartości wody pełnią rolę produktów nawilżających, napinających i wygładzających skórę. Posiadają lekkie, beztłuszczowe formulacje. Zawierają często ekstrakty roślinne (aloes, wąkrotka azjatycka), humektanty takie jak gliceryna, sorbitol, kwas hialuronowy, mocznik oraz witaminy rozpuszczalne w wodzie [Chung-Hwa & Hyun-Jeong 2020; Wang & Hwa Lee 2019; Kamińska & Zieliński 2017; Karłowicz-Bodalska i in. 2013; Lodén 2003; Śliwa i in. 2011]. W produktach kosmetycznych używana jest woda wysokiej jakości - woda destylowana. Stosowane są także inne rodzaje wód np. woda termalna z francuskiego - eau thermale (INCI: Thermal Spring Water). Do innych niszowych wód należy woda z lodowca (INCI: Glacier Water) [Budzowski 2012; Łubkowska 2016; Sapińska- Śliwa & Kurpik 2011; Chen i in. 2017].

Typ bazy kosmetycznej przekłada się także na wiele cech użytkowych. Dla konsumentów ważna jest łatwość rozprowadzania produktu na powierzchni skóry. Istotną wielkością jest więc lepkość dynamiczna podłoża kosmetycznego. Lepkość jest często mylona przez konsumentów z gęstością, chociaż to dwie różne wielkości fizyczne. Lepkość dynamiczna jest to właściwość dotycząca płynów, tj. cieczy i gazów. Lepkość ma wpływ m.in. na wygodne dozowanie produktu z opakowania. Lepkość kosmetycznych preparatów wodnych modyfikowana jest poprzez zastosowanie polimerów syntetycznych, półsyntetycznych i naturalnych. Do najpopularniejszych syntetycznych polimerów należą pochodne kwasu akrylowego. Jednak do zainicjowania żelowania i uzyskania odpowiedniej lepkości należy wyregulować pH do 6.8 [Kamińska & Zieliński 2017; Tal-Figiel i in. 2013]. Do modyfikowania lepkości kosmetyków służą także pochodne celulozy, np. karboksymetyloceluloza, hydroksyetyloceluloza, hydroksypropyloceluloza, hydroksymetylopropyloceluloza [Szymański i in. 2015]. Natomiast do polimerów pochodzenia naturalnego należą gumy, które są polisacharydami pozyskiwanymi z roślin (guma arabska, guma ghati, guma guar, guma karob, guma konjak, guma tara, guma tragakantowa), alg (agar, karagen, alginiany) oraz metodami mikrobiologicznymi (guma dekstran, guma gellan, guma

kurdlan, guma ksantanowa, guma pullan, guma ramsan, guma velan) [Zięba i in. 2018; Orczykowska i in. 2011; Nowak i in. 2018].

Guma guar (GG-ang. Guar Gum) jest otrzymywana z nasion indyjskiej rośliny jednorocznej *Cyamopsis tetragonoloba.* Guma ta zbudowana jest z mannozy i galaktozy w stosunku 2:1. Stosowana jest w przemyśle kosmetycznym, farmaceutycznym i spożywczym. W produktach kosmetycznych pełni różne funkcje. Stosowana jest głównie jako stabilizator i modyfikator lepkości w emulsjach oraz stabilizator piany w szamponach [Zięba i in. 2018; Nowak i in. 2018].

Guma ksantanowa (XG- ang. Xanthan Gum) otrzymywana jest biotechnologicznie przy udziale bakterii *Xanthomonas campestris.* Mikroorganizm ten rozmnaża się w środowisku cukrowym. Po procesie fermentacji guma ksantanowa jest wytrącana przy użyciu alkoholu. Następnie jest suszona i mielona. Guma ksantanowa składa się z łańcucha głównego zbudowanego z D-glukozy i łańcuchów bocznych utworzonych z dwóch jednostek D-mannozy i jednej cząsteczki kwasu glukuronowego. W roztworach wodnych tworzy wiązania helikoidalne związane ze sobą oddziaływaniami wodorowymi. Guma ksantanowa znalazła zastosowanie w przemyśle kosmetycznym, farmaceutycznym i spożywczym. Stosowana jest zarówno w kosmetykach pielęgnacyjnych jak i myjących. Gumy pochodzenia naturalnego stosowane są z powodzeniem, np. w szamponach do włosów, płynach do kąpieli dla dzieci, fazie wodnej dwufazowych produktów do pielęgnacji ciała [Zięba i in. 2018; Klimaszewska 2017; Wasyluk i in. 2019].

