Emulsions are defined as disperse systems consisting of two immiscible liquids which are stabilized by the addition of an emulsifying agent, called emulsifier (also known as emulgent) [1]. Two liquids can form different types of emulsions: oil and water can form, firstly, an oil-in-water emulsion (O/W), wherein water is the dispersed phase and oil is the external phase. Multiple emulsions are also possible, including a water-in-oil-in-water (W/O/W) emulsion and an oil-in-water-in-oil (O/W/O) emulsion [2]. Due to their applications in medicine and cosmetics the formulation of O/W emulsions gained recently an increased interest in scientific papers [3].

Skin care cosmetics and emulsions are closely related. The recent emulsion technology has advanced the quality of cosmetics [4]. Additional value can be conferred to these formulations by including active ingredients with specific cosmetic effects [5]. Particularly advantageous cosmetic emulsion preparations are obtained when natural proteins are used as active ingredients. Collagen is one of the natural proteins used in cosmetic preparations due to its biodegradability, availability and biocompatibility [6]. Collagen is the most abundant protein of the human body, is naturally present in the connective tissues and makes the dermis resistant, supple and elastic. In particular, it is an effective natural humectant as result of the extensive, ordered hydration network that surrounds the molecule, in combination with its high substantivity to the skin surface [7].

In the last years the interest in the pharmaceutical and cosmetic industry to use plant extracts for various fields of application was substantially growing, due to the adverse effects generated by synthetic ingredients [8]. Essential oils have been used to improve the health and physical appearance of the human body, and to protect the skin against the environment damage since ancient times [9]. Essential oils are complex mixtures containing dozens of substances of various chemical composition at different concentrations [10]. They are characterized by the compounds present in highest concentration which determine their flavour, fragrance and biological properties [11]. Biological properties of essential oils such as antibacterial, antifungal and antioxidant activity make essential oils suitable for use in cosmetics [12, 13].

Trends in the field of cosmetics target cosmeceuticals products which are hybrid products, intended to enhance the beauty through ingredients that provide additional health-related functions or benefits [14]. Dermocosmetics, performance cosmetics, functional cosmetics, dermaceuticals, active cosmetics and nutricosmetics are other terms used for cosmeceuticals [15]. Decorative cosmetics represent an important sector of cosmetics industry that adopted this trend [16]. Make-up products are no longer used just for decorative purposes but also for therapeutic properties. In this respect, cream foundation represent a good example, which become a dermocosmetic product, that not only have the ability to camouflage small skin imperfections but also have beneficial properties on skin such as moisture, sunscreen, and moreover is noncomedogenic and does not irritate skin compared to conventional products [17]. Recently CC-cream (color control or color correcting) and BB-cream (blemish balm or beauty balm) were developed, which are multitasking products correcting visible skin

The aim of this study was to formulate and evaluate two types of O/W emulsions based on collagen and other natural ingredients that can be used as color correcting (CC-cream) and cream foundation. Both types of emulsions obtained are stable at different temperatures and the pH values of emulsions correspond to the natural pH of the skin, indicating that emulsions can be safely applied to the skin. Results from the optical microscopy analysis show that all emulsions present foam-like appearance. The rheological properties of emulsions were studied and it was proved that all emulsions present a non-Newtonian pseudoplastic behaviour and thixotropic characteristics at two operating temperatures (24 and 33°C). It can be concluded that all emulsions can be used as a natural alternative to a CC-cream or a cream foundation. Further microbiological tests and clinical trials are necessary for the obtained emulsions.

Keywords: collagen, CC-cream, cream foundation, rheological behaviour

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imperfections, like a foundation, and also add other benefits by treating the skin like a traditional cream product [18].

Considering these aspects, the aim of this study was to prepare O/W emulsions, usable as CC-cream and cream foundation, based on naturals ingredients such as vegetable oils and butters, hydrolyzed collagen and essential oils, and to evaluate the rheological properties of these emulsions.

Experimental part
Materials and methods
Collagen hydrolysate was obtained by acid hydrolysis of wet white leather wastes at 125°C during 8 h according to the technology previously described [19].

The essential oils, lavender (Lavandula angustifolia), rosmarinus (Rosmarinus officinalis), cistus (Cistus ladaniferus) and pinus (Pinus sylvestris), were obtained in Department of Medicinal and Aromatic Plants, Faculty of Agriculture, Mustafa Kemal University, Hatay, Turkey from wild plants from the province of Hatay in the period of their blooming.

