Uniwersytet Morski
w Gdyni

Wydział Zarządzania
i Nauk o Jakości

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

Innovations in quality development of products and services, vol. 1

Innowacje w kształtowaniu jakości wyrobów i usług, tom 1

Red. Przemysław Dmowski

Gdynia 2022

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pod redakcją Przemysława Dmowskiego

Gdynia 2022

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Projekt dofinansowany przez Ministerstwo Edukacji i Nauki w ramach programu "Doskonała Nauka", numer umowy: DNM/SP/547067/2022.

PROJEKT OKŁADKI: Agnieszka Palka

WYDAWCA:

UNIWERSYTET MORSKI W GDYNI
ul. Morska 81-87
81-225 Gdynia
www.umg.edu.pl

ISBN 978-83-7421-436-0

Projekt i opracowanie graficzne:

Grafpol sp. z o.o.
ul. Żmudzka 21, 51-354 Wrocław
www.argrafpol.pl

SPIS TREŚCI

SAFETY OF MEDICAL DEVICES (MD) CLASS I BASED ON DIRECTIVE MDR

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Abstract
Medical devices, class I are the most comprehensive group of all medical devices. Orthopaedic footwear is classified as MD class I. Economic reasons encourage manufacturers, who produces footwear for people with reduced mobility, to attempt to market footwear that is a MD class I. However, registration of such a product is possible only after certain procedures are complied with The article presents the methods of testing seleted footwear components for certifications as a MD class I. The results of tests of footwear components selected at the footwear design stage and the test results of the footwear prototypes are also presented.

Keywords: medical devices, MDR directive, orthopaedic footwear, product safety

Introduction

Orthopedic footwear being a class I medical device have to meet certain requirements. Consequently, not only footwear, as a final product have to be tested but also footwear components.

The main aim of this article is to present the methods of testing footwear components for certification as a medical device. Moreover, paper shows the results of biomechanical tests which were carried out using prototype of designed footwear.

1.1. Medical device market

The medical device market is currently estimated at around EUR 115 billion. Medicale devices class I constitute the most numerous group among all medical devices. As specified in Art. 2 Regulation (EU) 2017/745 of the European Parliament and of the Council of 5 April 2017 on medical devices, amending Directive 2001/83/EC, Regulation (EC) No 178/2002 and Regulation (EC) No 1223/2009 and repealing Council Directives 90/385/EEC and 93/42/EEC (hereinafter: MDR DIRECTIVE) a medical device is: a tool, apparatus, device, software, implant, reagent, material or other device intended by the manufacturer for use (...) in humans for diagnosis, prevention, monitoring diagnosis, prevention, monitoring, prediction, prognosis, treatment or compensate of disability" by assigning it a specific purpose and medical use. Pursuant to the provisions of the MDR Directive, the manufacturer should: 1. classify the product in accordance with Annex VIll to the MDR DIRECTIVE 2. perform the conformity assessment procedure 3. issue an EU declaration 4. mark the product with the CE mark 5. submit a declaration in accordance with the MDR DIRECTIVE (Annex VIII). According to the MDR Directive, footwear is classified as a class I non-invasive medical device. Pursuant to the Act of 7 April 2022 on medical devices, the conformity assessment of class I medical devices with the essential requirements does not have to be carried out with the participation of a Notified Body.

The essential requirements set out in the Regulation are of a very general nature and do not define technical solutions. Details of such requirements that may be adopted with regard to design, manufacture and other aspects of product life are contained in harmonized standards, European standards adopted on the basis of a Commission proposal on the application of Union harmonization legislation" [EU Regulation 1025/201]. Therefore, using harmonized standards is the easiest way to demonstrate compliance with the requirements of the directive. Harmonized

standards include horizontal standards (for a wide range of medical devices) and vertical standards (for a narrow group of products it's included in the HS EU MDR 2017/745 list (Journal of the EU) and contains 5 horizontal harmonized standards. The analysis of the existing provisions for the MDD Directive showed as many as 268 harmonized standards.

May 26 this year. the Act of April 7, 2022 on medical devices entered into force. However, some rules enter into force on January 1, 2023 (advertising of medical devices) or July 1, 2023 (data register). During the transitional period of the regulations being in force, the applicable standards, harmonized with the previous MDD directive, are applied first. However, in the case of simple medical devices (including footwear), no harmonized standards have been developed that would define the technical requirements. In accordance with the requirements of the directive, products should be designed and manufactured in accordance with the state of the art. According to this definition, such knowledge may come from other European or national standards (if they are relatively new), ISO standards, professional literature and promotional materials of similar products.

1.2. Aging society

The phenomenon of population aging occurs in almost all developed countries. It is associated with a decrease in fertility and extending human life. According to data, 7,058,456 people over 65 years of age live in Poland (4,238,182 women and 2,820,274 men) [Cierniak-Piotrowska et al. 2020]. The average life expectancy of Poles is 81.7 years for women and 73.8 years for men, respectively [GUS 2018]. For comparison, the average age of men in the EU is 78.2 years and the average age of women is 83.7 years. Since 1990, the average age of men has increased by 6.5 years and that of women by 7.6 years. According to EUROSTAT data, the share of people aged 65 in Poland is lower than in other European Union countries, it is growing faster and thus is approaching the EU level (for comparison, in the years 2001-2018 the number of elderly people changed by 3.9 percentage point, while in Poland this change is as high as 4.7 percentage point) [Bąkowska et al. 2019, Corselli-Nordblad

& Strandell 2020]. Moreover, projections show that in the next decade we will become one of the oldest European societies. According to forecasts, in 2050 the percentage of people 65+ in the EU will amount to 28.5%. The aging of the society forces taking specific measures to improve the quality of life of seniors. Involutional changes occurring in the elderly lead to static-dynamic damage to the plantar part of the patient's foot [Drzał-Grabiniec et al. 2013]. For the elderly, a huge problem is choosing the right serial footwear due to foot problems. Research conducted at the Institute of Psychiatry and Neurology in 2017 showed that only 8.2% of people aged 60+ have feet without deformations and changes on the skin or nails (a sample of 180 women and 50 men with diabetes and RA) [Rajchel-Chyla et al. 2018]. Seniors undoubtedly need special footwear (comfortable, prophylactic, therapeutic) as well as prophylactic and orthopedic insoles. In addition, the materials from which footwear is made for this group of consumers should have very good hygienic properties, because the elderly are more likely to suffer from mycoses of the skin of the feet and nails. It should also be emphasized that seniors experience changes in the shape and size of the feet, and their mobility is largely limited by pain.

Data from The Polish National Health Fund (called NFZ show that in 2019 as many as 11,099 people were hospitalized for surgery related to deformation of the anterior segment of the foot (the so-called sensitive feet), of which as many as 31.16% (i.e. 8273 people due to hallux valgus correction)) [NFZ statistics]. It is a large group of consumers, requiring a specific providing of footwear. It should be emphasized, however, that the NFZ statistical data concern people with extreme deformities. As it was written, older people are a rapidly growing proportion of the Polish population, and sometimes they have milder problems with their feet, which doesn't require a surgery intervention. This group of consumers requires special, comfortable footwear which isnt't a kind of individual orthopaedic footwear. In addition, there is an increase in awareness of the prevention of foot diseases and the needs related to proper foot care and care for their proper functioning at every stage of life. Such activities allow seniors to participate in professional and social activities. The introduction of footwear, which is a medical device that meets the needs of people with reduced mobility, sensitive feet and diabetic feet, is a serious challenge.

However, it is a key element in the prevention of foot diseases.

The article presents the methods of testing selected footwear components for certification as a class I medical device. The results of tests of footwear components selected at the footwear design stage and the test results of the footwear prototypes are also presented.

1.3. Requirements for orthopedic footwear being a class I medical device

To cope with expectations of the market, it is necessary to take prophylactic measures, increasing the quality of life of an aging society. Therefore, a prototype of orthopedic footwear which meets the requirements of a class I medical device was developed. A feature that distinguishes the designed footwear from the products available on the Polish market is the fact that the inside of the footwear is properly dimensioned, which involves the use of an orthopedic insole with a thickness of 6-8 mm. This is a unique feature, unprecedented in mass production footwear. The extended dimensions of footwear interior will enable the customer, who requires an individual orthopedic insole, to place the insole in his footwear - without a neccesity of replacing shoe to another model.

The following requirements are crucial for the design process of orthopedic footwear that meets the requirements of a class I medical device. Unfortunately in the standards harmonised with the MDR Directive, there are no requirements that should be met by this type of footwear. Therefore, the requirements and procedures developed in the Institute of Leather Industry (currently Łukasiewicz – IPS) were used in the assessment of the shoes.

1.3.1. Last, sole and insole

According to many researchers, a key role in the safety of footwear is its correct fit to the foot. The last is a reflection of the foot, it determines the shape of the interior of the footwear, thus it is responsible for the comfort and "ergonomic quality" [Baumgartner et al. 2016; Muszyński 2016; Skidan et al. 2019; Sokolowski &

Winkler 2019; Ziajka 1994]. Last, however, is not a perfect copy of the foot shape. In the design process it is modified by adding, for example, functional excess and fashion excess (excess in the dimension of the length of the last which varies depending on the shape of the anterior part of the footwear called tip of the last e.g. square, rounded, pointed). In footwear intended for people with reduced mobility, with sensitive feet or diabetic feet, the dimensions of the last have to be wider to give a possibility of inserting an orthopedic insole. The requirements for last dimensions are presented in Table 1 [Rajchel-Chyla et al. 2012].

Table 1. Basic parameters of last for footwear which is dedicated people with diabetes mellitus and sensitive foot

Lp.	Feature	Women footwear		Men's footwear
		Casual	elegant	
1.	Size	24	24	27
2.	Fitting according to PN-87/O-91055	H ½ x/	G ½ x/	H ½ x/
3.	alfa angle	87°x/	85°x/	88°x/
4.	Gamma angle	84°x/	82°x/	82°x/
5.	Toe height	24 mmx/	22 mmx/	26 mmx?
6.	1st metetarsal head height	37 mmx/	35 mmx/	40 mmx/

x/ minimum;

xx/ maximum;

Source: [Łukasiewicz – ŁIT]

The use of an additional component in the form of an orthopedic insole significantly increases the comfort of using the footwear and contributes to the alleviation of pain. Moreover, the orthopedic insole changes the pressure distribution on the sole of the foot, thus relieving the diseased areas on the foot. Relieving insoles often use appropriate corrective elements, such as metatarsal pads or longitudinal arch support. An important element of the insole is also the heel pad, which stabilizes the heel in a neutral position.

Another important component is a specially constructed roller sole (Fig. 1 and Fig. 2) [Rajchel-Chyla & Gajewski 2020; van Schie et al. 2001]. It is a stiff cradle-like sole that limits the range of motion in the metatarsophalangeal joints and the metatarsal head area (places where the formation of wounds and ulcers arises) [Rajchel-Chyla & Gajewski 2016].

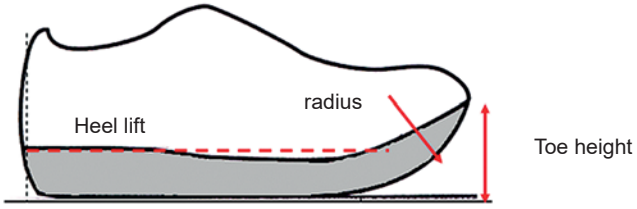

Fig. 1. Footwear with roller sole

Source: [Łukasiewicz – ŁIT]

In addition, the reduction of pressure in the metatarsophalangeal area of footwear having a rigid roller sole is about 50% compared to footwear having a flexible sole. [Brown et al., 2004; Deleu et al. 2010]. It is important especially from the point of view of the prevention of the development of the diabetic foot syndrome.

1.3.2. Materials

An important aspects for the suitability of materials for the production of footwear is their softness and high hygienic parameters ensuring proper comfort of footwear use. These features are especially important in footwear for diabetics.

The comfort of using special footwear for people with reduced foot mobility is a complex concept that covers both the issues of the appropriate design of the footwear, its size and the properties of the materials from which the footwear is made. From this point of view, it is important to assess both the physical and mechanical properties and the hygienic parameters of the materials used.

When selecting materials for the production of specialized footwear, the requirements of the feet from the point of view of physiology should be taken into account. By choosing the right materials, we can influence the microclimate inside the footwear and prevent the feet from getting wet.

Selected materials are tested in the scope of:

- physical and mechanical indicators,
- hygienic parameters,
- content of harmful substances.

Table 2. Selected requirements for the footwear materials

Kind of test	Parameter	requirement
parameters	Leather thickness	
	Determination of the abrasion resistance (dry condition)	≥ 30 000
	Determination of the abrasion resistance (wet condition)	≥ 13 000
Hygienic parameters	Water vapour permeability [mg/(cm^2*h)]	≥ 4,0
	Water vapour absorption [mg/cm^2]	≥ 1,0
	Water vapour ratio [mg/cm^2]	≥ 33,0
Harmful substances	formaldehyde [mg/kg]	< 125
	Aromatic amine [ppm]	≤30,0
	pentachlorophenol [mg/kg]	undetectable
	Chrome (VI) [mg/kg]	undetectable
	phtalate	undetectable

Source: [Łukasiewicz – ŁIT]

2. Material and methods

In accordance with the MDR Directive and the Act of April 7, 2022 on medical devices, a medical device should be assessed by means of certification of compliance with harmonized standards or other technical documents. In the case of orthopedic footwear, there is lack of harmonized standards with the MDR directive.

In connection with this, the tests of footwear components as well as footwear prototype were carried out with compliance with Łukasiewicz-ŁIT procedure.

In the article, the methods and results of testing the footwear components as well as footwear prototype are presented.

The following footwear components were selected for the testing: the last, lining materials from pig leather (sample A) and cow leather (sample B) and footwear prototype. The colour of lining materials is light (light brown – sample A and light beige – sample B). It is very important property, especially in footwear designed for diabetics. According to the requirements, the hygienic parameters of materials for footwear linings should be very high.

The last which was selected for testing was characterized by its anatomical shape, high tip (anterior part of a last) and widened fitting.

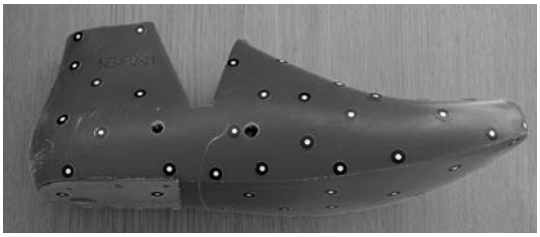

Fig. 2. Last fot orthopaedic footwear

Source: [Conhpol Henryk Konopka]

Sample A	Pig leather, light brown colour	
Sample B	Cow leather, light beige colour	

Fig. 3. Lining materials: pig leather (A) and cow leather (B)

Source: [Łukasiewicz – ŁIT]

Fig. 4. Orthopaedic footwesar with Roller sole

Source: [Conhpol Henryk Konopka]

The evaluation and last measurement was performed in accordance with the PN-O-91055: 1987 and BN-73/7781-04. The test was carried out using a tape measure, an altimeter and a caliper. For the evaluation of last bottom surface, special templates designed in Łukasiewicz - ŁITin accordance to PN-O-91055: 1987 and BN-73/7781-04 standard were used.

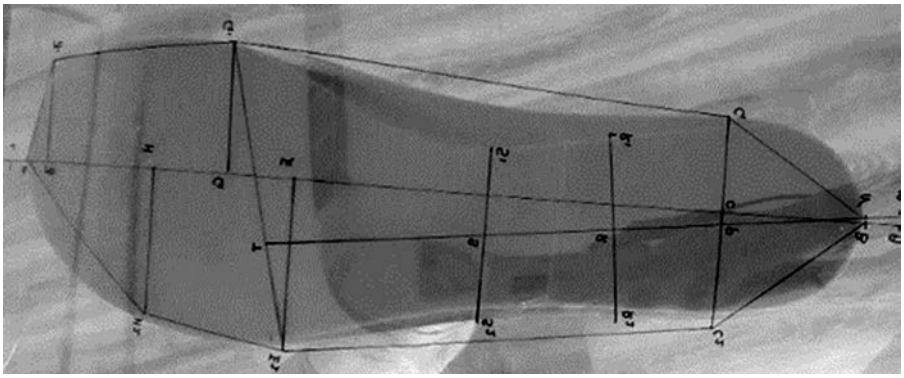

Fig. 5. Last bootom surface – template

Source: Łukasiewicz-ŁIT

In the case of materials for footwear linings, tests of physicochemical and hygienic parameters as well as the content of harmful substances were carried out. The tests were carried out in accordance with the procedure contained in PN-EN-ISO standards.

Table 3. Methods of testing materials

Rodzaj badania	Parametr	Aparatura	Standard
physicochemical parameters	Leather thickness	Leather Thickness Gauge	PN-EN ISO 2589:2005 Leather - Physical and mechanical tests - Determination of thickness
	Determination of the abrasion resistance (dry and wet condition)	ABRASION TESTER MARTINDALE 2000	PN-EN ISO 20344:2012 p.6.12 Personal protective equipment - Test methods for footwear
Parametry higieniczne	Water vapour permeability, water vapour absorption and water vapour ratio	apparatus for testing water vapor permeability and water vapor permeability JG / VDA	PN-EN ISO 20344:2012 Personal protective equipment - Test methods for footwear p. 6.6, 6.7, 6.8.
Hygienic parameters	formaldehyde	spektrofotometr UV/ VIS	PN-EN ISO 17226-2:2019-05 Leather - Chemical determination of formaldehyde content - Part 2: Method using colorimetric analysis (ISO 17226-2:2018)
	Aromatic amine	liquid chromatograph with diode detector (HPLC / DAD)	PN-EN ISO 17234-1:2015-07 Leather -- Chemical tests for the determination of certain azo colorants in dyed leathers -- Part 1: Determination of certain aromatic amines derived from azo colorants (ISO 17234-1:2015)
	Chrome (VI)	spektrofotometr UV/ VIS	PN-EN ISO 17075-1:2017-05 Leather -- Chemical determination of chromium(VI) content in leather -- Part 1: Colorimetric method (ISO 17075-1:2017)

Rodzaj badania	Parametr	Aparatura	Standard
Hygienic parameters	pentachlorophenol	Gas chromatograph with mass detector (GC / MS)	PB-5.4. version 3 z dn. 30.03.2018
	phtalate	Gas chromatograph with mass detector (GC / MS)	PN-EN ISO 17072-1:2019-07 Leather - Chemical determination of metal content - Part 1: Extractable metals (ISO 17072-1:2019)

Source: own study.

In the case of biomechanical tests, the effectiveness of the insole and the footwear in reducing pressure under the foot is assessed. The aim of the biomechanical tests is to assess the effectiveness of pressure reduction under the foot using the Pedar ® System. It is an accurate and reliable pressure distribution measuring system for monitoring local loads between the foot and the shoe.

The Pedar® system consists of insoles with sensors to measure the pressure exerted by the foot on the ground. Each of the inserts has 99 sensors arranged in 15 rows according to the diagram shown below.

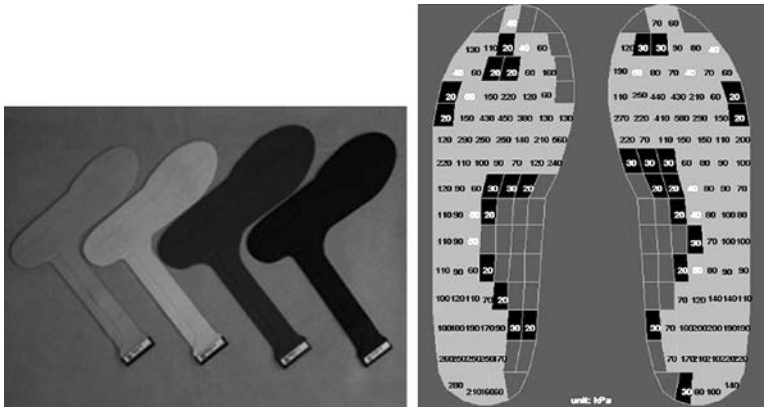

Fig. 6. Pedar insole with sensors (SYSTEM Pedar ®)

Source: [Łukasiewicz-ŁIT]

Each walk consisted of 20 steps at the appropriate speed on the treadmill (2 and 3 km / h). There were 2 walks at each speed. In this method, the pressure distribution under the feet was examined using the shoe with an insole. The reference for the test was barefoot walking with Pedar system at the same condition.

3. Results

3.1. Last

Last which is dedicated for orthopaedic footwear production have to meet the requirements of Standard PN-O-987 „Sizes. Lasts" as well as BN-73 / 77-04 „Lasts common use. Construction indexes of 2/3 of the last length ". The results of the last measurement are presented below.

Table 4. results of last measuring and evaluation according the standards

No.	Parameter	Result	Requirement from PN-O-91055:1987 standard	remarks
1	Metric size	27	-	-
2	French size (EU)	42	-	-
3	Foot lenght	270	-	-
4	Last botom Surface lenght	283	-	-
5	Functional excess	13	-	-
6	Forefoot width	97	98,0 (H-I)	tęgość H-I
7	Heel width	67	64,2 (H-I)	tęgość powyżej H-I
8	Ball girth	270	266 (I½)	tęgość powyżej I½ (J)
9	Alfa angle	prawidłowy	88	w porównaniu z szblonem kontrolnym ściółki kopyta
10	Beta angle	prawidłowy	82	w porównaniu z szablonem kontrolnym ściółki kopyta
11	Toe height	30-31	26	zgodne z wymaganiami norm

No.	Parameter	Result	Requirement from PN-O-91055:1987 standard	remarks
12	Last fitting according to the forefoot dimensions	above I½ (J)		
13	Last fitting after using 6mm insoles	Ball girth - 258 mm, fitting– H/H ½		

Source: own study.

According to the presented data, the tested last is suitable for the production of footwear for people with sensitive feet and diabetic feet. The dimensions of the last allow to put the insole in a shoe. The acceptable thickness of a insole is 6-8 mm.

3.2. Materials

Lining materials have to meet some requirements which coincern about hygienic parameters and content of harmful substances.

Data analysis show, that both samples, it means pig leather as well as cow leather meet requirements for the lining materials using in footwear for people with sensitive feet and diabetics. Both of them can be the component of footwear.

Table 5. Results of lining materials testing

Kind of tests	Parameter	Requiremenr	Pig leather Sample A	Cow Leather Sample B
physicochemical parameters	Leather thickness	-	0,7	0,8
	Determination of the abrasion resistance (dry condition)	≥ 30 000	30 000	30 000 superficial slight abrasions to the coating
	Determination of the abrasion resistance (wet condition)	≥ 13 000	13 000 (no holes)	13 000 (no holes) Coating abrasions

Kind of tests	Parameter	Requiremenr	Pig leather Sample A	Cow Leather Sample B
Hygienic parameters	Water vapour permeability [mg/(cm^2*h)]	≥ 4,0	15,2	9,7
	Water vapour absorption [mg/cm^2]	≥ 1,0	6,0	6,2
	Water vapour ratio [mg/cm^2]	≥ 33,0	128,0	83,8
Harmful substances	Formaldehyde [mg/kg]	< 125	Undetectable (<7,5 mg/kg)	7,9[1)]
	Aromatic amines [ppm]	≤30,0	No found	No found
	pentachlorophenol [mg/kg]	Undetectable	Undetectable	Undetectable
	Chrome (VI) [mg/kg]	Undetectable	Undetectable	Undetectable
	phtalate	Undetectable	Undetectable	Undetectable

[1)]wynik podano w przeliczeniu na suchą masę badanej próbki skóry

Source: [Łukasiewicz – ŁIT]

3.3. Fitting & biomechanical tests

The purpose of an using the insole in the footwear is to reduce the pressure on the plantar side of the patient's foot, especially in the area of the forefoot, which is exposed to overload, and thus (in the case of diabetics) to ulceration. Pressure reduction is therefore a desirable effect in footwear intended both for people with sensitive feet or RA (rheumatoid arthritis), as well as for diabetics.

The graphs of changes in the maximum pressures in the forefoot area are presented below, taking into account the barefoot passages and in footwear with an insole at two speeds: 2 km/h and 3 km/h.

The use of the insole reduces peak pressures by 42-43.4% in relation to the results obtained on the bare foot.

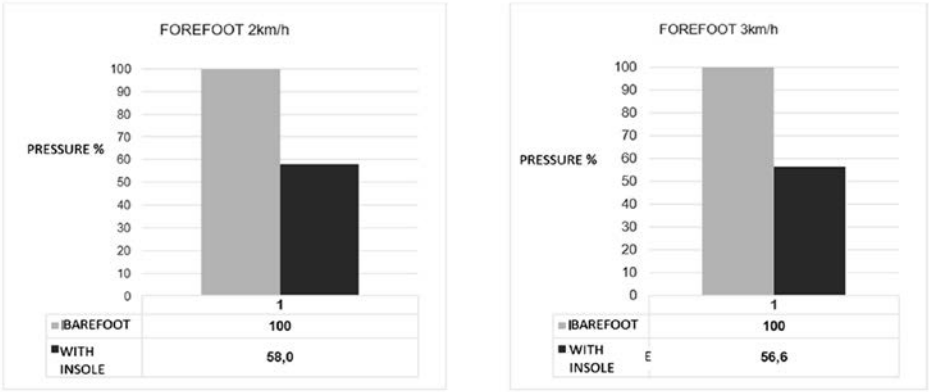

Fig. 7. Maximum pressure in the forefoot area

Source: [Łukasiewicz – ŁIT]

The midfoot area is a place at the foot where an increase in the pressure exerted by the foot on the ground should be expected. This is due to the bottom structure and corrective elements in the insole. The corrective elements used in the insole increase the contact surface of the foot with the ground, resulting in a more even distribution of pressure on the sole of the foot. The use of the insoles enhances this effect to 7-8%.

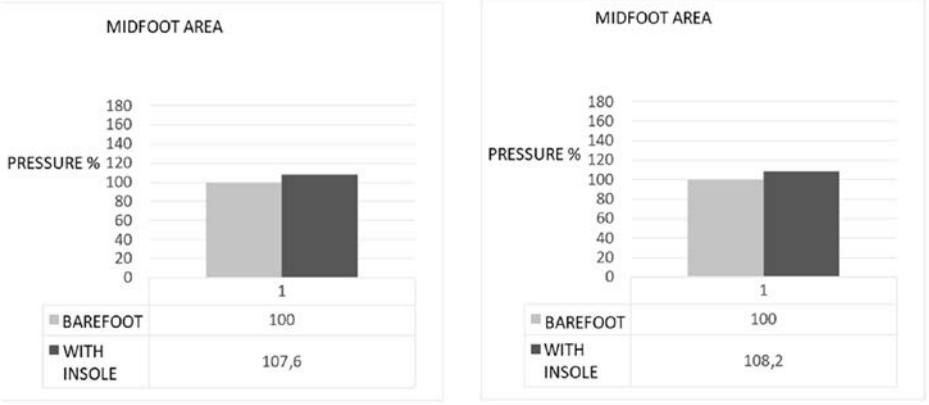

Fig. 8. Maximum pressure in the midfoot area

Source: [Łukasiewicz – ŁIT]

The use of an insole and a specially designed „roller" sole contributed to the reduction of pressure on the sole of the patient's foot. Below is a comparison of images of pressure distribution on the sole of the patient's foot.

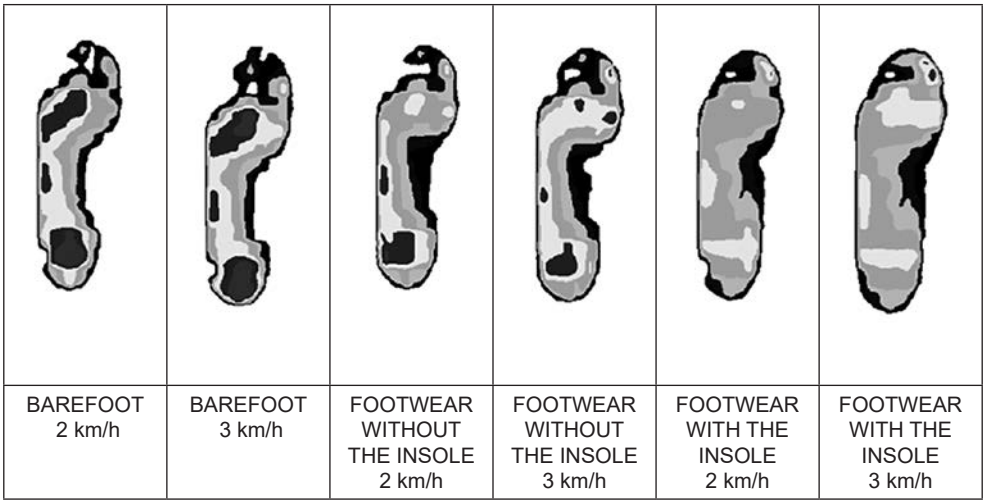

Fig. 9. Comparison of images of pressure distribution on the sole of the foot

Source: [Łukasiewicz – ŁIT]

Images of pressure distribution, presented in Figure 9, show a clear reduction of pressures both in the area of the heel and the forefoot.