Oprócz odczuć w czasie rozprowadzania produktu na powierzchni skóry ważne są także odczucia po aplikacji. Hydrożelowe bazy kosmetyczne nie dają uczucia tłustości i często wybierane są do cery tłustej i mieszanej. Mogą być wykorzystane do sporządzania różnych rodzajów kosmetyków. W zależności od dodatkowych składników mogą stanowić bazę kosmetyków myjących, pielęgnacyjnych, pod makijaż, czy też żelu do utrwalania włosów.

Na potrzeby niniejszej pracy wytworzono hydrożelowe bazy kosmetyczne z sumarycznym udziałem procentowym 1% wag. polimerów naturalnych (gumy guar i gumy ksantanowej) w formulacji. Receptury różniły się stosunkami wagowymi gumy guar do gumy ksantanowej (1:0; 0:1; 0,5:0,5; 0,3:0,7; 0,7:0,3 % wag.).

Prototypy baz poddano badaniu lepkości dynamicznej, tekstury, ocenie stopnia nawilżenia skóry, przeznaskórkowej utraty wody oraz analizie sensorycznej.

1. Materiały i metody

1.1. Materiały

Do sporządzenia hydrożelowych baz kosmetycznych użyto następujących składników: guma guar (Guar Gum; Biomus; Polska), guma ksantanowa (Xanthan Gum; Biomus; Polska), gliceryna (Glycerin; Cremerglyc; Cremer; Polska;), konserwant (Benzisothiazolinone and Methylisothiazolinone; Acticide MBS; Thor;), kwas cytrynowy (Citric Acid; HSH Chemie; Polska), woda destylowana. Podłoża wykonano według receptury w Tabeli 1.

Tabela 1. Skład prototypów baz kosmetycznych o zmiennych proporcjach polimerów (sumaryczny udział to 1% wag.)

Nazwa wg INCI*	**% wag.**				
Cynamopsis Tetragonoloba (Guar) Gum	1	-	0.5	0.3	0.7
Xanthan Gum	-	1	0.5	0.7	0.3
Glycerin	4				
Benzisothiazolinone (and) Methylisothiazolinone	q.s.				
Citric Acid	do pH 5.5				
Aqua (Water)	do 100				
Oznaczenie receptury	**P1**	**P2**	**P3**	**P4**	**P5**

Źródło: opracowanie własne.

INCI-International Nomenclature of Cosmetic Ingredients.*

W zlewce odważono glicerynę i za pomocą szklanej bagietki roztworzono w niej odpowiednią proporcję gum. Potem porcjami dodawano wodę destylowaną. Powstałą próbkę powoli mieszano przy użyciu mieszadła magnetycznego. Następnie wprowadzono konserwant. Na końcu wyregulowano pH za pomocą kwasu

cytrynowego i wymieszano całość. Tak wykonane podłoża zbadano pod względem fizykochemicznym, użytkowym jak i pielęgnacyjnym.

1.2. Metody badawcze

Podłoża kosmetyczne poddano badaniu lepkości dynamicznej za pomocą lepkościomierza Brookfield DV-I+. Badanie wykonano w temperaturze 22°C. Zastosowano prędkość obrotową równą 60obr./min. Pomiar przeprowadzono trzykrotnie. Wynikiem końcowym została średnia arytmetyczna otrzymanych pomiarów.

Badanie tekstury przeprowadzono na analizatorze tekstury CT3 Brookfield. Użyto sondy symulującej nacisk palcem (nylonowa sonda sferyczna TA43). Zadano następujące ustawienia: prędkość 0,1 mm/s, dystans 10 mm. Oznaczono takie parametry jak twardość i siła adhezji. Wyniki zostały wygenerowane przez oprogramowanie Brookfield Texture Pro CT. Dla każdego z badanych prototypów wykonano po 3 pomiary, które dalej uśredniono.

