Rheological Behaviour of Cold Creams with Cinnamon and Thuja Alcoholic Extract

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In this paper the rheological behavior of three cold creams obtained in laboratory have been made, such as: simple cold cream, one cream with cinnamon extract and one cream with thuja extract. All three creams have a pseudo-plastic time-dependent rheological behavior, also exhibiting a velvety feeling and being easily applied on skin. By adding the alcoholic extracts of cinnamon and thuja, the creams became more fluid and soft and could be applied better.

Keywords: rheology, cold cream, alcoholic extracts of cinnamon and thuja

Cosmetic creams are used for re-establishing the optimum level of skin hydration. Thus, by applying the cream on skin surface an occlusive film is formed that decrease water loss through stratum corneum. If there is an optimum water content, the skin is elastic, soft and velvet [1]. Most cosmetic creams are heterogeneous systems, namely emulsions that are complex and thermodynamically unstable, their structure and behavior being the theme for many scientific studies [2-7].

From those studies was concluded that rheology is one of the main methods used to analyze the properties of a cream, its stability and for quality control. Also, a change in cream rheology could imply the inevitable damage of the product [8,9]. Regarding the structure, creams have a three dimensional matrix, that must be stable when motionless and flow easily when the product is applied on skin. So, the most important characteristic of creams is to retrieve its shape after application. The rheological measurements allow the correlation of the information on viscoelastic behavior with the sensory perception and the ability to apply the cream. The correlation between microstructure and macroscopic behavior of a material can be detected using rheological oscillatory tests [7]. Since ancient times, natural ingredients have been used in cosmetic creams for their therapeutic properties [10-16]. But, besides that, natural extracts can induce changes in viscosity [10].

Because the influence of natural extract on rheological properties of cosmetic creams is an important aspect of great concern and in literature were not found such information, we thought to be interesting to study the effect that cinnamon and thuja alcoholic extracts have on a cold cream obtained in our laboratory.

Experimental part

Cinnamon and thuja extracts

For this study, the cinnamons from Cinnamomum Verum specie without further additions, in powder form and commercially available and the fresh Thuja leaves harvested from bushes grown in pollution free places have been used. Both extracts were obtained using Soxhlet apparatus and ethanol as solvent.

In order to obtain the cinnamon extract, about 30 g cinnamon powder were weighted and were inserted into the Soxhlet cartridge. The cartridge was covered with cotton-wool and was added from the top into the body of the extractor device. The body of the extractor was attached to the collecting flask and then about 400 mL solvent was introduced from the top until siphoned off 2-3 times. Next, the condenser was attached to the extractor body and the heat source was connected. The extraction occurred at 75-80°C for 7 h, with a refluxing rate of 5-6 siphoning per hour. Finally, the alcoholic extract was concentrated in a rotary evaporator until 30 mL concentrated cinnamon extract remained.

The thuja extract was obtained following the same steps, starting from 60 g fresh Thuja leaves, previously well homogenized and 300 mL solvent. The extraction was carried out for 8 h at 75-80°C and then the alcoholic extract was concentrated until finally 25 mL thuja extract were obtained.

Cold cream formulation

In this study have been used: yellow beeswax, directly from producers and harvested in 2015, commercial olive oil, manufactured in 2016, borax and sodium dodecyl sulfate (surfactant), the last one from Merck. The cream has been made using the method described in literature [17]. Into a Erlenmeyer flask 7 g beeswax and 250 mL olive oil have been introduced and the mixture was heated at T=68°C, under continuous stirring. Over the mixture, 0.5 g borax and 1 g surfactant solved in water and heated at the same temperature were added, under vigorous stirring. Sodium dodecyl sulfate is added in order to avoid lumps and fat sensation on skin and also to stabilize the emulsion. Finally, the raw cream (named Cream 1) was cooled at 45°C and poured into containers.

Creams with cinnamon and thuja extract

In order to obtain the cinnamon cream, 20 g raw cream are poured into a container and 2 mL cinnamon extract is added. The cosmetic cream obtained (named Cream 2) has a yellow-reddish color, a smooth texture and a specific cinnamon flavor that persist a long time after being applied on skin.

The thuja cream is made by mixing 2 mL thuja extract with 20 g raw cream. This product (named Cream 3) has an olive-green color, a fine texture and a specific thuja smell, that give a fresh note to the skin.