4. Discussion

The basic role that a medical device should fulfill is i.a. treating or alleviating disease. Medical device should obligatorily meet the safety requirements of use.

In the case of footwear, the safety of use includes not only correctly selected dimensions of the footwear inside but also the use of materials with good hygienic and rheological properties, ensuring a proper microclimate inside the footwear and preventing the multiplication of fungi and bacteria as well as containing no harmful substances [Frankowski 1969; Liszka 1696; Rajchel-Chyla et al. 2012].

Natural materials (pig lining leather - sample A and cow lining leather - sample B) were selected to make prototypes of the footwear. The selected components met the requirements for footwear materials for diabetics and people suffering from rheumatoid arthritis, both physically and mechanically as well as hygienically [Rajchel-Chyla et al. 2012]. Only for the cow lining leather sample, in the dry and wet abrasion resistance tests, slight superficial abrasions of the coating were observed after 30,000 cycles (dry conditions) and 13,000 cycles (wet conditions). However, the material can be applied for e.g. in shoes for diabetics. The advantage of the sample is also the light colour of the material. Thanks to this it is possible to recognize the blood stains that result from an injury. It is very important aspect in diabetic neuropathy.

The use of a wider fitting (J) allows tho insert an insole (6mm thick) to reduce the pressure - then the footwear fitting decreases to H-H ½.

Orthopedic footwear for a medical device is designed to alleviate problems with local overloads and deformities. This effect is achieved by obtaining the use of two different systems: using the insole with metatarsal pad which reduces plantar pressure and the using the roller sole.

A literature study indicates a positive effect of the using a metatarsal pad on the reduction of forefoot pain [Chang et al. 2012; Chen et al. 2014; Holmes 1990; Janaszek & Kolaszyńska 2012; Koenraadt et al. 2012; Lee et al. 2014]. It is one of the key aspects of footwear comfort assessment in people with sensitive feet (the term sensitive feet, was introduced by Professor Piątkowski, means the subjective feeling of ailments in the feet reacting with pain to hard ground and uncomfortable footwear [Piątkowski 1969]). Diabetics often do not feel pain due to diabetic neuropathy.

In the tested insole, the reduction of pressure on the sole of the foot in the forefoot area was approximately 43%. The obtained results confirm the results of studies conducted with the use of the analogous Pedar system [Lee et al. 2014].

As it was mentioned, the reduction of pressure in the forefoot is a desirable effect, especially in diabetics, where the risk of ulceration in the forefoot region is high [Huppin 2012; Ahmed et al. 2020; Collings 2020; Kato et al. 1996; Lott et al. 2007; Musab et al. 2013; Guldemon et al. 2017].

The key aspect is the method of placing the metatarsal pad - in front of the metatarsal heads - then the pressure reduction value is the highest [Ahmed et al. 2020; Chang et al. 1994; Chen et al. 2015; Guldedmondt et al. 2017; Hastings et al. 2007; Rajchel-Chyla & Gajewski 2016]. Such an insole construction does not affect the comfort of footwear use [Lee et al. 2005; Ashry et al. 1997].

Another component of footwear to reduce pressure is the roller sole [Brown et al. 2004; Colemann 2001; Collings et al. 2020; Zwaferink et al. 2020]. The tested footwear has a „roller type" sole.

The biomechanical tests carried out with the use of the sole system of the designed footwear (the system consists of a roller sole and a pressure-reducing insole) showed a reduction in pressure in the forefoot area by 43% and an increase in pressure by 8% in the metatarsal area. This is a normal phenomenon - the expected effect of therapeutic footwear is to reduce the pressure in the forefoot. On the other hand, the metatarsus is the area of the foot in which one should expect an increase in the pressure exerted by the foot on the ground. The corrective elements used in the insole increase the contact surface of the foot with the ground, resulting in a more even distribution of pressure on the sole of the foot.

Summing up, the obtained results of biomechanical studies confirmed the reduction of pressure on the plantar side of the foot, which contributes to the alleviation of pain in the foot area. Moreover, reducing the pressure on the foot tissues is a prophylaxis against the formation of foot ulcers, which in the case of diabetics is an important element in the prevention of partial or total feet apmutation.

In addition, the results of the hygiene tests and the content of harmful substances comply with the requirements.

The tested footwear can therefore be marketed as a class I medical device.

5. Conclusions

According to the definition of a medical device contained in the MDR Directive, it is the manufacturer who indicates the specific properties of the product, thanks to which he classifies the device as a medical device. In the case of footwear, which is a

class I non-invasive medical device, the assessment of compliance with the essential requirements is based on the existing normative documents (national and European standards), professional literature and in accordance with the current state of knowledge.

For footwear, access to new European standards is limited to professional footwear only. Among the current standards for footwear there are 112 standards concerning mainly methods of testing footwear and professional footwear.

The tests carried out on the basis of the requirements and internal procedures of Łukasiewicz-ŁIT and the obtained results qualify the designed footwear as a class I medical device. The footwear is recommended for placing on the market.

The advantage of the product is not only alleviating pain by reducing pressure on the sole of the foot. Equally important advantage is a prevention the formation of ulcers and deformation of the feet. It is possible thanks to the use of an insole reducing pressure and increasing the dimensions of the footwear's inside.

6. Acknowledgements

The work uses the knowledge obtained during the implementation of the project with Conhpol Henryk Konopka, co-financed by the Polish Agency for Enterprise Development (Project number POIR.02.03.02-12-0051 / 20).

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GREEN POLYURETHANE COMPOSITES AS AN EXAMPLE OF INNOVATION IN PRODUCT MANAGEMENT

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Abstract
The purpose of shaping the product (here: composites) is to adapt it to the requirements of the selected target group - the client (here both: consumer and natural environment). Product management is based on product shaping and it is one of the key elements of this process.
The aim of the article is to show the achievements in obtaining an environmentally friendly product. This was done through a literature review on the modification (shaping) of polyurethane composites into green materials. The analysed articles indicate that these composites can be synthesized in sustainable economy processes and can be modified with substrates of natural origin, often waste from agriculture and the food industry; they can be formed into innovative materials, (bio)degradable in the natural environment.

Keywords: product management, green products, polyurethane composites, innovative materials, modification

Introduction

One of the elements of product management is to improve the product quality. The quality of the product cannot be separated from the quality of the material from which it is made. By optimizing the physicochemical and biological properties of the material, better and better products are obtained. Taking into account the condition of the natural environment, diminishing non-renewable resources and the safety of consumers, all sectors of the economy should modify their products so that they are as safe as possible and not harmful to the environment.

Composites exist in nature almost from the beginning of life, e.g. in bones, muscles and tendons, wood, etc. As early as in the first half of the last century, decorative phenolic laminates, the first glass-reinforced resins and polyesters were produced. The composite industry, as materials composed of at least two components (matrix and reinforcement), has developed significantly since then. At the moment, huge amounts of composite products are to be found on the market, and even more are waste that pollutes the natural environment. And although we appreciate the comfort of traveling on a luxury yacht, whose light and durable hulls are made of laminates, as well as obtaining energy using wind farms with unusual mechanical properties of composite propellers, we have been struggling with the problem of recycling them for a long time.

One of the proposals for solving the problem of utilization of composites is to make them, at least partially, (bio)degradable, i.e. susceptible to decomposition under the influence of abiotic and biotic environmental factors. The use of natural fillers to obtain composites cannot be called innovative because it has been used for a long time. However, the type of filler, modification of its surface to increase its compatibility with the polymer matrix, or the source of these fillers, are innovative methods.

Despite of the use of natural fillers, the polymer matrices themselves are very often synthesized from natural or biodegradable raw materials. These both modifications correspond to two of the 12 principles of Green Chemistry. Thus, in addition to their standard characteristics of properties corresponding to specific applications, composites can become environmentally friendly materials. Given the pressures of increasing consumer environmental awareness, this has the potential to significantly add value to these materials in the marketplace. Bearing these principles in mind, you can manage the product so that its value, also from the point of view of environmental protection, increases.

Product management of such composites consists of three basic levels:

i) Product core: basic functions of the green composite - e.g. construction, sorption, etc.

ii) Real product: functions and features that make up the entire green composite and respond to the expectations of the natural environment - e.g. reducing the volume of non-degradable polymers in the environment, reducing CO_2 production, using less non-renewable resources, etc.

iii) Extended product: additional benefits of using a green composite - e.g. it can be modified with waste materials, etc.

Generally, product extensions are physical products and related accessories or services [Thoben et al. 2001]. In the case of polymer composites, in addition to, for example, services related to the finished product for a specific application (such as extended warranty, service care, collection after use, etc.), an additional benefit may be the use of waste materials as a substrate for product construction. Such waste often disturbs the aesthetics of the landscape, smells bad, pollutes surface waters, etc. The constant collection of this waste and processing into substrates will reduce the burden on the environment and potential consumers living in the vicinity.

As stated long ago: "*Competitive pressures notwithstanding, manufacturers have to come up with novel new ideas to market their wares - including attracting the customers by supplying them with extended products. In order to do that efficiently and effectively, they have to form alliances of their on to develop comprehensive packages for the customer*" [Thoben et al. 2001]. Therefore, the cooperation between the producer of composites and the manufacturer, whose by-product is a material that can become a substrate in a polymer composite system, can bring not only the quality benefit of the product, but also the improvement of the environment and the comfort of the local population, as well as increasing the competitiveness of this market.

The future of green composites remains a separate issue, which is the fourth level - potential product (any improvements and transformations that the product may undergo in the future). It can be assumed that the principles of green chemistry will evolve and the development of the methods used in accordance with them will lead products made of composites towards even more environmentally friendly materials.

Of all polymers, polyurethanes (PURs) are of major importance. As the production volume of PURs is currently in 6th place in the world [PlasticsEurope 2020], the amount of waste generated from them is enormous. And since also PURs are

a matrix for the construction of the composite, all solutions leading to the reduction of this waste are desirable.

The aim of this paper is a short review of achievements in the field of synthetic PUR modifications with natural materials. Main directions of these plastics modification and examples of used materials are presented. Attention is paid to the influence of modifiers addition on the physicochemical and biological properties of PUR composites and their susceptibility to degradation, as well as on the potential application.

1. Materials and methods

In order to achieve the goal set in the paper, the resources of scientific literature collections available in the UMG library were analysed, guided by the following entries: Environmental impact of polyurethanes; Supercitical fluids for polyurethanes; Environmental management in the company; Green chemistry in polyurethanes; Biocatalysis of polyurethanes; and Natural polyurethane composite fillers. An in-depth analysis of the scientific literature (the method of critical analysis of the literature on the subject) made it possible to select the main directions of research carried out in recent years on the production of polyurethane composites with characteristics that allow to improve the quality of the environment.

2. Polyurethane composites

The benefits of using polymer composites instead of pure polymers are enormous. First of all, composites have significantly increased strength (e.g. in the construction of windmill blades) and barrier properties (e.g. in packaging). Fillers are often a waste material from the production of other products, which reduces the cost of producing composites. As it was said before, a significant advantage is the replacement of synthetic fillers, obtained from non-renewable sources, with natural fillers. The fillers are materials usually the most abundant in the world, often post-production waste (mainly from agriculture and the food industry), light, low-density and,

above all, biodegradable. However, too poor compatibility between the synthetic polymer matrix and the natural fibre requires preliminary chemical or physical treatment of the fibres [Jadhav et al. 2019]. In addition, green composites are currently used in applications that require less mechanical resistance, such as packaging, garden supplies, automotive panels, furniture, etc. [Mhatre et al. 2019]. However, work is underway to ensure that the properties of these composites do not differ from those of standard materials and can already be found in the aircraft, construction, sporting and electronic industries, as well as in the transport and energy sector [Potluri 2019].

The main natural fillers for composites are plant fibres, examples of which are shown in Fig. 1, and animal fibres (silk, wool, feathers and hair). Their size varies, from long particles of several centimetres to a milled powder with particles of micrometre or nanometre size. For many years, asbestos and mineral wool, which are also a natural but mineral fibres, have been used.

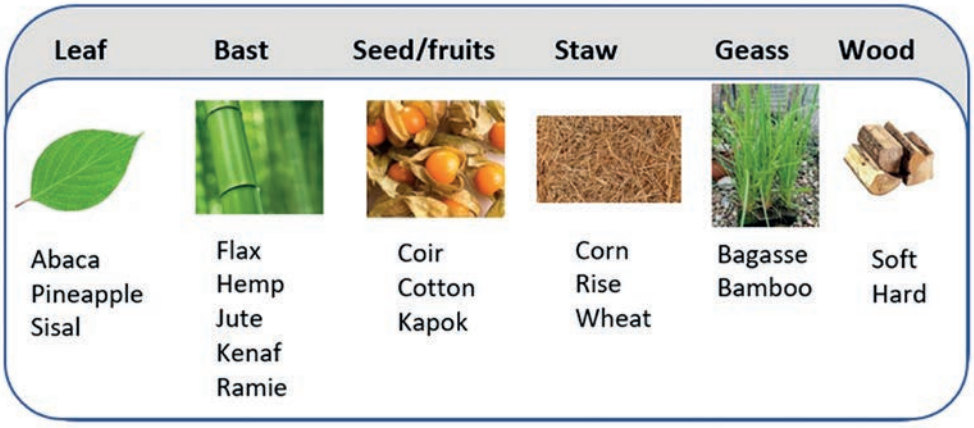

Fig. 1. The most popular plant fibres used in the modification of polymers

Source: prepared on base of [Thompson at al. 2001].

Natural fillers can be organic or inorganic compounds. Table 1 shows examples of composites with natural organic and inorganic fillers, and the properties that have improved with the addition of filler, and the potential use of these composites.

Table 1. Examples of natural modifiers used to obtain polyurethane composites, the affected (mostly improved) properties and potential composite application

No	Type of natural modifier	Modifier	Affected properties in comparison to native PUR	Potential application	Ref.
1	organic	Araucaria pine nut shell fibres	Flexural strength, density, water absorption, and swelling in thickness	Composite panels	[Protzek et al. 2021]
2		Hemp fibre	Insulating properties	Building insulation	[Sair et al. 2018]
3		Bambusa balcooa fibre	Tensile strength, tensile modulus and chemical resistance	Construction materials	[Kumar & Siddaramaiah, 2004]
4		Butter tree seed waste	Mechanical properties	Automotive sectors	[Madhukar et al. 2015]
5		Powdered buckwheat husks	Tensile strength	Construction, automotive, and sports industries	[Włoch & Landowska 2022]
6		Water hyacinth fibre	Mechanical and sound absorption properties	Sound absorption materials	[Sukhawipat et al. 2022]
7		Modified chitosan	Flame-retardant and smoke-suppressed properties, tensile strength	Flame retardant materials	[Xu et al. 2022]
8		Gallic acid	NIR light triggered shape memory performance	Multifunctional intelligent materials responsive to stimuli, e.g. for lighting controls	[Liu et al. 2022]
9		Spirulina Platensis algae biomass	Thermal stability, water sorption, chemical resistance	Structural applications	[Syed et al. 2022]
10	inorganic	ZnO crystals	The adsorption and retention of the acetic acid	Acetic acid removers	[Zulliani et al. 2022]
11		nanoSiO_2	Biodegradability	Biodegradable products	[Das et al. 2017]
12		diatomite (diatomaceous earth)	Mechanical, thermal and morphological properties	Various applications as thermoplastic materials	[Kucuk et al. 2021]
13		multiwalled carbon nanotubes	Mechanical properties and electrical conductivity	Conductive composite material, e.g. effective EMI-shielding material	[Luo et al. 2019]

14	organic/ inorganic hybrids	chitin modified with natural gum rosin + ZnO-SiO_2-NPs	Mechanical, wettability, thermal stability, water, and oxygen barrier properties, flammability behaviour, and antimicrobial activity	Food packaging materials	[Moustaffa et al. 2022]
15		ZnO with palm sheath residues	Resistance to heat absorption, crystallinity and stiffness	Heat resistance foams	[Zanini et al. 2021]
16		TiO_2 with dopamine	Mechanical and thermal properties, and water resistance	Waterborne adhesives, coatings, printing inks and textile finishing agent	[Deng et al. 2019]
17		Graphite and nanomagnetite (Fe_3O_4) / chitosan	Stability in time and sensitivity for epinephrine	Sensitive sensors for epinephrine	[Mattioli et al. 2020]

Source: own study.

2.1. Polyurethanes with natural organic materials as fillers

The most popular among bio-based PUR composites is their plant fibre reinforcement. The main reason of this is their availability, low-density and price compared to synthetic fibres. Moreover, they are often waste materials from e.g. agriculture. These organic fibres, like the synthetic ones, improve some selected parameters of the composite, make it more desirable. For example, PUR composites with hemp fibres were characterized by high thermal insulation and mechanical strength [Sair et al. 2018]. As Sair and his co-workers point out, the estimated properties make obtained PUR composites an excellent candidate for the preparation and development of a new ecological insulating material with high added value and a low cost.

A separate group of organic, natural modifiers are oligo- and polysaccharides. The second most common in nature, after cellulose, is chitin. It is extracted from the shells of crustaceans and the walls of some mushrooms. However, due to its insolubility in water and organic solvents, it is often converted into chitosan. The use of chitosan as a filler improved oil sorption by composite PUR foam [Piotrowska-Kirschling et al. 2021].

Spent coffee grounds are rich in carbohydrates, lipids, proteins, and minerals [de Bomfim et al. 2022]. The filler in the form of coffee grounds was found to reduce the permanent deformation of the foams in the compression test by 75% [Auguścik-Królikowska et al. 2021]. Moreover introduction of 20% by mass of the filler caused a reduction in the rate of heat and smoke release during the foam combustion [Auguścik-Królikowska et al. 2021].

2.2. Polyurethanes with natural inorganic materials as fillers

Also, natural, but inorganic fillers change the properties of composites, making them more desirable, and at the same time often cheaper materials.

An interesting solution for obtaining an environmentally friendly adsorbent of acids is the PUR/ZnO composite [Zuliani et al. 2022]. Zinc oxide is a natural mineral that is often used in cosmetics. Research indicates that the dispersion of ZnO particles in the PUR matrix, and the weak interactions of these materials, facilitate the transport of the absorbed acid to the oxide surface, where it reacts to form zinc acetate. The connection of this process with the presence of free hydroxyl groups in the PUR structure makes the sorption of the acid even more efficient than when using ordinary ZnO packed in containers.

2.3. Polyurethanes with natural organic/inorganic hybrids as fillers

Often the use of organic/inorganic hybrids for PUR modification allows for obtaining additional or enhanced properties of these composites.

When ZnO-doped-SiO_2 nanoparticles (ZnO-SiO_2-NPs) were used to chelate chitin, improved properties of PUR nanocomposites were obtained [Moustaffa et al. 2022]. All investigated properties: mechanical, wettability, thermal stability, water, and oxygen barrier properties, flammability behaviour, and antimicrobial activity were proved to be better. The mechanical properties of thermoplastic PURs were also improved by the use of diatomaceous earth, consisting of amorphous silica (SiO_2) with an admixture of the crystalline phase [Kucuk et al. 2021].

The organic-inorganic hybrid of ammonium polyphosphate with chitosan proved to be an excellent flame retardant PUR material by creating a graphitized char layer on the surface of the composite [Xu et al. 2022]. At the same time, these composites were characterized by enhanced tensile strength without sacrificing the ultimate elongation [Xu et al. 2022].

2.4. Polyurethanes with fillers of nanoparticles obtained by green methods

One of the principles of green chemistry indicates the use of environmentally safe methods for the compound/product obtaining. Undoubtedly, one of them is the use of plant reducing agents in the reaction of obtaining nanoparticles. Cobalt nanoparticles, obtained using green tea extract, were loaded into a PUR matrix [Khidhir et al. 2022]. The resulting composites were decoupled by electrospinning into high-strength fibres to form scaffolds with potential cardiac application. Very popular is nanocellulose. It can be obtained from a vast range of sources, such as plant, tunicates, and bacteria. Nanocellulose produced by bacteria, such as from the *Acetobacter* species, has identical structure to plant-based cellulose [Seydibeyoğlu et al. 2013].

Soybean based PURs were additionally modified with nanosized cellulose produced from bacteria [Seydibeyoğlu et al. 2013]. Seydibeyoğlu and others observed that fine dispersion of the bacterial cellulose was achieved and as a result of both flexural strength and modulus improved over the unfilled samples by 100 and 50%, respectively.

2.5. Green modification of polyurethane matrix

Very often the PUR matrix of the composite is also modified in the pro-environmental direction.

One of the most important modifications is the use of plant oils instead of synthetic polyols. The most popular is castor oil. The presence of free hydroxyl groups in this oil chains allows binding of the absorbed acetic acid [Zuliani et al. 2022].

Das et al. [2017] synthesized nanocomposites with PUR based on transesterified castor oil and palm oil isocyanate, which facilitated biodegradation of these materials. Palm oil [Sukhawipat et al. 2022] and soil oil [Luo et al. 2019] are also used as bio-based polyol.

Another interesting group of natural compounds used in the synthesis of polyurethanes are plant polyphenols, e.g. gallic acid [Liu et al. 2022]. Also, carbohydrates such as starch are introduced into the chemical structure of PUR chains as cross-linkers [Paprota et al. 2022].

3. Discussion

The examples of modifications of PUR composites shown above are an element of product quality development. They make it possible to obtain products that will degrade after the end of their use, especially if both the filler and the PUR matrix are made of degradable natural materials. The introduction of natural organic and inorganic modifiers, hybrids and nanoparticles obtained with green methods as fillers to the PUR matrix, as well as to the chemical structure of this polymer, has a direct impact on the properties of the composites obtained in this way. At the same time, it offers hope for reducing the amount of waste in the natural environment. Thus, often such innovative methods of changing the composition of products can directly affect the state of the environment and indirectly the quality of life of the population.

Moreover, often these modifiers come from post-production waste, which further reduces the environmental impact of their production. **Thus, there is a close relationship between the quality of the composites themselves, the quality of the products obtained from them and the environmental quality.** Therefore, the question arises: is it allowed in the discipline of Management and Quality Sciences to talk about product management without taking into account the quality of the material and the quality of the environment (where the environment can be a human-consumer, the natural environment, the work environment, etc.)?

4. Conclusions

The paper discusses the general structure of composites, and the individual sections present examples of natural organic and inorganic fillers and their hybrids, as well as nanofillers obtained through green chemistry, and discuss the methods of green modifications of the polyurethane matrix.

The examples of the use of natural and ecologically obtained fillers as well as the modification of the chemical structure of the polymer matrix presented in the article indicate the production of environmentally friendly composites with excellent biological and physicochemical properties. It offers a great opportunity to replace plastics made of crude oil, to reduce the still arising polymer waste and to manage post-production waste. These innovative ideas for shaping the quality of composite materials, at the same time affect the quality of finished products obtained from them, and, consequently, the quality of the natural environment and the lives of its users.

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INNOVATIVE LAMINATES WITH GLASS POLYESTER RECYCLATE

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Abstract
The glass reinforced polyester waste was ground and added to produce new laminates with glass mats. The effect of adding recyclate on some properties of laminates has been tested. The laminates with recyclate had a similar hardness to the laminate without recyclate. The study showed that using glass reinforced recyclate in laminates decreases the tensile strength. The shredded glass polyester waste can be used as a filler in laminates to less responsibility elements. Obtained results were promising for a global waste management solution for glass reinforced polyester waste and end-of-life products that will lead to a more sustainable composite materials industry.

Keywords: composites, glass polyester waste, recycling

Introduction

Glass reinforced polyester materials are used in a wide range of applications such as the automotive industry, aerospace and wind turbines. The moulding process (hand lay-up and spray-up) is often the method of choice especially in the field of bespoke and custom-made products or small batch sizes and due to their low investment costs. Spray-up and hand lay-up are the original techniques for processing glass reinforced polymers and they continue to perform very well in the production of large, highly complex components or products. They are the second largest segment in the European glass reinforced polymer market the production of volume over all years (more than 20%). In 2020 the production volume of the European glass fibre reinforced polymers market was 996,000 tonnes [Witten & Mathes 2020].

A few years ago, the European Composites Industry estimated that there were approx. 10,000 companies in the European composites sector, employing a total of approx. 125,000 staff. Glass fibre accounts for well over 90% of fibre reinforced plastics/composites production. Glass fibres are used in very different variations. The main differentiation is the fibre length and the type of semi-finished products. The three main types of fibres are short fibres, long fibres and endless fibres. Short fibres have a length of less than 2 mm, long fibres are between 2-50 mm. Every fibre which is longer than 50 mm is called endless fibre. Short fibre reinforced plastics are a very big group of materials. On the other hand, polyester resins are the most polymer matrix in composites. The two main application areas for glass polyester composites remain the construction/infrastructure and transport sectors. Due to the increasing use of composites in various applications, a steady increase in their waste amounts is expected. Today, approximately 30,000 tonnes of post-consumer glass and carbon reinforced polymer waste are produced annually in Europe. Additionally, 40 – 50,000 tonnes of commercial production waste are generated [FiberEUse 2017]. Technical advantages of composites (mainly great durability and resistance to environment) influence became a serious disadvantage during tests on their utilization. Consumer interest and government legislation are now driven to encourage the recycling of polymer composites. This should contribute to reducing environmental pollution. Especially under many national legislations (for example in Germany and Sweden), the landfilling of organic waste is prohibited. The European Waste Framework Directive (2008/98/EC) defines basic concepts related to waste management. This directive introduces a five-step hierarchy, which applies as a priority order in waste prevention and management. The European waste hierarchy designates five successive stages of waste management: prevention, preparing for re-use, recycling, other recovery, e.g. energy recovery and disposal. It emphasises the need for increased recycling and highlights the reduced availability of landfill. However, it does not apply to glass reinforced polyester which is not properly recycled due to its inherent nature of heterogeneity. By the principle of sustainable development, entrepreneurs should make maximum use of recyclable products to close the chain of materials. Composite materials can be recycled or recovered through mechanical

grinding, thermal (pyrolysis, fluidised bed), thermo-chemical (solvolysis) or cement co-processing [Job 2015, Yang et al. 2012, Oliveux et al. 2015, Jastrzębska 2016]. Mechanical recycling presents significant environmental and economic advantages over other proposed recycling processes and it is positively accepted from an ecological point of view. Mechanical recycling is a commonly used technology due to its effectiveness, low cost and low energy requirement. Mechanical recycling would be the best recycling method for scrapped glass fibre reinforced polyester in Poland, where waste dispersed in various locations in the north is generated. There are an increasing number of companies that offer composites recycling services for example Thornmann Recycling in Poland. The material after recycling should be inexpensive and possess good exploitation properties and its production should be harmless for the natural environment. The possible fields of application depend on the final size of the scraps of the recyclate. Usually, the comminuted recyclate contains various fractions, from fine particles to long fibres and every size grade can be applied to different purposes. It does however drastically decrease the value of the recycled materials. The recycled products, short fibres and ground matrix (powder), can be used respectively as reinforcement or fillers. Because of the deterioration of the mechanical properties, the incorporation level of filler material is extremely limited in thermoset composite applications (less than 10%). For re-use of the fibres as reinforcement in thermoset applications, the variation in composition and potential contamination with resin particulates has a negative impact on manufacturing speed and thermoset resin quality. This could be minimised if the separating and dismantling processes were upgraded and could be suitable in cases where no more value retention is possible. The recycling of composites will play a vital role in the future, especially for sectors that depend on composites such as aerospace and automotive. These industries will require different recycling options for their products that will fit with current legislation and business models. To commercialise what is technically proven, appropriate business models need to be developed that integrate existing waste management supply chains using associated capital investment. Recycling composites are an important aspect of sustainable development, based on the constant balance between the three aspects: economical, human, and environmental.

