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Polymer-Stabilized Emulsion Systems: Structural Characteristics and Physical Stability Evaluation

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ABSTRACT

In the course of investigation of the effects of polymeric emulsifier (Simulgel®A) on the structural characteristics and physical stability (during storage time) of semisolid o/w emulsion systems with different emulsifier concentrations, dispersed droplets of an internal oil phase (4.5–11.5 μm size) were discovered. The degree of dispersity was increased along with increasing polymeric emulsifier concentration (from 1 to 5% m/m), which was shown by microscopic analysis. Experiments were also carried out using pH, electrical conductivity, and rheological (rotational and oscillatory) measurements. Emulsion samples expressed a mild acid value acceptable for topical preparations during a 6-month period. Electrical conductivity of fresh samples ranged from 0.423 to 2.009 mS/cm and after a 6-month period this slightly increased to 0.663–2.890 mS/cm. All emulsion samples revealed plastic flow behavior in fresh state, with changes in flow pattern during storage time. Viscoelastic properties defined by the oscillatory rheometry results were in good correlation with parameters of rotational rheometry and degree of internal phase dispersity. High yield stress values (flow tests) and favorable low values of damping factor (oscillatory studies) both indicated good internal structuring and long-term stability of sample containing 3% m/m of polymeric emulsifier.

Key Words: Polymeric emulsifier; O/W emulsions; Rheological parameters; Rotational and oscillatory rheometry; Optical microscopy; Aging; Physical stability.

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INTRODUCTION

Traditionally, emulsion systems are very popular formulations for topical delivery (pharmaceutical and cosmetic). Since the structure of these systems is responsible for its physical and sensorial properties, investigations of systems structure are essential.

In most topical pharmaceutical and cosmetic formulations, primary emulsifiers are low molecular weight surfactants. The use of polymeric emulsifiers (associative thickeners) has been recently suggested as a nonirritant alternative to low molecular weight surfactants.[1,2]

Due to their large molecules, polymeric emulsifiers do not penetrate the skin nor do they enhance an unwanted penetration of other formulation compounds. Thanks to their excellent emulsifying and thickening properties they also fulfill the need of industry to lower low molecular weight emulsifier concentration without any impact on the stability or flexibility of formulation.[2,3]

Liquid dispersion polymers (LDPs) recently have been used for emulsions stabilization. The system (LDPs) consists of a polymer phase, a carrier phase (carrier oil), and an activator. The polymer phase can be of anionic or cationic nature. The carrier oil can be a mineral oil, cosmetic ester, or natural oil. The activator functions in the same way as the emulsifier. The emulsifier is nonionic with a high HLB. The activator enables water molecules to move through the small polymer particles by osmosis and allows them to swell.[3]

Polymeric emulsifier Simulgel®A (INCI: Ammonium polyacrylate/isohexadecane/PEG-40 castor oil) is a new polymer based on inverse latex technology with rapid gelling action and can be used at room temperature. Neither neutralization nor preswelling operations are required, making it very safe for use in production processes. Just by adding water to Simulgel A, the emulsifier inverts and the polymeric network expands instantly to form stabile gel in a few seconds. These special properties are above and beyond its thickening activity, common to all polyacrylates.[4]

Formulations containing the polymeric emulsifier have acceptable sensory properties (good skin feel, low degree of stickiness and/or tackiness) common to so-called "cream gels." They differ greatly from the gelatin-like appearance, often achieved in formulations with the traditional combination of surfactant emulsifier and polymeric thickener. A significant advantage of such preparations is the ability to provide the "right" rheology in personal care products, which plays an important role in physical stability and correlates to the performance expected by the consumer. For example, the flow and the feel of moisturizing and hydrating body lotion is expected to be light and fast breaking; the lotion should spread easily and be absorbed quickly.[5]

Previous studies examining the model emulsions containing 3% m/m of this polymeric emulsifier with different ratio of oil phase (10–30% m/m) revealed good macroscopic characteristics accompanied with remarkable stability within a 2-month testing period.[6]

The aim of this study was to evaluate structural characteristics and physical stability of semisolid o/w emulsion systems containing polymeric emulsifier (at different concentrations) by means of pH and electrical conductivity measurements, rheology, (rotational and oscillatory rheometry), and microscopic analysis (optical light microscopy).

