# HAIR MASKS BASED ON KERATIN AND COLLAGEN

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The study aimed to develop and characterize some O/W emulsions, designed as nourishing hair masks. The cosmetic formulations based on collagen hydrolysate, keratin, and natural ingredients (essential and vegetable oils) were organoleptically evaluated. The pH, morphological, superficial, and rheological properties were assessed as a physicochemical background. The rheological measurements were performed at 23 and 32°C, and the shear stress versus shear rate ascending and descending rheograms were built, together with the flow profiles of viscosity as a function of shear rate. The cosmetic emulsions were stable at temperature variation and the pH values were considered physiologically acceptable for the skin, indicating that formulations can be safely applied for cosmetic purposes. Results from the optical microscopy analysis showed that all emulsions presented a creamy and non-greasy appearance. The superficial profiles, quantified through contact angle at solid/liquid interface, were specific for hydrophilic formulations. The emulsions showed pseudoplastic and thixotropic behavior, facilitating the formulations' flow and the topical application. The Power law model was used to quantify the flow properties, and the thixotropic analysis was conducted using particular descriptors, namely thixotropic area, and thixotropic index. The designed emulsions presented appropriate physicochemical properties for cosmetic applications in hair care.

Keywords: collagen/keratin-based emulsions, hair masks, physicochemical characteristics

## INTRODUCTION

Hair represents an essential component in terms of a person's physical appearance, with a high social impact on both women and men. For this reason, to make it as visually pleasing as possible, the hair is often subjected to thermal or chemical treatments affecting its structure (Tinoco *et al*., 2018).

Keratin is a protein found in the structure of the hair and is directly involved in maintaining its resistance, flexibility, and durability by ensuring a proper degree of hydration and a shiny appearance (Basit *et al*., 2018, Tinoco *et al*., 2018). Collagen, as essential protein for the human body, is also found in the connective tissue surrounding hair follicle. It contributes to the process of hair growth and regeneration by facilitating the formation of stem cells, giving birth to new hair follicles (Natsuga *et al*., 2019).

Emulsions are soft coarse dispersions intensively selected in cosmetic applications and body care (Talianu *et al*., 2019). To incorporate proteins with role in hair regeneration (keratin, collagen) into an emulsion component, they must be soluble in water and have a reduced ability to aggregate the peptides in its structure (Dănilă *et al*., 2019b). Thus, the use of protein hydrolysates in the formulation of cosmetic products is indicated due to their ability to prevent damage to the hair strand or to repair the already damaged one (Tinoco *et al*., 2018, Dănilă *et al*., 2020).

The purpose of this study consisted in the research of new hair care products in the

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form of O/W emulsions that can be used as hair masks based on keratin and collagen, but also other natural ingredients such as panthenol, vegetable oils, and essential oils.

## MATERIALS AND METHODS

### Materials

Vegetable oils (avocado oil, argan oil), emulsifiers (Varisoft emulsifier: cetearyl alcohol, behentrimonium methosulfate), floral water, panthenol, and essential oils and keratin were purchased from a local pharmacy. Type I collagen hydrolysate was obtained by acidic hydrolysis (Dănilă *et al*., 2019b).

### Preparation of the O/W Emulsions

According to Table 1, the ingredients of phase A (oils and emulsifier) and phase B (floral water, distilled water, keratin, collagen hydrolysate) were heated in a water bath in two heat-resistant Berzelius beakers, under homogenisation. When both phases reached a temperature of about 75°C, they were removed from the water bath. The content of phase A was slowly added over phase B under continuous stirring. The mixing continued for a few minutes, avoiding the aeration of the emulsions. Over the obtained composition, C phase ingredients were added and mixed for about one minute. The beaker was placed in a cold-water bath under continuous stirring for 3 minutes. In the cooled composition, the ingredients of phase D were gradually added and mixed after each one. The obtained emulsions, coded as Emulsions 1-3, were transferred through sterile containers.