Stopień nawilżenia skóry zmierzono przy użyciu sondy korneometrycznej podłączonej do urządzenia firmy Courage+Khazaka electronic GmbH. Na skórze przedramienia wyznaczono pola o powierzchni 2x2 cm: pole kontrolne (skóra nie pokryta preparatem) i pole badane na które aplikowano po 0,5 ml kosmetyku. Nawilżenie skóry odczytano po 30 i 60 minutach od aplikacji preparatów. Za wynik końcowy przyjęto średnią arytmetyczną 10 wyników przeprowadzony przez kobiety w wieku 23 lat. Rezultaty badań przedstawiono w jednostkach arbitralnych [a.u.].

Pomiar przeznaskórkowej utraty wody (TEWL) wykonano za pomocą tewametru firmy Courage+Khazaka electronic GmbH. Na skórze przedramienia wyznaczono pola 4 cm^2 (pola kontrolne nie pokryte preparatem oraz pola badane na które aplikowano po 0,5 ml preparatu). Po czasie 30 i 60 minut od aplikacji podłoży wykonano po 10 pomiarów, które następnie uśredniono. Wyniki przedstawiono na wykresie w jednostkach TEWL [$g/m^2/h$].

Analizę sensoryczną przeprowadziła grupa uprzednio przeszkolonych probantów w wieku 23-28 lat. Badanie wykonano w odpowiednich warunkach (stałe światło i temperatura pomieszczenia). Ocenie poddano takie parametry jak: efekt poduszki,

jednolitość, konsystencja, przyczepność, rozprowadzanie, kleistość oraz wygładzenie. Parametry te opisano w Tabeli 2. Każdy parametr oceniono w skali 1-5 (1 oznacza zły, a 5 bardzo dobry). Za wynik końcowy przyjęto średnią arytmetyczną ocen zaokrąglonych do liczb całkowitych, przeprowadzonych dla każdej z cech.

Tabela 2. Parametry podłoży w analizie sensorycznej

Parametr	Objaśnienie
Efekt poduszki	Oznacza ilość wyczuwalnego preparatu pomiędzy palcami (kciuk i palec wskazujący) podczas pocierania.
Jednolitość	Opisuje jednorodność i gładkość powierzchni podłoża. Ocenę przeprowadzono w naczyniu oraz po rozprowadzeniu próbki na powierzchni skóry.
Konsystencja	Stanowi gęstość i spójność preparatu.
Przyczepność	Oznacza możliwość pobrania produktu na opuszek palca.
Rozprowadzanie	Łatwość rozprowadzenia próbki na skórze i stopień oporu podczas aplikacji.
Kleistość	Oznaczenie stopień kleistości po aplikacji produktu na skórze.
Wygładzanie	Stanowi gładkość obszaru na której zostało zaaplikowane podłoże z obszarem bez aplikacji próbki.

Źródło: opracowanie własne na podstawie [Kuta i in.2017].

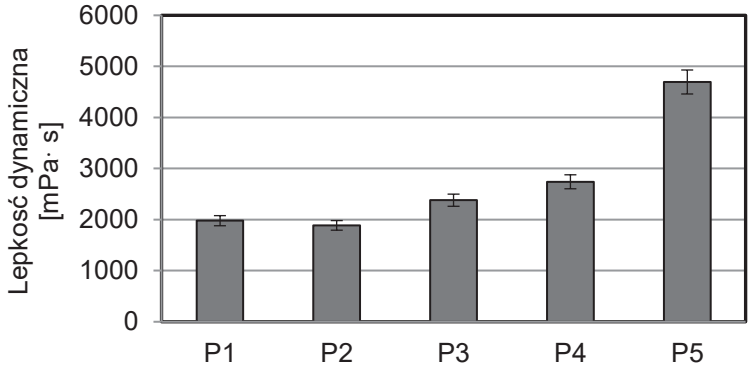
1.3.Analiza statystyczna wyników

Przedstawione wyniki są średnią arytmetyczną z trzech lub dziesięciu pomiarów. Oszacowano przedziały ufności, które stanowią błąd pomiarowy na poziomie +/- 5%. Wartości błędów są widoczne na wykresach.

