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Original article

Running title: Textural properties of emulsions containing natural thickeners

The Influence of Selected Thickeners on the Textural Properties of Oil-In-Water Emulsions

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SUMMARY

Introduction. Texture profile analysis, as the most popular method of texture analysis today, is used for relating the mechanical characteristics of the samples to their sensory characteristics. Thickeners have an important influence on the mechanical properties of semi-solid products, and thus on the physical stability of creams. Choosing the right one often requires more skill than knowledge.
Aims. The aim of this study was to evaluate the influence of thickeners - natural (xanthan gum) as well as naturally modified polymers (hydroxyethylcellulose, hydroxypropylmethylcellulose) at the concentration of 1% w/w on the textural properties of oil-in-water emulsions.
Results and Discussion. The following parameters of the tested emulsions were determined: adhesiveness, cohesiveness, and hardness. All tested creams reached higher adhesiveness values at the end of the study compared to the originally measured values. However, the presence of thickeners did not increase the stickiness of the formulations since the adhesiveness of the tested samples did not differ much compared to the control sample. Almost similar values of cohesiveness were measured for all samples compared to the initial values. The values of hardness showed that the deformation after two compression cycles did not disrupt the structure and that all preparations were of similar spreadability.
Conclusion. The results obtained by texture analysis could be used in the formulation of a cosmetic product with predefined sensory characteristics. Also, they could help in finding an adequate combination and concentration of thickeners for their application in the formulation. Further research should be directed towards the application of more different thickeners and different ranges of their concentrations in the formulation.

Keywords: **texture profile analysis, thickener, xanthan gum, hydroxyethylcellulose, hydroxypropylmethylcellulose**

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INTRODUCTION

Technologies that have been recently developed can imitate our perception of semi-solid products in terms of consistency, firmness, stickiness, cohesiveness, spreadability, etc. Texture analysis represents a multidisciplinary approach that has different areas of application, especially in the characterization of food structure. However, there is a growing interest in the application of texture analysis in the cosmetic and pharmaceutical industry. Texture profile analysis (TPA) is the most popular and the most commonly used method of texture analysis today. By applying the TPA method, the mechanical characteristics of the samples could be related to their sensory characteristics. Szczesniak was one of the first authors to use texture analysis in food characterization and, together with his colleagues, defined terms that correlated with the results obtained by sensory evaluation (1, 2). Jones et al. (3, 4) were among the first to propose texture profile analysis (TPA) for the characterization of semi-solid dosage forms of drugs and as a suitable method for characterizing semi-solid formulations containing bioadhesive polymers.

By application of various modes of measurement and choosing the right probe, it is possible to examine different groups of semisolids using modern texturometer (5).

Proteins and polysaccharides are substances that are very often used as emulsifiers in emulsions. Proteins are most commonly used because of their surface activity and gelling properties to improve the texture characteristics and stability of emulsions, while polysaccharides are usually added to increase viscosity and allow the formation of a gel-like product (6).

In the International Nomenclature of Cosmetic Ingredients (INCI), there are more than 500 thickeners that have been registered. Choosing the right thickener often requires more skill than knowledge. Unfortunately, the "universal thickener" does not exist yet (7).

There has been a trend in the cosmetic industry to use raw materials of natural origin for many years now, but it is not always easy to find natural materials that would replace those of synthetic origin. Natural polymers, such as starches and other polysaccharides, were the first used thickeners since ancient times. Their advantage is that they fit into the current trends of application of "natural" personal care products. These products are obtained from nature with minimal processing, but also with certain functional shortcomings in relation to synthetic products. The most commonly used natural thickeners are polysaccharides, such as sugar polymers. Some of the examples are cellulose derivatives, xanthan gum, alginates and carrageenan. This type of thickeners are effective for thickening aqueous solutions as well as oil-in-water emulsions and have a long history of safe application. However, there are certain disadvantages considering their application. For example, their tactile properties are not ideal, which leads to the stickiness of the formulations when used in high concentrations. They can also lead to poor appearance and unsatisfactory sensory properties of the final product (8).