Table 1. Composition of the O/W hair balm emulsions

| Phase | Ingredients (%) | Emulsion 1 | Emulsion 2 | Emulsion 3 |
|---|---|---|---|---|
| A | avocado oil (mL) | 5 | 10 | 15 |
| A | argan oil (mL) | 5 | 10 | 15 |
| A | emulsifier* (g) | 5 | 8 | 10 |
| B | floral water (mL) | 40 | 30 | 20 |
| B | distilled water (mL) | 41 | 38 | 36 |
| B | collagen hydrolisate (g) | 1 | 1 | 1 |
| B | keratin (mL) | 1 | 1 | 1 |
| C | panthenol (mL) | 1 | 1 | 1 |
| D | Cosgard preservative (mL) | 0.5 | 0.5 | 0.5 |
| D | essential oils (mL)** | 0.5 | 0.5 | 0.5 |

* Varisoft emulsifier: cetearyl alcohol, behentrimonium methosulfate; **essential oils: Eucalyptus, pine, rosemary, oregano

#### *pH Determination*

The pH of dermatocosmetic emulsions was evaluated using an inoLab pH meter.

#### *Optical Microscopy Analysis*

The morphology of the designed emulsions was carried out using a LEICA optical microscope model S8AP0, with the increased power of 20-160x.

#### *Goniometric Evaluation*

The superficial properties were performed with CAM 101 (KSV Instruments), using the *contact angle method*: liquid drop (water) was spread on a solid surface (emulsion-coated slide test), analyzing the modifications of liquid drop shape on this surface.

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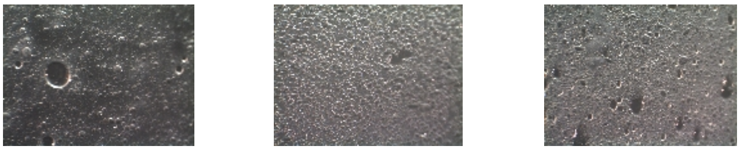
*Rheological Analysis*

The flow properties of the emulsions were performed using a rotational viscometer Multi-Visc Rheometer (Fungilab), equipped with TR 9 standard spindle, and a ThermoHaake P5 Ultrathermostat to ensure a constant temperature (23±0.1°C and 32±0.1°C). The operational conditions were previously reported (Ghica *et al*., 2016).

## RESULTS AND DISCUSSION

All emulsions were homogeneous, stable, with no phase separation, and a sweet scent, well defined by the selected ingredients. The O/W emulsions presented a pH of 5.5, compatible with the skin pH. Optical microscopy was used to study the morphology of the emulsions. The images of the samples are presented in Figure 1.



Emulsion 1 Emulsion 2 Emulsion 3

Figure 1. Optical microscopy images of O/W cosmetic hair balm emulsions

It can be noticed that all emulsions had a white aspect, with non-greasy structure. Emulsion 1 was characterized by a foam-like appearance, while the other two emulsions had creamy appearance. Differences between the microscopic images were attributed to various vegetable oils with different content in fatty acids, used as oil phases.

Contact angle values (CA°) represent a benchmark to quantify the superficial properties of the emulsions. Drops dynamic was monitored with a digital camera and the contact angle was mathematically depicted for each emulsion, as previously (Popa *et al*., 2013).

a) CA = 17.40°±2.13 b) CA=22.18°±1.08 c) CA=30.04°±1.89

Figure 2. Images of the drop shape for the W/O dermatocosmetic emulsions:
a) Emulsion 1; b) Emulsion 2; c) Emulsion 3

It can be observed that CA values increased proportionally with the oil content. For Emulsions 3 it was found the maximum value of contact angle of 30.04° which was 1.72 fold higher than Emulsion 1. Globally, the recorded CA values indicated a marked hydrophilicity of the emulsions, an important quality in their design, with direct implications for skin hydration and hair nourishing potential.

The rheograms – viscosity as a function of shear rate – were built (Figure 3) and the Power law model was used to quantify the flow behavior of the formulations:

$$\eta = m \cdot \dot{\gamma}^{-n} \qquad (1)$$

where m parameter represents the viscosity obtained for the shear rate value of $1 \cdot s^{-1}$, and n is the flow behaviour index (Dănilă *et al*., 2019a), and determined through the linearization of equation (1) by double logarithmic method (Figure 4).