3. Wyniki

Lepkość dynamiczna

Lepkość jest istotną cechą warunkującą funkcjonalność podłoża. Odpowiednia lepkość preparatu dobierana jest do danego opakowania. Opakowanie z kolei powinno umożliwiać łatwe dozowanie produktu. Wyniki lepkości dynamicznej przedstawiono na Rys.1.



Rys. 1. Lepkość dynamiczna hydrożelowych baz kosmetycznych w zależności od proporcji gumy guar do gumy ksantanowej

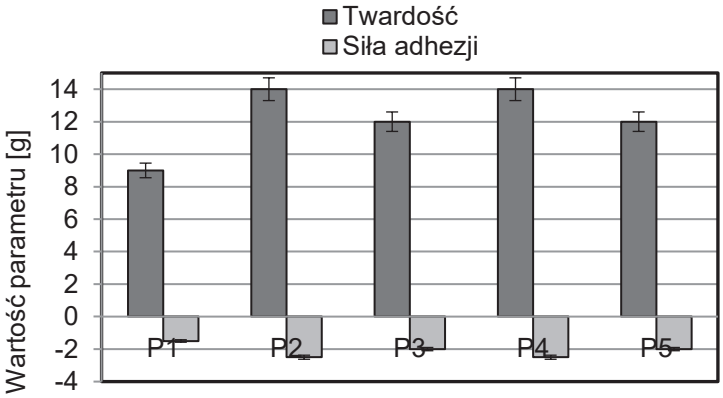
Źródło: badanie własne.

Lepkość badanych podłoży przy prędkości 60 obr./min. wynosiła od 1887 do 4695 mPa·s. Najwyższą lepkość (4695 mPa·s) oznaczono dla próbki P5 z zawartością 0,7% wag. gumy guar i 0,3% wag. gumy ksantanowej. Najniższą lepkość, tj. 1887 mPa·s odnotowano dla preparatu o oznaczeniu P2. Połączenie gumy guar i gumy ksantanowej pozwala osiągnąć wyższą lepkość bazy niż zastosowanie tych gum osobno. Otrzymane wyniki są zgodne z literaturą [Gustaw i in. 2001].

Tekstura

Tekstura jest to szereg cech wpływających na konsystencję produktu. Badanie tekstury przy użyciu analizatora tekstury pozwala na obiektywne oznaczenie wielu parametrów, np. twardości i siły adhezji. Parametry te oznaczane są za pomocą zmysłów i instrumentalnie. Według definicji sensorycznej [Kuta i in. 2017] twardość jest to siła niezbędna do ściśnięcia (kompresji) badanej próbki i odzwierciedla się w stopniu łatwości rozprowadzaniu produktu po powierzchni skóry. Natomiast według definicji instrumentalnej jest to maksymalna siła zarejestrowana przez urządzenie w trakcie pierwszego cyklu kompresji.

Siła adhezji określa przyczepność próbki do sondy. W praktyce jest określana jako przyczepność kosmetyku do palca przy jego nabieraniu. Pomiary tekstury powtórzono trzykrotnie, wyniki uśredniono i przedstawiono na Rys.2.



Rys. 2. Twardość i siła adhezji badanych baz kosmetycznych

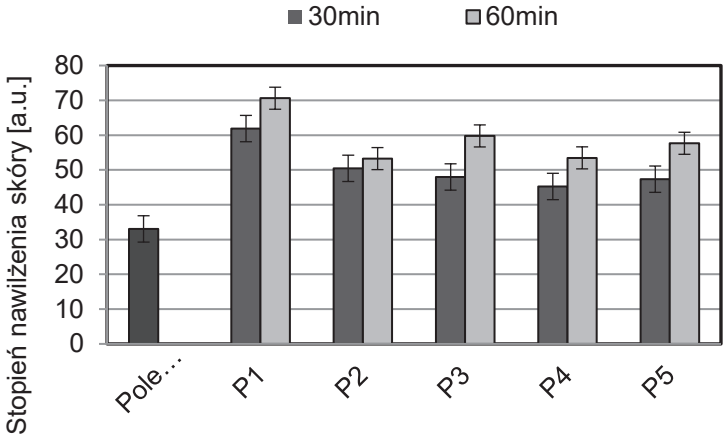
Źródło: badanie własne.