Adequate combination of thickeners, as well as their application in the appropriate concentration is a challenge in the formulation of stable and effective formulations with satisfactory sensory characteristics (9). Lemaitre-Aghazarian et al. (10) studied the effects of changing certain parameters of the fatty phase of water in oil emulsions (W/O) on their texture properties, also using texture analysis. Lukić et al. (11, 12) examined the influence of emollients on the textural properties of W/O cosmetic creams in order to predict their sensory characteristics. The results showed the correlation that exists between physical measurements and the corresponding sensory properties. Calixto et al. (13), have set as a challenge the formulation of stable and effective cosmetic products that, among other ingredients, contain a combination of polymers and waxes. The conclusion of this study was that wax has a greater impact compared to polymer when it comes to texture characteristics.

The aim of this study was to evaluate the influence of different natural polymers on the textural properties of oil-in-water (O/W) emulsions. To date, there have not been enough data available on this impact. Given the growing presence of "natural products" on the market and claims about the benefits of their application on the skin, the impact of natural (xanthan gum) as well as naturally modified polymers (hydroxyethylcellulose, hydroxypropylmethylcellulose) was assessed. Each of them was incorporated individually into the O/W emulsion at the concentration of 1% w/w.

MATERIALS AND METHODS

Materials

Ingredients

For preparation of the emulsions, following reagents were used: Myritol® 318 (INCI: Caprylic/capric triglycerides) was purchased from Henkel (Germany), isopropyl myristate (INCI: isopropyl myristate) from Centrohem (Serbia), while Paryol 165 OL/R (INCI: Olive oil) and Euxyl PE 9010 (INCI: Phenoxyethanol (and) Ethylhexylglycerin) were from Comcen (Serbia). MontanovTM82 (INCI: Cetearyl alcohol (and) Coco-glucoside) and MontanovTM14 (INCI: Myristyl alcohol (and) Myristyl glucoside) were bought from Seppic (France), while propylene glycol (INCI: Propylene glycol) was from Fagron (Netherlands). Thickeners - xanthan gum, hydroxyethylcellulose and hydroxypropylmethylcellulose were purchased from AvenaLab Cosmetics (Serbia) and purified water was obteined from Faculty of Medicine (University of Niš, Serbia).

Preparation of emulsions

Four O/W emulsions were prepared as typical cosmetic creams (ingredients list given in Table 1). The creams differed only in the type of added texturing agent. Xanthan gum, hydroxyethyl cellulose (HEC) and hydroxypropylmethylcellulose (HPMC) were used as thickeners. Propylene glycol, preservative and thickener were dissolved in purified water. In order for the thickener to adequately disperse and achieve a smooth consistency, the mixture was left to swell for 24 hours. Each texturing agent was incorporated at the concentration of 1% w/w in the emulsion. Also, an additional O/W emulsion, without any hydrophilic polymer was prepared to serve as a placebo. The samples were then prepared using the hot-cold emulsification process, by adding the aqueous phase to the heated fat phase (heated to 60°C) and mixing with a propeller rotary stirrer RW16 basic (IKA Werke, Germany) until room temperature was reached.

Table 1. *Composition of the developed formulations*

	Ingredients (INCI name)	Function in the formulation	Content (% m/m)
Oil phase	Caprylic/capric triglycerides	Emollient	11,00
	Isopropyl myristate	Emollient	7,50
	Olive oil	Emollient	3,00
	Cetearyl alcohol (and) Coco-glucoside	O/W emulsifier	7,00
	Myristyl alcohol (and) Myristyl glucoside	O/W emulsifier	1,50
Aqueous phase	Xanthan gum/HEC/HPMC	Thickener	1,00
	Propylene glycol	Humectant	10,00
	Phenoxyethanol (and) Ethylhexylglycerin	Preservative	1,00
	Aqua (Water)	Water phase	q.s. 100,00