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Qualitative analysis of extracts and raw materials

Because this study follows the influence of the extract on the rheological properties of the creams, it was not required an evaluation of the active compounds found in the extracts, but the TLC analysis have been made in order to confirm the presence of the main active ingredient in each extract. The TLC analysis has been made by using the method presented in literature [18].

One of the most important aspects in cream behavior is the nature of the waxes and of the emollient; thus the physico-chemical characteristics have been analyzed for both the beeswax and the olive oil used in this experiment. For the beeswax the acidity index, saponification index, ester index and peroxide index were determined using the methods described in Romanian Pharmacopoeia [19].

For the olive oil, free fat acids (FFA) compared to the amount of oleic acid (%), saponification index and iodide value (IV) have been determined, using an analytical method described in literature [20]. For olive oil also an FTIR analysis have been made using a Perkin Elmer Spectrum 100 spectrometer.

The reagents used for the physico-chemical determinations for both the beeswax and the olive oil have been bought from Merck.

Rheological measurements for the cinnamon and thuja creams

The rheological properties of the creams have been measured with an Anton Paar, Physica MCR 501 modular rheometer equipped with a Peltier system for temperature control. The measurements were made with a plane-plane ribbed geometry with a 50 mm diameter. The tests were carried out both in an oscillating mode and in the rotational mode.

Results and discussions

In table 1 are showed the physico-chemical characteristics for beeswax used for cream formulation

The experimental data obtained for the beeswax used for cream formulation shows that is a quality product and can be used as an excipient in cosmetic products. It also has a good skin tolerance, a protective effect and good coverage by forming a waterproof film on skin that prevents skin dehydration. Table 2 shows the characteristics for the analyzed olive oil.

As can be seen from the table, the analyzed olive oil has a very high quality with low oxidation tendency, the values of analyzed index enrolling in the existing limits found in literature. Also, the degree of unsaturation of the olive oil has been realized with the FT-IR analysis (fig. 1).

In figure 1 are observed the peaks in range 3100-2800 cm^{-1}, the most illustrative being those at 2920 and 2852 cm^{-1}. According to literature [22] these peaks belong to the symmetrical and asymmetrical C-H stretching vibration of the CH_2 and CH_3 aliphatic groups from the alkyl part of the triglycerides that are found in vegetable oils. Also, in the range 1800-1600 cm^{-1} could be observed two bands at about 1750 and 1660 cm^{-1}. According to literature, the absorbency at 1743 cm^{-1} is characteristic for oils with a high amount of saturated fat acids and short carbohydrate chain, and the spectral band close to 1660 cm^{-1} corresponds to the double C=C bond that can be correlated with the polyunsaturated fat acids found in oil [23].

Identification of active compounds from the alcoholic extracts of cinnamon and thuja have been made by the means of thin layer chromatography and the retention coefficients (R_f), for the two extracts are presented in table 3.

According to literature, Rf values showed in table 3 belong to the main ingredients from cinnamon and thuja: cinnamaldehyde and thujone, respectively [24, 25].

As mentioned above, the purpose for the rheological tests is to obtain information on structural properties and stability of cosmetic creams. Rheological measurements that allows to estimate the structural stability of studied creams are achieved through viscoelastic parameters

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS FOR BEESWAX.

Product	Melting point, °C	Acidity Index, mg KOH/g	Saponification Index, mg KOH/g	Ester Index mg KOH/g
Beeswax from literature [19]	62-66	17,5 – 23	83 -106	68-80
Beeswax analyzed	65	20	98	73

Table 2
CHARACTERISTICS FOR ANALYZED OLIVE OIL

Product	FFA(oleic acid) %	Saponification number (SN)	Iodine value (IV)
Olive oil from literature [21]	14.5	187-195	70-88
Analyzed olive oil	13.87	190	78