EXPERIMENTAL

Materials

Polyacrylate polymeric emulsifier, Simulgel A (kindly provided by Seppic, France) was used as emulsifying agent in concentration of 1, 3, and 5% m/m respectively. Medium-chain triglycerides (Mygliol 812, BP grade) in concentration of 30% m/m and double distilled water were used as ingredients for all samples. The composition of test emulsion samples is listed in Table 1.

Preparation of Emulsions

All the samples were prepared at room temperature (20 ± 2°C) by direct method: the polymeric emulsifier was dispersed into the water phase under

Table 1. Composition and labels of test emulsion samples.

	Sample label		
Ingredients (% m/m)	E1	E2	E3
Medium-chain tryglicerides	30.0	30.0	30.0
Simulgel®A	1.0	3.0	5.0
Purified water ad	100.0	100.0	100.0

turbulent agitation, during 10-minute stirring period, until a homogenous gel was obtained. After that the oil phase was progressively introduced while stirring was maintained for another 15 min. A laboratory mixer (Heidolph RZR 2020, Germany) at 1050 rpm was used for mixing operations. After the preparation emulsions were placed into appropriate plastic opaque containers, tightly closed and stored at room temperature (20 ± 2°C).

Testing Methods

The testing methods were performed for the first time using fresh (48 hours old) samples and for another three tests in 1-, 2- and 6-month periods, respectively.

Macroscopic Behavior

The emulsions were observed for consistency, color, shine, homogeneity, and eventually creaming or phase separation during storage.

pH Measurement

Measurements of the pH values were carried out directly in prepared samples by pH meter Hanna Instruments INC 8417.

Electrical Conductivity

Measurement of electrical conductivity was performed directly in prepared samples in order to obtain emulsion type and structural changes during storage using conductometer CDM 230 (Radiometer, Copenhagen, Denmark). Before the measurement, the conductometer was calibrated with 0.01 M KCl solution at temperature (20 ± 2°C).

Rheological Measurements

Rheological measurements were performed using rotational and oscillatory rheometer (Rheolab MC 120, Paar Physica, Stuttgart, Germany) coupled with the cone and plate measuring device MK 22 (radius 25 mm, 1° angle) for rotational and MK 24 (radius 37.5 mm, 1° angle) for oscillatory measurements. The CSR (controlled shear rate) procedure was selected for flow curve evaluation. Continuous (rotational) flow tests were performed by increasing a shear rate from 0 to 200 s^{-1} and back to 0, each stage lasting 200 s.

Oscillatory (dynamic) measurements were performed in order to determine linear viscoelastic region of the samples (amplitude sweep). The investigations were carried out at constant frequency of 1 Hz and amplitude sweep ramp from 0.6 to 100%. A frequency sweep ramp from 0.1–10 Hz was performed at the constant strain of 10%, which was within the previously determined linear viscoelastic region for all the samples. Yield stress value and minimal apparent viscosity for characterization of the samples were used in rotational, while storage (G') and loss (G'') modulus alongside with damping factor ($\tan \delta$) were used in oscillatory measurements.

Microscopy

The optical microscope Olympus, (BX50F4), connected to a video camera (Sony) was used for evaluation of microstructure of the tested emulsion samples. A small amount of each batch of prepared fresh sample was placed in a separated vial in order to be kept exactly in the same condition as the test emulsion samples. For the purpose of the microscopic analysis, each vial was opened and fully mixed. After dilution 1:1 with distilled water, measurements of 500 particles per sample were performed to obtain mean droplet diameter and standard deviation. Measurements were repeated over storage time for all the samples.

Statistical Evaluation

Student *t*-test for comparative studies with significance level of 0.05 was used.

RESULTS AND DISCUSSION

Obtained emulsions were white, smooth, glossy, homogeneous, of semisolid consistency, without a sticky/tacky skin feel, and were breaking diffently on the skin providing a fresh sensation. Consistency of prepared emulsions depended on emulsifier concentration and varied from softer (for sample E1) to thicker (for sample E3). During storage time changes in macroscopic behavior were observed.

Sample E1 exhibited significant macrosopic change in consistency and became much softer after a 2-month period. Color and shine, together with a pleasant feel during application were unchanged.

Stability of sample E2 during storage time was maintained and no significant changes were notified.

In sample E3 an appearance of sticky/tacky feel and emulsion break during application was observed after a 6-month period.

