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Rheological and sensory properties of hydrophilic skin protection gels based on polyacrylates

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Introduction. With the current increases in occupational skin diseases, literature data attesting the decreasing efficiency of barrier creams with respect to the manufacturer's declarations and legal regulations granting skin protection gels for employees, research is required to analyse and evaluate the recipes used for hydrophilic skin protection gels based on polyacrylates. *Methods*. This study investigated the rheological properties, pH and sensory perception of hydrophilic barrier gels based on polyacrylates. *Results*. The acrylic acid derivatives used were good thickeners, and helped to form transparent gels of adequate durability. They could be used to create hydrophilic films on the surface of the skin to protect it against hydrophobic substances. A correlation was shown between the results of the rheological properties and the barrier properties of the gels. This confirms the possibility of monitoring the quality of the gels at the stage of recipe development. *Conclusions*. Polyacrylates are viable for use in industry to produce hydrophilic barrier creams suitable for skin protection.

Keywords: skin protection gels; polyacrylates; rheological and sensory measurement correlation

1. Introduction

There are a number of factors in the work environment that can be harmful to human skin, and some may cause different types of serious dermatoses. The incidence and development of work-related dermatosis among employees depend on their age, professional experience, skin type, perspiration, gender, other co-existing skin diseases, general hygiene and the use of personal protection measures [1,2].

In workplaces where the use of protective gloves is impossible, the only way to limit contact between the skin and harmful substances is the use of skin protection agents, such as barrier creams, gels and protective masks. The means used for skin protection can be divided into three groups: hydrophilic creams, gels and masks; hydrophobic creams, gels and masks; and products designed to protect against ultraviolet (UV) rays.

Hydrophilic preparations smeared on the skin create an impermeable elastic film or layer that blocks organic substances. They also protect against substances insoluble in water, such as organic solvents, resins, oils, fuels, etc. The film should not hinder the manipulation of the fingers, or disturb heat exchange or skin transpiration [3,4]. The basic component of a hydrophilic skin protection cream is a gel, i.e., a semi-translucent and semi-solid substance with a colloid texture, which easily transforms into a liquid and is thus easy to smear over the surface of the skin. After evaporation of the water or other solvent content, it creates a film that blocks organic substances. When the work has been completed, the product should be easily washable with water, which includes the removal of such impurities as grease or paint [5]. These are the characteristics of polyacrylates (Carbopols) [6,7]. In cosmetics and pharmaceuticals, Carbopols are used to thicken the solutions. They have bio-adhesive properties, they are present in the composition of dermatological preparations, such as masks or gels, and their irritation potential is low [7].

Based on the increase in occupational skin diseases, the literature data attesting the decreasing efficiency of barrier creams with respect to the manufacturer's declarations and the legal regulations granting skin protection creams for employees, this research analysed and evaluated the recipes used for hydrophilic skin protection creams utilizing polyacrylates [8–10]. The research was extended to include established correlations between the rheological and sensory properties of the preparations. The analysis shows that it is possible to monitor product quality even at the stage of recipe development. This has a significant impact on analysing the possibility of using polyacrylates in the production of hydrophilic skin protection creams.

2. Materials and methods

2.1. Materials

A hydrophilic barrier gel consists of four main components: a synthetic hydrocolloid solid from the polyacrylate

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Table 1. Raw materials used in the research.

Trade mark	INCI name	Chemical name (IUPAC)	Producer	Function
Optasense™ G40-PW-(RB)	Carbomer	Polyacrylic	Croda Poland	Solid component
Triethanoloamine	Triethanoloamine	Tris(2-hydroxyethyl)amine	POCH Poland	Consistency, pH balancer
Glycerine	Glycerine	Propane-1,2,3-triol	POCH Poland	Softening agent
Propylene glycol	Propylene glycol	Propane-1,2-diol	POCH Poland	
Water	Aqua	Water	–	Thinner agent
Ethanol	Ethyl alcohol	Ethanol	POCH Poland	
Sorbic acid	Sorbic acid	2,4-Hexadienoic acid	POCH Poland	Preservative
Sodium benzoate	Sodium benzoate	Sodium benzoate	Galfarm Poland	

Table 2. Composition of hydrophilic barrier cream.