Methods

Textural analysis

Textural analysis was performed using a texturometer (CT3 Texture Analyzer, Brookfield Engineering Laboratories) by carrying out a TPA test that performed two compression cycles on the sample and reported five established Texture Profile Analysis results. The trigger value was set at 10 g, target deformation (travel distance into the sample) at 2 mm and the test speed at 2 mm/s. After penetrating the sample placed into female cone probe, the male cone probe returned to the initial position. From the obtained graph force (load) vs. distance, the maximum force (firmness) and the negative area (adhesiveness) were calculated. All the measurements were taken in triplicate, at room temperature (21°C). The textural analysis was performed at the time of making, one and two weeks, and one and three months after the preparation of formulations.

The results were recorded using the software (Brookfield Engineering Laboratories), and then the mean ± standard deviation was determined for each parameter.

RESULTS AND DISCUSSION

Polymers are one of the most used class of ingredients used in cosmetics and personal care products. A large number of polymers used in this field play an important role in the formation of the film and act as rheological modifiers, fixatives, thickeners, emulsifiers, conditioners, foam stabilizers, as well as antimicrobial substances. Water-soluble polymers significantly contribute to the textural properties of emulsions, among other ingredients. Therefore, these hydrophilic polymers are widely used in O/W emulsions as thickeners and rheological modifiers, but also as emulsion stabilizers, emulsifiers or wetting agents (14).

Xanthan gum is a natural heteropolysaccharide, discovered in the 1950s, which consists of glucose, mannose and glucuronic acid. The presence of acetic and pyruvic acid makes xanthan gum an anionic polysaccharide. As a non-absorbing polysaccharide, it stabilizes O/W emulsions by increasing the viscosity of the aqueous phase and acts synergistically with other polysaccharides, which is an important characteristic when it comes to viscosity. It is very often used in the food industry due to its temperature stability, compatibility with food ingredients and pseudoplastic rheological properties, but also for stabilizing suspensions and emulsions. Xanthan gum solution is very viscous even when this polysaccharide is in a very low concentration. Therefore, this is exactly the reason why xanthan gum is used as a thickener (15, 16).

Cellulose is an effective thickener in systems with a higher water content. Cellulose derivatives are, among other thickeners, most often used in all types of cosmetic products, as well as in the drug development, considering their physical and sensory characteristics. This type of polymers are intensively used for thickening solutions and dispersion systems such as emulsions and suspensions. They can increase shelf life as well as resistance to mechanical and thermal changes of emulsions. Among them, cellulose ethers, especially those with higher molecular weight, are more suitable for regulating viscosity and stabilizing liquid dispersion systems such as suspensions and emulsions. Therefore, there is a direct proportionality between viscosity of cellulose ether solutions and their molecular weight. Examples of the most commonly used cellulose ethers are: methylcellulose (MC), ethylcellulose (EC), hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), hydroxypropylmethylcellulose (HPMC), carboxymethylcellulose (CMC) and sodium methylcellulose. Ethylcellulose and hydroxyethylcellulose have been used successfully in cosmetic products for many years as thickeners and film agents (17).

Thickeners have an important influence on the mechanical properties of semi-solid products, and thus on the physical stability of creams. Increasing the amount of thickener can have a positive effect on physical stability when it comes to creams. However, the application of higher concentrations of thickeners can also lead to an increase in hardness, adhesiveness, viscosity as well as more difficult spread ability of these formulations (9). Gilbert et al. (18), observing the textural characteristics of nine O/W emulsions, which differed in only one ingredient (polymer), confirmed the positive influence of polymers on viscosity and viscoelastic parameters and found a statistically significant correlation between rheology and texture analysis.

Based on the results obtained from the deformation curve of the force versus time, which is characteristic of the texture analysis, the appropriate parameters of the tested emulsions were determined: adhesiveness, cohesiveness and hardness.