The best way of solving the problem with composite waste after production is mechanical recycling via collection, shredding and milling down into fractions. Then the recyclate can be reused as a filler in new formulations and has other industrial uses. The recycling process lowers the negative loads on the natural environment. There must be created market for recyclate. Actions must be taken due to existing and forthcoming regulations. In most cases, the waste producers must act according to the present situation on the market. Commercialising recycled glass fibres is difficult due to their low cost: generally €1-3/kg for the most common E-glass fibre type. This leaves little margin for recycled fibres, and companies struggle to find sufficient recyclate markets to operate at commercially viable levels. The fibrous fragment can come in a wide variety of forms (e.g. powders, fibre-particulate bundles, fibre tows and woven platelets), which all partly consist of resin. This makes it hard to say what the exact recycled fibre properties are, so in most experiments the performance is mainly judged by integrating the material into a new resin.

The production process of moulding composites with glass polyester recyclate was proposed by Błędzki at the University in Kassel in cooperating with the Institute of Polymers of the Szczecin University of Technology [Błedzki et al. 2019, Scheibe et al. 2019]. Whereas Amico et al. [2012] did positive effects by adding polyester waste glass between two glass mats in the resin polyester to replace the used calcium carbonate filler. Similar studies were performed by placing glass polyester waste for "sandwich" profiles in the process of pultrusion [Adolphs & Branca 2002]. Recycled contents obtained in these studies range between 10% and 30% of the total laminate weight. Works assessing the applicability of glass polyester recyclate were carried out also at the Silesian University of Technology in Katowice [Rutecka et.al. 2004, 2005]. Polyester laminates with facings were tested with one and two layers of glass mat with the addition of waste in the amount of 20%, 35% or 50% by weight. Tests have shown that the recyclate has a negative effect on the strength properties of the new laminate. In subsequent studies it was used recyclate for polyester laminates, folding made of 10 layers of glass mat made by contact lamination. Optimal properties showed a ten-layer polyester laminate with 4 wt.% addition recyclate (improvement in impact strength by 11%, slight change of other properties). The greater

amount of waste (10 wt.% and 20 wt.%) in laminates worsened the mechanical properties and additionally necessitated the use more of a mixture of polyester resin and recyclate to supersaturate the composite, which increased product cost. It is difficult to solve the problem of glass polyester waste recycling in Poland, so in connection with this, we have decided to perform research in this area. The earliest our study [Jastrzębska 2016] showed that glass reinforced polyester recyclate may be used as fillers in new polyester composites with dolomite dust.

This case study was carried out the mechanical recycling of glass reinforced polyester waste. With a ban on the disposal of glass reinforced polyester waste into landfill and the ever-increasing costs of waste disposal, the stabilising of waste in the composite system has increasing attraction. The paper aimed to demonstrate the possibility of obtaining new laminates with glass polyester recyclate. The materials used for the laminates were unsaturated ortophthalic polyester resin and glass mats. The influence of the different amounts of glass reinforced polyester recyclate on the mechanical properties of composites has been tested. An important goal of the research was to introduce as much glass polyester recyclate as possible.

1. Material and methods

In this paper laminates with glass reinforced polyester recyclate were obtained. The waste of glass fibre reinforced cold-cured polyester laminates was ground in a shredder manufactured in Kubala Sp. z o.o. This device was equipped with a rotor (length 338 mm, ø 270 mm), which rotated at a speed of 820 rpm, and its efficiency was about 100 kg/h. The grains of recyclate were smaller than 0.75 mm. The recyclate was a mixture of cured polyester resin particles and glass fibre (45.3%).

The materials used for the laminates were ortophtalic polyester resin Polimal 109-32 K in the amount of 75% by weight manufactured Organica-Sarzyna S.A. and glass mat with a weight of about weight 300 g/m^2 from Krosglass®. Initiator in the amount of 0.01 wt.% and accelerator in the amount of 1 wt.% have been used to catalyse the process. Laminates were manufactured by hand lay-up. The application

of the manual laminating method is associated with unavoidable defects such as air voids between the laminate layers and in the laminate itself.

In the prepared samples, a glass mat (5 layers) or a glass mat (4 layers) with the addition of glass polyester recyclate in various amounts (5, 10, 15% by weight) was used as reinforcement. The density of laminates was determined [PN-EN 1926: 2007] and their Barcol hardness [PN-EN ISO 2039-1: 2004] and tensile strength [PN-EN ISO 527-1: 2012] were tested. The Barcol hardness test is generally used on soft materials such as rigid plastics. It measures hardness based on the indentation of a sharp point with a flat tip. Barcol hardness is measured on a scale from 0 to 100. To determine the hardness of the materials, 10 measurements were performed on samples of each material. Static tensile tests were performed on a universal testing machine Zwick & Roell (Ulm, Germany). Material testing was done in triplicate to ensure statistically significant values. The tensile strength and density data were analysed by using statistical software (Microsoft® Excel® of Microsoft 365). Additionally, functions describing test results and values of correlation coefficients have been shown in the figures.

2. Results

The study determined the impact of polyester glass recyclate on some properties of glass fibre reinforced polyester laminate. It was expected that the introduction of the recyclate consisting of short glass fibres and polyester resin would strengthen the polyester laminate with the glass mat and improve their tensile strength and hardness. The tensile strengths of polyester laminate with 5 layers of glass mat and laminates with 4 layers and different amounts of glass polyester recyclate are given in Fig.1. In this study the sought relationship has been determined in the form of linear functions. Conformity of the relationship to experimental data was evaluated using determination coefficient R^2. The model partially predicts the outcome. The estimated regression function only with a certain approximation reflects the actual relationships between the examined features. Tests of a larger number of samples with glass polyester recyclate will allow for a through statistical analysis.

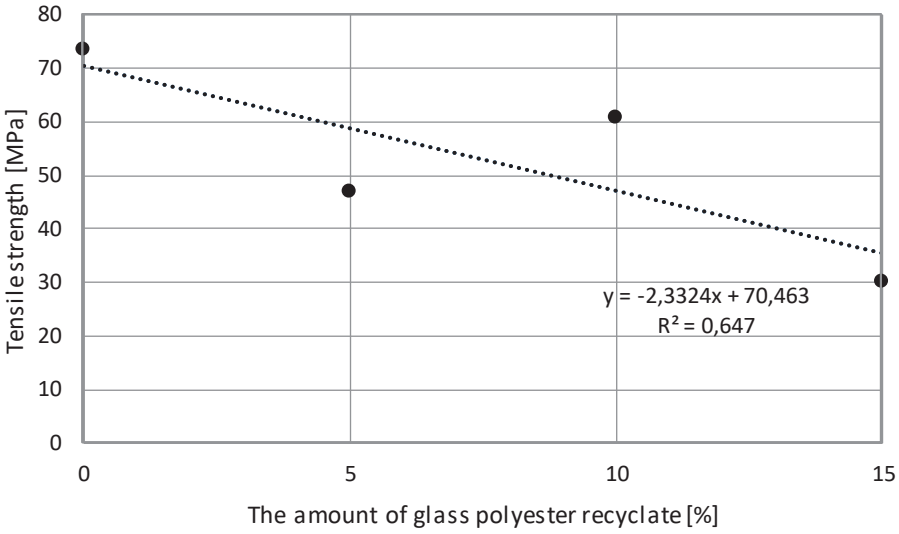

Fig. 1. Tensile strength of laminates depending on the amount of glass polyester recyclate

Source: own study.

It was found that the addition of glass polyester recyclate to the laminate with glass mat results in a decrease in tensile strength as compared to the properties of the laminate without recyclate. Replacing one glass mat by 10 wt.% recyclate lowered the tensile strength of laminate about 20%, but adding 15 wt.% the tensile strength of laminates decreased as much as 60%. Adding 15% of the recyclate causes a sharp decrease in the mechanical properties of the manufactured laminates. Additionally, large amounts of granulate induce problems with composite curing and forming. It has been shown that the content of the recyclate influenced studied mechanical properties. The effects of stretching depend primarily on resin adhesion to fillers. The decrease in quality characteristics after adding recyclate can be explained by a weaker connection of the filling and polyester warp caused residues contained in the waste cross-linked resin, making it difficult to wet glass fibres. The problem turned out to be numerous voids, significantly lowering properties mechanical. In Table 1 the results of the hardness of laminates are presented.

Table 1. The hardness of laminates with glass polyester recyclate

The amount of glass polyester recyclate [%]	The hardness
0	39.3
5	37.9
10	46.8
15	40.9

Source: own study.

Replacing one layer of glass mat by glass polyester recyclate does not improve the hardness of laminates and reduces the strength stretching, which applies them to producing undemanding items of high strength, e.g. for the production of components fence, barriers or various types of tiles and road engineering (signs, bollards, etc.). These results demonstrated the potential of reusing glass polyester waste, at present landfilled, to manufacture elements such an automotive components, profiled sheets and architectural cladding materials. Obtained results were promising for a global cost-effective waste management solution for glass reinforced polyester waste and end-of-life products that will lead to a more sustainable composite materials industry.

The density of polyester laminate with 5 layers of glass mat and laminates with 4 layers and different amounts of glass polyester recyclate are given in Fig. 2. It was observed that glass polyester recyclate replacing one layer of glass mat with a weight of 300 g/m^2 reduces the density of polyester laminates.

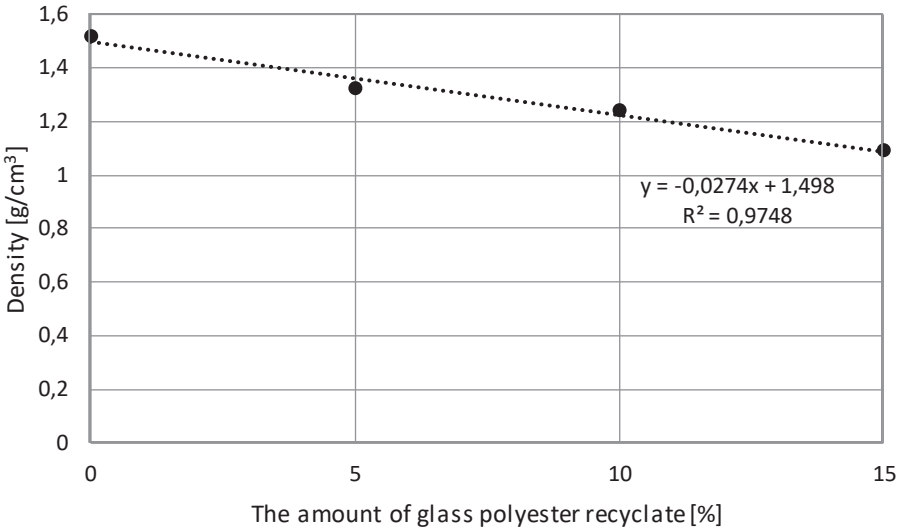

Fig. 2. Density of laminates depending on the amount of glass polyester recyclate

Source: own study.

Probably in a relationship with a random arrangement in space recyclate, there was no complete supersaturation of their polyester resin. The resulting pores during contact lamination are the result large area of shredded waste. The recyclate has a lower density than conventional fillers as it contains a significant proportion of low-density polymer. This could lead to weight savings compared to using not only glass fibre but also calcium carbonate for example in other composites. Also, although filler substitute recyclates are more expensive by weight than traditional fillers, the lower density means they are cheaper per unit volume. This could be favourable for industries where weight and cost savings are very important, such as the transport industry.

3. Conclusions

The purpose of this study was to estimate recycling application for finely ground glass reinforced polyester waste in polyester laminates production. Some properties of new polyester laminates based on glass polyester waste and glass mats are presented. The laminates consist of an internal layer created from glass polyester recyclate and of two external layers created from two of the glass mat. The laminate with waste was characterized using the Barcol hardness test and the static tensile test, and the obtained results were compared with the results of laminates without the addition of recyclate. The tests showed that the use of polyester-glass recyclate does not improve the selected properties of the polyester laminate reinforced with glass mats. The addition of recyclate does not affect the hardness of the laminate but lowers its tensile strength, which allows the use of such material only in structures that do not require high mechanical strength. Reuse of glass reinforced polyester recyclate in the amount of 5 wt.% and 10 wt.% in laminates is possible. The results demonstrate the potential of incorporating glass reinforced polyester recyclate to manufacture laminates. Because of the enduring and increasingly strict statutory processing regulations, especially for unsaturated polyesters/styrenes, it is very interesting to use recyclate not only in hand lay-up but in many other industrial sectors using different technologies (i.e. resin transfer moulding, vacuum infusion, etc.) in the composite industry. A key note will be the price of this glass polyester recyclate on the end market. New possibilities for application of glass polyester recyclate as a filler laminates have been presented. It also will be contribute to achieving the objective of sound environmental management. Glass reinforced polymer waste will be fed back into the technical loop.

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EFFECT OF THE MOLECULAR MASS OF HYALURONIC ACID ON THE PHYSICAL AND CHEMICAL PROPERTIES OF FACE CREAMS

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Abstract
In this paper an attempt was made to determine the effect of molecular weight of hyaluronic acid on physicochemical and functional properties of face creams. A reference cream formulation and formulations differing in molecular weight of hyaluronic acid were developed. Ultra - low molecular weight (below 10 kDa), low molecular weight (below 500 kDa) and high molecular weight (0,85 - 1,15 MDa) hyaluronic acid were selected for the study. The following tests were performed for the produced prototypes of face creams: dynamic viscosity, yield point, consistency evaluation, skin hydration level, transepidermal water loss and sensory tests.
It was found that the application of hyaluronic acid of different molecular weight significantly influences physicochemical and functional properties of face creams and consumer perception. The most advantageous properties were observed for cosmetics containing ultra - low molecular acid.

Keywords: cosmetics, hyaluronic acid, quality

Introduction

Hyaluronic acid is a linear polysaccharide belonging to glycosaminoglycans (GAGs), which are the most important components of the extracellular matrix ECM (Extracellular Martix) of all tissues. The presence of GAGs in tissues causes many

biochemical processes that occur inside and outside the cell. This is due to their interaction with different types of molecules such as growth factors and their receptors, enzymatic proteins, structural proteins of the extracellular matrix. GAGs determine the characteristics of the extracellular matrix, affecting its elasticity, cohesiveness, and the degree of hydration [Jaszczuk et al. 2009; Kucia 2017, Bukhari et al. 2018, Vasvani et al. 2020].

Hyaluronic acid occurs naturally in organisms, and its chemical structure is the same in humans as in other vertebrates. In humans, most, or half, of hyaluronic acid is contained in the skin. It is a highly hydrophilic biopolymer, so it functions in the human body as a moisturizer and ensures proper hydration of the skin. It protects against free radicals and is a kind of link between collagen and elastin, responsible for skin elasticity. From the age of about 25 the skin begins to age, imperceptibly at first. This is caused, among other things, by the decreasing amount of hyaluronic acid in the skin, which decreases with age. The largest amount of this component a person has right after birth, in a person who is 40 years old there is already half as much, while around the age of 80 it completely disappears [Kucica 2017; Wang et al.2007].

Hyaluronic acid is widely used in cosmetology and aesthetic medicine. Used as a filler and injected into the skin [Kaniowska 2019]. For example, in the United States, 1 million out of 12 million cosmetic procedures per year are those using hyaluronic acid [Wang et al. 2007, Noszczyk 2017]. Hyaluronic acid and its derivatives are also conventionally used in cosmetic products. Most commonly, this ingredient is found in anti-aging cosmetics. However, there are more and more new products on the cosmetic market, which contain hyaluronic acid in their composition. The most common form of cosmetics with hyaluronic acid are cosmetic emulsions, which are systems of two immiscible liquids, in which one is suspended in the other in the form of droplets. These include creams. In their composition they contain water, emulsifiers, active substances modifying rheology, fragrances, preservatives, etc. [Klonowska 2022; Kupper et al. 2017; Bernat et al. 2017; Klauzinska et al. 2017 Venkataramani et al. 2020, Hosoi et al. 2017]. Moreover, the formulations of this type of cosmetics differ, among others, in its concentration, degree of crosslinking, molecular weight

and also in the ingredients with which they are combined. Although many articles on hyaluronic acid can be found in the literature [Zheng et al. 2022; Klauzinska et al. 2017; Vasvani et al. 2020; Kupper et al. 2020; Kucia 2017] no studies have been reported on the effect of the molecular weight of this ingredient on the physicochemical and functional properties of personal care cosmetics, which translate, in effect, into the quality of the final product. This provided an asumpt to try to develop formulations of facial care creams with hyaluronic acid and determine the effect of the molecular weight of hyaluronic acid on the physicochemical and performance properties of these products.

1. Material and methods

1.1. Formulations

Four prototypes of face creams were developed and made. The formulations (K2-K4) differed in molecular weight of hyaluronic acid. For the purposes of this study, the following acids were used: ultra - low molecular (M_w less than 10 kDa), low molecular (M_w less than 500 kDa) and high molecular (M_w in the range from 0.85 to 1.15 MDa). This component was used at a concentration of 0.5%. Cream K1 was the reference sample, which did not contain hyaluronic acid in its composition. It was the reference preparation in the analysis of the obtained results.

Table 1. Formulation of face creams with different molecular weight of hyaluronic acid

Ingredients (INCI Name)	DESIGNATION OF FACE CARE CREAMS			
	K1	K2	K3	K4
	Concentration [wt%]			
Butyrospermum Parkii Butter	0.5			
Ceteary lAlcohol	6.0			
Ceteareth 20	2.5			
Glycery Stearate	4.0			
Oryza Sativa Seed Oil	2.0			
HyaluronicAcid (ultra-low molecular – less than 10 kDa)		**0.5**		
Hyaluronic Acid (low molecular – less than 500 kDa)			0.5	
Hyaluronic Acid (high molecular – 0,85 – 1,15 MDa				**0.5**
Sodium Benzoate and Potassium Sorbate	1.0			
Aqua	up to100			
Citric Acid	up to pH≈6			

Source: own research

Hyaluronic acid (ultra - low molecular weight (Rec. K2), low molecular weight (K3) and high molecular weight (K4) was added to preheated water (depending on the formulation) and allowed to hydrate for about 7 hours. The oil phase components were then heated in a water bath to 75 ºC while stirring with a magnetic stirrer at 400 rpm and at 22 ºC .The hydrated hyaluronic acid was also heated to about 75 ºC. After which the two phases were combined. After thorough mixing of both phases, the preparation was cooled to about 30ºC, preservative (sodium benzoate and potassium sorbate) was added, mixed again and homogenized using a Silent Crusher-M-homogenzer, from Heidoplph, at about 30 °C, at 10 rpm for 5 min. Finally, the pH was adjusted to approximately 6 with citric acid.

1.2. Materials

The following have been used as raw materials in skin care creams:

- Butyrospermum Parkii Butter. Masło Shea from Standard Sp. z o.o;
- Cetearyl Alcohol. Lanette O from BASF Polska;
- Ceteareth 20. Emulgin B2 from BASF Polska;
- Glyceryl Stearate. Cithrol GMSfrom CRODA Polska;
- *Oryza Sativa Seed Oil*.Raw material from ECOSPA;
- HyaluronicAcid. Hyaluronic acid ultra - low molecular weight(M_w less than 10 kDa), low molecular weight (M_w less than 500 kDa) and high molecular weight (M_w between 0.85 and 1.15 MDa) from online shop Zrób sobie krem;
- Citric Acid. Producer HSH Chemie Polska. Concentration of active ingredient 98-99 %;
- Sodium Benzoate (and) Potassium Sorbate. Raw material KEM BS from Pol Nil S.A. Concentration of active ingredients: 50 %;
- Aqua.

1.3. Methods

1.3.1. Dynamic viscosity

The dynamic viscosity of the skin care creams was tested using a Brookfield HADV III Ultra rheometer. The measurement was carried out at 22 °C at a speed of 10 rpm. The RV/SSRZ S spindle set was used. The volume of the tested samples was 250 cm^3.

1.3.2. Yield point

The yield point is the lowest value of shear stress at which a substance begins to flow. Creams characterized by a lower liquid limit have a „lighter" consistency and spread more easily on the skin [Klimaszewska et al.2016]. The flow limit of the tested skin care creams was determined with a viscosity meter (model HA DV III

Ultra from Brookfield Engineering Laboratories, USA) equipped with a set of paddle spindles. Measurements were carried out at spindle speed: 1 rpm. Measurement results were recorded and analyzed using EZ-Yield software.

1.3.3. Texture analysis

Consistency was evaluated using a texture analyzer (model CT3 4500 from Brookfield Engineering Laboratories, USA). The test allows for the evaluation and objective comparison of a number of characteristics that are typically assessed by the senses, including hardness, viscosity, brittleness, and elasticity. These parameters translate into the ease of spreading creams on the skin and the adhesion of these products (Klimaszewska et al.2016). The test was performed with a measuring probe made of nylon, with a load of 0.1 g and a measurement speed of 0.1 mm/s. The results were recorded by Texture Pro CT software. The texture profile analysis (TPA) consisted of evaluating the following properties: hardness (the mass required to push the probe to a depth of 10mm, i.e., the maximum force recorded during 1 test cycle) and adhesion force (the mass that must be applied to the probe to pull it out - a measure of the adhesion of the product to the probe).

1.3.4. Hydratation of the skin

Skin hydration was tested using a corneometer (Corneometer CM 825), which determines the capacitive resistance of the stratum corneum. Skin hydration was measured on clean, degreased ski n as a reference. Then 1 g of the tested skin care cream was applied to a 20 x 20 mm area of the forearm. The measurements were taken 2h after applying the cosmetic at a temperature of 22° C. The measurements were performed for 5 women aged 35-40 years. The results are presented as the arithmetic mean from 5 measurements.

1.3.5. Transepidermal Water Loss

Transepidermal water loss (TEWL) was measured with a Tewameter TM 300 on clean, degreased skin (reference point) and 2 hours after application of a skin care cream. Measurements were taken on 5 women aged 35-40 years.

1.3.6. Sensory evaluation

Sensory analysis was conducted for four manufactured samples of skin care creams. Each of them was evaluated in terms of parameters such as: smell, consistency, uniformity, cushion effect, spreading, smoothing, stickiness, greasiness and absorption. The parameters were evaluated on a scale of 1 to 5, with the number 5 indicating a high level of quality, 4 indicating good, 3 indicating sufficient, 2 indicating acceptable, and 1 indicating insufficient. Prototypes of skin care creams differing in the molecular weight of the hyaluronic acid used were evaluated by a team of ten with appropriate sensory sensitivity. Selection of candidates with regard to the sensitivity of the sense of smell was carried out by the method of direct evaluation of odors in the flasks, in accordance with the PN-EN ISO 5496 standard. A two-stage tactile sensitivity test was also carried out. In the first stage, the ability to distinguish surface roughness, the so-called surface feeling. In the second stage, the sense of deep feeling was verified [Szakiel & Turek 2010; Jędryka 2001].

2. Results and discussion

2.1. Rheological properties

The rheological properties of aqueous HA solutions have been extensively described in the literature. In general, it was found that aqueous HA solutions are characterized by non-Newtonian, shear-thinning and viscoelastic behavior. In aqueous solution, aggregation of polymer chains occurs with the formation of an extended three-dimensional network due to the formation of a tertiary ß-sheet structure. The formation of this network depends on the molecular weight of HA and its

concentration. It has been shown that as the molecular weight and concentration increase, the HA network is strengthened, resulting in a gradual increase in the viscosity and viscoelasticity of HA solutions [Fallacara et al. 2018]. In addition, the rheological properties of HA in aqueous solutions are affected by factors such as ionic strength, pH and temperature. It has been found that as these factors increase, the viscosity of HA decreases markedly, suggesting a weakening of interactions between polymer chains [Rwei et al. 2008]. However, there are few reports in the literature on the effect of hyaluronic acid on the rheological properties of emulsions. Which was confirmed by the authors of the paper by Kibbelaar et al [Kibbelaar et al. 2021]. The same authors undertook a paper on the effect of different HA molecular weights on the rheological properties of a concentrated model emulsion, while focusing only on the elongation properties, using a rheometer to stretch the fibers and the effect of tensile speed. It was shown that when making cosmetic emulsions with HA of different molecular weights, elongation flow as a function of molecular weight is more important than the shear-thinning behavior of the emulsion.

The effect of molecular weight of hyaluronic acid on dynamic viscosity (η) values was evaluated and the results are shown in Fig.1. Dynamic viscosity is an important quality characteristic of face creams. It largely determines the functional properties of cosmetics, affecting the ease of application and dosage of the product.

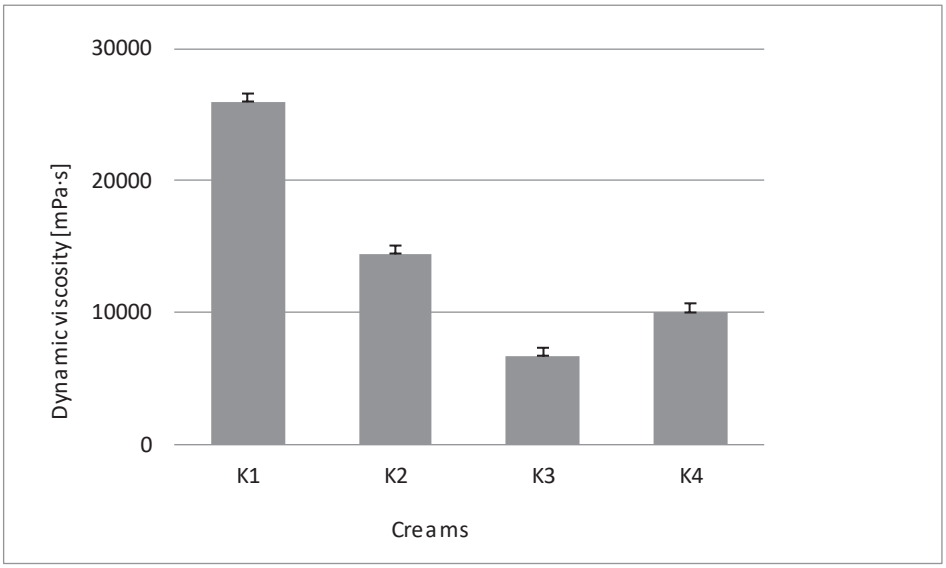

Fig. 1. Dynamic viscosity of face creams with different molecular weight of hylauronic acid. K1- reference sample, K2- cream with ultra - low molecular weight of hyaluronic acid, K3 - cream with low molecular weight of hyaluronic acid, K4- cream with ultra high molecular weight of hyaluronic acid

Source: own research

The highest dynamic viscosity value (26030 mPa·s) was observed for the base cream. This preparation did not contain hyaluronic acid in its composition. The addition of this component of different molecular weight led to a decrease in the tested parameter. The results oscillated from 6750 to 14500 mPa·s depending on the applied molecular weight of hyaluronic acid. The lowest decrease in viscosity was observed for the sample K2 containing in its composition ultra - low molecular hyaluronic acid, by about 44 % in comparison with the base cream. On the other hand, the addition of low molecular weight hyaluronic acid (K3) led to a significant decrease in dynamic viscosity by about 74 % in comparison to the base cream. The values of the studied parameter can be ranked as follows $\eta K1 < \eta K2 < \eta K4 < \eta K3$. According to the conclusions of Authors Kibbelaar et al, the observed decrease in

emulsion viscosity after the addition of HA may be due to the shear-thinning properties of this type of system. On the other hand, the differences in viscosity as a function of molecular weight for emulsions may be due to differences in elongated flow during emulsion formation. Under the influence of increasing shear rates, HA chains deform and align with flow streamlines, and this causes a decrease in viscosity [Fallacara et al. 2018].

Fig. 2 shows the values of the liquid limit for skin care creams differing in the molecular weight of hyaluronic acid. Testing the yield point of face creams is extremely important from the point of view of both the consumer and the manufacturer. The lower the value of this parameter, the better the cosmetic will spread on the skin. For the manufacturer, the yieldpoint values are helpful in selecting the appropriate type of packaging as well as the dosage method [Klimaszewska et al.2016].