	Parts by weight (%)			
Ingredient	Sample 1	Sample 2	Sample 3	Sample 4
Optasense™ G40-PW-(RB) water solution	45.45	31.82	27.27	35.64
Propylene glycol	9.10	6.36	5.46	6.72
Glycerine	45.45	31.82	27.27	35.64
Ethanol	–	30.00	40.00	20.00
Triethanoloamine	–	–	–	2.00

family, a solvent, a softener and an antimicrobial. Table 1 presents the suppliers and functions of the different raw materials used for the study.

2.2. *Hydrophilic barrier gel preparations*

The hydrophilic barrier gels based on polyacrylates were obtained using a mechanical stirrer (RW 20 digital IKA; IKA, Poland). The process was carried out at a constant temperature of 25 ± 1 °C.

Optasense™ G40-PW-(RB) was dissolved in water to obtain an 8% aqueous solution. Propylene glycol, glycerine and preservatives were then added. The result was stirred to obtain a homogeneous texture. Ethanol was added to a gel sample if its viscosity was too high.

The possibility of reducing the quantity of thickener used in the gel was tested. The replacement of the thickener by another raw material caused some modification of the rheological properties of the preparation. For that purpose the concentration of Optasense™ G40-PW-(RB) in the recipe was reduced to obtain a 2% aqueous solution, and then triethanolamine was added as a replacement.

Table 2 presents the details of the recipe.

2.3. *pH measurements*

The proper pH value of the skin should lie between 4.5 and 6. The acidic environment of the skin's protective layer forms a barrier to bacteria, UV rays and environmental pollution. Barrier creams applied to the skin should not disrupt its natural acid–base balance.

We analysed the pH of the filtrate obtained by dissolving 4 g of gel in 30 g of water using a pH-meter (HANNA HI 221; HANNA Instruments, Poland).

2.4. *Rheological studies*

The flow and viscosity curves of the preparations were determined using a rotational rheometer (Brookfield RS Plus; Brookfield, Poland). The measuring system was a C 25-2 cone plate (cone diameter 25 mm, cone angle 2°): range of shear rates, 1–1000 s^{-1}; measurement time, 30 s; number of measurement points after setting the blocks, 30. The rheometer was supported by RheoWin3000 software version 1.2. Each measurement was repeated three times with a fresh sample. The flow curve and viscosity for each formulation were expressed as the average. Measurements were carried out at a constant temperature (25 °C) using a Huber Ministat 125 (Huber, USA).

2.5. *Sensory analysis*

A study of the organoleptic properties was carried out in a group of 10 people. During the test, each of a number of properties was evaluated on a scale of 0–5. These parameters were: colour, smell, texture (homogeneity of the gel, smearing capacity, drying time, film residue on the skin), film adhesion, greasiness, viscosity, degree of softening and skin hydration.

The data from both the rheological and sensory measurements, and their coupling, are presented in Section 3.4.

2.6. *Stability of hydrophilic skin protection gels*

A stability test was carried out for the hydrophilic skin protection gels. The samples were stored at different temperatures, i.e., at 4, 22 and 40 °C. The sample storage time was 8 weeks for temperatures of 4 and 22 °C, and 24 h for the temperature of 40 °C.

3. Results and discussion

3.1. *pH measurements*

The aqueous solution of Optasense™ G40-PW-(RB) was pH 2.1, the hydrophilic barrier cream samples 1, 2 and

3 were all pH 3.5, while sample 4 was pH 6.0. The pH of barrier creams should be between 3.5 and 9 [4]. All of the preparations manufactured matched this criterion. The low pH for gels could be caused by the fact that acrylic acid polymer is an anionic polymer sensitive to the pH of the environment. There are functional groups derived from weak acids present in its chains. Adding triethanolamine to the recipe caused the pH to rise, which is the result of creating complexes between the acrylic acid polymer and cationic triethanolamine. Those polymers are used as buffering agents for triethanolamine intended for dermatologic use [11,12].