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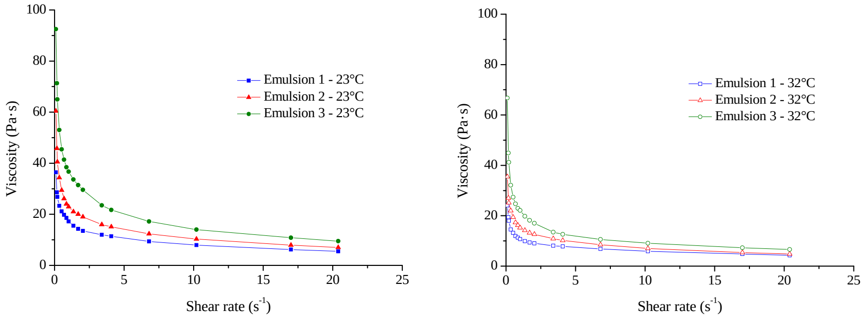
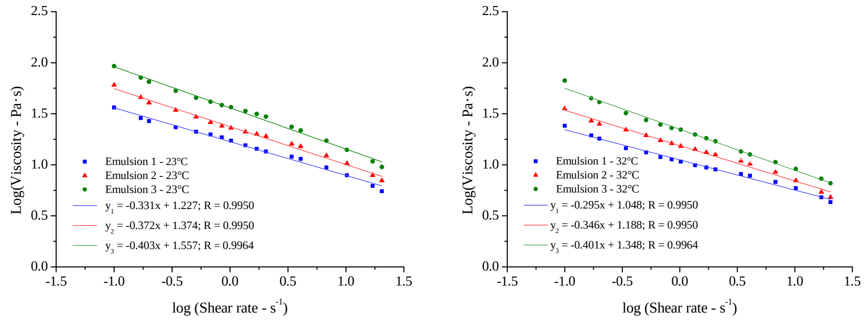



a) b)

Figure 3. Plots of viscosity versus shear rate for the Emulsions 1-3, evaluated at: a) 23°C; b) 32°C




a) b)

Figure 4. Log-log plots of viscosity versus shear rate, for the Emulsions 1-3 evaluated at: a) 23°C; b) 32°C

Analyzing Figure 3a-b, the emulsions viscosity decreased at shear rate increase, showing a pseudoplastic behavior at both working temperatures, aspect which was well defined through the log-log plots presented in Figure 4a-b. The pseudoplastic behavior is a requirement for the dermatocosmetic emulsions, both conditioning aspect and spreading as a continuous film on the hair surface. The parameters n and m, specific to the Power law model, are listed in Tables 2 and 3 for both working temperatures.

Table 2. Values for the determination coefficient and parameter specific to the Power law model, and the thixotropic descriptors determined at 23°C

| Formulation | R | m | n | $S_{asc}$ (Pa·s$^{-1}$) | $S_{thix}$ (Pa·s$^{-1}$) | $T_{hyst\%}$ (%) |
|---|---|---|---|---|---|---|
| Emulsion 1 | 0.9950 | 16.869 | 0.331 | 1507.694 | 127.699 | 8.47 |
| Emulsion 2 | 0.9960 | 23.664 | 0.372 | 1951.959 | 201.807 | 10.34 |
| Emulsion 3 | 0.9960 | 36.107 | 0.403 | 2697.663 | 317.649 | 11.77 |

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Table 3. Values for the determination coefficient and parameter specific to the Power law model, and the thixotropic descriptors determined at 32°C

| Formulation | R | m | n | $S_{asc}$ ($Pa \cdot s^{-1}$) | $S_{thix}$ ($Pa \cdot s^{-1}$) | $T_{hyst\%}$ (%) |
|---|---|---|---|---|---|---|
| Emulsion 1 | 0.9950 | 11.168 | 0.295 | 1129.760 | 88.713 | 7.85 |
| Emulsion 2 | 0.9950 | 15.417 | 0.346 | 1332.160 | 126.726 | 9.51 |
| Emulsion 3 | 0.9964 | 22.284 | 0.401 | 1756.404 | 188.342 | 10.31 |