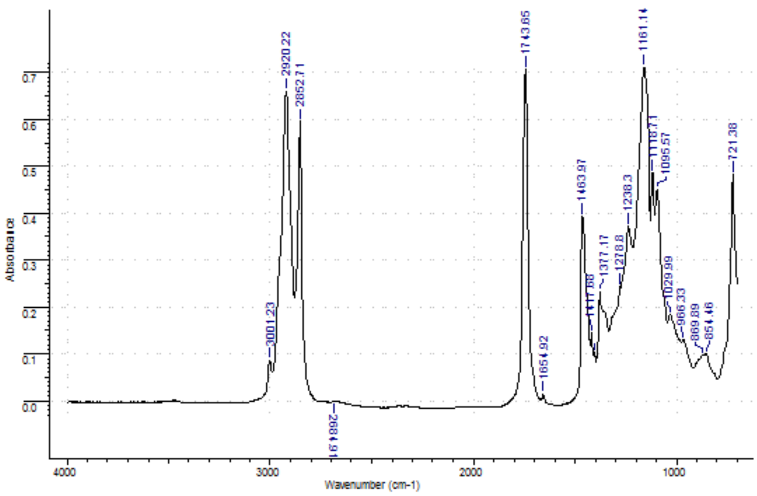

Fig 1. The FT-IR spectrum for olive oil sample

measured, namely: module storage G' (a measure of the deformation energy stored by the sample during the shear process, representing the elastic behavior of the material [7]), module loss G" (a measure of the deformation energy used by the sample during the shear process, representing the viscous behavior of the material [7]), phase angle δ, loss factor tan δ (tan δ = G"/G', revealing the ratio of the viscous and the elastic portion of the viscoelastic deformation behavior) and complex viscosity η^*.

For the analyzed samples two testes have been made: amplitude sweep test and the frequency sweep test.

The first oscillating test applied for the samples was the amplitude sweep test (fig. 2) in order to establish both the linear viscoelastic range limit and to assess the structural stability of creams. The tests were conducted at two different temperatures: 25° C (room temperature) and 37° C (physiological temperature). In this test, the frequency was kept constant (ω = 10 rad/s), but deformation was varied in the range from 0.001 to 100%.

As showed in figure 2, the studied samples have a good stability in the field of small deformations, the limit value for the linear viscoelastic range vary between 0.01-0.03% for the analyzed samples at both temperatures. At 37°C, the structure became flexible (lower G' values) that means that all samples are characterized by a smooth aspect and are easily to apply on skin.

For cream 2 with cinnamon extract (fig. 2b) the two dynamic modules exhibit lower values, which suggest that this cream has a soft consistency, is smoother and easier to apply on skin. This fact can be explained by the cinnamon alcoholic extract that has been introduced in the raw cream. In this case two physical effects can occur: 1) mixing two fluids with different viscosities (alcohol from extract and olive oil from the cream) and 2) solving of some ingredients from the cream, such wax and/or surfactants in the alcohol from the extract, thus decreasing the viscosity of the final product, fact confirmed by the rheological measurements. Beside these two effects also a chemical reaction can occur, especially an esterification between the OH group of the alcohol and the free acids from the olive oil used in cream formulation.

Cream 3, with thuja extract (fig. 2.c) shows an even bigger decrease of the values for the two dynamic modules, which suggests that this cream is also characterized by a soft consistency, smooth aspect and is easier to apply on the skin. The phenomenon cans also be explained by the alcohol from the thuja extract that can have one of the effects mentioned above.

The second rheological oscillatory test made for the studied samples was the scanning frequency test (fig. 3). In this case, the amplitude is maintained constant in the limits of linear viscoelastic range (γ=0.01%÷0.03% for both temperatures, the frequency varying between 0.1 ÷ 100 rad/s.

From figure 3 could be observed that G' values are higher than those for G" for all the frequencies range and for all the samples, which represent an solid type behavior for both temperatures. The dynamic modules are almost parallel and vary very little with the frequency, thus suggesting the existence of a stable tridimensional structure due to intermolecular interactions. The smaller values for the two dynamic modules at 37°C demonstrate that creams 2 and 3 are softer, smoother and could be applied better on skin. Also, the bigger values for complex viscosity for the studied samples at low frequency shows that the studied samples have a stable structure in stationary state and are easy to apply on skin. Moreover, the small values of the limit voltage at 37°C (table 3) reinforces the idea that, compared to the raw cream, those with alcoholic extracts show very good display capabilities on skin.

Experimental data obtained in this study shows that the performances for a commercial cosmetic product depends on the composition and formulation and on the ingredients used to obtained it. A secret formulation of ingredients leads to obtain a quality product that flow easily from the container and does not allow the sedimentation of solid particles during storage, is stable (shear viscosity is zero) and has a good display capacity (pseudo plastic behavior), forming a uniform film on skin.