3.2. *Rheological measurement*

The repeated measurements of flow and the viscosity data exhibited practically identical curves. Hydrophilic barrier gels based on Optasense™ G40-PW-(RB) belong to the group of non-Newtonian shear thinning fluids. Figures 1 and 2 illustrate the impact of added ethyl alcohol on the flow and viscosity curves.

Comparing the flow curves from Figure 1 it can be observed that adding alcohol to the recipe lowers the yield value (a reduction from 76.900 to 37.590 Pa). Lowering of the yield point is also observed when triethanolamine (rheology modifier) is added to the recipe (Figure 3, yield point of 21.292 Pa).

Introducing ethanol and triethanolamine to the recipe allows the viscosity of the hydrophilic barrier gels to be lowered in comparison with their equivalents without rheological modifiers.

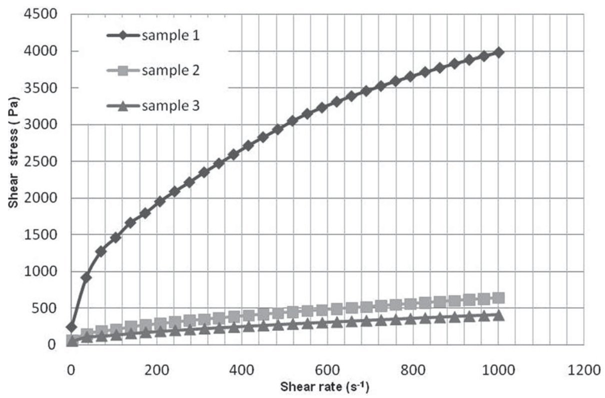

Figure 1. Effect of ethyl alcohol on the flow curves for samples 1, 2 and 3.

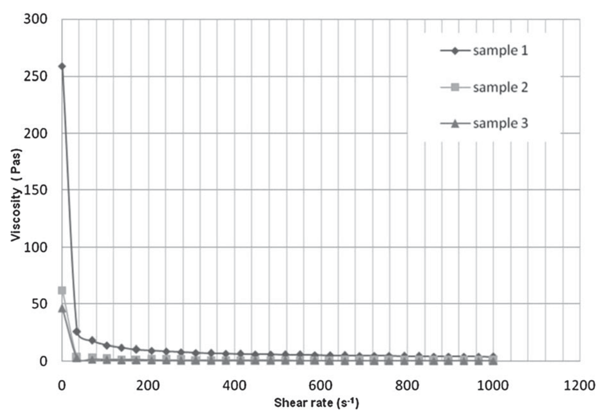

Figure 2. Effect of ethyl alcohol on the viscosity curves for samples 1, 2 and 3.

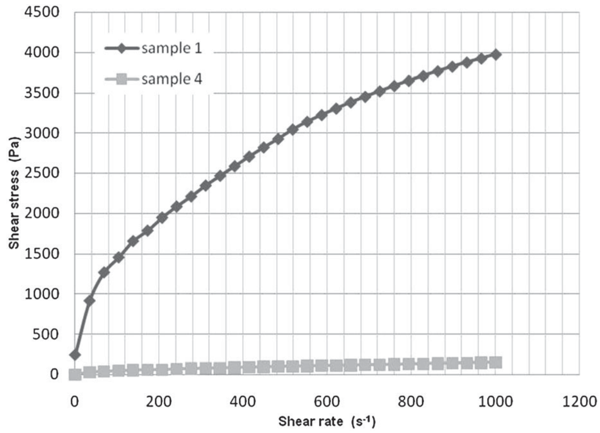

Figure 3. Effect of adding triethanolamine on the flow curves for samples 1 and 4.

3.3. *Sensory analysis*

Table 3 and Figure 4 present the results of the sensory analysis for hydrophilic gels based on polyacrylates.

The property of smell had one of the lowest ratings, caused by the lack of masking agents for the thickening substances and additional fragrant constituents.

Table 3. Results of the sensory analysis.