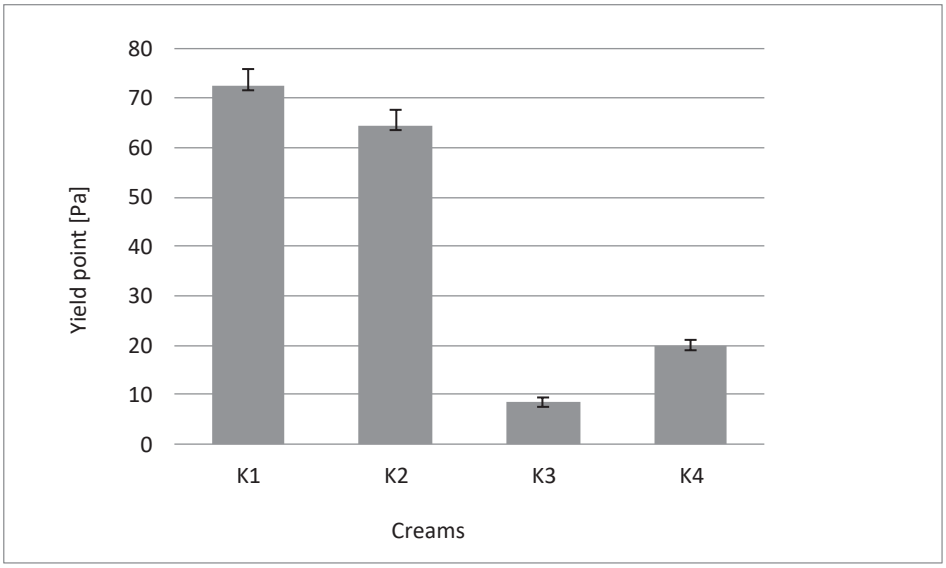

Fig. 2. Yield point of face creams with different molecular weight of hylauronic acid. K1- reference sample, K2- cream with ultra - low molecular weight of hyaluronic acid, K3 - cream with low molecular weight of hyaluronic acid, K4- cream with ultra high molecular weight of hyaluronic acid

Source: own research

It was found that the molecular mass of hyaluronic acid influenced the values of yield point of the tested skin creams. The decrease of this parameter was noted for all creams differing in molecular mass of hyaluronic acid in comparison with the base cream. At the same time for K2 cream containing ultra - low molecular weight acid the values of yield point were comparable to the results obtained for the base cream. Addition of low molecular and high molecular acid contributed to significant decrease of the tested parameter from about 72-88 % in comparison to cream K1 (base sample), which in consequence may determine a good application of the cosmetic on the skin. In addition, it should be noted that the obtained results of the yield point of the developed emulsions correspond with the results of dynamic viscosity.

Fig. 3. shows the evaluation of the consistency of facecreams differing by the molecular weight of hyaluronic acid. Hardness and adhesion are extremely important parameters during product application. They translate into ease of spreading on the skin and dosage.

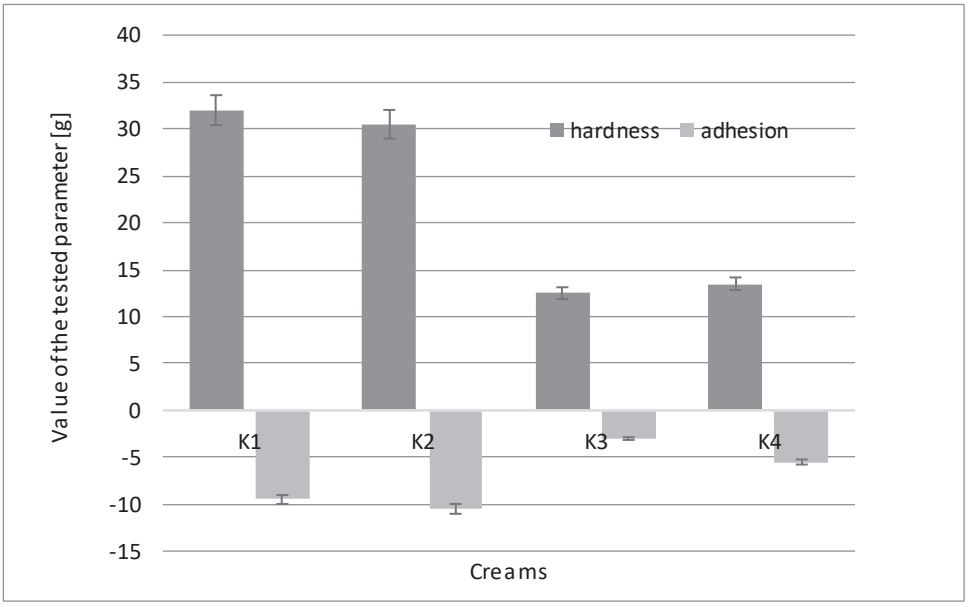

Fig. 3. Hardness and adhesive force of face creams with different molecular weight of hylauronic acid. K1- reference sample, K2- cream with ultra - low molecular weight of hyaluronic acid, K3 - cream with low molecular weight of hyaluronic acid, K4- cream with ultra high molecular weight of hyaluronic acid

Source: own research

The highest hardness (32 g) was achieved by the base cream without hyaluronic acid, the adhesion strength for this formulation was (-9.5 g). The addition of ultra - low molecular hyaluronic acid (K1) contributed to a slight decrease in hardness and adhesion compared to the base cream. The use of low and high molecular weight acid in the K3 and K4 skin creams resulted in a significant decrease in hardness (by about 60%) and led to an increase in adhesion (by about 42-68%) compared to the base cream.

In conclusion, the effect of the molecular weight of hyaluronic acid on the values of hardness and adhesion strength of the tested face creams was noted. The results of the study correspond to the results obtained in the study of dynamic viscosity and yield point.

2.2. Moisturizing properties

Face creams should be characterized by a high degree of skin hydration. For this purpose, various moisturizing substances, called humectants, are added to such formulas [Arct & Pytkowska 2009]. Recently, hyaluronic acid has become very popular. In cosmetic preparations, hyaluronic acid functions not only as a viscosity modifier but also a skin conditioning agent [Juncan et al. 2021].

Fig. 4. shows the results of studies on skin hydratation after application of face creams differing in molecular weight of hyaluronic acid.

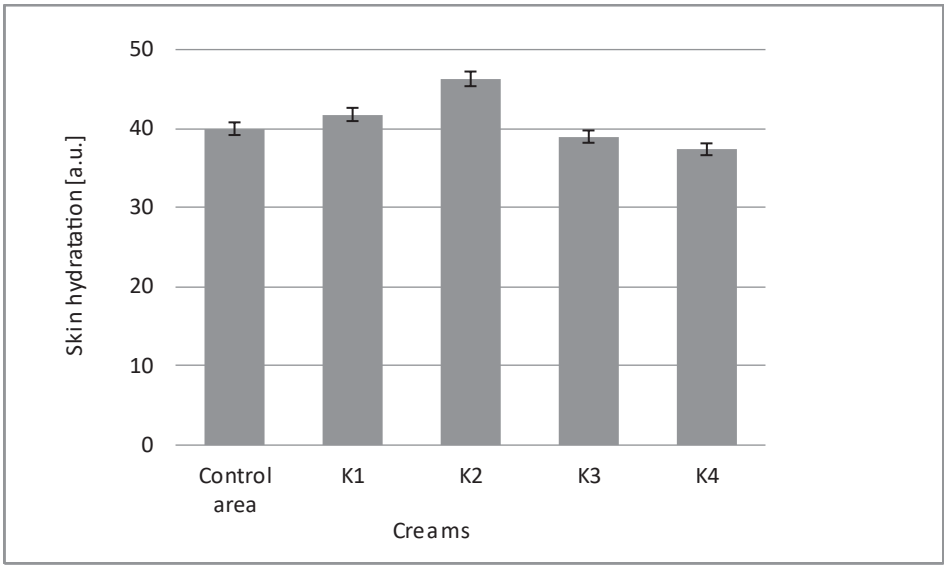

Fig. 4. Skin hydratation level after 2h from application the face creams with different molecular weight of hylauronic acid. K1- reference sample, K2- cream with ultra - low molecular weight of hyaluronic acid, K3 - cream with low molecular weight of hyaluronic acid, K4- cream with ultra high molecular weight of hyaluronic acid

Source: own research

Skin hydration level after application of all creams ranged from 37.4 to 46.3 a.u. On the basis of the obtained results, it can be concluded that only after application of the cream K2 containing hyaluronic acid ultra - low molecular weight (the result above 45 a.u.) the skin was sufficiently moisturized.

The results of skin hydration studies are consistent with those reported in the literature. Among others, Pavicic et. al. [Pavici et.al. 2011] showed that the highest skin hydration was recorded after applying a cream involving the lowest molecular weight (in this case 50 Da). According to the authors, low-molecular-weight hyaluronic acid is able to penetrate deeper layers of the skin than high-molecular-weight acid. The use of high-molecular-weight hyaluronic acid, on the other hand, allows the formation of a lipid mantle on the surface of the skin, preventing water loss and protecting it from internal factors [Pavici et.al. 2011; Kucia 2017].

TEWL determines the amount of water that is lost from the epidermis through evaporation. It has a direct impact on the level of skin hydration. When the TEWL level is high the skin becomes dehydrated [Arct& Pytkowska 2009, Klauzińska et al.2017].

Figure 5. shows the results of TEWL tests after application of face creams differing in the molecular weight of hyaluronic acid.

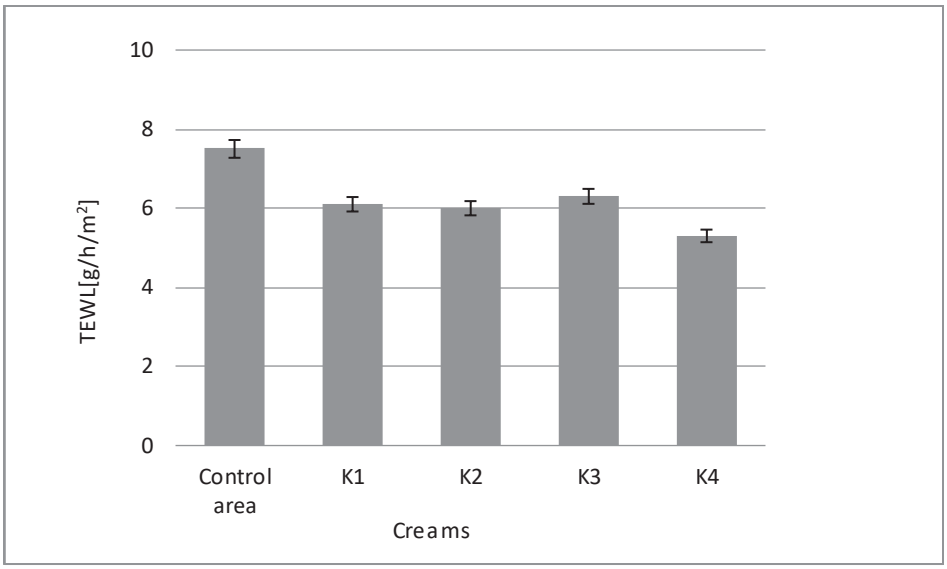

Fig. 5. TEWL after 2h from application the face creams with different molecular weight of hylauronic acid. K1- reference sample, K2- cream with ultra - low molecular weight of hyaluronic acid, K3 - cream with low molecular weight of hyaluronic acid, K4- cream with ultra high molecular weight of hyaluronic acid

Source: own research

TEWL for the control area was 7.5 g/h/ m^2. After application of all face creams a decrease in transepidermal water loss was observed in relation to the control area to about 6.0-5.3 g/h/ m^2. The smallest value of TEWL was observed after the application of K4 cream containing a high molecular acid.

In conclusion, it can be said that the addition of hyaluronic acid to facial creams affects the reduction of traspeidermal water loss. Among others, Kwon et al. in their work [Kwon et.al 2013] proved that the addition of hyaluronic acid to a cream leads to a reduction in traspeidermal water loss. In addition, in their work [Bukhari et.al 2018] they confirmed that the anti-wrinkle efficacy of hyaluronic acid depends on the molecular weight, which may be related to differences in the transdermal absorption of this ingredient with different molecular weights in the stratum corneum.

2.3. Sensory evaluation

The evaluation of product attributes perceived through the senses plays an important role in the perception of cosmetic quality. The result of this evaluation can largely determine the acceptability and purchase of a product by the consumer [Szakiel & Turek 2019, Kulawik-Pióro et al. 2020].

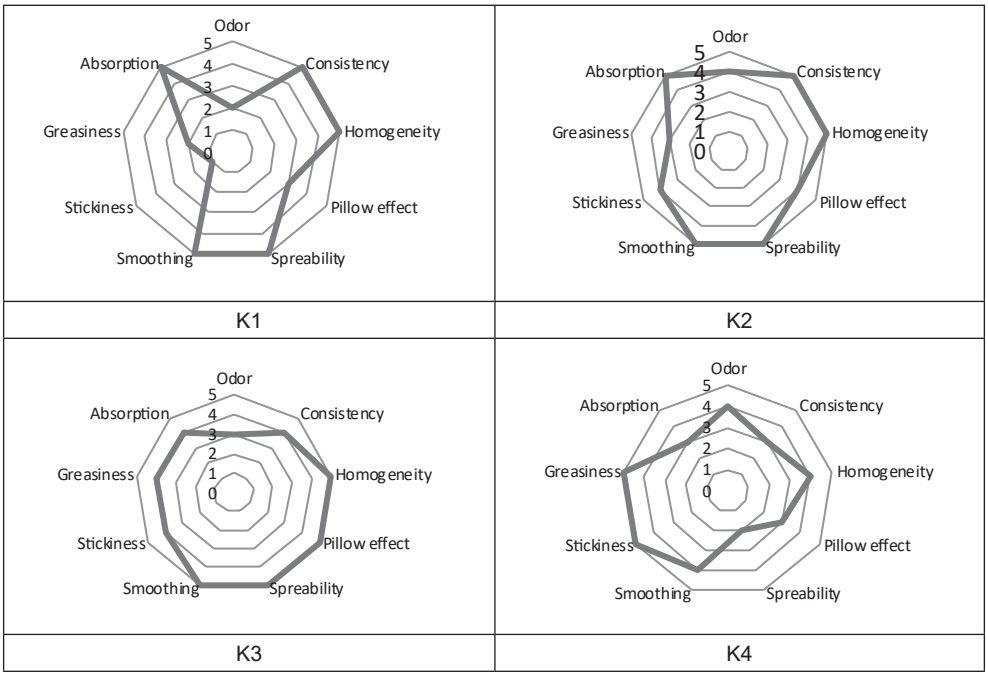

Fig. 6. Sensory evaluation of face creams with different molecular weight of hylauronic acid. K1- reference sample, K2- cream with ultra - low molecular weight of hyaluronic acid, K3 - cream with low molecular weight of hyaluronic acid, K4- cream with ultra high molecular weight of hyaluronic acid

Source: own research

The cream with ultra - low molecular hyaluronic acid (K2) was rated the highest by the testers. Five parameters i.e. consistency, absorption and homogeneity were rated at the maximum number of points. This prototype also had the lowest number

of parameters, among the tested creams, rated 4 (good), these were: odor, pillow effect and stickiness. The greasiness of this cream was rated 3 (sufficient), from which it can be concluded that this cream has a light consistency and would be good for people with oily, combination skin or under makeup.

The second place in the sensory evaluation can be given to the cream with low molecular hyaluronic acid, its highest rated parameters (5 - very good) are: homogeneity, consistency,pillow effect, spreability, smoothing. Slightly weaker, with a rating of good (4) were consistency, stickiness, greasiness and absorption. The lowest rating (3) was given for the scent of the cream.

The cream with high molecular hyaluronic acid was rated very good (5) for its greasiness and stickiness. It was rated good - 4 - for its homogeneity, smoothness and odor, which according to the test persons was pleasant and sweet. The consistency, pillow effect, and absorption were rated as sufficient (3). This cosmetic had the „heaviest" consistency and absorbed poorly. On the other hand, the worst rating of acceptable (2) was given for spreading on the skin.

The testers rated the base cream very well in as many as five categories (consistency, homogeneity, spreading, smoothing, absorption), so it would seem that this would be the perfect cream, but the other categories effectively disqualified it. The pillow effect was rated as sufficient (3), followed by the greasiness and odor as acceptable (2) and a failing grade (1) was given for stickiness.

3. Conclusions

The main aim of the article was to work out formulas of face care creams with hyaluronic acid and to determine the influence of molecular weight of hyaluronic acid on the quality of this type of cosmetics. The following acids were selected: ultra - low molecular, low molecular and high molecular.

On the basis of the conducted research it was found that:

- The molecular weight of hyaluronic acid influenced the dynamic viscosity values of the tested face creams. The highest value of dynamic viscosity (26030 mPa·s) was characteristic for the base cream, without hyaluronic acid. The

addition of hyaluronic acid in the formulations led to a decrease in the dynamic viscosity value. The highest values of this parameter in relation to the base cream were noted for the cream containing ultra - low molecular hyaluronic acid and the lowest for the cream containing low molecular hyaluronic acid;

- The values of the yield point of the creams ranged from 8.5 to 72.57 Pa. The lowest value, indicating the possibility of „easy" application of the cosmetic, was recorded for the cream containing low molecular weight hyaluronic acid;
- The highest hardness and adhesion strength was observed for the base sample and the cream with ultra - low molecular hyaluronic acid. However, the lowest hardness and adhesion was observed for the cream with low molecular weight hyaluronic acid. Thus, the molecular weight size of hyaluronic acid affects the application properties of the product. Additionally, it can be stated that the results corresponded with the results obtained in the dynamic viscosity and yield point;
- The highest skin hydration was observed after the application of the cream with ultra - low molecular hyaluronic acid - 46.3 (a.u.), while the lowest was observed after the application of the cream with high molecular hyaluronic acid - 37.4 (a.u.);
- Each of the creams has an effect on reducing transepidermal water loss; the skin retains water best after application of a cream with high molecular hyaluronic acid;
- In sensory tests the cream with low molecular and ultra - low molecular hyaluronic acid received the best marks, while the cream with high molecular hyaluronic acid received the lowest marks.

In conclusion, a significant effect of the molecular weight of hyaluronic acid on the physicochemical properties of the developed emulsions can be stated. A similar trend of changes was shown for the results of viscosity, yield point and hardness of the tested creams. It is possible to indicate in all cases a decrease of the analyzed parameters for the studied emulsions depending on the molecular weight of hyaluronic

acid in the following series: K2>K4>K3, where K2, K4 and K3 contain ultra - low molecular weight, high molecular weight and low molecular weight HA, respectively. Moreover, it was shown that the cream containing ultramolecular hyaluronic acid has the best moisturizing properties among the analyzed emulsions and obtained, according to the members of the sensory panel, the best sensory evaluation.

4. Acknowledgements

The work performed under the project no. 3501/188/P titled: „Application of innovative raw materials of natural and synthetic orgin in care and suport of treatment of skin diseases in various clinical conditions" and Project no.3086/35/P titled:„Development of formulations and technologies for the manufacture of innovative cosmetics, pharmacy supplies, household and industrial chemicals". Projects financed by the Ministry of Education and Science.

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EVALUATION OF FUNCTIONAL PROPERTIES OF BAR SHAMPOOS AVAILABLE ON THE POLISH MARKET

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Abstract
Currently, there is a great variety on the shampoo market in terms of additional functions and product form. However, bar shampoos are new. They are gaining popularity among consumers, especially due to the convenience of their use and also due to the ecological aspect.
In this study, an attempt was made to evaluate some of the usage properties of bar shampoos. Wetting, surface and foaming properties of these products were compared with classic liquid shampoo. The analysis of the obtained results shows that the tested bar shampoos in terms of the analyzed quality determinants are not inferior to classic liquid shampoos.

Keywords: shampoos, cosmetics, usage properties

Introduction

In 1933, the first non-alkaline shampoos for washing hairs appeared on the market, until then soap was used to maintain the hygiene of the scalp and hair [Urbano 1995]. Competition on the market and growing consumer expectations mean that modern shampoos, apart from the basic washing functions, should meet additional requirements. Therefore, shampoos should have foaming properties both in hard and

soft water as well as in contact with greasy hair. Consumers expect, that not only will they not dry their hair, but it will also have a conditioning effect. Additionally, shampoos should have low irritating properties, be biodegradable and inexpensive. All this means that nowadays shampoos are products with a complex recipe, usually composed of 10-30 ingredients [Trüeb 2007]. The ingredients of shampoos can usually be divided into three groups: cleansing base, conditioning and active ingredients, and functional additives [Luengo et al. 2021].

The cleansing base consists of surfactants and it is this group of compounds that the shampoos have the ability to remove environmental dirt. Depending on the type of hair, the washing base contains various proportions and types of surfactants, although the main components are usually anionic and amphoteric surfactants [Bouillon 1996]. Over the years, alkyl and alkyl ether sulfates have been used most often in shampoo formulations. They owe their popularity mainly to the price and good washing properties. Moreover, they exhibit the expected foaming and rheological properties. The trend visible on the market is to limit the use of products with alkyl and alkyl ether sulfates, which is caused by consumers' concerns about the irritation of these compounds on the skin and eyes. Alternatively to them, taurates and sulfoacetates and sulfosuccinates are used in formulations [Cornwell 2018]. In addition, other anionic surfactants are often used in shampoo recipes: alkyl ether carboxylate, acyl peptides, and olefin sulfonate. They are used particularly eagerly because they are well tolerated by the skin and are compatible with other anionic and amphoteric surfactants [Trüeb 2007]. The literature indicates that anionic and amphoteric surfactants can form complexes reducing the ability of anionic surfactants to attach to proteins. Amphoteric surfactants are seen as potential ingredients in mild shampoos because they are well tolerated by the skin and condition the hair [Bouillon 1996]. Among the amphoteric surfactants, cocamidopropyl betaine and coco-betaine have the most applications in hair washing products. A limitation in the use of cocamidopropyl betaine is sensitivity to pH, moreover, a high proportion of cocamidopropyl betaine in systems containing anionic surfactants reduces the foaming activity of the system [Cornwell 2018].

In order for the product to meet the expectations of the consumer, it is necessary to use a number of additives to improve its functionality and stability. Ensuring the stability of the product is related to the protection against microorganisms, for this purpose it is necessary to add preservatives. It is also necessary to ensure oxidative stability and for this purpose antioxidants are added to protect the sensitive substances from oxidation. The durability of the shampoo is also related to ensuring the appropriate pH, therefore an inherent component of the shampoo recipe are also buffers [Trüeb 2007]. Another determinant of the quality of shampoos is its viscosity, providing the correct viscosity makes it easier for the consumer to dose the product, but also consumers perceive high-viscosity products as „rich in composition", hence viscosity modifiers in shampoo formulas. Manufacturers achieve the attractiveness of shampoos by adding dyes, opacifiers (e.g., dispersions of styrene acrylic copolymers) and fragrances [Arct 2007].

Shampoos often gain therapeutic properties through the addition of active ingredients, usually to help fight: dandruff, seborrhea, seborrheic dermatitis, and psoriasis [Schwartz et al. 2016; Trüeb 2007]. The main property of these active substances will be antifungal activity. Until recently, the biocide most commonly used in shampoos since the 1950s was zinc pyrithione. Usually, its amount in the product ranged from 0.5% to 2%, it was readily used by producers due to its effectiveness, cost and compatibility with other ingredients of the shampoo. Currently, its use in cosmetic products available on the European Union market is prohibited. In addition, the compounds that exhibit fungicidal properties that have been used in shampoos are: ketoconazole and selenium sulfide. Climbazole and octopirox are also used as fungicidal compounds, but their use in hair washing products is less frequent [Schwartz et al. 2016]. In 1987, Procter and Gambel introduced a 2-in-1 shampoo, and since then conditioners have become a common additive to shampoo formulations [D'Souza & Rathi 2015]. The main task of the conditioning ingredients is to neutralize the negative charge. In addition, they improve the hydrophobicity of the hair and mimic the natural lipid layer of the hair. They improve detangling, provide shine and smoothness [Draelos 2005]. Usually, the conditioning ingredients are: polymers, oils, waxes, hydrolyzed aminoacids and cationic molecules [Robbins 2013]. It is estimated

that the most frequently used conditioning agents are silicones. They show high substantivity in relation to hair due to non-polar van der Waals interactions. Particularly popular in 2in1 shampoos is dimethicone but also siloxysilicates. The action of dimethicone is to protect the hair shaft from abrasive action, while siloxysilicates increase the volume of the hair [Dias 2015; Arct 2007]. Protein hydrolysates of plant and animal origin have also been used. From feathers, horns, hair and hooves, keratin hydrolysates are obtained, useful in products for hygiene and hair care [Dias 2015]. High molecular weight hydrolysates tend to form a film on the hair surface, while low molecular weight hydrolysates are credited with penetrating the cuticle. The effect is smoothing the hair and improving hydration, additionally, hydrolysates soothe the irritating effect of anionic surfactants [Arct 2007]. An important conditioning agent are also mineral and vegetable oils. They can reduce the penetration of water into the hair structure, and they can also prevent surfactants from penetrating the hair follicle by sealing the epidermis cells [Dias 2015]. However, it should be remembered that introducing them into the product requires the formation of an emulsion, moreover, they destabilize the foam, which may have a limiting effect on their use [Arct 2007]. Ammonium compounds, in particular cationic surfactants, are also widely used in hair hygiene and care products. They show high substantivity due to ionic and van der Waals interactions. Simple cationic surfactants such as alkyltrimethylammonium chloride and dialkyldimethylammonium chloride face limitations in use, namely they are incompatible with anionic surfactants. This compatibility is achieved by modifying the molecule by introducing hydrophilic groups. Polymeric derivatives of quaternary ammonium salts have also found use as conditioning compounds. They can be used without limitation in formulations containing anionic surfactants, but do not exhibit antistatic activity like their monomeric precursors [Arct 2007].

The shampoos available on the market differ not only in formulation but also in the form in which they are sold, it can be distinguish: liquids, liquid creams, gels, mousses, powders [Bouillon 1996] and for some time also bars. Taking into account the purpose and cosmetic positioning, shampoos can be divided into several groups: ordinary, mild, beauty, conditioning and special care shampoo [Kwaśniewska &

Wieczorek 2017]. Shampoo formulations and their form are subject to constant modification, it is related to the competition on the market and the growing expectations of the consumer. The cosmetics industry is expected to become a fully circular industry and cosmetic formulations should use eco-sustainable, bio-based and biodegradable ingredients [Luengo et al. 2021]. Another observed trend concerns the use of greener packaging, currently it is most visible in the increase in ratio of refill consumption [Okada et al. 2021]. It seems that bar shampoos, which have recently been available on the market, are in line with the trend of ecological packaging. For this reason, an attempt was made to evaluate some of the quality determinants of the above-mentioned shampoos and compare them with the classic liquid shampoo.

1. Material and methods

1.1. Materials

3 shampoos in a bar and one liquid shampoo purchased on the Polish market were tested. According to the manufacturers declarations, the shampoos had the following composition:

- Shampoo 1 (product for normal hair): Sodium Coco-Sulflate, Butyrospermum Parkii Butter, Threobroma Cocao Seed Butter, Olea Europea Fruit Oil, Hydrated Silica, Sodium Lauroyl Glutamate, Parfum, Citrus Aurantium Bergamia Fruit Oil, Limonene, Geraniol, Citral, Citronellol;
- Shampoo 2 (product with a regenerative effect): Triticum Vulgare (Wheat) Starch, Potassium Lauryl Sulfate, Cetearyl Alcohol, Sodium Lauryl Sulfate, Aqua (Water, Eau), Glycerin, Butyrospermum Parkii (Shea) Butter, Stearic Acid, Lactic Acid, Parfum (Fragrance), Persea Gratissima (Avocado) Oil, Hydrolyzed Jojoba Esters, Limonene, Linalool, Biosaccharide Gum-1, Sodium Levulinate, Glyceryl Caprylate, Sodium Anisate, Benzyl Alcohol, Ascorbyl Palmitate;
- Shampoo 3 (product with a pomegranate scent) Disodium Lauryl Sulfosuccinate, Sodium Coco-Sulfate, Triticum Vulgare (Wheat) Starch, Cetearyl

Alcohol, Hydrogenated Palm Glycerides, Aqua, Lauryl PCA, Cocamidopropyl Betaine, Ricinus Communis Seed Oil, Glyceryl Stearate, Olea Europaea Fruit Oil, Parfum, Sodium Chloride, Limonene, Linalool, CI 77891;

- Shampoo 4 (liquid product): Aqua, Sodium Laureth Sulfate, Sodium Lauryl Sulfate, Cocamidopropyl Betaine, Glycol Distearate, Sodium Citrate, Sodium Xylenesulfonate, Parfum, Dimethiconol, Dimethicone, Citric Acid, Sodium Benzoate, Guar Hydroxypropyltrimonium Chloride, Sodium Chloride, TEA--Dodecylbenzenesulfonate, Tetrasodium EDTA, Sodium Hydroxide, Trisodium Ethylenediamine Disuccinate, Trideceth-10, Panthenol, Panthenyl Ethyl Ether, Hexyl Cinnamal, Hydroxycitronellal, Magnesium Nitrate, Methylchloroisothiazolinone, Benzyl Alcohol, Magnesium Chloride, Sodium Borate, Methylisothiazolinone.