The pH values (Table 2) were in range 5–7, indicating that all samples expressed a mild acid value acceptable for topical preparations. Changes in pH value during storage time could be atributed to ionization of hydrophylic polymer chains in continuous phase, which had influenced the values of electrical conductivity (Table 2).

Decrease in electrical conductivity during storage time has been already observed in systems stabilized by polymeric emulsifier and was attributed to structuration of the polymer chains in continuous phase.[7]

The flow data of the test emulsion samples are shown in Figs. 1–2 and Table 3.

All the fresh samples revealed the nonNewtonian, shear-thinning plastic flow behavior described in basic rheological literature,[8] without significant thixotropy (Fig. 1).

Shear-thinning behavior is a desirable property of creams, since they should be "thin" during application and "thick" otherwise.[9]

Flow pattern of all samples was very similar in fresh state and within a 3-month period. It is noticeable from Fig. 2 that sample E3 showed a dramatically different pattern on longer storage. Considerably larger thixotropy at this stage indicated the presence of structure that is more susceptibile to break down under shear than in the other samples.

Table 2. The pH and electrical conductivity values of test emulsion samples.

	pH value				Electrical conductivity (mS/cm)			
Sample label	After 48 h	After 1 month	After 2 months	After 6 months	After 48 h	After 1 month	After 2 months	After 6 months
E1	6.67	6.03	6.08	5.66	0.423	0.316	0.267	0.663
E2	6.21	6.19	6.06	5.82	1.234	0.803	0.635	1.860
E3	5.98	5.99	6.04	5.71	2.009	1.297	0.667	2.890

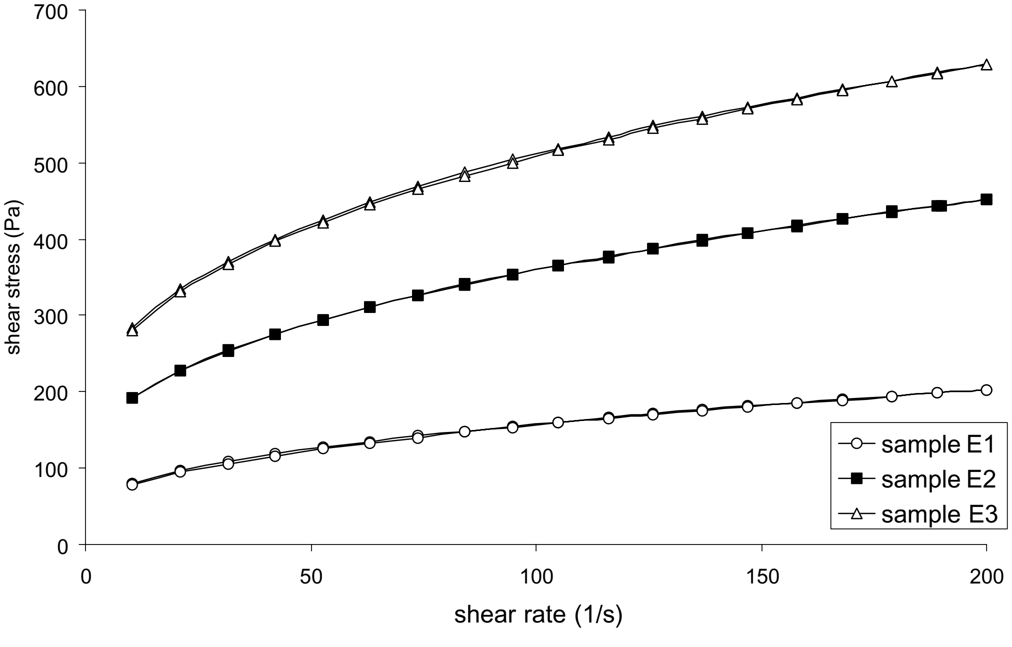

Figure 1. Flow curves for the fresh emulsion samples E1–E3 (48 hours after preparation).