Assessed property	Descriptive term	Most frequent description
Smell	Extremely nice, very nice, nice, neutral, unpleasant, unsavoury	Neutral, unpleasant
Colour	Pretty, nice, ugly	Nice
Texture – homogeneity of the gel	Very good, good, satisfactory, bad, very bad	Very good, good
Spreading on the hand	Optimal, satisfactory, bad, very bad	Optimal, satisfactory
Adhesion of film	Very good, good, bad, very bad	Good
Drying time	Very quick, good, long, very long	Very quick, good
Viscosity	Optimum, high, too high	Optimum
Feeling after application	Smooth, warm, rough, drying out	Smooth

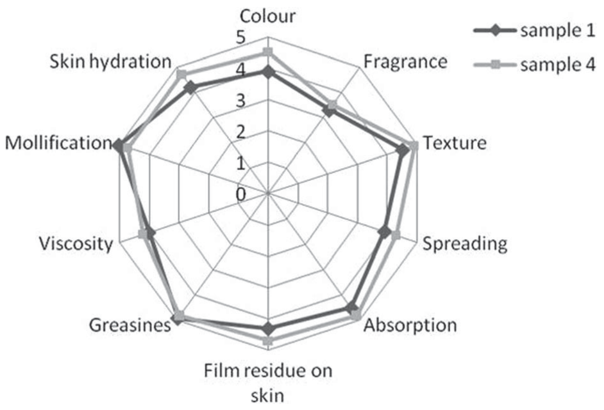

Figure 4. Results of the organoleptic evaluation of hydrophilic gel samples 1 and 4.

Table 4. Results of the sensory analysis, selected parameters.

Characteristic	Sample 1	Sample 2	Sample 4
H	90	92	98
SH	78	80	86
T	90	94	96
Ad	86	90	94

Note: Mean values, scale 0–100. *Ad* = film adhesion; *H* = homogeneity; *SH* = spread on the hands; *T* = drying time.

The largest discrepancies in the ratings concerned gel colour. The colour was directly related to the concentration of Optasense™ G40-PW-(RB) in the recipe. The lower the concentration, the more transparent the gel.

The high ratings for gel texture confirm the possibility of using polyacrylates in preparations for hydrophilic barrier creams.

In terms of application, the most important properties of the gel were homogeneity (*H*), film adhesion (*Ad*), drying time (*T*) and ease of spreading on the hands (*SH*). Table 4 presents a detailed breakdown of the ratings.

3.4. *Correlation between rheological and sensory measurements*

In order to determine any correlations between the sensory evaluation parameters and the specific rheological parameters, the obtained flow curves were approximated. The most appropriate mathematic model to describe the curves was the Herschel–Bulkley model ($R^2 > 0.990$). See Table 5 for the results of the study.

A linear dependency between the sensory evaluation parameters and rheological parameters was defined (k and n in the Herschel–Bulkley model) [13,14]. See Table 6 and Figures 5 and 6 for the results.

Table 5. Values of the parameters of the rheological models for modern skin protection creams.

	Herschel–Bulkley mathematic model			
Cream	τ_y (Pa)	k (Pas^n)	n (–)	R^2
Sample 1	76.900	147.03	0.4960	0.998
Sample 2	59.110	9.293	0.5967	0.999
Sample 3	37.590	6.054	0.6023	0.999
Sample 4	21.292	2.858	0.6230	0.999

Note: k = consistency (Pas^n); n = flow index (–); τ_y = yield shear stress (Pa).

Table 6. Correlation coefficients between rheological and sensory parameters.

Characteristic	k (Pas^n)	n (–)
H	0.520	0.674
SH	0.520	0.674
T	**0.916**	**0.981**
Ad	0.783	**0.897**

Note: Statistically significant relations in bold. *Ad* = film adhesion; *H* = homogeneity; k = consistency (Pas^n); n = flow index (–); *SH* = spread on the hands; *T* = drying time.