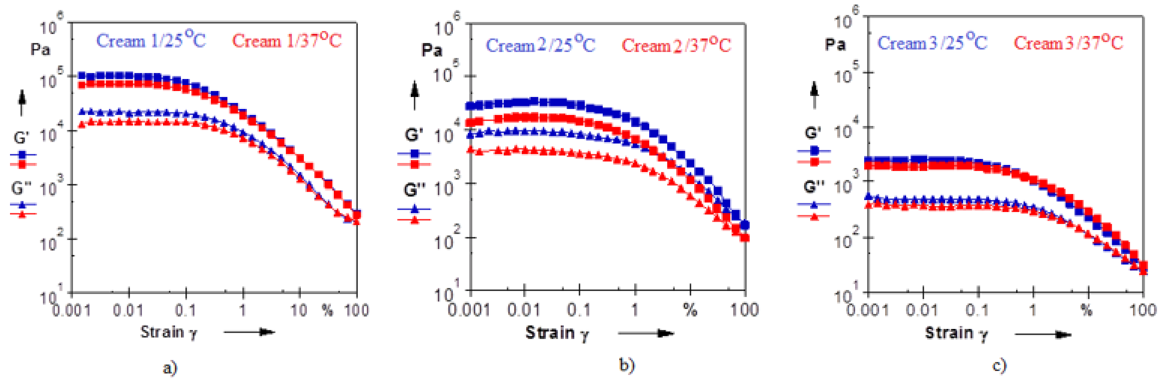

Fig. 2. Amplitude sweep test at 25°C and 37°C for the samples. a). Raw cream; b). Cinnamon extract cream; c). Thuja extract cream

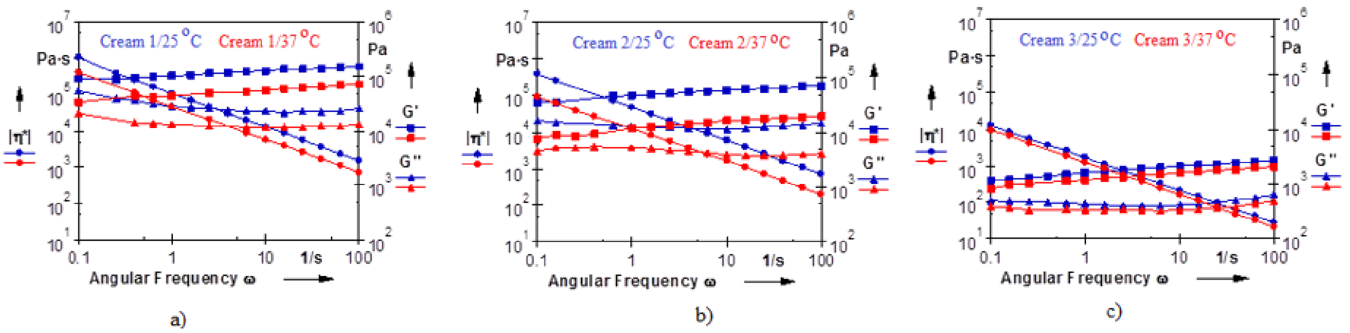

Fig. 3. Scanning frequency test for the analyzed samples at 25°C and 37°C. a) Raw cream; b) Cinnamon extract cream; c) Thuja extract cream

Table 3
R_f VALUES FOR THE TWO ALCOHOLIC EXTRACTS

No. crt.	Sample	R_f
1.	Cinnamon alcoholic extract	0.60
2.	Thuja alcoholic extract	0.54

Table 4
VALUES FOR VOLTAGE LIMIT FOR ANALYZED CREAMS AT THE TWO

Sample	Voltage limit (τ_0), Pa	
	T=25ºC	T=37ºC
Raw cream (Cream 1)	1.21	0.98
Cinnamon extract cream (Cream 2)	16.72	8.43
Thuja extract cream (Cream 3)	10.4	7.51

Conclusions

Rheological tests made at both 25°C and 37°C for the three cold creams obtained in laboratory provided information about their structural properties and stability. It was found that at 37°C, the structure is flexible for all creams analyzed (smaller values for G'), samples being characterized by a velvety appearance and easily application to the skin.

By adding alcoholic extracts of cinnamon and thuja, respectively, the values for dynamic modules decreases, suggesting that the products have a soft consistency, a smoother appearance and are easier to apply on skin.

Also, high values for complex viscosity at low frequencies shows that the studied samples have a stable structure at rest and are easily applied on skin. Moreover, small values for limit voltage at 37°C reinforces the idea that the creams with alcoholic extracts very good application behavior on skin comparing with the raw cream

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