Twardość badanych podłoży wahała się od 9 do 14 g. Najwyższą twardość zanotowano dla podłoża P2 i P4 a najniższą dla P1.

Natomiast siła adhezji analizowanych próbek kształtowała się w przedziale od -2,5 do -1,5 g. „Najlepszą" przyczepność z badanych podłoży osiągnęła próbka P2 i P4, najsłabszą zaś próbka P1 (1% GG i 0% XG). Uzyskane wyniki siły adhezji są zbliżone, np. do szamponów z gumami naturalnymi [Zięba i in. 2018].

Stopień nawilżenia skóry

Podłoża mają przede wszystkim spełniać rolę medium dla substancji aktywnych. Aczkolwiek mogą niekiedy wykazywać samodzielne działania kosmetyczne. Stopień nawilżenia warstwy rogowej naskórka po aplikacji prototypów podłoży przedstawiono na Rys. 3.



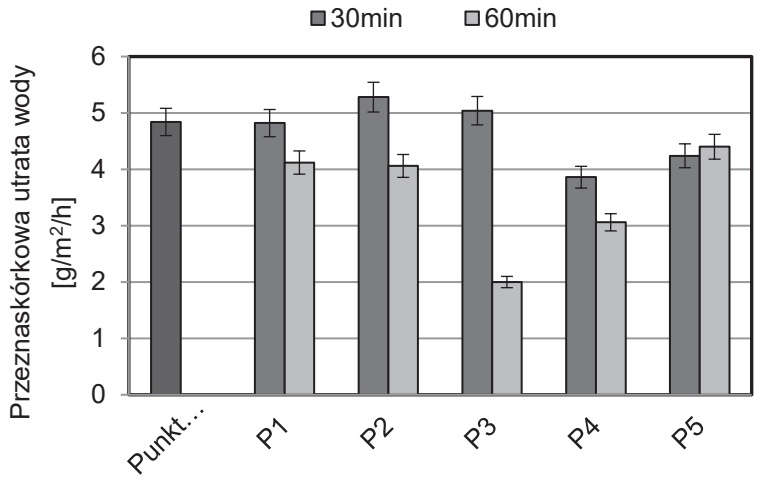
Rys. 3. Stopień nawilżenia skóry po aplikacji badanych baz kosmetycznych

Źródło: badanie własne.

Pole kontrolne (niepokryte preparatem) odznaczało się nawilżeniem na poziomie ok. 33 a.u. Wszystkie badane podłoża spowodowały poprawę nawilżenia warstwy rogowej naskórka w stosunku do pola kontrolnego. Po czasie 30 minut od aplikacji podłoży odczytane nawilżenie to od 45,2 do 61,9 a.u. Natomiast po 60 minutach od 53,3 do 70,6 a.u. Najwyższy wzrost w stosunku do pola kontrolnego odczytano dla podłoża P1 (1% gumy guar i 0% gumy ksantanowej). Następnie kolejno dla podłoży oznaczonych jako P2, P5, P3 i P4. Wzrost nawilżenia po 60 minutach od aplikacji bazy z gumą ksantanową jest zgodny z żelami stanowiącymi produkt gotowy [Kamińska & Zieliński 2017].

Przeznaskórkowa utrata wody

Polimery mogą wykazywać działanie błonotwórcze, które ogranicza przeznaskórkową utratę wody. Przeznaskórkowa utrata wody po zastosowaniu podłoży w zależności od proporcji gum została zobrazowana na Rys. 4.



Rys. 4. Przeznaskórkowa utrata wody po aplikacji badanych baz kosmetycznych

Źródło: badanie własne.

Odczyt transepidermalnej utraty wody dla pola kontrolnego (niepokrytego preparatem) to 4,84 g/m^2/h. Natomiast po czasie 30 minut od nałożenia preparatów TEWL to wartości od 3,86 do 5,28 g/m^2/h, zaś po 60 minutach to od 2 do 4,4 g/m^2/h. Otrzymany spadek TEWL jest zjawiskiem korzystnym po zastosowaniu kosmetyków pielęgnacyjnych.

Analiza sensoryczna

Analiza sensoryczna jest badaniem subiektywnych odczuć panelistów. Pozwala na oznaczenie preferencji konsumentów. W Tabeli 3 przedstawiono wyniki analizy sensorycznej.