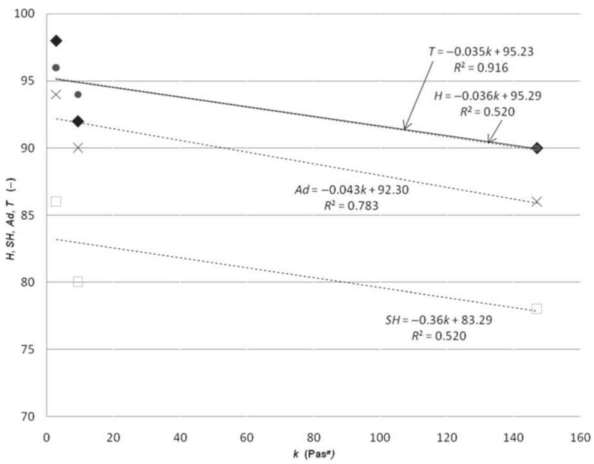

Figure 5. Relationship between sensory parameters and consistency parameters.
Note: × *Ad* = film adhesion; ♦ *H* = homogeneity; k = consistency (Pas^n); □ *SH* = spread on the hands; ● *T* = drying time.

As shown by the results, a strict correlation was obtained for the following pairs: drying time k, drying time n; and film adhesion n.

No correlation was found for parameter k and spreading. This might be due to the shear rate.

3.5. *Stability of hydrophilic skin protection gels*

The samples of hydrophilic skin protection gels stored for a period of 8 weeks remained stable, with no observed

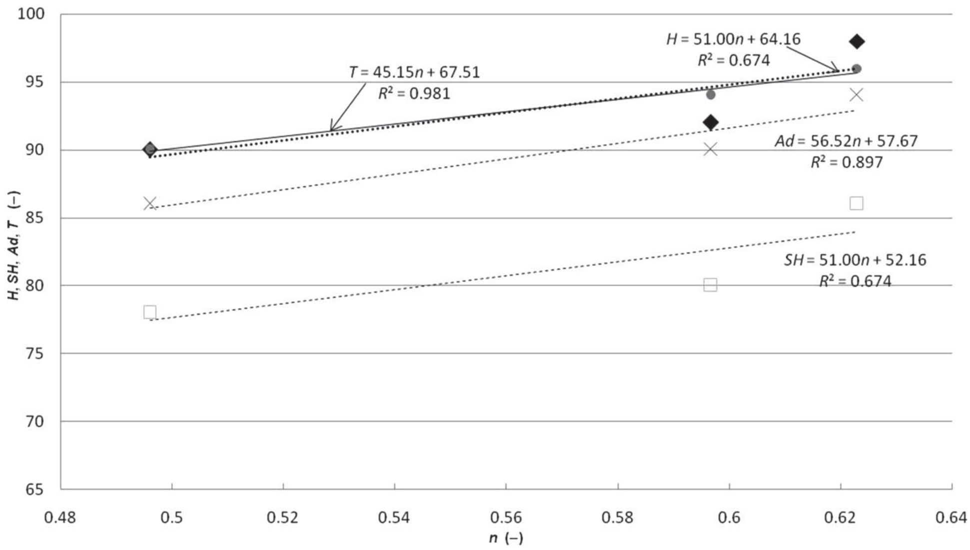

Figure 6. Relationship between sensory parameters and flow behaviour index.
Note: × Ad = film adhesion; ♦ H = homogeneity; k = consistency (Pas^n); n = flow behaviour index (–); □ SH = spread on the hands; • T = drying time.

changes in consistency or mouldability. Those samples stored at room temperature had a more intense odour.

The samples left in daylight changed in colour to pale yellow. This may have been caused by constant exposure to UV radiation.

Our study showed that those protective hydrophilic gels stored at elevated temperatures became more viscous, with the evaporation of water being the main cause of this effect.

Compared with the temperature of the skin, it may be concluded that the process of water evaporation would occur in a similar manner. This would create the expected protective layer on the skin.

4. Conclusions

1. The acrylic acid derivatives used in the study were good thickeners, forming transparent gels of adequate durability. They created hydrophilic films on the surface of the skin, protecting it against hydrophobic substances. These films were easy to remove using water. Polyacrylates can thus be used in industry to produce hydrophilic barrier creams for skin protection.
2. The hydrophilic barrier gels with a lower yield point had a lighter texture, and hence were easier to spread on the skin.
3. The correlation demonstrated between the rheological analysis results and the barrier property evaluation of the creams confirmed the possibility of defining the characteristics which are important from the user's point of view.

By applying an objective and quick instrumental analysis it is possible to reduce the time and cost of a sensory analysis.

Disclosure statement

No potential conflict of interest was reported by the authors.

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