1.2. Evaluation of the wetting properties

The wetting properties were assessed using a Kruss K100 tensiometer. The Wilhemy method was used to determine the contact angle. The tested shampoo solutions had a concentration of 1.25%. Paraffin was selected as the analyzed surface and it was treated as a model surface imitating human skin.

1.3. Evaluation of the surface properties

The surface tension was measured according to the Wilhelm method. Testing of the analyzed aqueous solutions of shampoos was carried out with a Kruss K 100 tensiometer. The obtained results allowed to plot the surface tension isotherms and to determine the values of the critical micellization concentration (CMC).

1.4. Evaluation of foaming properties

10% solutions of the analyzed shampoos were tested to determine the foaming properties. The method of the perforated disc was used in accordance with the Polish standard PN-EN 12728:2001. The test solutions were whipped with a perforated disc in a measuring cylinder for 1 minute. All solutions were whipped at the same speed

by making movements of a specified length and frequency. The foam volume was determined 1 and 5 minutes after the end of the measurement.

2. Results

The parameter that allows to determine this ability is the contact angle, its measured values are given in Table 1. For all tested solutions, the value of the contact angle was lower than 90°. The lowest value was recorded for shampoo solution 2, it was 58.4°.

Table 1. Values of the contact angles of the tested shampoo solutions

Shampoo	Contact angles [°]
Shampoo 1	69.87
Shampoo 2	58.4
Shampoo 3	68.98
Shampoo 4	65.07

Source: own study

On the basis of tensiometric measurements, surface tension isotherms were plotted, which in turn made it possible to determine the critical micelle concentration (CMC) value. The obtained values are presented in Table 2. The bar shampoos exhibited varying CMC values. Two of the test subjects, i.e. shampoo 1 and 2, showed lower CMC values than the classic liquid shampoo.

Table 2. Values of critical micelle concentration (CMC)

Shampoo	CMC value [%]
Shampoo 1	0.019
Shampoo 2	0,006
Shampoo 3	0,223
Shampoo 4	0.147

Source: own study.

The volume of the foam column produced in the perforated disc test are shown in Tables 3. These values made it possible to calculate the values of the foam stability index. The stability of the foam was defined as the ratio of its volume after 1 minute and 5 minutes from the moment of its formation. During this time, the generated foam for all tested solutions was characterized by high stability from 81.54% to 96.26%.

Table 3. The volumes of the foam column and the values of the foam stability index of the tested shampoo solutions

Shampoo	V_1 [cm^3]	V_5 [cm^3]	Y_5 [%]
Shampoo 1	550	496.6	90.29
Shampoo 2	502.8	410	81.54
Shampoo 3	446.6	430	96.28
Shampoo 4	360	340	94.44

Source: own study.

3. Discussion

In the solid-liquid system, in order to obtain data on the degree of wetting, it is necessary to determine the size of the contact angle. This parameter is widely used in the evaluation of wetting properties [Yuan & Lee 2013]. At the basis of the description of these phenomena is the Young's equation, proposed in 1805:

$$\gamma_{lv}\, cos\theta_Y = \gamma_{sv} - \gamma_{sl} \tag{3.1}$$

where: γ_{lv}, γ_{sv}, γ_{sl}, - liquid-vapor, solid-vapor, and solid-liquid interfacial tensions and θ_Y is a contact angel [Kwok & Neumann 1999]. In the practical assessment of wetting properties, it is assumed that when the value of θ_Y is less than 90°, the liquid wetting the tested surface. Complete surface wetting occurs when θ_Y is 0° [Bruel et al. 2019]. The obtained data indicate that all of the tested shampoo solutions wetted the paraffin surfaces. The values of the contact angle are in the range from 58.4°

to 69.87°. Among the analyzed products, the bar shampoo no 2 solution had the lowest values of the contact angle, proving the best wetting properties.

Consumers equate dense and durable foam created in the washing process with a high content of surfactants and thus with effective removal of dirt. This all makes foaming ability an important factor in determining product quality [Sułek & Zięba 2010]. In thermodynamic terms, foam is an unstable structure that disappears over time. So far, three mechanisms of its destabilization have been known: drainage, coalescence, and coarsening [Fameau & Salonen 2014]. Moreover, a number of physical and chemical factors can influence its stability. Based on the data in Table 3, it can be concluded that the analyzed shampoos in the bar were characterized by a greater ability to generate foam compared to the liquid shampoo. However, when looking at bar shampoos only, it can be seen that the foaming tendency of this group was varied. For the obtained data, the foam stability index was calculated after 5 minutes, proceeding analogously to the methodology proposed in the literature [Małysa & Kowalska 2016]. The foam stability index (Y_5) was calculated according to the formula:

$$Y_5 = \frac{V_5}{V_1} \cdot 100\% \tag{3.2}$$

were, V_5- foam volume measured after 5 minute, V_1- foam volume measured after 1 minute. The obtained values are in a large range from 81.54% to 96.28%. Shampoos 3 and 4 showed the highest foam durability. The difference in the foam stability index for these two products was only 1.84%. The foam stability is influenced by a number of factors, one of them may be lipophilic compounds, which would explain the low stability of foam shampoo 2. The manufacturer declares that this product contains shea butter, avocado oil and jojoba oil derivatives. Taking into account only the analyzed shampoos in the bar, it can be noticed that this product group showed a high variability in terms of foam stability, as indicated by the calculated values of the foam stability index.

The washing effect of surfactants contained in shampoos varies depending on the type of dirt, usually it is: sebum, dead epidermis cells, solid impurities, and hair care and styling products. The mechanisms of removing greasy dirt are well known and described. It is assumed that the mechanism of effective sebum removal from hair and scalp is based on four stages: roll-up, spontaneous emulsification, penetration and solubilization [Cornwell 2018]. Literature data show that sebum removal is correlated with low value of critical micelle concentration (CMC) [Clarke et al. 1989 a, b], therefore a low CMC value is a desirable feature of shampoos. In this study, the CMC values of the test products were determined on the basis of surface tension isotherm. The CMC of shampoos in bars 1 and 2 take values order or two orders of magnitude less than the CMC of the liquid shampoo. In turn, the shampoo in the bar 3 is characterized by a CMC value comparable to that of a liquid shampoo. As a result, it cannot be clearly stated that bar shampoos have better washing properties.

4. Conclusions

The wetting, foaming and surface properties can be considered as one of the many determinants of the quality of hair shampoos. In this study, an attempt was made to evaluate these determinants in relation to bar shampoos. Bar shampoos are a relatively new element of the cosmetics market but they are gaining popularity. Growing consumer interest in these products results mainly from the fact that they are considered a more ecological product than traditional liquid shampoos. This view is due to the fact that they are devoid of plastic packaging. In addition, bar shampoos are convenient to use.

Characteristic for the assessed bar shampoos were very good foaming properties, higher than for the classic liquid shampoo. However, the stability of the generated foam for these two types of products was similar.

In this study, paraffin was treated as a surface imitating human skin. The analyzed solutions of the tested shampoos in the bar acted on its surface as partially wetting solutions. The classic liquid shampoo solution also showed partially wetting properties.

Micelles generated by cleaning agents are directly involved in the process of removing dirt, therefore CMC values were determined in this study. Among the analyzed bar shampoos, large differences of up to three orders of magnitude were noted. These values were comparable or lower than the CMC values of the liquid hair shampoo.

The obtained results indicate that the tested bar shampoos, in terms of the analyzed quality determinants, are not inferior to classic liquid shampoos. It seems that in the future they may become an alternative to classic liquid shampoos.

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APPLICATIONS OF HYDROXYETHYL URAE IN SKIN CARE COSMETICS

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Abstract
In this study an attempt was made to evaluate the possibility of using a urea derivative (INCI: Hydroxyethyl Urea) in personal care cosmetics. A series of prototypes of care creams in the form of O/W emulsions, which differed in the mass ratio of Glycerin to Hydroxyethyl Urea, was prepared. It was found that an increase in the content of Hydroxyethyl Urea with a simultaneous decrease in the content of Glycerin in the tested skin care creams significantly affects their physicochemical and functional properties. Moreover, an increase in the degree of skin hydration was found after the application of the tested emulsions with increasing concentrations of Hydroxyethyl Urea.

Keywords: skin care products, emulsions, humectants, quality

1. Introduction

The efficiency of the epidermal barrier depends on a properly formed stratum corneum. It is composed of keratinocytes connected by a lipid matrix composed of ceramides, cholesterol esters and fatty acids. On the surface of the stratum corneum there is a hydrolipidic barrier. Weakening of this barrier can be caused by bacteria, allergens or pathological conditions. Then a defect in the functioning of the natural skin barrier occurs, associated with increased transepidermal water loss TEWL

[Welz-Kubiak & Reich 2016; Jaworek et al. 2020]. Water can diffuse through the epidermis via intercellular lipids, corneocytes, water pores, or by shunt diffusion. It is widely recognized that intercellular lipids are the major barrier to water loss from the epidermis [Potts & Francoeur 1991; Berkey et al. 2021]. A malfunction of the natural skin barrier can give rise to symptoms such as dryness, irritation, intense itching or even skin inflammation. The level of hydration of the stratum corneum is also important for the feel, firmness and cosmetic aspects of the skin. In their work, authors Berkey and colleagues [Berkey et al. 2021] found that the biomechanical properties of the epidermis (mechanical tension and stiffness) play an important role in skin health. Because they control processes such as chapping and cracking of the epidermis, which in turn affects a person's perception of skin firmness and stiffness. Therefore, the process of skin care is a desirable and even required element [Jaworek et al. 2020; Rudyk & Jurzak 2012]. It consists, among others, in the systematic and regular use of appropriate cosmetic products that moisturize and lubricate the skin. That is why emollients and humectants are key raw materials used in skin care formulations. Emollients are materials with occlusive properties, causing the formation of a thin protective film on the surface of the epidermis, protecting against excessive water evaporation from the deeper layers of the skin. The vast majority of emollients have an epidermal effect - on the surface of the epidermis. There is a group of emollients, e.g. lanolin and ceramides, which, as a result of penetration into the intercellular cement structures of the stratum corneum, lead to the reconstruction of the epidermal barrier [Kamińska 2021; Welz-Kubiak & Reich 2016]. Humectants are hygroscopic substances with the ability to bind and retain water in the stratum corneum, which has a positive effect on the restoration of its protective barrier. Among the cosmetic materials with moisturizing properties we can distinguish: glycerin, urea, sorbitol, propylene glycol, lactic acid, hyaluronic acid, lactates, hydroxy acids, panthenol, amino acids. Some of the presented humectants are part of the Natural Moisturizing Factor (NMF), which binds water in the outer layers of the epidermis. Humectants in skin care products are most often used together with emollients because of their ability to form a continuous film on the skin surface, which contributes to water retention, i.e. reduces TEWL [Rudyk & Jurzak 2012; Kraft & Lynde 2005;

Lynde 2001]. Moreover, humectants are widely used in cosmetic, pharmaceutical or food industries due to their excellent ability to retain moisture in products during long-term use, storage and transportation [Lin et al. 2020]. In the cosmetic market, we can observe a continuous demand for novel raw materials that contribute to the increase of skin hydration and decrease of water loss from the stratum corneum. The moisturizing effect of traditional humectants does not meet their industrial demand, especially for products for atopic skin [Dong et al. 2021]. There are scientific reports in the literature dedicated to the acquisition, evaluation of new raw materials with moisturizing activity. For example, in [Song et al. 2021] a newly obtained natural polysaccharide - konjac glucomannan oligosaccharide kojic acid - was studied, where its moisturizing effect was demonstrated and possible applications in skin care were indicated. Whereas Authors Dong et al [Dong et al. 2021] synthesized new type of carmine cochineal-derived CDs (Car-CDs) via one-pot solvothermal method. They analyzed the moisture retention function of Car-CDs in human skin in their work. They have successfully applied Car-CDs as nano additives in a moisturizing lipstick. So they demonstrated the potential use of Car-CDs in health care, skin care and cosmetic industry. An interesting alternative to the commonly used moisturizers in the formulations of cosmetic care products is a derivative of urea - hydroxyethylurea (INCI: Hydroxyethyl Urea). Its commercial form is a 50% aqueous solution, has no smell and no color, is biodegradable. It is characterized by high solubility and stability. Hydroxyethyl Urea can be used in the pH range from 5 to 8. In order to evaluate the possibility of using Hydroxyethyl Urea, a series of prototypes of skin care creams in the form of O/W emulsion were made. Glycerin was also selected for testing as a commonly used humectant in skin care formulations. It serves as a reference substance. The developed and manufactured care creams differed in the mass ratio of Glycerin to Hydroxyethyl Urea (8:0; 6:2; 4:4; 2:6 and 0:8 wt%). The following tests were performed for the formulated products: stability, dynamic viscosity, field point, consistency evaluation, sensory testing and skin hydration after application of the skin care creams.

1. Material and methods

1.1. Materials

The following raw materials were used for making a series of prototypes of care creams in the form of O/W emulsions: Glycerin (Cremerglyc from Cremer); Cetearyl Olivate and Sorbitan Olivate (Olivem 1000 from Ecospa); Oleyl Erucate (Cetiol J600 from BASF SE); Capric/Caprylic Triglyceride (Crodamol GTTC from Croda S.A.); Cetearyl Alcohol (Lanette O by BASF SE); Butyrospermum Parkii Butter (Shea Butter by Standard Sp. z o.o.); Prunus Amygdalus Dulcis (Sweet Almond) Oil by Standard Sp. z o.o.); Hydroxyethyl Urea (Hydrovance from Akzo Nobel); Sodium Benzoate (and) Potassium Sorbate (KEM BS from Pol Nil S.A.) and Citric Acid (Citric Acid from HSH Chemie Polska).

1.2. Methods

Stability

The stability of skin care creams was analyzed using a Turbiscan LabCooler instrument from Formulaction, which allows characterization of physicochemical phenomena (e.g. particle migration, flocculation, coalescence, sedimentation or creaminess). The instrument's measurement head (a light source along with two synchronized transmission and backscatter sensors) scans the formulation moving from the bottom to the top of the vial collecting data every 40μm over the entire sample height (up to 50mm). Samples were stored for 4 weeks at 40˚C. Measurements were taken every 7 days. The results are presented in a graph generated by Turbiscan LAB software version 2.0.0.19.

Dynamic viscosity

The dynamic viscosity of skin care creams was tested using a Brookfield DV-I+ viscosity meter. Measurements were conducted at 10rpm and at 22°C. The measurements were performed 5 times. The results presented in the graph are averaged values.

Yield point

The values of field point of the tested skin care creams were determined using a Brookfield HADV III Ultra viscosity meter equipped with a set of vanespindle. Measurements were conducted at a constant spindle speed of 1rpm and at 22°C. EZ-Yield Software was used to record the measurements and analyze them.

Consistency evaluation

Brookfield's CT3 texture analyzer was used to determine the hardness and adhesion strength of the manufactured skin creams. The results of the measurements were recorded by Texture Pro CT software. The measurements were carried out using a spherical nylon sampler, with a depth of immersion of the sampler of 10 mm, a head travel speed of 0.1 mm/s and a load of 0.1 g. Measurements were performed at 22°C.

Degree of skin hydration

Moisturizing effect of the tested creams was evaluated using Corneometer CM 825 probe and Courage-Khazak MPA 580 adapter. Two 2 cm x 2 cm areas (test and control) were marked on the skin of the test persons (forearm skin). Then 1g of the test product was applied to the test area and gently spread. After 2 hours, corneometric measurements were taken. The results are presented as the arithmetic mean of the 5 measurements.

Sensory evaluation

Sensory evaluation of the tested skin care creams was conducted in a group of five adult women aged up to 25 years. The proband evaluated individual emulsions in terms of the following sensory indicators: adhesion, texture, uniformity, cushion effect, spreading, absorption, stickiness, greasiness, oiliness, and smoothness [Kossowska & Zielinski 2017]. The parameters were evaluated on a point scale from 1 to 5, where: 1 - bad, 2 - average, 3 - poor, 4 - good, 5 - very good.

2. Results

2.1. Formulation development of skin care creams

Basing on the source data, market analysis and own experience, the formulations of care creams in the form of O/W emulsions have been worked out (Tab.1.). The formulations differed in mass ratios (8:0; 6:2; 4:4; 2:6 and 0:8) of two humectants: commonly used glycerin (G) and the tested derivative of urea (H).

Table 1. Care cream formulations in the form of emulsion O/W

Ingredients (INCI Name)	Concentration [wt %]				
	G8:H0	G6:H2	G4:H4	G2:H6	G0:H8
Cetearyl Olivate and Sorbitan Olivate	6.0				
Oleyl Eructate	1.0				
Cetearyl Alcohol	2.0				
Capric/Caprylic Triglyceride	1.0				
Butyrospermum Parkii Butter	2.0				
Prunus Amygdalus Dulcis (Sweet Almond) Oil	4.0				
Glycerin	8.0	6.0	4.0	2.0	-
Hydroxyethyl Urea	-	2.0	4.0	6.0	8.0
Aqua	to 100				
Sodium Benzoate and Potassium Sorbate	0.5				
Citric Acid to pH 5,0-6,5	q.s				

Source: own study.

The preparation of the care creams consisted in heating to a temperature of about 70ºC and mixing separately the components of the oil phase (Cetearyl Olivate and Sorbitan Olivate, Oleyl Eructate, Cetearyl Alcohol, Capric/Caprylic Triglyceride, Butyrospermum Parkii Butter, Prunus Amygdalus Dulcis (Sweet Almond) Oil) and the components of the water phase (Aqua, Glycerin, Hydroxyethyl Urea,) on a water

bath until they were completely dissolved. Then the two phases were combined while stirring to form a homogeneous system. The resulting emulsion was homogenized (Heidolph SilentCrusher homogenizers). Subsequently, a preservative was introduced at 30°C and again mixed thoroughly. Finally, the pH of the creams was adjusted (about 5.0-6.5) with Citric Acid.

The next stage of the work was evaluation of the stability of the produced care creams using Turbiscan Lab Cooler device from Formulaction, which allows for characterization of the actual state of dispersion and long-term analysis of the destabilization processes occurring in it without disturbing the structure of the system during measurement. Based on the obtained test results, it was clearly stated that all produced creams showed no signs of emulsion instability. Figure 1 shows an example of the backscattering (BS) and transmission (T) relationships as a function of cell height at a given time for a G4:H4 skin care cream containing 4 % Glycerin and 4 % Hydroxyethyl Urea made from 4 measurements over 4 weeks.

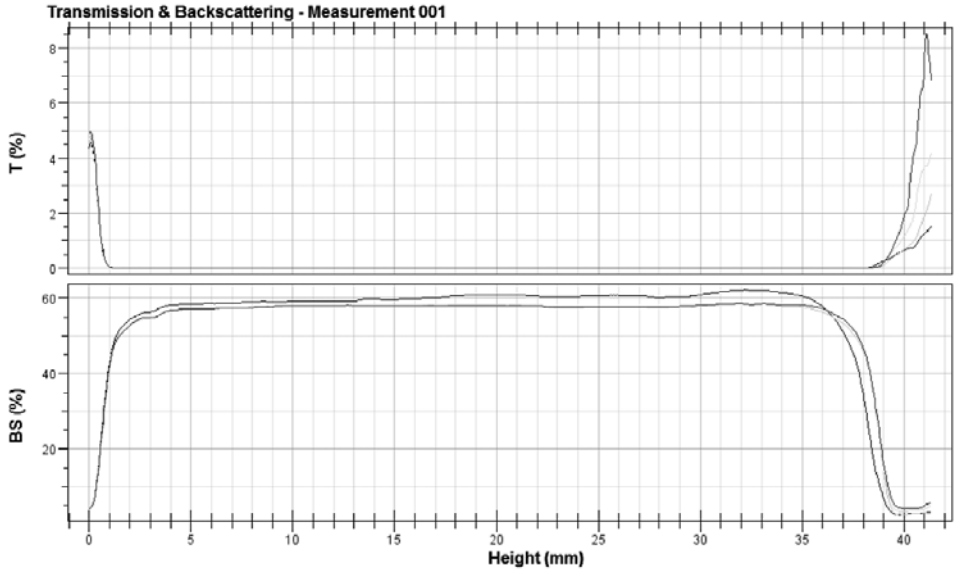

Fig. 1. Dependence of transmission (T) and light scattering (BS) on sample height for G4:H4 skin care cream containing 4 % Glycerin and 4 % Hydroxyethyl Urea

Source: own study.

2.2. Dynamic viscosity

Introduction of humectant to the emulsion formulation can affect the viscosity of the finished cosmetic product. Authors Masson et al. [Masson et al. 2005] analyzed in their work rheological behavior of prepared O/W emulsions depending on the type of humectant used. It was found that the addition of glycerol increased the emulsion viscosity, while propylene glycol decreased the viscosity of all the formulations studied. On the other hand, sorbitol increased the viscosity of the preparations containing additionally peach oil in their formulation. The results of dynamic viscosity measurements of the tested caring creams containing in various proportions humectants Glycerin and Hydroxyethyl Urea are presented in Fig. 2.

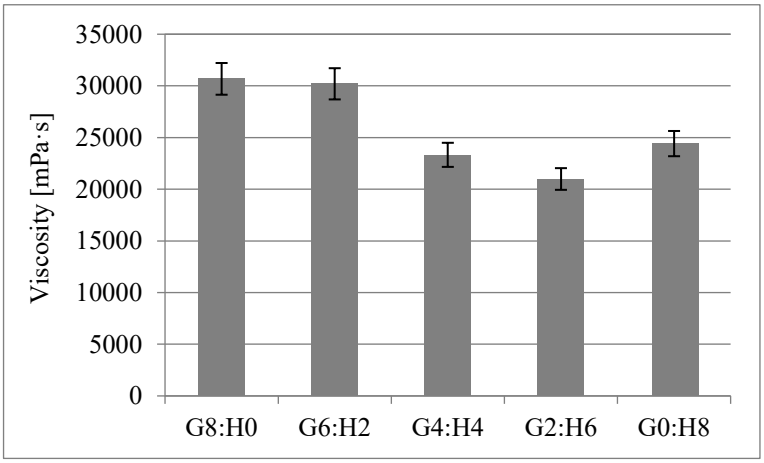

Fig. 2. Dynamic viscosity of skin care creams

Source: own study.

Based on the results obtained, the effect of the type of humectant used (G8:H0 and G0:H8) on the viscosity of the developed skin care creams was found. The emulsion containing 8 wt % Glycerin (G8:H0) has a higher viscosity value (30680 mPa·s) in comparison with the cream containing 8 wt % Hydroxyethyl Urea (G0:H8), which obtained a viscosity result of 24000 mPa·s. Also the simultaneous use of both tested

moisturizing raw materials in the formulation, in different mass ratios, leads to differences in the viscosity results of the tested emulsions. A decrease in viscosity of emulsions (G6:H2 and G4:H4 and G2:H6) can be observed with increasing content of Hydroxyethyl Urea in the formulation. The lowest viscosity value of 20992 mPa·s was observed for emulsion G2:H6, where two moisturizers were used in a weight ratio of 2 wt % Glycerin to 6 wt % Hydroxyethyl Urea. Authors Sandi and Susiani [Sandi & Susiani 2021] in their paper claim that the good viscosity of moisturizing cream is 2,000-50,000 cPs. Thus, the obtained results of dynamic viscosity of the tested formulations are within the range observed for standard creams presented in the literature.

2.3. Yield point

Rheological properties of emulsions significantly affect the level of utility of personal care cosmetics. An important rheological parameter in the case of emulsions is the yield point. It is the lowest value of shear stress at which the so-called "flow" of the substance occurs. The results of yield point in case of emulsions are important for selection of optimum packaging of the cosmetic and the method of dosing. They also give information about the efficiency of spreading the product on the skin during use and about the stability of the system. The authors Savić and co-workers [Savić et al. 2020] studying anti-wrinkle creams found that the preparation with the highest value of the yield point is characterized by a better structure and stability of the emulsion system. The results of the measurements of the yield point of the tested skin care creams containing in different proportions humectants Glycerin and Hydroxyethyl Urea are shown in Fig. 3.

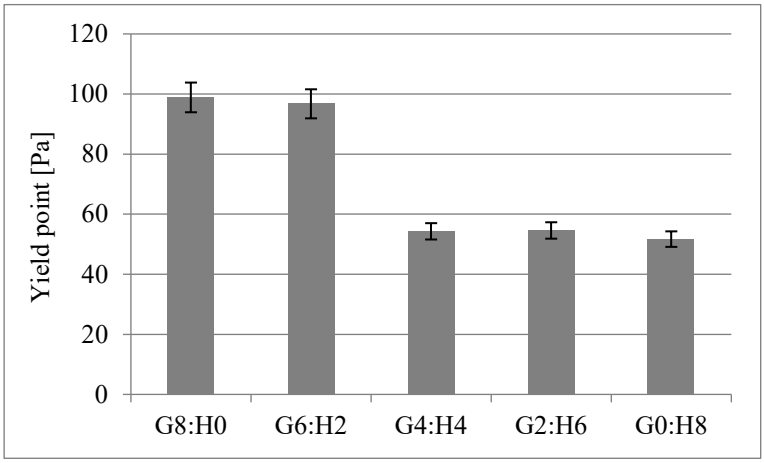

Fig. 3. Yield point of skin care creams

Source: own study.

The results obtained for yield point properties of the tested creams correlate well with the results of dynamic viscosity measurements (Fig. 2). Also in this case the effect of the type of humectant used (G8:H0 and G0:H8) on the yield point of the developed emulsions was observed. The cream containing 8 wt % Glycerin (G8:H0) shows a higher yield point (99Pa) compared to the cream (G0:H8) containing 8 wt % Hydroxyethyl Urea (52Pa). Moreover, a decrease in emulsion viscosity can be observed with increasing Hydroxyethyl Urea content in the formulation. The lowest value of the yield point (about 54Pa) was observed for emulsions G2:H6, (2 wt % Glycerin, 6 wt % Hydroxyethyl Urea) and G4:H4 (4 wt % Glycerin, 4 wt % Hydroxyethyl Urea), where two moisturizing agents were used. Lower values of the tested parameter for skin care creams imply a lighter texture and potentially better spreadability of the product on the skin. The indicated tendency was also demonstrated by Klimaszewska and coworkers [Klimaszewska et al. 2021]. The authors studied face masks with different concentrations of Lonicera caerulea Fruit Powder. They showed that the formulation containing the highest amount of blue honeysuckle powder (0.9%) and obtaining the lowest value of yield point is characterized by the best spreadability on the skin among the tested face masks.

2.4. Evaluation of consistency

The evaluation of the consistency of the skin care creams was analyzed using the two parameters of hardness and adhesion force. Hardness represents the maximum force recorded during the test, while adhesion force represents the lowest (negative) value recorded during the test. The evaluation of emulsion consistency gives information about, among other things, the application and spreading efficiency of the product on the skin during use [Huynh et al. 2017, Moldovan et al. 2017]. Textrometric studies of emulsion formulations were also conducted by authors Moldovan and colleagues [Moldovan et al. 2017], where they showed that the addition of a mixture of glycerol stearate and Ceteareth-25 determines higher values of consistency, hardness, lower values of adhesion force, which consequently has less influence on the spreadability of the product. The results obtained from texture analysis for skin care creams containing Glycerin and Hydroxyethyl Urea humectants in different proportions are shown in Figure 4.