Adhesiveness, defined as the maximum positive force required to overcome the attractive forces between any surfaces of a sample (cream), characterizes the degree of stickiness of the sample. Adhesive properties define the sensory properties of cosmetic creams and affect consumer acceptance (5, 19). By visual inspection of the graph (Figure 1), it can be seen that all creams (including placebo cream) showed an increase in adhesiveness after one week of preparation, with the raise being the largest in the samples with xanthan gum and HEC. After that period, the values of adhesiveness did not change much. However, it can be said that all tested creams reached higher adhesiveness values at the end of the study (after 90 days) compared to the originally measured values. Nonetheless, the obtained values from all tested samples did not differ much in relation to the adhesiveness of the control sample, which means that the presence of thickeners does not increases the stickiness of the formulations significantly.

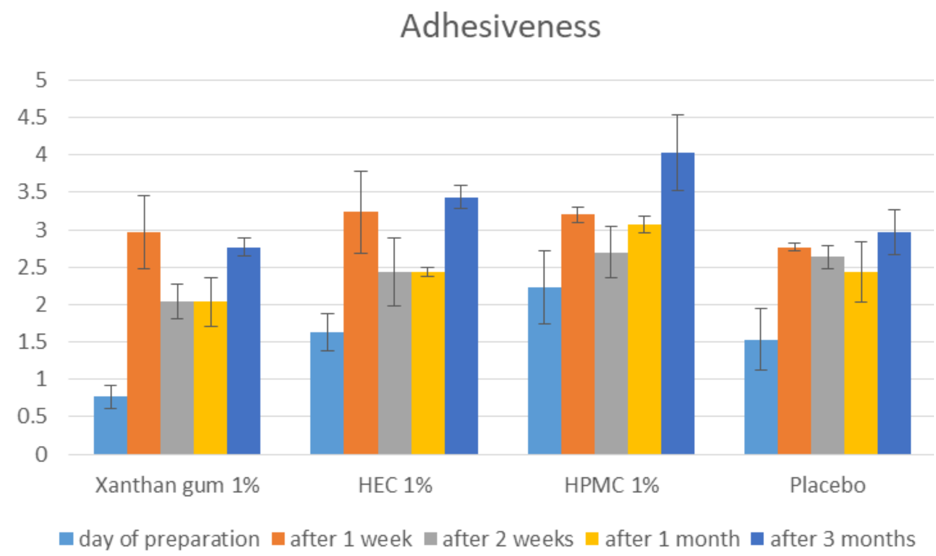

Figure 1. *Results of adhesiveness of the formulations evaluated on the day of preparation, one and two weeks, and one and three months after preparation (mean values ± SD, n = 3)*

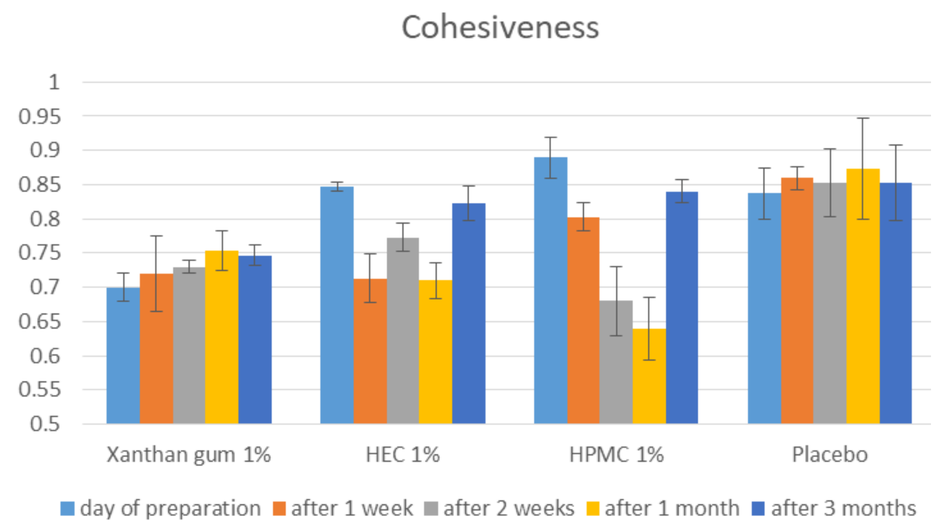

Figure 2. *Results of cohesiveness of the formulations evaluated on the day of preparation, one and two weeks, and one and three months after preparation (mean values ± SD, n = 3)*