Vegetable oils (almond oil, rice oil, avocado oil), mango butter, emulsifiers (glyceryl stearate, cetearyl olivate, sorbitan olivate), mineral pigments brown, yellow and pearly beige (iron oxides: CI 77491, CI 77492, CI 77499, CI 77019, CI 77891), floral waters (chamomile and lavender), glycerin, xanthan gum, rice powder, panthenol, preservative cosgard (benzyl alcohol, salicylic acid, glycerin, sorbic acid) and titanium oxide were purchased from https://www.elemental.eu/ro/.

Formulation of O/W emulsions
The chemical composition for both types of emulsions, CC-cream (color correcting cream) and cream foundation, is presented in table 1.

The ingredients of phase A and phase B are heated in a water bath in two heat-resistant Berzelius beakers, periodically homogenizing the composition. When both phases reach a temperature of about 70-75°C, they are removed from the water bath; then, the content of phase B is slowly added over phase A by mixing constantly. The mixing continued for a few minutes, avoiding as much as possible the aeration of the emulsion. The ingredients from phase C were then added to the composition and mixed for a few minutes. The beaker was placed in a cold water glass and the composition was continuously stirred. In the cooled composition, the ingredients of phase D are added and mixed slowly. The obtained emulsion is transferred to a sterile container.

Characterization of O/W emulsion
Physical characterization, stability and pH
For the obtained emulsions the organoleptic (color, appearance, smell) and physical (phase separation) properties were optically observed. pH was evaluated using a inoLab pH meter. For all obtained emulsions, stability tests were performed at different temperatures: room temperature (20-23°C), 4-5°C (refrigerator) and 40°C (incubator).

Optical microscopy analysis was performed using a LEICA optical microscope model S8AP0, with Increase Power: 20-160x.

Rheological analysis was performed with a rotational viscometer Multi Visc-Rheometer (Fungilab) equipped with a TR 10 standard spindle and a ThermoHaake P5 Ultrathermostat to maintain constant the sample temperature during the measurements. The operational conditions were detailed in our previous studies [20]. The creams flow ability was determined at 24 and 33°C. For each cream a rotational speed over the range from 0.3 to 60 rpm was applied at both temperatures, corresponding to a shear rate between 0.08-16.8 s⁻¹. The rheological data were fitted according to Power law model expressed as viscosity as a function of shear rate (eq. 1):

\[ \eta = m \cdot \gamma^{-n} \]  

where, m and n are parameters correlated with the formulation factors of the designed creams and determined by linearization of eq. (1) by double logarithmic method [21]. It can be appreciated that the value of m parameter corresponds to the viscosity obtained for the shear rate value of 1·s⁻¹. To assess the thixotropic behaviour of the cosmetic cream stested, the up- and down-curves shear stress as a function of shear rate were built. The thixotropic character was quantified by two parameters [22].

1) Thixotropy area (Sₜₕᵢₓ) defined as the area between the up- and down-curve. The up-curve represents the area bounded by the ascending curve (Sₚₛₜₐᵢₗ) and is associated with the manipulation time of the cosmetic product when it is exposed to the skin. The down-curve corresponds to

| Phase | Ingredients | CC-cream | Cream foundation |
|-------|-------------|----------|------------------|
| A     | almond oil, mL | 20       | 15               |
| A     | mango butter, g | 10       | 15               |
| A     | titanium oxide, g | -     | 15               |
| A     | rice oil, mL | -       | 20               |
| A     | avocado oil, mL | -     | 10               |
| A     | emulsifier, g | 5         | 6                |
| A     | brown pigment, g | 0.05 | 0.02             |
| A     | yellow pigment, g | 0.1   | 0.05             |
| A     | pearly beige pigment, g | - | 0.05             |
| B     | chamomile water, mL | 60 | -                |
| B     | lavender water, mL | - | 36               |
| B     | glycerin, mL | 1         | -                |
| B     | collagen, g | 1.15      | 1.23             |
| C     | xanthan gum, g | 0.2       | 0.1              |
| C     | rice powder, g | 0.5       | 1                |
| C     | panthenol, mL | 1         | 1                |
| D     | cosgard preservative, mL | 0.5 | 0.5              |
| D     | essential oil, mL ** | 0.05 | 0.05             |

* CC-cream: glyceryl stearate; cream foundation: cetearyl olivate, sorbitan olivate
** CC-cream: 1-rosmanin, 2-lavender; cream foundation: 1-cistus, 2-pinus.
the descending area (S\text{desc}) and it refers to the restoration of the initial structure of the shear formulation.