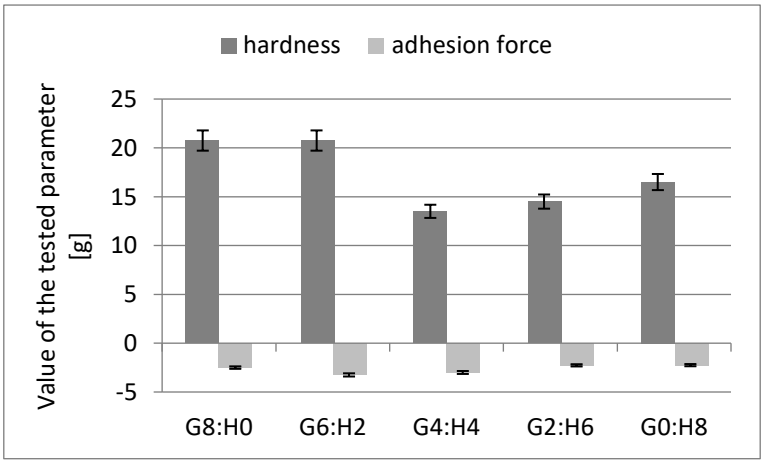

Fig. 4. Hardness and adhesion force of skin care creams

Source: own study.

Analyzing the results of the texture tests it was observed that the highest values of hardness are characterized by creams G8:H0 and G6:H2 containing in their composition the highest concentrations of Glycerin. On the other hand the lowest values of hardness are characterized by creams containing in their formulation both Glycerin and Hydroxyethyl Urea in mass ratios (4:4 and 2:6). The effect of the type of humectant used (G8:H0 and G0:H8) on the hardness of the developed skin care creams was also observed. The skin care cream containing 8 wt % Glycerin (G8:H0) obtained a higher hardness value (20.8g) compared to the emulsion containing 8 wt % Hydroxyethyl Urea (G0:H8), which obtained 16.5g. The adhesion strength results for the tested skin creams oscillated at similar levels ranging from -3.25 to -2.25g.

2.5. Degree of skin hydration

Of all the care cosmetics, preparations with moisturizing properties have the widest application. When water is lost from the stratum corneum faster than it is received from the lower epidermal layer, then the skin becomes dehydrated and loses elasticity. [Mohiuddin 2019; Spada 2018]. The problem of dry skin is extremely common. It can be caused by low ambient temperature, low humidity, exposure to chemicals, microorganisms, aging, psychological stress, atopic dermatitis, and eczema, among others [Mohiuddin 2019]. The process of skin hydration involves repairing the skin barrier; increasing water content, reducing transepidermal water loss, restoring the lipid barrier and its ability to attract, retain and redistribute water [Kraft & Lynde 2005; Lynde 2001]. The moisturizing properties of the developed skin care creams are shown in Figure 5.

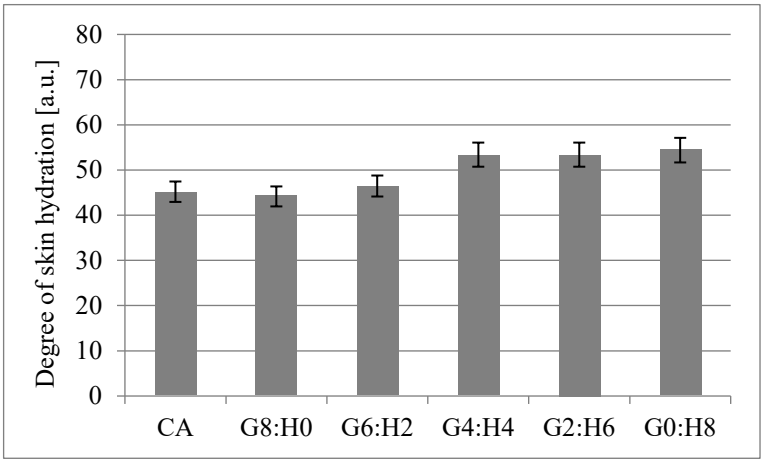

Fig. 5. Degree of skin hydration after the application skin care creams

Source: own study.

On the basis of the presented results it has been found that the degree of skin moisturizing after the application of skin care creams, containing as a humectant Hydroxyethyl Urea, is higher than the results obtained for emulsions with Glycerin. It was also observed that the content of 4 wt % and higher of Hydroxyethyl Urea in the formulation leads to a comparable degree of skin hydration (about 54 a.u.) after the application of these preparations.

2.6. Sensory testing

The aesthetics of a product and its sensory qualities can influence consumer acceptance of a cosmetic product. There are numerous scientific reports in the literature using sensory tests to evaluate cosmetic products, despite the possibility of using instrumental methods. [Kulawik-Pióro et al. 2020, Kossowska & Zieliński 2017]. For sensory evaluation of developed and manufactured creams, 10 discriminants (adhesion, consistency, homogeneity, pillow effect, spreability, absorption, stickiness, greasiness, lubrication, smoothing) characterizing the quality of cosmetic emulsions were selected. The results obtained are presented on sensory profiles (Fig. 6).

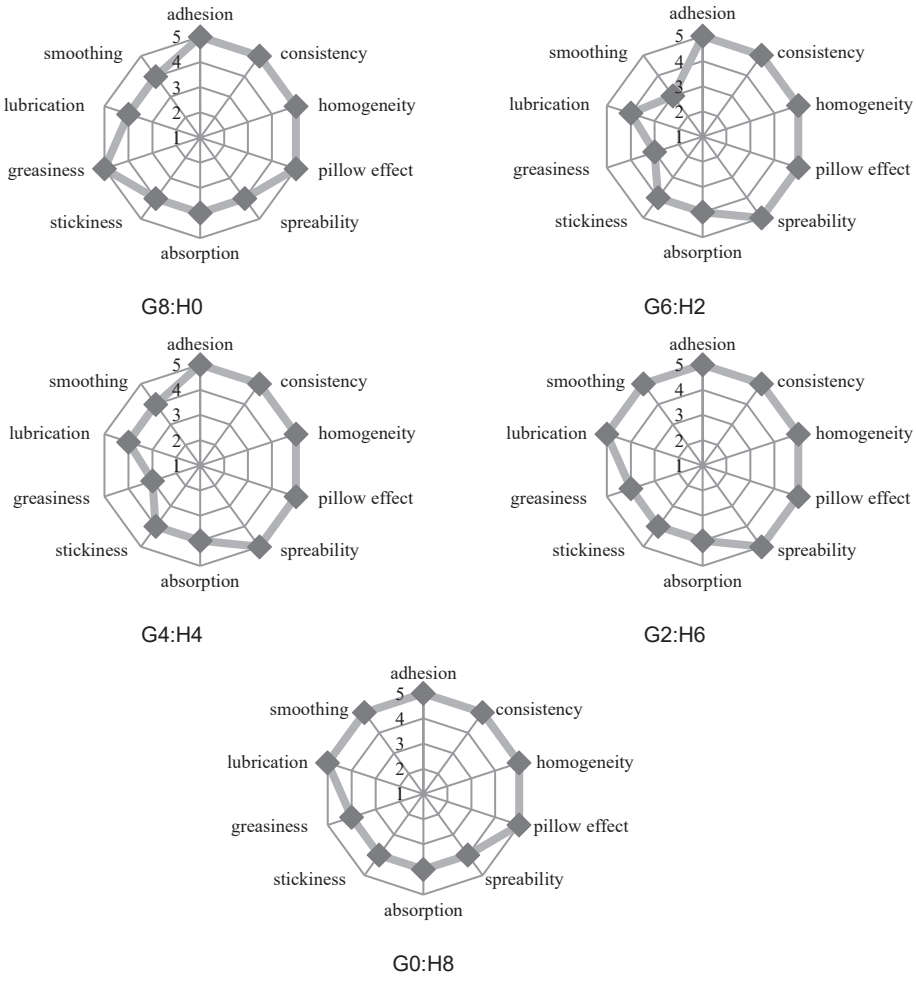

Fig. 6. Sensory profiles of skin care creams

Sensory analysis of the developed skin care creams showed that all tested emulsions received maximum points for such sensory parameters as adhesion, consistency, uniformity, and cushion effect. Equal sensory impressions (4 points) during the evaluation of the tested creams, according to the members of the sensory panel, also applied to parameters such as absorption and stickiness. The skin care creams containing 8 wt% and 6 wt% Hydroxyethyl Urea received the highest scores for

oiliness and smoothness. It can therefore be concluded that this humectant improves the sensory properties of such preparations. It should also be noted that emulsions containing in the recipe both Hydroxyethyl Urea and Glycerin in mass ratio 4:4 and 6:2 (versions G4:H4 and G6:H2), according to the test persons, were evaluated sensorially the lowest.

3. Conclusions

In this study an attempt was made to evaluate physicochemical and performance properties of the care creams containing Hydroxyethyl Urea as a humectant. For this purpose a series of nursing cream prototypes were prepared in the form of O/W emulsions differing in mass ratio of Glycerin (commonly used humectant) to Hydroxyethyl Urea. All prepared and manufactured emulsions were characterized by stability of the system.

On the basis of the results obtained it was found that the addition of Hydroxyethyl Urea to the formulation of skin care creams leads to a decrease in dynamic viscosity, melt flow limit and hardness in comparison with the values obtained for the reference formulation containing only Glycerin (G8:H0). Thus, these emulsions according to the interpretation of other authors [Huynh et al. 2017, Moldovan et al. 2017**;** Klimaszewska et al. 2021] will be characterized by a lighter consistency and potentially better spreadability of the product on the skin during use. It was also found that the degree of skin hydration after application of skin care creams containing Hydroxyethyl Urea as a humectant is higher than the results obtained for emulsion G8:H0 containing 8 wt % Glycerin. On the other hand, sensory analysis showed that the use of the humectant Hydroxyethyl Urea in the formulations of skin care creams improves their sensory properties.

Thus, it can be clearly stated that the introduction of Hydroxyethyl Urea into the formulation of cosmetic emulsions has quite a significant effect on the functional and physicochemical properties of this type of products. The use of urea derivative in skin care creams not only has a beneficial effect on the effect of skin moisturizing, but also has a positive influence on sensory evaluation of emulsions.

4. Acknowledgements

The work performed under the project no. 3086/35/P titled: „Development of formulations and technologies for the manufacture of innovative cosmetics, pharmacy supplies, household and industrial chemicals" and project no. 3501/188/P titled: „Application of innovative raw materials of natural and synthetic orgin in care and suport of treatment of skin diseases in various clinical conditions". Projects financed by the Ministry of Education and Science.

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POTENTIAL POSSIBILITIES OF USING PLANT WASTE FROM POLISH VINEYARDS FOR THE PRODUCTION OF COSMETIC COMPONENTS

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Abstract
The growing interest in grapevine cultivation and wine production observed in Poland in recent years results in the demand for management of an increasing amount of wastes, such as grape pomace, stems, leaves, buds and young shoots, as well as woody grapewine osiers removed in winter. Currently, these wastes are mainly managed as biocompost, biofuel or possibly animal feed. However, each of these solutions is associated with many problems. Taking into account all the aspects related to sustainable development, work is being carried out on the possibilities of using this type of wastes in biotechnological processes or to produce raw materials for the food industry.
In this paper the possibility of using vineyard wastes to produce full-value cosmetic raw materials was analyzed. Waste of plant material from Regent, Rondo and Solaris grapevine varieties grown in the vineyard in Opole region, was selected for the

study. Particular types of wastes were processed into cosmetic components using solvent and micellar extraction. The obtained extracts were evaluated regarding the content of substances that are valuable from the cosmetological point of view. For this purpose, the extracts were characterized by liquid chromatography - tandem mass spectrometry (LC-MS/MS) and their antioxidant capacity was investigated. Grape pomace, stems, buds and young canes were found to be particularly valuable waste materials. The cosmetic components obtained on their basis were characterized by a high content of polyphenols, such as flavonols (quercetin, kaempferol), flavanols (catechins, epicatechins), anthocyanins (malvidin 3-O-glucoside, peonidin 3-O-glucoside, petunidin 3-O-glucoside) and stilbenes (resveratrol) as well as organic acids (tartaric, citric, malic).

Keywords: vineyard wastes, cosmetics components, sustainable development.

Introduction

Winegrowing is one of the most important agricultural activities in the world. According to the data presented by *Food and Agriculture* Organization of the United Nations (FAOSTAT), in the 2019-2021, vineyards covered a total of 7.3 million hectares. Data for 2018-2020 shows an average global harvested area of 6.91 million hectares with an average yield of 113376 hg/ha and an average production of 78.36 Mt. Average global wine production for 2018-2019 according to FAOSTAT data reached 28.10 Mt.

Taking into account the total area, the European Union member countries rank first worldwide (3.3 million ha). The leaders in grapevine cultivation are Spain, France and Italy. Relatively large area of vineyards can be also found in Portugal, Romania, Bulgaria, Hungary and Germany. Besides the European countries, significant area is cultivated in China (0.78 million ha), South America (0.5 million ha) and the USA (0.4 million ha) (OIV International Organization of Vine and Wine – Activity Report 2021).

In the last decade, there has been in Poland a significant increase in interest in viticulture, vineyards establishment for commercial as well as enotourism purposes and wine production. According to the data from the National Agricultural Support

Centre (KOWR), the total vineyards area in Poland in the 2021/2022 marketing year is estimated at 619.37 ha, and the number of registered producers at 380. Apart from the registered vineyards, there are estimated about 100 unregistered vineyards in Poland. The trend from 2009 to 2022 indicates a significant increase in both the area and the number of registered producers, respectively from 36.01 to 619.37 ha and from 21 to 380 producers, and it will continue to grow each year due to the improving climatic conditions in Poland. Comparing the 2010/2011 and 2020/2021 marketing years on the basis of the KOWR data in terms of grape harvest, wine production and sales, a minimum 19-fold increase in each of the compared aspects is noticeable.

Changes in the vineyard areas and in the number of wine producers in recent years are presented in Figure 1. and 2. respectively.

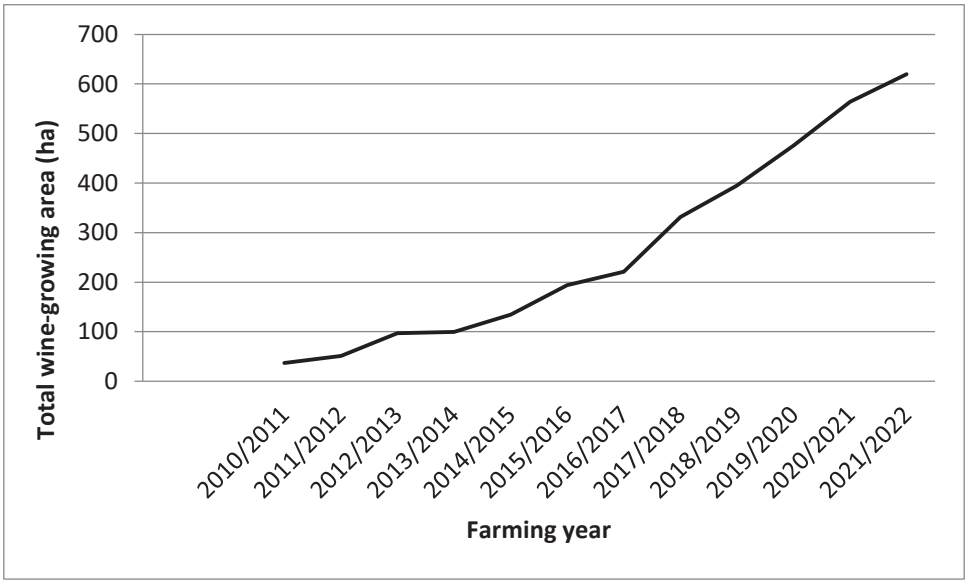

Fig. 1. Total wine-growing area over the farming years in Poland
(prepared by the authors based on the KOWR data)

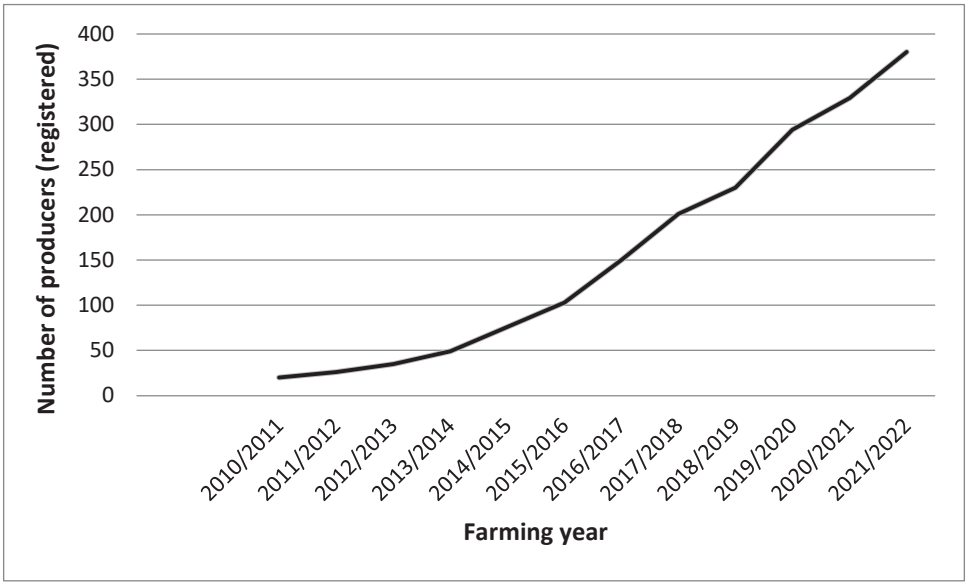

Fig. 2. Number of producers over the farming years in Poland
(prepared by the authors based on the KOWR data)

The increase in the area and number of vineyards is in direct correlation with the increase in the weight of grape fruit produced every year. In the 2020 - 2022 marketing years, grape production in Poland is estimated at 22.000 - 27.000 quintals (2.200 - 2.700 tonnes). The tendency observed in Poland in recent years is shown in Figure 3.

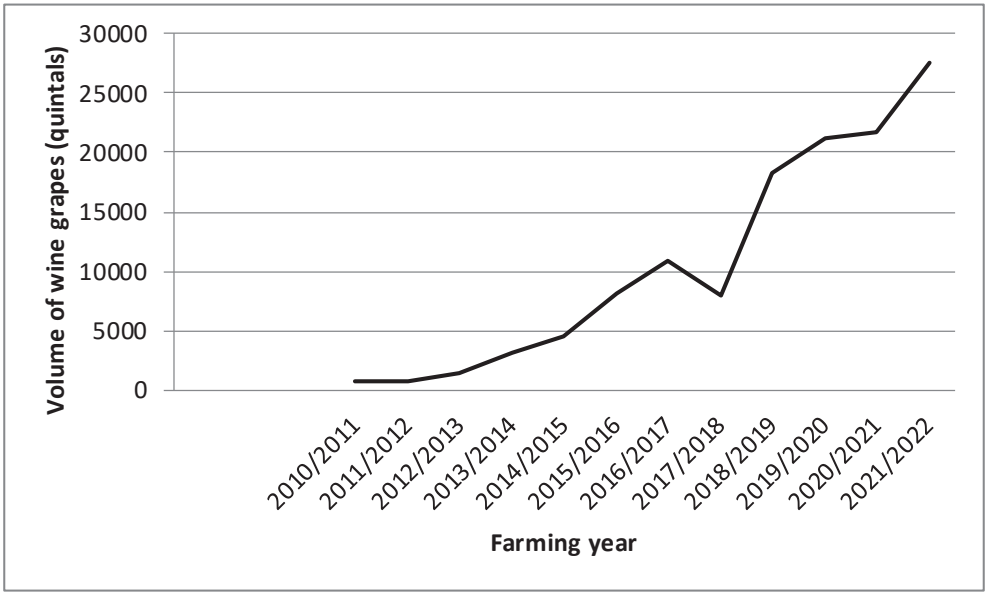

Fig. 3. Volume of wine grapes over the farming years in Poland (prepared by the authors based on the KOWR data)

The grape growing increase is integrally related to the increase in wastes generated [Arvanitoyannis et al. 2006]. It is assumed that one ton of harvested and processed grapes generates an average 130 kg of pomace, 60 kg of lees and 30 kg of stalks [Ruggieri et al. 2009, Oliveira & Duarte 2016]. Additionally, during vine cultivation, canes from the previous season and excess leaves are removed, and the number of buds is reduced. The grape bunch and grapevine elements which are the source of waste material during the viticulture process are shown in Figure 4. and 5. respectively.

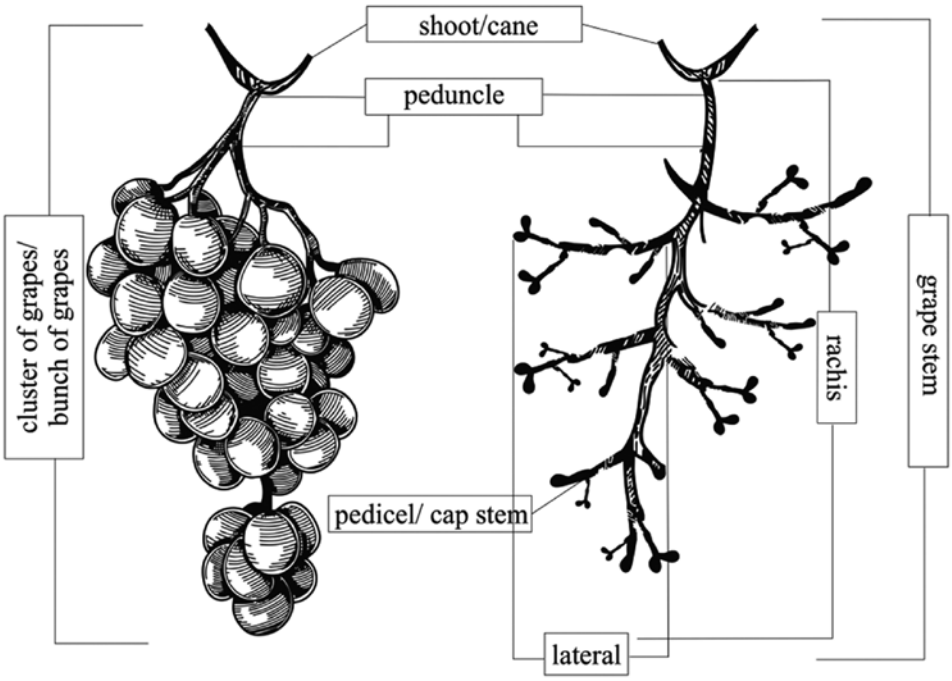

Fig. 4. Diagram of grape bunch elements (prepared by the authors).

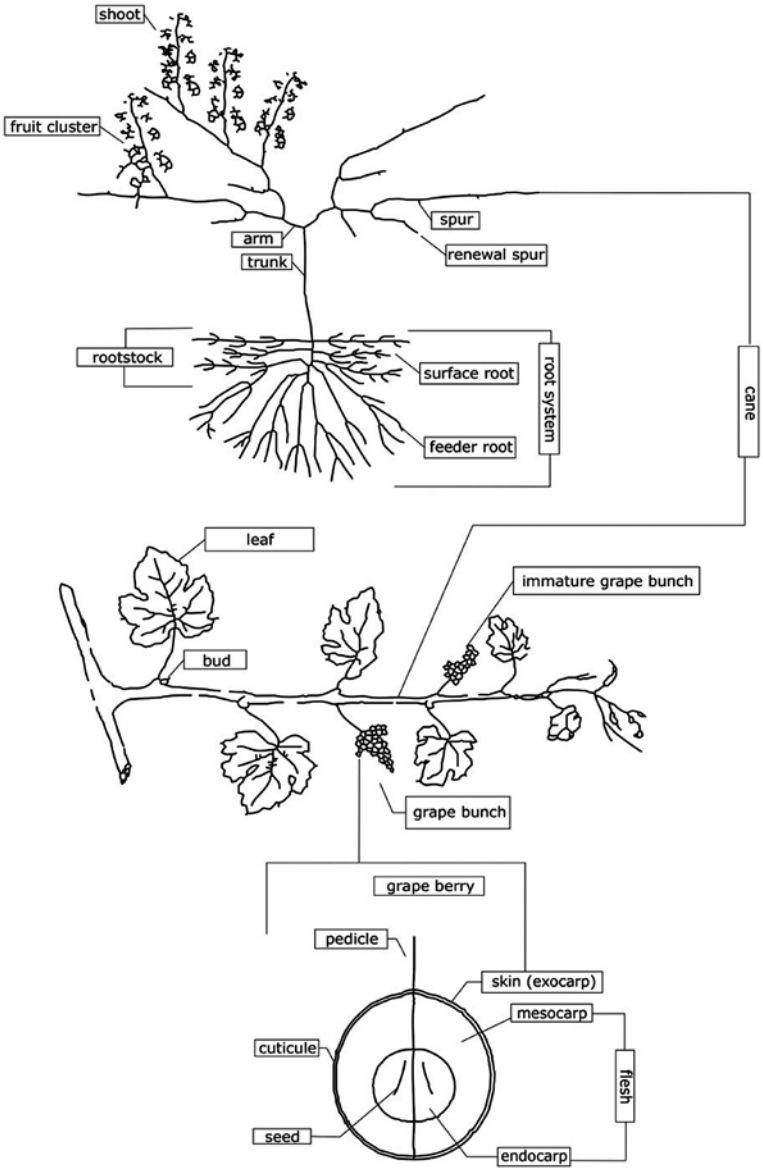

Fig. 5. Diagram of grapevine elements (prepared by the authors).

The growing interest in grapevine cultivation and wine production observed in Poland in recent years results in the demand for management of an increasing amount of wastes, such as grape pomace, stems, leaves, buds and young shoots, as well as woody grapevine osiers removed in winter. Currently, in countries where grapevines have been grown for hundreds of years, these wastes are mainly managed as biocompost, biofuel, coloring-agents, food pharmaceutical and cosmetic industry, skin protection agents, in biotechnological industry of flavorings and aroma compounds or possibly animal feed [Rubio et al. 2013, Burg et al. 2014, Schönnenbeck et al. 2016, Fabbri et al 2015, Rajha et al. 2014, Rodríguez et al. 2010, Egüés et al. 2013, Corbin et al. 2015, Bertran et al. 2004, Prozil et al. 2012].

The aim of the study was to evaluate the possibility of using the waste from grapevine cultivation and wine production from Poland to obtain valuable components of cosmetics. Waste of plant material from different grapevine varieties grown in the vineyard in Opole region – Estro Vineyard, was selected for the study. Particular types of wastes were processed into cosmetic components using solvent or micellar extraction. The obtained extracts were evaluated regarding the content of substances that are valuable from the cosmetological point of view. The extracts were characterized by liquid chromatography-tandem mass spectrometry (LC-MS/MS) and their antioxidant capacity was investigated.

1. Material and methods

The study was performed for wastes, such as grape pomace, stems, leaves, buds, and young shoots, as well as woody grapevine osiers removed in winter. Regent, Rondo, and Solaris grapevine varieties were selected for the study (plant material was used from vineyards in which all three of the above-mentioned varieties were used in the same ratio). Photos of grape waste material obtained from the Estro Vineyard are shown in Figure 6.

Fig. 6. Grape wastes from Estro Vineyard

1.1. Extraction

The various types of grape waste obtained were processed by solvent or micellar extraction.

1.1.1. Micellar extraction (grape pomace)

The micellar extraction process was performed using a mechanical stirrer. An aqueous solution of surfactant—decyl glucoside was used as the extraction medium. Grape pomace was frozen and grounded with dry ice in a laboratory knife mill. Grounded grape pomace was added to the extraction medium and stirred vigorously at 380 rpm. The process was carried out for 3 h at room temperature.

The obtained extract was filtered under vacuum using a non-woven polyester filter. The filtrate was centrifuged at 7500 rpm for 5 min and used directly in further studies [Wasilewski et al. 2022].

1.1.2. Solvent extraction (steams and canes)

The solvent extraction process was performed using a mechanical stirrer. Demineralized water was used as the extraction medium. Canes and stems were frozen

and grounded separately with dry ice in a laboratory knife mill. Grounded material, in appropriate amount, was added to water and stirred vigorously at 380 rpm for 3 hours at room temperature.