Cohesiveness is another parameter that indicates the strength of internal bonds but is also responsible for the overall elegance of the cream (5, 19). Mathematically, it represents the ratio of work performed during two cycles. Based on the results of the texture analysis (Figure 2), we can notice that throughout the period of study, cohesiveness of all creams, including placebo, did not change much. The most variations were in sample with 1% HPMC. Still, at the end of the study (after 3 months of production), almost similar values of cohesiveness were measured for all samples compared to the initial values.

Hardness of any semi-solid product can be expressed as the maximum positive force required to deform the sample with a finger. Higher values of this parameter indicate less spreadability of the sample (5, 19). Initial values of hardness of tested creams can be put in the following order: cream with HPMC > cream with HEC > cream with xanthan gum. Not only did a sample with 1% HPMC show the highest values at the time of preparation, but also during measurements after 7, 14, 30 and 90 days. It can be noticed that hardness of all creams containing thickening agent increased over time, which was not the case with the placebo sample. This comfirms that the thickener affects the firmness of the creams. In the study, we examined hardness measured after the first and second cycle. The obtained values for both cycles were very similar, thus it can be said that there was no weakening of the structure after the first compression cycle in all preparations. Therefore, the deformation did not disrupt the structure. After 90 days of production, the tested emulsions achieved close values of hardness among each other, which indicated that they were of similar spreadability (Figure 3).

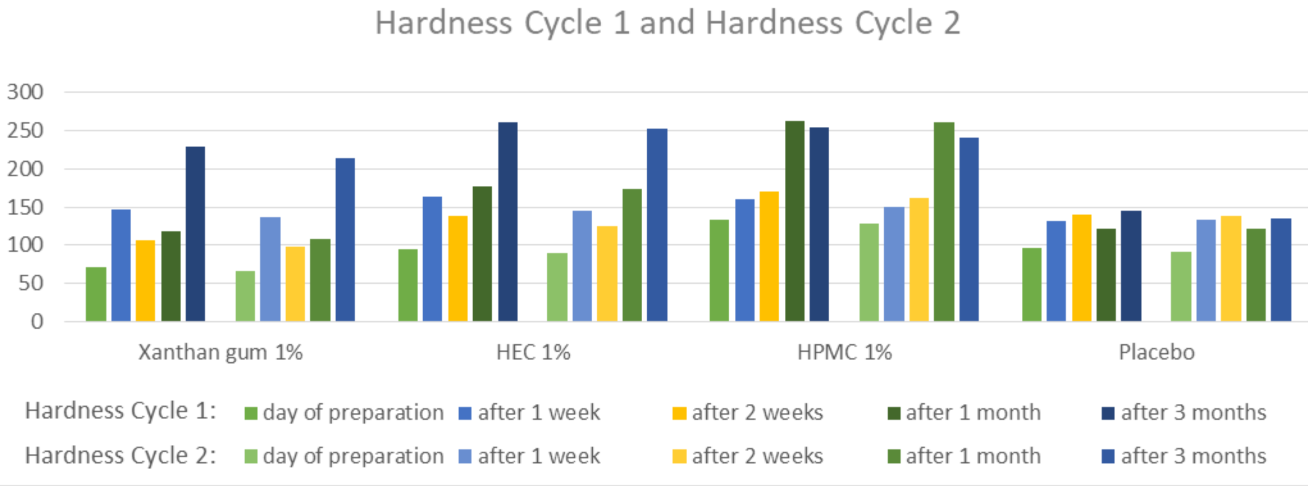

Figure 3. *Results of hardness (hardness cycle 1 and hardness cycle 2) of the formulations evaluated on the day of preparation, one and two weeks, and one and three months after preparation (mean values ± SD, n = 3)*