2) Thixotropy index (T\text{hyst}%) represents the relative thixotropy area and is computed as a percentage of the rheodistruction area caused by agitation at the maximum rotational speed, reported to the ascending area (eq. 2). Thixotropic systems are those with T\text{hyst}% values greater than 5%.

\[
T_{\text{hyst}[]} = \left( \frac{S_{\text{asc}} - S_{\text{desc}}}{S_{\text{asc}}} \right) \times 100
\] (2)

Results and discussions

Physical characterization, stability and pH

The emulsions obtained are homogeneous and present different colors, as shown in figure 1, depending on the quantity of pigments used.

Rheological analysis

Pseudoplastic behaviour

The results of the rheological experiments obtained at two operating temperatures (24 and 33°C) for the designed cosmetic emulsions, are presented in figure 4a-b.

From figure 4a-b the influence of the composition on the viscosity of the formulations tested at both operating temperatures can be noticed. Thus, the CC-cream 1 is more viscous than the CC-cream 2, respectively the cream foundation 1 has a higher viscosity compared to the cream foundation 2.

The rheological patterns recorded in figure 4a-b also show the influence of the temperature on the tested emulsions viscosity, which decreases with temperature increase due to the fluidization of the system.

All emulsions have a pleasant, creamy, moisturized appearance and a smell specific to the essential oils in the composition. No phase separation was observed shortly after preparation. On the skin the CC-creams present a light coverage, while the cream foundation present a medium coverage due to titanium oxide and the combination of the three pigments used. Titanium oxide also adds sun protection factor (SPF) to the cream foundation formulations.

Following the stability tests, all emulsions were found to be stable at all three working temperatures.

The pH values of the obtained emulsions are shown in table 2.

### Table 2

|            | CC-cream 1 | CC-cream 2 | Cream foundation 1 | Cream foundation 2 |
|------------|------------|------------|--------------------|--------------------|
| pH         | 6.4        | 6          | 6.1                | 6.3                |

The natural pH of the skin varies between 4.5 - 6.5 and this interval is considered to be optimal for cosmetic products that are indirect contact with the skin [5]. The values obtained for the emulsions are in this interval, indicating that emulsions can be safely applied on the skin.

Optical microscopy analysis results are presented in figures 2 and 3.

From the optical microscopy images, it can be seen that all emulsions have foam-like appearance, even if slightly aerated in the case of cream foundation due to the titanium oxide form the composition. The size of the pigments incorporated in emulsions is of hundreds of micrometers (200-500µm), due to the fact that during the process of production, heat tend to form aggregates of the primary pigment particles which are then closely attached and become very difficult to separate [23].
All rheograms show that the viscosity of the tested systems decreases with shear rate increase at both operating temperatures, indicating a pseudoplastic non-Newtonian behaviour with shear thinning of the emulsions.

For the quantification of the pseudoplastic behaviour, the Power law rheological model that express the relationship between viscosity and shear rate was applied (eq. 1). The values of the rheological parameters, m and n, and the determination coefficient R² specific to the above model are listed in Table 3 for the formulations tested at 24°C and in Table 4 for the formulations analyzed at 33 °C, respectively.

For the formulations tested, values of determination coefficient R² between 0.9953 and 0.9992 are recorded, indicating that the experimental data verify this rheological model.

For the emulsions analyzed at the two operating temperatures, it is observed that at increasing temperature the rheological parameter m recorded a decrease of about 1.60-1.85 times.

For CC-cream 1 a value of the parameter m higher than 1.13 times is recorded compared to CC-cream 2 tested at 24°C, and 1.22 times higher at 33°C. For the cream foundation 1, a value of the parameter m 1.49 times higher is recorded compared to the cream foundation 2 tested at 24°C, and 1.38 times higher at the temperature of 33°C.

Thixotropic behaviour

The study of thixotropic behaviour is achieved by obtaining the rheogram corresponding to the up-curve (ascending curve) at increasing shear rate, and down-curve (descending curve) recorded at decreasing shear rate. For the same shear rate, the points on the return curves correspond to shear stresses lower than those on the up-curves. The thixotropy phenomenon is characteristic to plastic and pseudoplastic flow dispersion systems [22].