Tabela 3. Uśrednione wartości oceny sensorycznej badanych podłoży

Parametr	Oznaczenie receptury				
	P1	P2	P3	P4	P5
Efekt poduszki	5	4	4	5	5
Jednolitość	5	5	5	5	5
Konsystencja	5	5	5	5	5
Przyczepność	4	4	3	4	4
Rozprowadzanie	5	4	4	4	4
Kleistość	4	4	4	4	4
Wygładzenie	5	5	5	4	4

Źródło: badanie własne.

Maksymalna możliwa wysokość oceny sensorycznej w niniejszych badaniach to 5 punktów, zaś najniższa to 1 punkt. Niemal wszystkie analizowane podłoża kosmetyczne osiągnęły wysokie noty (5 lub 4 punkty). Jedynie dla podłoża P3 dla parametru przyczepność oznaczono 3 punkty. Otrzymane wyniki analizy sensorycznej świadczą o dobrych właściwościach pożądanych przez konsumentów.

4. Podsumowanie

W pracy podjęto próbę opracowania i wytworzenia bazy kosmetycznej o wysokiej zawartości wody. Jako modyfikator reologii wykorzystano polimery pochodzenia naturalnego o łącznym stężeniu 1% wag. Zbadano wpływ stosunku gumy guar do gumy ksantanowej na właściwości takie jak lepkość dynamiczna, tekstura (twardość i siła adhezji), stopień nawilżenia warstwy rogowej naskórka, transepidermalna utraty wody i parametry sensoryczne.

Lepkość dynamiczna badanych prototypów podłoży była w kolejności następującej: P5>P4>P3>P1>P2. Odczytana najniższa lepkość była ponad dwukrotnie niższa od oznaczonej najwyższej lepkości. Najwyższą lepkość uzyskano dla kosmetyku zawierającego polimery o stosunku wagowym 0,7% gumy guar i 0,3% gumy ksantanowej. Próbka o takiej kombinacji gum najefektywniej wpływa na zwiększenie lepkości. Stosując taką proporcję dwóch gum możliwe jest również zmniejszenie

łącznej zawartości polimerów w celu osiągnięcia pożądanej lepkości. Jest to istotne z punktu widzenia obniżania kosztów produkcji.

W wyniku badania tekstury stwierdzono, iż najwyższą twardość z badanych próbek otrzymano dla podłoża P2 (1% gumy ksantanowej) i P4 (0,3% gumy guar i 0,7% gumy ksantanowej). Najlepszą przyczepność uzyskano również dla próbki P2 i P4.

Wytworzone hydrożelowe bazy kosmetyczne odznaczały się dobrymi właściwościami pielęgnacyjnymi. Stopień nawilżenia skóry po aplikacji próbek w stosunku do pola kontrolnego był znacznie większy. Wzrost nawilżenia w stosunku do pola kontrolnego był widoczny już po 30 minutach. Jednak jeszcze wyższe nawilżenie odczytano po 60 minutach. Badane podłoża także efektywnie ograniczały przeznaskórkową utratę wody po 1 godzinie od aplikacji preparatów. To działanie wynika z zastosowania polimerów o właściwościach błonotwórczych w tym gum pochodzenia naturalnego.

Analiza sensoryczna wodnych podłoży wykazała, iż preparaty spełniają zadowalające właściwości organoleptyczne i użytkowe. Wskazują na to wysokie oceny poszczególnych parametrów sensorycznych.

Reasumując można stwierdzić, iż przygotowane preparaty mogą stanowić zarówno samodzielny kosmetyk pielęgnacyjny lub ochronny, jak i bazę do gotowych kosmetyków. W zależności od dodania komponentów można uzyskać kosmetyki różnego przeznaczenia. Dodając do podłoża detergenty można otrzymać żele do mycia twarzy i ciała, szampony do włosów, mydła w płynie lub specjalistyczne pasty do mycia rąk. Także wzrost stężenia modyfikatorów lepkości może stanowić odpowiednią bazę dla tzw. żelu do utrwalania fryzury. Zatem istnieje możliwość sporządzenia naturalnego i funkcjonalnego podłoża kosmetycznego o wszelakich zastosowaniach.

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