It has been demonstrated that the adhesiveness of aqueous gels composed of hydroxyethylcellulose (HEC) is a function of polymer concentration and is attributed to the reported adhesive nature of this polymer (4, 20). In the study by Estanqueiro et al. (9), the formulation with 1% of cellulose ether (sodium carboxymethylcellulose) showed the highest values of adhesiveness, compared to lower values of formulation with 1% of xanthan gum. Also, it was shown that the formulation which also contained 1% of xanthan gum did not undergo significant variations in hardness over six months (9). Gilbert et al. (21), concluded that the presence of xanthan at 1% in O/W emulsions, in comparison with a gum-free emulsion, did not affect their spreading characteristics but affected hardness and high degrees of stringiness and stickiness. Dubuisson et al. (22) showed that the effect of xanthan gum on the texture properties of emulsions was similar but obviously diminished when compared to polymer solutions.

To our knowledge, this is the first paper where texture properties of preparations with xanthan gum, HEC and HPMC were compared. Taking this into consideration, these results may be the basis for further research of formulations with more different thickeners and their combinations as well as their different concentration ranges.

CONCLUSION

Consumer acceptance and the effectiveness of topical products include the optimal mechanical characteristic (hardness and cohesiveness), appropriate adhesiveness and good spreadability. The results of previous studies have shown that there is a direct correlation between texture analysis and sensory characteristics; also, the sensory profile of cosmetic products can be predicted based on instrumental measurements. The obtained results show that the data obtained by texture analysis could be used in the formulation of a cosmetic product of predefined sensory characteristics or in the process of reformulation. Further research should be done using more different thickeners and their different concentration ranges in the formulation.

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Article info

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Uticaj odabranih ugušćivača na teksturne karakteristike emulzija ulje u vodi

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SAŽETAK

Uvod. Najpopularnija metoda teksturne analize je analiza profila teksture. Primenom ove metode, mehaničke karakteristike uzoraka dovode se u vezu sa njihovim senzornim karakteristikama. Ugušćivači imaju važan uticaj na mehaničke osobine polučvrstih proizvoda, pa samim tim i na fizičku stabilnost kremova. Izbor pravog ugušćivača često zahteva više umeća nego znanja.

Cilj. Cilj ovog istraživanja bila je procena uticaja često korišćenih prirodnih (ksantan guma), kao i prirodno modifikovanih polimera (hidroksietilceluloza, hidroksipropilmetilceluloza), u koncentraciji od 1% m/m, na teksturne osobine emulzija tipa ulje u vodi.

Rezultati. Na osnovu dobijenih rezultata određeni su odgovarajući parametri testiranih emulzija: adhezivnost, kohezivnost i čvrstina. Svi testirani kremovi dostigli su veće vrednosti adhezivnosti na kraju studije, u poređenju sa prvobitno izmerenim vrednostima. Međutim, adhezivnost ispitivanih uzoraka nije se mnogo razlikovala u odnosu na adhezivnost kontrolniog uzorka, što znači da prisustvo ugušćivača ne povećava lepljivost formulacija. Izmerene vrednosti kohezivnosti za sve uzorke u poređenju sa početnim vrednostima bile su gotovo slične. Vrednosti čvrstine kremova pokazale su to da deformacija nakon dva ciklusa kompresije nije narušila strukturu kremova, kao i da su sve formulacije slične razmazivosti.

Zaključak. Rezultati dobijeni teksturnom analizom mogu biti iskorišćeni pri formulisanju kozmetičkog proizvoda unapred definisanih senzornih karakteristika. Takođe, mogu biti od pomoći u pronalaženju adekvatne kombinacije ugušćivača, kao i u određivanju odgovarajućih koncentracija za njihovu primenu u formulaciji. S obzirom na to, dalja istraživanja trebalo bi usmeriti na primenu više različitih ugušćivača i različitih opsega njihovih koncentracija u formulaciji.

Ključne reči: **teksturna profilska analiza, ugušćivač, ksantan guma, hidroksietilceluloza, hidroksipropilmetilceluloza**