The up-and down-curves shear stress as a function of shear rate are illustrated in Figures 5 and 6 for the formulations analyzed at 24 and 33°C.

The rheograms presented in Figures 5 and 6 show that all the tested formulations have a thixotropic character at both temperatures, the descending curve being placed under the ascending curve.

**Table 3**

THE VALUES OF THE RHEOLOGICAL PARAMETERS m AND n AND THE DETERMINATION COEFFICIENT R² SPECIFIC TO THE POWER LAW MODEL APPLIED TO THE EMULSIONS ANALYZED AT 24°C

| Emulsion        | m    | n    | R²    |
|-----------------|------|------|-------|
| CC-cream 1      | 61.142 | 0.537 | 0.9696 |
| CC-cream 2      | 23.811 | 0.524 | 0.9953 |
| Cream foundation 1 | 64.530 | 0.501 | 0.9959 |
| Cream foundation 2 | 43.107 | 0.618 | 0.9974 |

**Table 4**

THE VALUES OF THE RHEOLOGICAL PARAMETERS m AND n AND THE DETERMINATION COEFFICIENT R² SPECIFIC TO THE POWER LAW MODEL APPLIED TO THE EMULSIONS ANALYZED AT 33°C

| Emulsion        | m    | n    | R²    |
|-----------------|------|------|-------|
| CC-cream 1      | 35.401 | 0.478 | 0.9984 |
| CC-cream 2      | 28.986 | 0.479 | 0.9988 |
| Cream foundation 1 | 37.729 | 0.582 | 0.9992 |
| Cream foundation 2 | 26.974 | 0.604 | 0.9972 |

**Tabel 5**

THE THIXOTROPIC PARAMETER VALUES DETERMINED FOR THE EMULSIONS ANALYZED AT 24°C

| Emulsion        | S_{max} (Pa·s) | S_{max} (Pa·s) | S_{max} (Pa·s) | T_{thix} (%)
|-----------------|----------------|----------------|----------------|-----------|
| CC-cream 1      | 2631.182       | 2333.290       | 317.382        | 11.99     |
| CC-cream 2      | 2283.766       | 2024.327       | 261.439        | 11.43     |
| Cream foundation 1 | 2677.723 | 2341.49 | 336.233        | 12.55     |
| Cream foundation 2 | 1946.314 | 1732.568 | 213.746        | 10.98     |
The values corresponding to the ascending area, descending area, thixotropy area and thixotropy index are given in tables 5 and 6 for the formulations analyzed at 24 and 33°C.

The values of the thixotropy index listed in tables 5 and 6 are superior to 5%, indicating that the designed cosmetic formulations are thixotropic at both operating temperatures. It is noted that the increase of temperature decreases the values recorded for ascending, descending and thixotropy areas.

**Conclusions**

Both types of emulsions (CC-cream and cream foundation) obtained are stable at different temperatures and the value obtained for the pH of the emulsions correspond to the natural pH of the skin, indicating that emulsions can be safely applied to the skin.

Results of the optical microscopy analysis shows that all emulsions have foam-like appearance and the cream foundation is slightly aerated.

The emulsions tested present a pseudoplastic non-Newtonian behaviour with shear thinning at both operating temperatures. The pseudoplastic behaviour of the designed cosmetic formulations was quantified through the rheological model of the Power law - viscosity as a function of shear rate.

Pseudoplastic behaviour is a desirable requirement for systems with topical application both in terms of conditioning and spread on the skin and the formation of a continuous film at the application site. At high shearing speeds, such as when dispensing from the conditioning vessel, the material will flow rapidly by facilitating administration, while at low shear rates, such as the product being spread on the skin, the material will adopt a high consistency by recovering the original rheological properties possessed before administration.

Thixotropic analysis was performed using specific descriptors such as thixotropic area and thixotropy index. The thixotropic nature is also a quality parameter sought in order to convert an initially viscous emulsion in a thin product, easy to spread on the skin.

Both flow parameters and thixotropy characteristics determined are strongly influenced by the composition of the cosmetic formulations and the operating temperature.

It can be concluded that all the emulsions prepared are stable, safe for the skin and present adequate rheological properties, so it can be used as a natural alternative for a CC-cream or a cream foundation. In the future microbiological tests and clinical trials are necessary for the obtained emulsions.

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