The obtained extracts were filtered under vacuum using a non-woven polyester filter. The filtrate was centrifuged at 7500 rpm for 5 min and used directly in further studies.

1.2. Antioxidant activity

1.2.1. DPPH method

The radical-scavenging activity of extracts was evaluated according to a modified version of the method of [Brand-Williams et al. 1995].First, a volume of 1 mL methanol extract (20 µL of an extract with 980 µL of MeOH) was mixed with 3 mL of a methanolic solution of DPPH radical (0.1 mM). The mixture was mixed and allowed to stand in the dark for 30 min. The absorbance was measured at 517 nm against the blank (methanol). The percentage of inhibition of $DPPH^{\bullet}$ by extracts was calculated according to the following equation:

$$AA\ [\%] = 100\ x\ (A_{control} - A_{sample})/\ control \qquad (1.1)$$

where: $A_{control}$ is absorbance of DPPH solution, A_{sample} is absorbance of a mixture of extract and radical solutions.

1.2.2. ABTS method

The ABTS method was performed as described by [Re at al. 1999]. ABTS radical cation was obtained in the reaction of 1 mL ABTS [0.01 M 2,2-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt] with 1 mL potassium persulfate (0.005 M). The mixture was left to stand in the dark for 20 h to reach optimal absorbance at 734 nm. Then 300µL of each solution (20 µL extract with 980 µL of distilled water) was mixed with 2 mL of the $ABTS^{\bullet+}$ solution and after 6 min, the absorbance

was measured against a blank (water). The antiradical activity was calculated according to the following equation:

$$AA\ [\%] = 100\ x\ (A_{control} - A_{sample})/\ A_{control} \quad (1.2)$$

where: $A_{control}$ is absorbance of ABTS solution, A_{sample} is absorbance of a mixture of extract and radical solutions.

1.3. UHPLC-MS/MS evaluation of selected bioactive compounds

Extract solutions were separated using ultra-performance liquid chromatography (UHPLC) and considerate compounds were detected by tandem mass spectrometry (MS/MS). Based on this approach, bioactive compounds were qualified and quantified according to a detailed method published by [Wasilewski et al. 2022].

Targeted qualitative antocyanins data analysis was performed using a database built from a literature search. These compounds were identified and confirmed based on MS^2 fragmentation of selected m/z signals.

1.4. Color measurement

The color of the grape pomace, stem, and cane extracts was determined using a Konica Minolta CM-3600 colorimeter, based on the methodology described by [Wasilewski et al. 2022].

The brightness of extracts in the range from 0 (darkness) to 100 (brightness) was determined by the L* index. The a* parameter determined the color change from green (negative values) to red (positive values) and the b* parameter determined the field from blue (negative values) to yellow (positive values).

2. Results

2.1. Antioxidant activity

The role of the antioxidants is to neutralize the free radicals in biological cells. Free radicals have a negative impact on living organisms and result in the occurrence and spread of degenerative diseases. The determination of antioxidant activity is a good way to define the ability to prevent the formation of free radicals [Pham-Huy et al. 2008]. The antioxidant effects of the tested extracts was evaluated by combination of different tests, such as DPPH and ABTS methods. More than one type of antioxidant measurement needs to be performed to take into account the various mode of action of antioxidants [Huang et al. 2005]. The results of conducted antioxidant tests were presented in Figure 7.

Overall, grape pomace showed highest antioxidant capacity (DPPH: 60%, ABTS: 56%) followed by grape steams (DPPH: 53%, ABTS: 52%), while canes extract (DPPH: 12%, ABTS: 20%) showed the lowest value. Similar behavior patterns were observed in both test, regardless of their action mechanism. This observation can be explained by a greater concentration in total and individual phenolic content in grape pomace than steams or canes. The obtained results are consistent with the results of work carried out for waste from vineyards from other regions of the world [Baroi et al. 2022, Fia et al. 2021, Yammine et al. 2020, Gharwalová et al. 2018]. Based on polyphenolic content vineyard by-product, several studies have shown their high antioxidant activity, suggesting this product as an interesting source for natural antioxidants for application in pharmacology, cosmetic and food industries [Brahim et al. 2014, Deng et al. 2011, Sánchez et al. 2009].

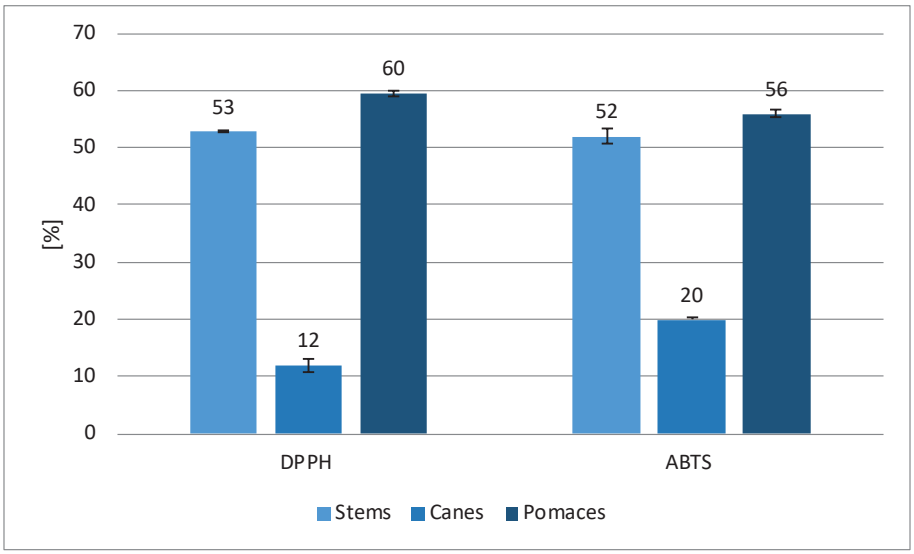

Fig. 7. Antioxidant activity of grape stem, cane and pomace extracts (mean ± SD)

2.2. UHPLC-MS/MS evaluation of selected bioactive compounds

The bioactive compounds presented in fruit waste by-products are mainly polyphenols, fatty acids, minerals, and vitamins. The cosmetic industry can take advantage of these bioactive components by extracting them from the by-products of the wine industry and using them in skin care products which have recently received increasing interest [Cádiz-Gurrera el al. 2021, Matos et al. 2019]. Antioxidant and anti-inflammatory activities in plants are usually associated with flavonoids and other phenolic compounds.

To evaluate the amount of selected compounds in grape pomace, stem and cane extracts, quantitative analysis was conducted by UHPLC-MS/MS. The results, expressed in mg/L, are displayed in Figure 8. The examined compounds were divided into five classes: carbohydrates (xylose, glucose, sucrose, fructose, maltose, mannose, sorbitol), organic acids (maleic acid, malic acid, citric acid, lactic acid, tartaric acid), amino acids (phenylalanine, aspartic acid, lysine, serine, leucine, histidine,

threonine, isoleucine, valine, methionine, tryptophan), ascorbic acid and polyphenols (gallic acid, quinic acid, rutin, syringic, vanillic, apigenin, hydroxybenzoic, trans-resveratrol, catechin, epicatechin).

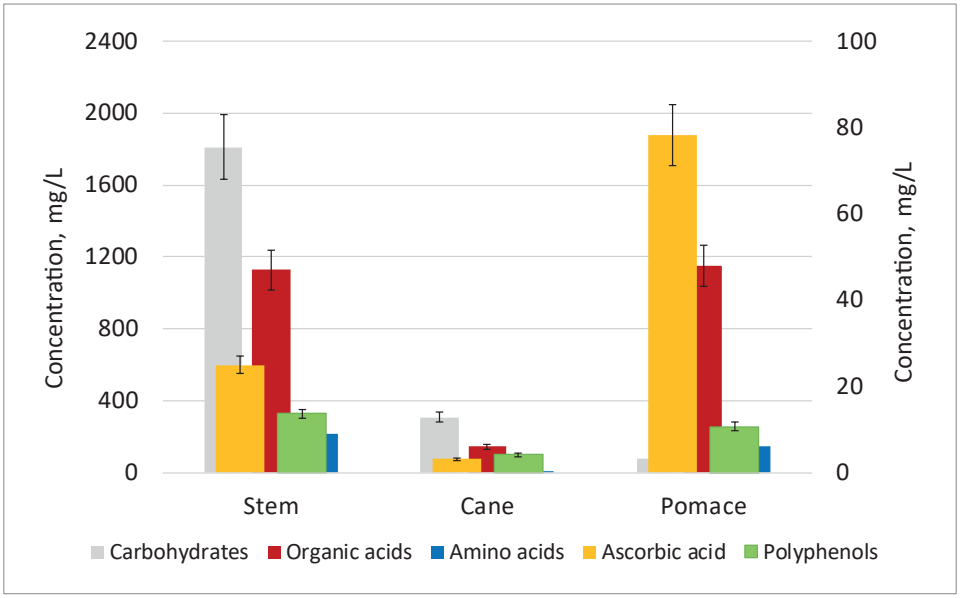

Fig. 8. Content of selected bioactive compounds. The superscripts a, b and c denote significant ($p < 0.05$) differences between the concentrations of each compound class (distinguished by color) in the stem, cane, and pomace.

As can be seen, stem and pomace extracts are rich sources of bioactive compounds, while cane extracts seem to be the most deficient in the determined compounds. However, stem and pomace extracts differ in the content of carbohydrates, which level is significantly higher in stem extracts while the carbohydrates contained in pomace were most likely processed at the fermentation stage. This is in the contrast to the ascorbic acid (vitamin C) content, which grape pomace extracts are richer in. Among the organic acids, tartaric and citric were the most abundant in winemaking by-products. Both acids have become common ingredients in skin care products due to their keratolytic and astringent properties. They moisturize the skin,

stimulate the metabolism, promote healing, and also have an anti-aging effect. The major phenolic compounds were quinic and gallic acids while lysine, phenylalanine, and tryptophan were dominant among the amino acids. Tryptophan is the most important compound for the intradermal synthesis of melatonin, which is a substance with a strong cyto- and tissue-protective effect on many levels and mechanisms of molecular and cellular damage, both at physiological and pharmacological concentrations [Tan et al. 2003].

Anthocyanins have attracted considerable global interest, mainly due to their health-promoting benefits associated with their antioxidant properties. The reddish-purple pigmentation of grapes is associated specifically with anthocyanins, a common group of compounds that gives color to flowers and fruits. Red to blue colored anthocyanins with different aglycone forms (cyanidin, peonidin, petunidin and malvidin), were qualitatively detected in grape pomace extract. The chemical structures of the representative compounds with their corresponding color are presented in Figure 9. However, these compounds were not found in the stems and canes.

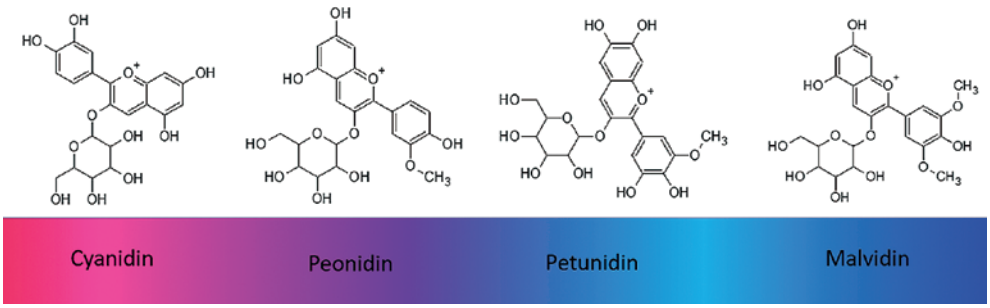

Fig. 9. The visible color range of analyzed anthocyanins in grape pomace extract

This observation shows that grape pomace can be used as a potential coloring ingredient as the anthocyanins they contain are strong antioxidants and are used as natural colorants [Mathur et al. 2020] in the cosmetics industry. Furthermore, the prophylactic and inhibitory effects of anthocyanins, are also used in the treatment

of various types of skin diseases including melanoma skin cancer [Diaconeasa et al. 2020]. Even low concentrations of anthocyanins can reduce the amount of UVB radiation interacting with the epidermis, demonstrating the benefits of anthocyanins in preventing UV-induced skin damage [Chan et al. 2020].

1.3. Color measurements

Figure 10 shows the extracts obtained from the wine waste such as grape pomace, stem, and cane.

Fig. 10. Color comparison of grape pomace, cane and stem extracts

To determine the color difference between individual extracts, colorimetric tests were performed and the results were presented in Figure 11.

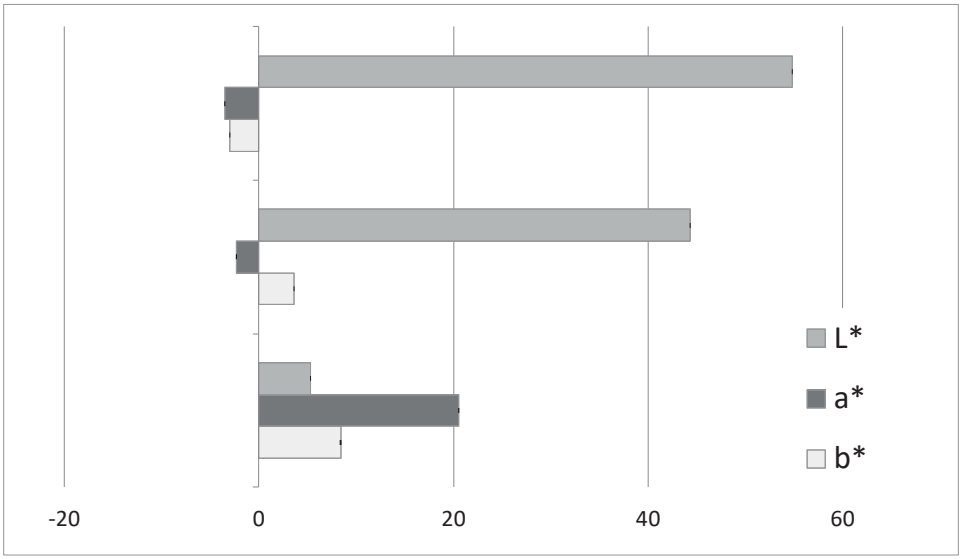

Fig. 11. Spectrophotometric data of the grape pomace, stem and cane extracts. The superscripts a, b and c denote significant ($p < 0.05$) differences between the color parameters (distinguished by color) in the stem, cane, and pomace

In the analyzed by-products of the winemaking process, the value of the L* parameter, determining brightness, ranged from 5.3 to 54.8. The highest value, therefore the brightest color, was recorded for the cane extract, while the lowest and thus the darkest - for grape pomace. The a* parameter (color change from green to red) was positive only for pomace extract, which indicates a significantly higher proportion of red color. The value of parameter b*, (color change from blue to yellow) was in the positive range for stems and pomace extracts (8.4 and 3.6 respectively) which indicates a higher proportion of yellow in these extracts.

On a 100-point scale, the difference in ΔL* between pomace and canes and also stems extract was 49.5 and 39.0 respectively, indicating a significant difference in the brightness of the extracts.

2. Conclusions

The present study showed that the extracts obtained from waste materials of grapevine cultivation, such as grape pomace, stems and canes, showed relatively high antioxidant potential. Chemical composition studies of the obtained extracts revealed the presence of bioactive compounds such as polyphenols, fatty acids, minerals and vitamins. Moreover, the extracts from grape pomace contained in their composition anthocyanins. These compounds, in addition to antioxidant properties, are natural pigments, which gives the possibility to use them as natural components to obtain colored cosmetics.

Wastes from grapevine cultivation can be a rich source of biologically active compounds that exhibit antioxidant properties and thus can protect the skin against negative environmental effects. Therefore, the use of waste raw materials from wine production as a source of phytochemicals in cosmetic preparations can contribute to the development of this industry and, consequently, to environmental and economic sustainability.

Biological activity of compounds obtained from grapevine cultivation waste supports its valorization as a source of bioactive phytochemicals to be used in cosmetics and is an effective and environmentally friendly alternative for waste management.

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COMPARISON OF SELECTED SPECTROSCOPIC METHODS FOR THE IDENTIFICATION AND QUALITY ASSESSMENT OF ENGINE GASOLINES

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Abstract
The research material consisted of commercial samples of gasolines with an octane number of 95 and 98 from various distributors. The analysis of medium infrared and fluorescence spectra showed differences between the tested samples due to their composition. Based on the principal component analysis (PCA), the possibility of grouping gasolines according to their octane number was investigated. Partial least squares regression analysis (PLS) was used to correlate the determined physico-chemical parameters of the tested samples with the spectra obtained for them.
The obtained research results confirm the application potential of the possibility of using spectroscopic methods in assessing the quality of motor gasolines.

Keywords: quality, gasoline, spectroscopy, PCA, PLS

Introduction

Engine gasoline is intended for the majority of vehicles equipped with spark ignition drive units. A typical gasoline is primarily composed of volatile hydrocarbons such as paraffins (alkanes), naphthenes (cycloalkenes), and olefins (alkenes), though it may also contain oxygen, nitrogen, or sulfur compounds. Automotive gasoline is one of the most refined products, and the process of producing it determines the final chemical composition of gasoline fractions and the resulting gasoline quality [Corsetti, Zehentbauer, McGloin, & Kiefer, 2015].

Experimental qualitative identification and quantitative determination of components which are present in gasolines is a difficult analytical task due to the high complexity of their chemical composition, as well as due to the physicochemical similarity between the components present in such mixtures.

For this reason, alternative methods are sought to enable precise determination of the composition and identification of gasolines.

Spectroscopic methods are based on fast and non-destructive measurements, therefore they are also called "green technologies" [Casson, Beghi, Giovenzana, Fiorindo, Tugnolo, & Guidetti, 2019; Grassi et al., 2021]. In times of sustainable development, it is important to develop methods that will allow to precisely determine the quality of a product / product without the use of chemical reagents.

Multivariate statistics techniques have increased the use of spectroscopic instruments, which have been widely used to predict physicochemical properties and authenticate gasoline samples based on infrared spectra [Balabin, Safieva, & Lomakina, 2010]. Some calibration methods were used for gasoline properties and quality coefficients prediction [Balabin et al., 2010; Brudzewski, Kesik, Kołodziejczyk, Zborowska, & Ulaczyk, 2006; Pasadakis, Gaganis, & Foteinopoulos, 2006; Silva, Lira Pontes, Pimentel, & Pontes, 2012].

In this paper the comparison of the MIR spectroscopy and fluorescence spectroscopy coupled witch chemometrics (for the identification and quality assessment of engine gasolines) was presented.

1. Materials and methods

1.1. Materials

The tested material consisted of 95 and 98 octane number gasolines. Samples were taken from various petrol stations located in Włocławek. Table 1 presents Producers' data on physicochemical characteristics of eight out of ten gasolines. Only Producer 5 did not make its safety data charts available.

Table 1. Characteristics of physicochemical properties of gasolines

Long Name	Short Name	R	Color	Boiling point (°C)	Density (Kg/m³)	Kinematic viscosity (Mm²/s)	N-hexane content
Producer 1_95	P1_95	Min. 95	Colorless or light yellow	25-210	720 to 775	≤7	None
Producer 1_98	P1_98	Min. 98				≤7	≤3%
Producer 2_95	P2_95	Min. 95		30-210		-	None
Producer 2_98	P2_98	Min. 98				-	≤3%
Producer 3_95	P3_95	Min. 95		25-210		≤1	-
Producer 3_98	P3_98	Min. 98				≤1	-
Producer 4_95	P4_95	Min. 95		30-210		≤1	None
Producer 4_98	P4_98	Min. 98				≤1	≤3%
Producer 5_95	P5_95	-	-	-	-	-	-
Producer 5_98	P5_98	-	-	-	-	-	-

Source: Own elaboration based on charts.

1.2. Measurement of physiochemical properties of gasoline

A PetroSpec instrument (PetroSpec GS-1000 plus VOC Gasoline Analyzer) was used to measure the physicochemical properties of gasoline. Through spectrophotometric analysis in infrared it allows to determine essential components of petrols and to calculate their octane number. Table 2 provides an explanation of the symbols tested along with the units.

Table 2. Explanation of symbols used during the analysis

Symbol	Description	Unit
R	Research octane number	
M	Motor octane number	
T50	Distillation temperature of 50% of gasoline by volume	F
T90	Temperature of distillation of 90% by volume of gasoline	F
MeOH	Methanol	(V/V) [%]
EtOH	Ethanol	(V/V) [%]
MTBE	Methyl tert-butyl ether	(V/V) [%]

Symbol	Description	Unit
DIPE	Diisopropyl ether	(V/V) [%]
ETBE	Ethyl tert-butyl ether	(V/V) [%]
TAME	tert-Amyl methyl ether	(V/V) [%]
TBA	tert-Butanol	(V/V) [%]
Wt%0	Percentage oxygen content	(V/V) [%]
Toluene	Toluene	(V/V) [%]
Total Xylenes	Xylens	(V/V) [%]
Olefins	Olefins	(V/V) [%]
SAT	Saturated compounds	(V/V) [%]
AROMATICS	Aromatic hydrocarbons	(V/V) [%]
Benzene	Benzene	(V/V) [%]
DI	Driveability index	

1.3. Spectra measurements

The medium infrared (MIR) spectra were measured using a Jasco FT/IR-4700 spectrophotometer. The measurement range was 4000-600 cm^{-1} with a resolution of 8 cm^{-1}. Three replicates per sample were performed, giving a total number of scans of 30.

Synchronous fluorescence spectra were measured using a Fluorolog 3-11 spectrofluorometer, from Jobin Yvon-Spex. Measurements were performed in quartz cuvettes, in a reflection geometry (front face). The excitation wavelength range for measuring synchrotron fluorescence spectra, was from 240 to 700 nm, with emission and excitation wavelength differences of $\Delta\lambda$ = 10, 20, 30, 40, 50, 60, 70, and 80 nm. The slit widths of the excitation and emission monochromators were 2 nm, while the integration time was 0.05s.

1.4. Data Analysis

Principal component analysis (PCA) was performed on the MIR or synchronous fluorescence spectra of gasolines to distinguish samples. PCA is a multivariate technique that linearly transforms an original set of variables into a substantially smaller

set of uncorrelated variables that represents most of the information in the original data set. Data for PCA are arranged in two-way matrix, in which column vectors represent variables and row vectors represent "objects" of which the variables are measured [Esbensen & Geladi, 2009].

The PLS regression method was used to determine relations between the spectra and the chemical properties of studied gasolines. Independent variables (*X*) were the MIR spectra or synchronous fluorescence spectra while dependent variables (*Y*) were the obtained parameters. Full cross-validation was applied to the regression model. The regression models were evaluated using the adjusted R^2 and the root mean-square error of cross-validation. The quality models were evaluated by the ratio of the standard deviation of reference data to the root mean-square error of calibration (RMSEC).

The PCA and PLS analysis was carried out using the Unscrambler 9.7 software (CAMO, Oslo, Norway).

2. Results and discussion

2.1. Physicochemical parameters

All gasolines show very similar properties to each other. The exception is the petrol from the Producer 1, whose viscosity differs significantly from the others, table 3. Analyzing the results presented in table 3, it can be concluded that 98 octane gasoline from Producer 4 is unrivalled in terms of octane number value. The value declared by the manufacturer is lower than the test results. However, this petrol also has its disadvantages - very low DI value. It is lower even than a cheaper alternative of the same manufacturer (Producer 4). Another factor worth mentioning is ETBE which is responsible for increasing the octane number in petrol. In larger amounts it is added to premium petrol (98 octane). However, in the case of gasoline from Producer 4, its value is much lower than in the case of the competition. Here, in order to achieve an octane value of R=99.4 more benzene was added, which itself has high octane value, as well as MTBE. On the other hand, what is surprising in this case is

the DI value, which is lower for the higher octane number gasoline (1167) than for the cheaper substitute (1217).

When the 95 octane gasolines were analyzed, samples from the Producer 1 and Producer 2 were different from the others. Both of them had almost identical results for research octane number (R) which were higher than in other gasolines. Gasoline from Producer 3 had lower R value which was probably due to the inaccurate mixture of additives.

Table 3. Physicochemical parameters obtained for studied gasolines

	P1_95	P1_98	P2_95	P2_98	P3_95	P3_98	P4_95	P4_98	P5_95	P5_98
R	96.6	98.2	96.5	98.3	94.3	98.1	94.6	99.4	95	98.2
M	85.6	87.8	85.6	87.8	84.7	87.8	84.8	88.7	85	87.8
T50	100.3	102	100.3	102.7	105	103.6	106.3	103	103	104.6
T90	159	145.6	159.6	145.6	160.3	146.6	162	164	158.3	147.6
DI	1221.7	1605	1229.8	1592.8	1226.4	1585.8	1217.4	1167.4	1227	1575
MeOH	0	0	0	0	0	0	0	0	0	0
EtOH	5.2	0.6	5.2	0.6	5	0.6	5.1	0.3	5	0.5
MTBE	0.5	0	0.4	0	3.7	0.3	3.5	14.8	2.7	0.9
DIPE	0	0	0	0	0	0	0	0	0	0
ETBE	2.1	12.3	2.4	12	0.6	11.6	0.3	0.9	1.4	11.3
TAME	0	0	0	0	0	0	0	0	0	0
Wt%O	2.4	2.2	2.4	2.1	2.6	2.1	2.6	2.9	2.6	2.1
Toluene	7.8	10.2	7.5	10.4	11.7	10.5	12.1	10	10.8	10.4
Xylenes	7.4	8	7.2	8	7.1	8.2	7.4	7.3	7.3	8.1
Ole	10.6	4	10.6	4.1	1.4	3	0.5	0	4.4	2.4
SAT	51	50.8	51.6	50.9	58	51.8	58.4	52	55.7	52.1
Aromatics	30.6	32.3	29.9	32.4	31.3	32.8	32.1	32	30.9	32.7
Benzene	0.5	0.4	0.5	0.4	0.6	0.4	0.6	0.7	0.6	0.4

2.2. MIR spectra

Figure 1 shows the MIR spectra that were taken for all studied gasolines. The spectra for a given petrol grade are virtually impossible to distinguish. For gasoline 98, bands with absorption maximum at 1033 - 1286 cm^{-1} are visible, which cannot be observed in gasoline 95.

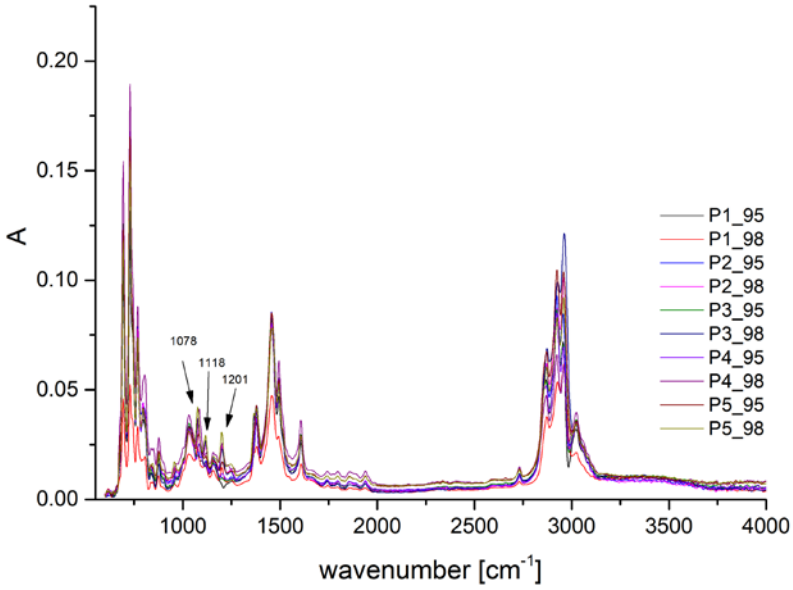

Fig. 1. MIR spectrum of all studied gasoline in the range of 600-4000 cm^{-1}

Figure 2 shows the MIR spectrum of P2_95 gasoline in the range of 600-4000 cm^{-1}. The vibration of the first overtone of the cis-HCCH bond is revealed at 694 cm^{-1}. At a wave number of 1030 cm^{-1}, a pyridine-derived band is presented (Al-Ghouti, Al-Degs, & Amer, 2008). In the range of 1086-1231 cm^{-1}, C-H bond bending vibrations can be observed, while in the next range of 1460-1606 cm^{-1}, asymmetric stretching vibrations are seen, aromatic ring vibrations and phenyl compounds also appear [Al-Ghouti et al., 2008]. At wave number 3028 cm^{-1}, bands originating from sp^2CH_2 olefins appears [Al-Ghouti et al., 2008].