The experimental data well fitted the Power law model, and correlation coefficients had high values, up to 0.9960 at 23°C and 0.9964 at 32°C. The most fluid system was Emulsion 1, the m parameter having the lowest value. In the case of Emulsion 2, it was recorded an intermediate value of the m parameter, being correlated with a medium viscosity. The maximum values for the m parameter were recorded for Emulsion 3. The forward and backward rheograms – shear stress as a function of shear rate – were also recorded (Figure 5) and the thixotropic behavior was quantified through the thixotropy area ($S_{thix}$) and thixotropy index ($T_{hyst\%}$). Thixotropic systems are those with $T_{hyst\%}$ values greater than 5% (Dănilă *et al.*, 2019b), and can be depicted from Table 2 and Table 3, where $S_{asc}$, $S_{thix}$, and $T_{hyst\%}$ were presented for both working temperatures alike.

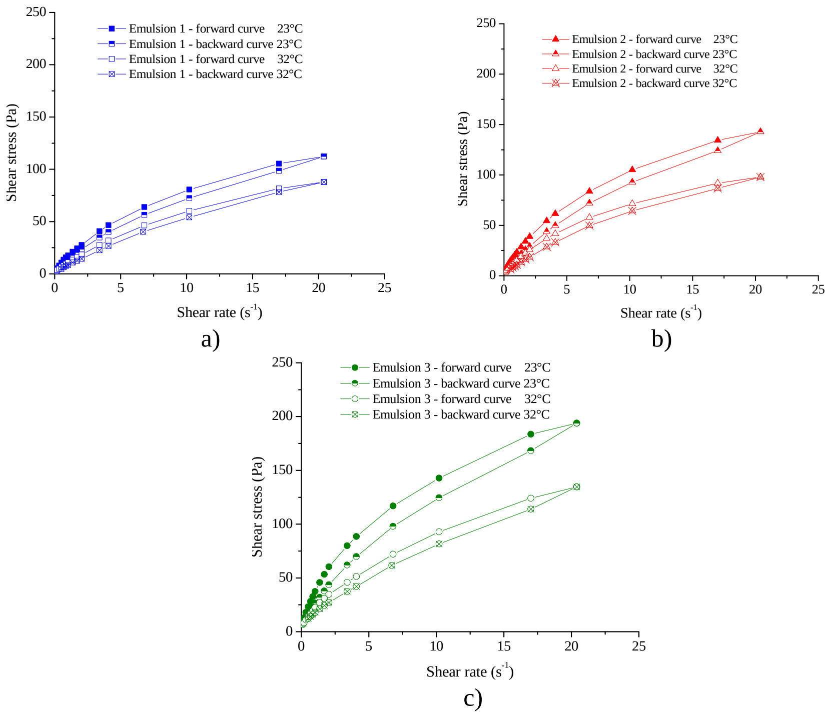


Figure 5. Forward and backward rheograms, shear stress versus shear rate, evaluated at 23°C and 32°C, for: a) Emulsion 1; b) Emulsion 2; c) Emulsion 3

Figure 4a-c indicates that the backward curve is positioned under the forward curve. Thus, for the same shear rate, the shear stress for the backward curve is smaller. The thixotropic character is defined by the thixotropy index higher than 5% for both

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temperatures. The thixotropic behavior is also a quality requirement targeted in emulsions design, allowing the transition of a viscous product into a more fluid one, easy to spread. Another influencing factor is related to the temperature. Thus, for temperature increase, it can be noticed that m parameter decreases for all emulsions, about 1.5-1.6 times, and a decrease of thixotropic parameters by about 1.4-1.68 times.

## CONCLUSIONS

All emulsions obtained were stable and the pH values corresponded to the skin physiological one, indicating that hair masks can be safely applied to the skin and hair. The optical microscopy analysis shows that all emulsions presented a creamy and foamy appearance with a non-greasy structure. The superficial profiles, quantified through contact angle, indicated a high degree of hydrophilicity. The emulsions showed a pseudoplastic and thixotropic behavior, facilitating the formulations flow and the application as hair balms. It can be appreciated that the designed emulsions presented adequate physicochemical properties for a cosmetic purpose, being considered suitable hair balm formulations for hair care.

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