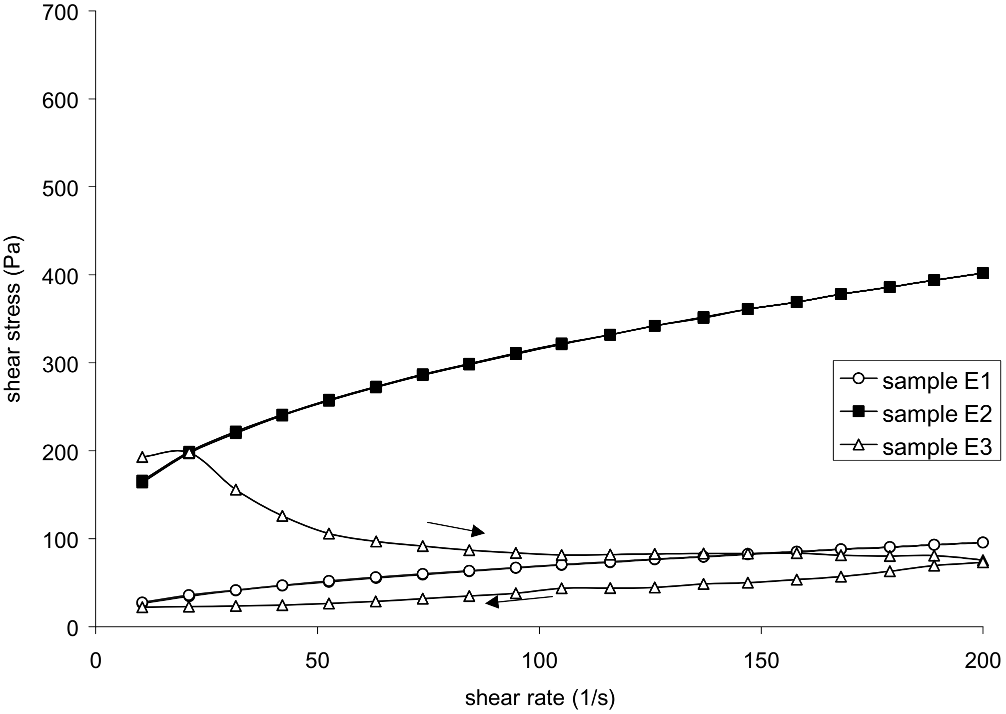

Figure 2. Flow curves for the emulsion samples E1–E3 (6 months after preparation).

Table 3. Yield stress values of test emulsion samples ($N = 3$).

	Yield point value τ_γ (Pa)			
Sample label	After 48 h	After 1 month	After 2 months	After 6 months
E1	36.68 ± 7.64	33.32 ± 1.67	11.92 ± 2.36	9.04 ± 3.36
E2	86.97 ± 4.35	80.89 ± 3.86	83.07 ± 5.69	75.41 ± 4.89
E3	109.95 ± 6.60	103.14 ± 5.54	121.33 ± 4.85	/

The stress yield and apparent viscosity values, as characteristics of plastic systems, were related to emulsifier concentration (Table 3, Fig. 3).

A possible reason for this phenomenon lies in the fact that stronger gel structure around dispersed oil drops had caused mixing and overlapping i.e., interaction of polymer chains that created new secondary bounds. Higher concentration of emulsifier, as expected, formed stronger gel structure of continuous phase accomplished by yield stress and viscosity increase.[7] The magnitude of yield stress relates to the strength of interparticle interaction of three-dimensional network microstructure in creams, while minimal apparent viscosity is an indicator of spreadability upon topical application.[10]

Trying different mathematical models, the ascendent curves were analyzed using data analysis software,[11] provided with measuring equipment. The Bingham, Hershely-Bulkey, and Casson mathematical models describing the viscoplastic fluids were selected. The best fitting ($R > 0.9999$) seemed to be the Hershel-Bulkey model:

$$\tau = \tau_0 + K\gamma^n$$

where τ is shear stress, τ_0 is yield stress (yield value), K is the consistency or the Hershel-Bulkey coefficient, γ is shear rate, and n is power law exponent or rate index for pseudoplastic fluids ($n < 1$).

Yield stress values were calculated using this regression mathematical model, while the values of minimal apparent viscosity were extrapolated from controlled rate flow curves.

The fitted K and p values for the Hershel-Bulkey model are listed in Table 4.