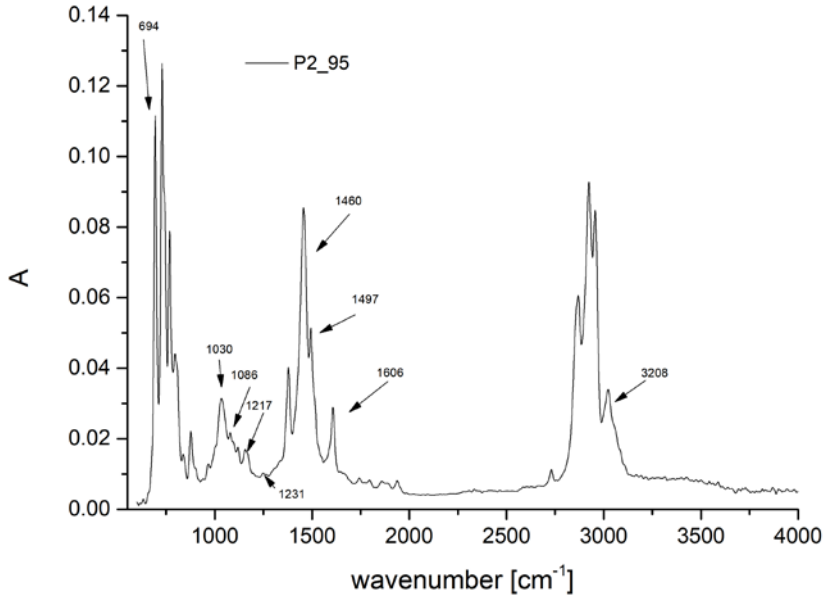

Fig. 2. MIR spectrum of P2_95 gasoline in the range of 600-4000 cm^{-1}.

Figure 3 shows the spectra in the range 600-4000 cm^{-1} of gasoline 95 and 98 coming from Producer 3. Noticeable differences were observed in the range 1000-1500 cm^{-1} and 2805-3030 cm^{-1}. These differences result from the different composition of the tested samples.

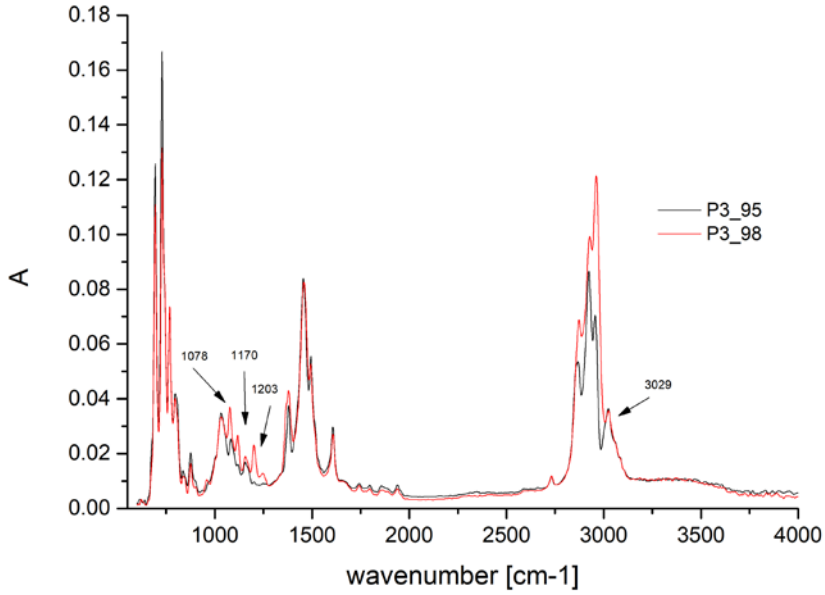

Fig. 3. MIR spectrum of Producer 3 gasoline 95 (black) and 98 (red) in the range of 600-4000 cm^{-1}

Producer 4 gasoline spectra can be seen in Figure 4. Olefinic hydrocarbon compounds are more prominent in gasoline with octane number 95, as evidenced by bands in the range 2869-2998 cm^{-1}. The absorbance at a wave number of 728 cm^{-1} was the highest of all studied gasolines. The level of the spectrum for the entire MIR range disqualifies the competition for 98-octane gasoline. It probably depends on the octane number, which is 99.5 (Table 3).

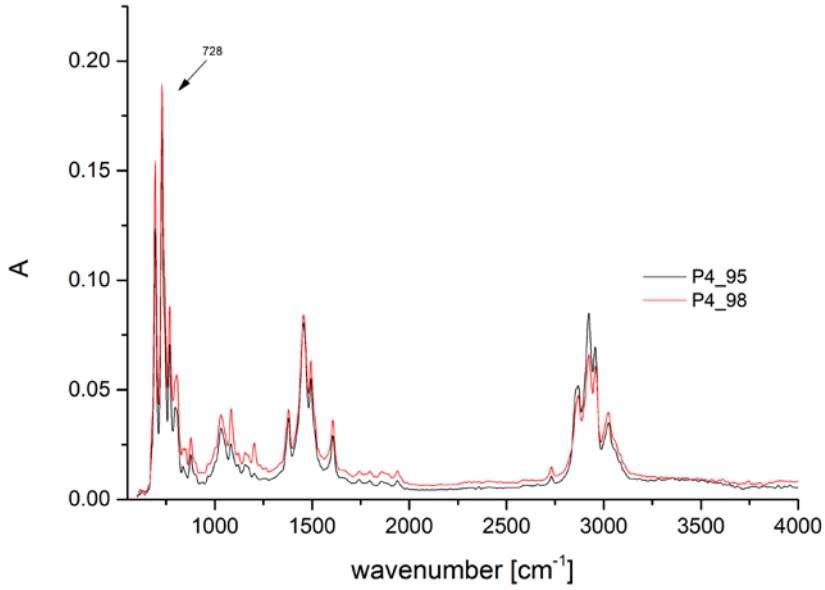

Fig. 4. MIR spectrum of Producer 4 gasoline 95 (black) and 98 (red) in the range of 600-4000 cm^{-1}

Petrol from Producer 1 and Producer 2 are presented on Figure 5 and Figure 6, respectively. The differences between 95 and 98 gasolines are visible in the whole spectrum.

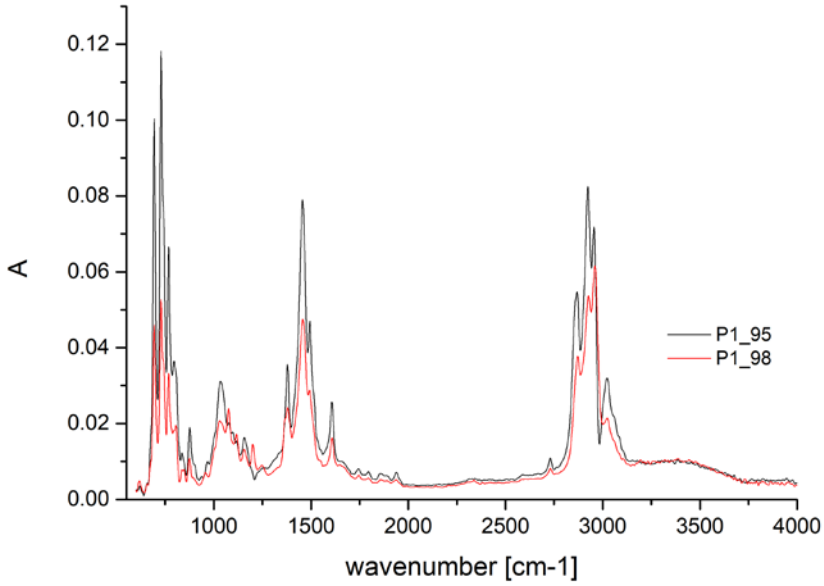

Fig. 5. MIR spectrum of Producer 1 gasoline 95 (black) and 98 (red) in the range of 600-4000 cm^{-1}

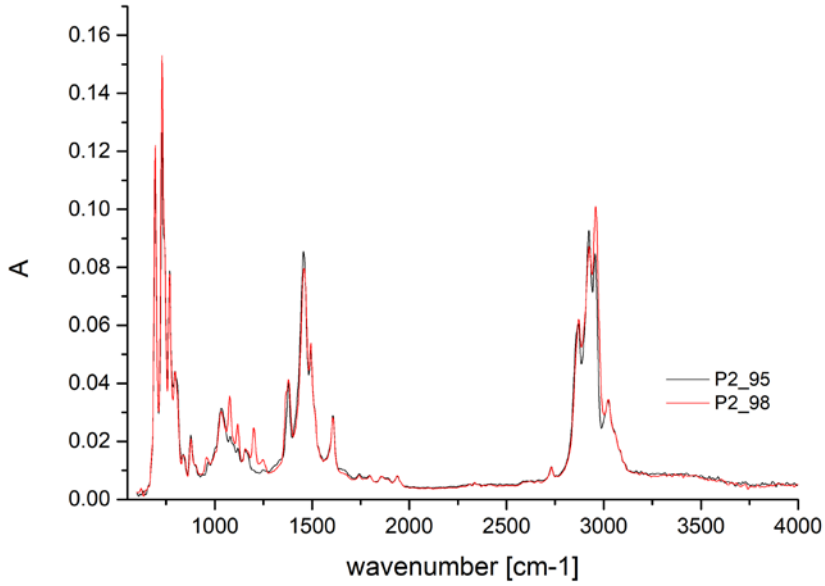

Fig. 6. MIR spectrum of Producer 2 gasoline 95 (black) and 98 (red) in the range of 600-4000 cm^{-1}

Figure 7 shows the spectra of gasoline from the Producer 5. This is one of two petrol samples where 95 octane gasoline outperforms 98 octane gasoline, as presented in table 3. This results are also confirmed by the bands in the range 2840 - 3087 cm^{-1} .

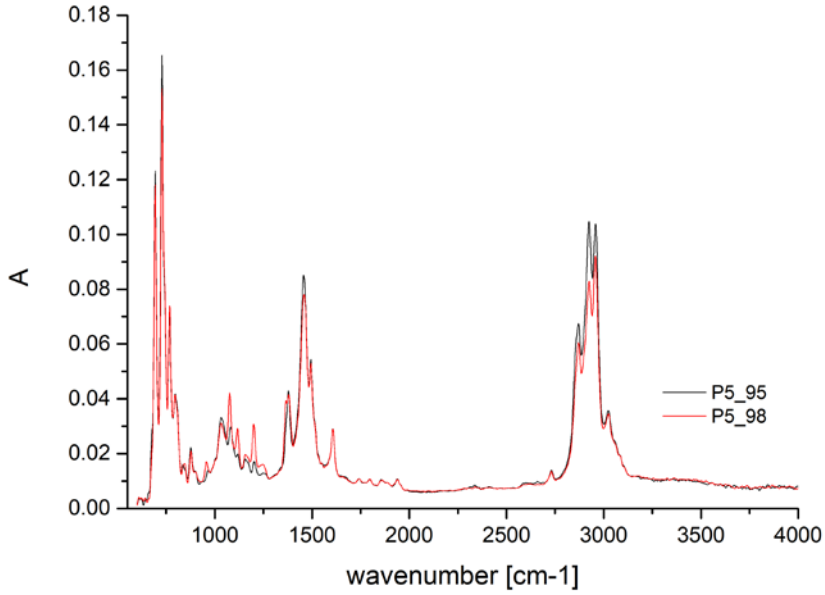

Fig. 7. MIR spectrum of Producer 5 gasoline 95 (black) and 98 (red) in the range of 600-4000 cm^{-1}

2.3. Fluorescence spectra

All synchronous fluorescence spectra of the studied gasolines were measured in the full spectral range of 240-720nm, at $\Delta\lambda$ = 10, 20, 30, 40, 50, 60, 70, 80 nm. A characteristic feature noticeable from the obtained graphs is that with decreasing value of $\Delta\lambda$, the spectra shift towards longer wavelengths. In addition, it can be seen that the width of the spectra changes directly proportional with the change in $\Delta\lambda$, which affects the formation of peaks. As the value of $\Delta\lambda$ decreases, the peaks become sharper and the entire spectrum becomes clearer. In contrast, spectra measured at higher values of $\Delta\lambda$ are difficult to interpret. Thus, the proper choice of the difference between the excitation and emission wavelengths affects the clarity of the synchronous spectrum [Patra & Mishra, 2002].

The peaks seen in the spectra characterize certain fluorescing compounds, more specifically aromatic compounds. In the 250-290 nm range, fluorescence of monocyclic compounds (benzene, toluene xylenes or phenols) can be observed [Steffens, Landulfo, Courrol, & Guardani, 2011]. Hydrocarbons with more elaborate structures fluoresce in higher wavelength ranges, for example those with two rings (e.g. naphthalene) fluoresce between 310-330nm, while phenanthrene (three benzene rings) have fluorescence peaks in the 345-355nm range. The higher the degree of ring structures, the higher the range in which the fluorescence peaks of the given aromatics fall [Pharr, McKenzie, & Hickman, 1992]. Figures 8 and 9 illustrate examples of synchrotron fluorescence spectra for a sample from a Producer 1 station at specific values of Δλ, Figure 8 (Δλ = 10, 20, 30, 40 nm), Figure 9 (Δλ = 50, 60, 70, 80 nm).

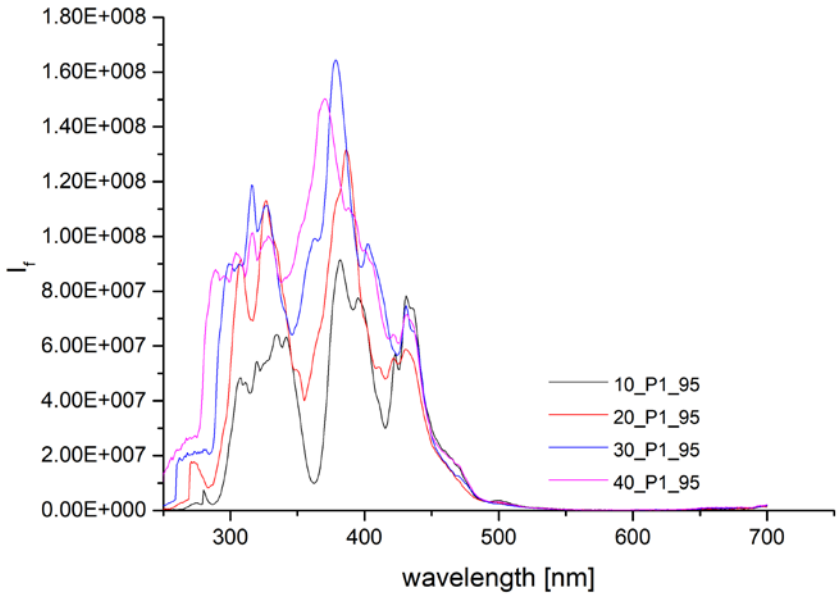

Fig. 8. Synchronous fluorescence spectra of P1_95 gasoline for Δλ= 10, 20, 30, 40 nm

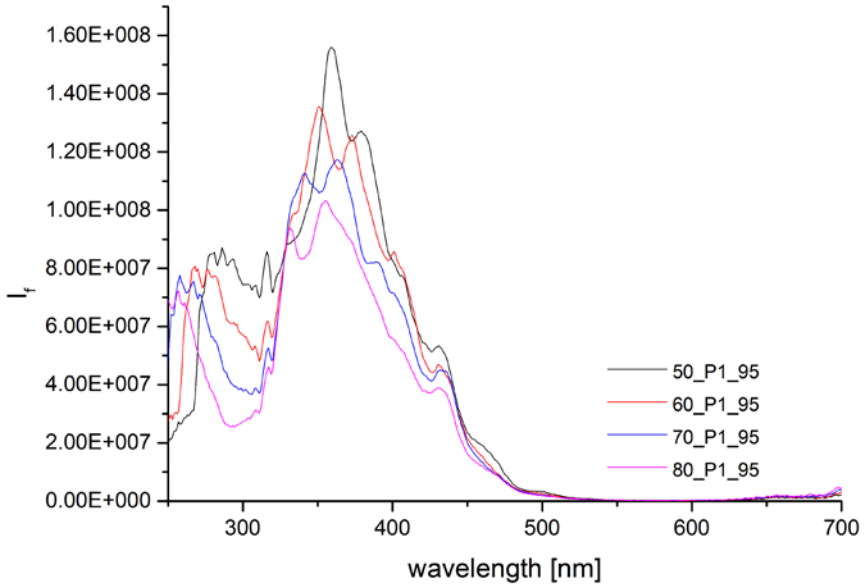

Fig. 9. Synchronous fluorescence spectra of P1_95 gasoline for Δλ= 50, 60, 70, 80 nm

Figure 10 shows the fluorescence spectra of all the tested gasolines for selected Δλ (10, 30, 60 and 80 nm). They are characterized by a similar distribution of fluorescence peaks. Their intensity depends mainly on the concentration of a given substance, but also on the fluorescence efficiency. This fact proves the similarity in composition of the blends, while differences in intensity of the peaks between 95 and 98 octane gasolines from the same manufacturers result from differences in concentrations of aromatic compounds fluorescing at a given wavelength. It is also possible to compare gasoline of the same type from different manufacturers, here the spectra are also characterized by high consistency of distribution and differences in intensity, which would allow for example to identify the sample of unknown origin. In the short-wave range, the intensity is higher for gasoline 95, which indicates a higher content of monocyclic aromas, while in the long-wave range (polycyclic aromas) the situation is reversed. It can also be noted that the spectra of Producer 3, 95 octane

gasoline are significantly different from the rest, this indicates the lowest content of aromatic hydrocarbons in this mixture.

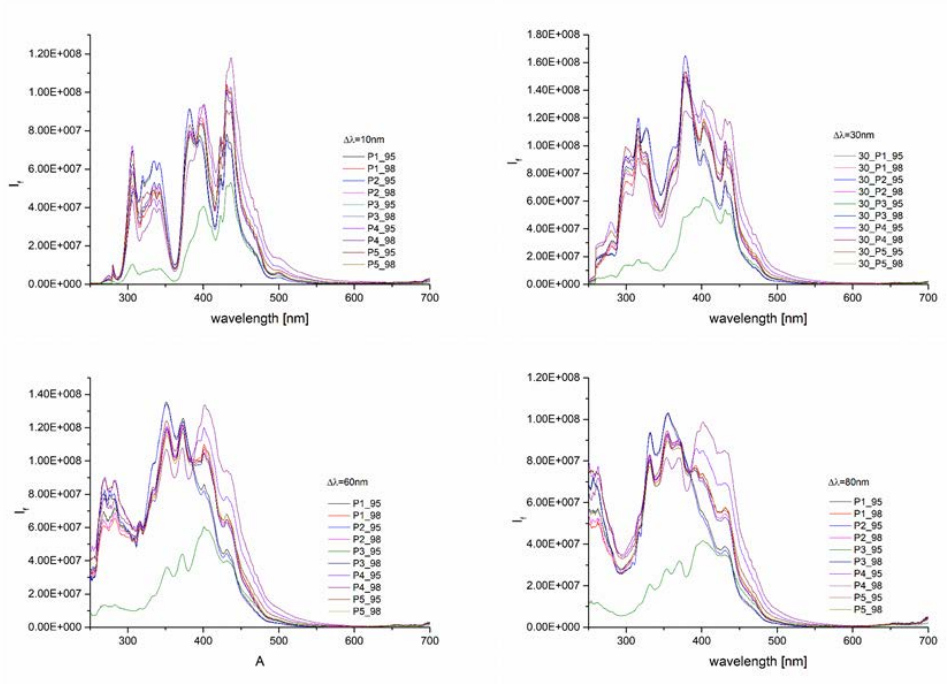

Fig. 10. Synchronous fluorescence spectra of all the tested gasolines for ∆λ= 10, 30, 60 and 80 nm.

2.4. PCA results

In order to compare the MIR spectra of the studied gasolines, a principal component analysis (PCA) was performed in the range 4000-400 cm^{-1}. It was possible to divide the gasolines into two groups based on the analysis: (1) Gasolines 95; (2) Gasolines 98. For the studied gasolines, the first two principal components describe 92% of the total variance of the original data set, where PC1 accounts for 85% of the total variance and PC2 for 7%. All 95 gasolines have positive PC2 values, while 98 gasolines have negative PC2 values. The results are shown on Figure 11.

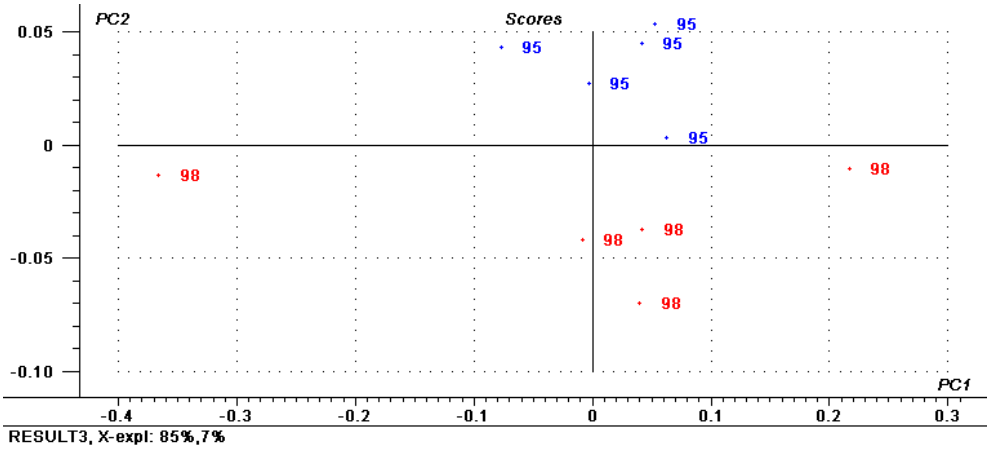

Fig. 11. The results of PCA for the MIR spectra in the range of 4000-400 cm^{-1}

To compare the synchrotron fluorescence spectra, principal component analysis of PCA was again performed for high-octane gasoline samples measured in a reflective geometry (front fraction) with excitation and emission wavelength differences of $\Delta\lambda$= 10, 20, 30, 40, 50, 60, 70, and 80 nm, respectively.

Based on the results obtained for all $\Delta\lambda$ it was possible to divide the samples due to the first two principal components, using the spectral range of 240-298nm as shown in Figure 12. The total variance of the origin data set various from 96-100%. For all the obtained results, 98 gasoline were placed together (near each other). Only P3_95 gasoline stood out from the others in its class, Figure 12.

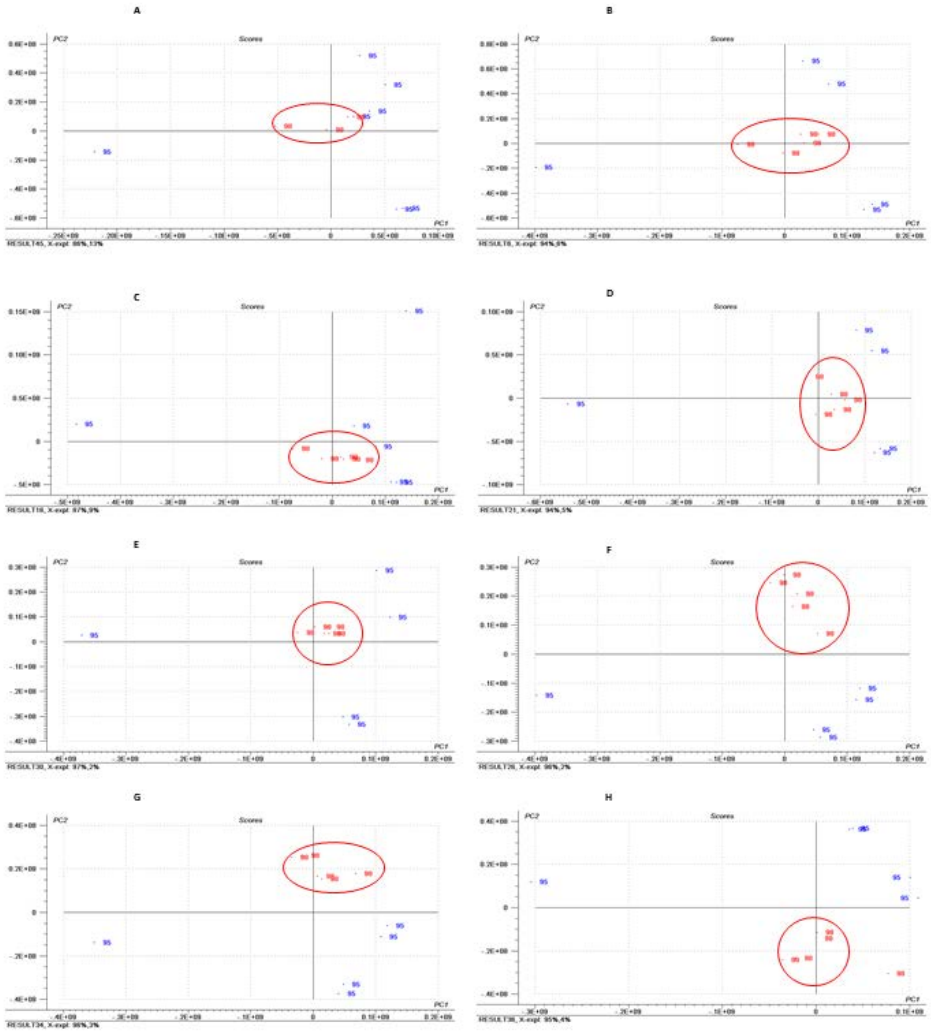

Fig. 12. Results of PCA analysis of synchronous spectra in the range of 270-325 nm for all tested 95 (blue color) and 98 (red color) gasolines. (A) Δλ= 10 nm, (B) Δλ= 20 nm, (C) Δλ= 30 nm, (D) Δλ= 40 nm, (E) Δλ= 50 nm and (F) Δλ= 60 nm, (G) Δλ= 70 nm and (H) Δλ= 80 nm.

2.5. PLS results

Table 4 illustrates the results of the PLS analysis, where the set of X variables were measured spectra (MIR or fluorescence). The set of Y variables consisted of corresponding values of independently measured parameters which were presented in table 3. The PLS1 model was used to correlate a multidimensional matrix of spectroscopic data and a one-dimensional matrix containing the values of the obtained physicochemical parameters.

The regression results confirmed the possibility of applying the NIR spectra to predict the quality of studied gasolines. In most of the obtained results for both spectroscopic techniques the R^2 values were high and RMSEC (Root Mean Square Error of Calibration) were low. The results for medium infrared were more accurate than for fluorescence, Table 4.

Table 4. Partial least squares (PLS) regression analysis results

	Medium Infrared			Fluorescence		
	Range [cm^{-1}]	R^2	RMSEC	Range [nm]	R^2	RMSEC
R	2813–2940	0.971	0.29		0.89	0.57
M	1687-1751	0.998	0.06		0.89	0.47
T50	607-944	0.995	0.12		0.77	0.86
T90	1035-1174	0.993	0.55		0.98	1.08
DI	607-1511	0.999	5.31		-	-
EtOH	2742-3060	0.988	0.24		0.96	0.45
MTBE	1079-1211	0.999	0.06		0.91	1.36
ETBE	599-1525	0.997	0.26	240-720	0.98	0.77
Wt%0	655-1257	0.998	0.008		0.95	0.06
Toluene	784-806	0.992	0.12		0.91	0.42
Xylenes	1392-1548	0.971	0.06		0.94	0.10
Olefins	663-825	0.998	0.15		0.93	0.92
SAT	603-784	0.996	0.16		0.90	0.87
Aromatics	950-1083	0.967	0.17		0.91	0.28
Benzene	609-1500	0.999	0.0009		0.96	0.02

3. Conlusions

The obtained results proved that MIR and fluorescence spectroscopy coupled with chemometrics could be a promising tool to predict the quality of gasoline samples. The PLS results for medium infrared were more accurate than for fluorescence due to the main components of gasoline. However, the models developed in this study need to be further tested on independent data sets from other gasoline producers to assess their stability and accuracy.

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ISBN 978-83-7421-436-0