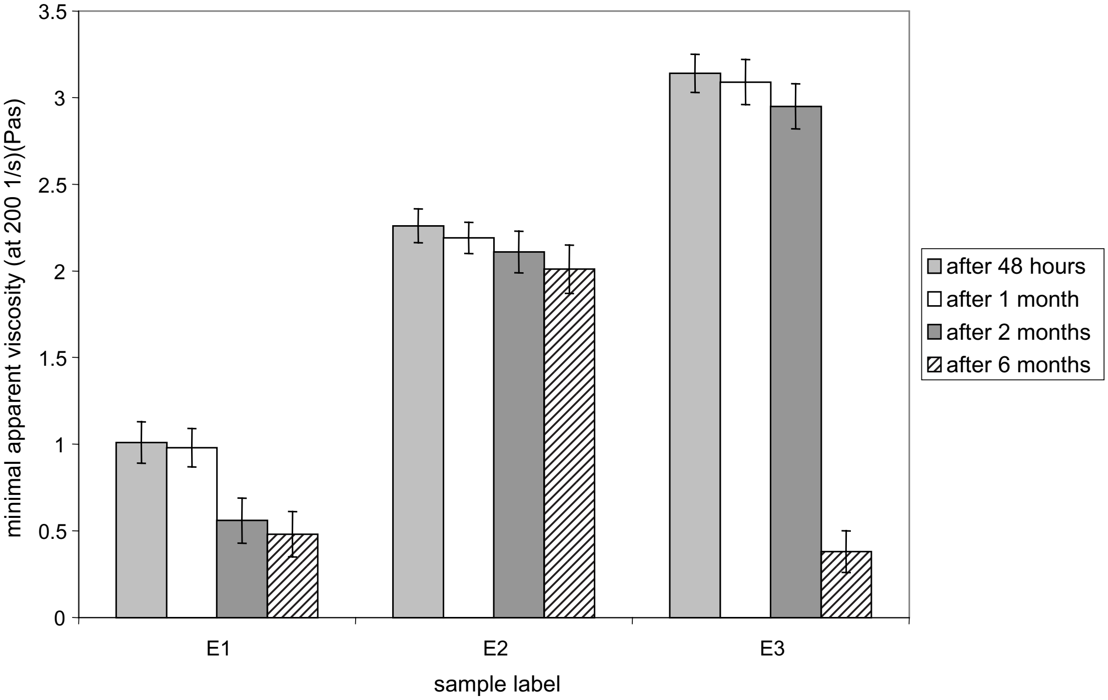

Figure 3. Minimal apparent viscosity (at $200\,s^{-1}$) of the test emulsion samples.

Table 4. The fitted parameters *K* and *p* for the Hershel-Bulkey model, during testing period.

	K				*p*			
Sample label	0	1	2	3	0	1	2	3
E1	15.01	14.63	6.22	5.02	0.45	0.45	0.52	0.54
E2	38.67	37.87	33.67	32.77	0.42	0.42	0.44	0.43
E3	72.59	73.68	54.79	/	0.37	0.37	0.41	/

0—After 48 hours.
1—After 1 month.
2—After 2 months.
3—After 6 months.

This model was consistent for all the samples at all time points during the testing period, with an exception of sample E3 after a 6-month storage time.

Irregular flow of sample E3 could not be described with the Hershel-Bulkey model. This kind of behavior, characterized by a sudden increase in thixotropic area, has already been observed in some macromolecular gels. A possible reason for this is structural degradation and establishing of new bonds during shearing induced by breaking of original structure.[12] This observation is very interesting because it supports the earlier finding that greater amount of emulsifier did not always lead to a more stabile system.[5] The best fitting model ($R = 0.9836$) for this flow behavior was the polynomial of 3rd power:

$$\tau = a + b\gamma + c\gamma^2 + d\gamma^3$$

where a, b, c, and d are coefficients of 0th, 1st, 2nd, and 3rd power, respectively. The fitted values were: $a = 239.8\,\text{Pa}$; $b = -3.6771\,\text{Pas}$; $c = 0.027595\,\text{Pas}^2$ and $d = -6.6766\text{E-}5\,\text{Pas}^3$.

The existence of yield stress plays an important role in emulsion stability, determining not only the shelf life of the product but also making the application easier to use.[13]

The rank order of yield values was found to be similar to that of the viscosity values, i.e., sample E1 was with the lowest, and sample E3 with the highest yield stress value (Table 3 and Fig. 1). It is known that "cream gels" have a much higher yield stress than aqueous gels, indicating on oil/polymer interaction.[5] The presence of relatively high yield stress values in samples E2 and E3 (Table 3) was taken as an indicator of high emulsion stability, since good correlation between yield value and elastic parameters of semisolids had been established.[14]

According to previous findings,[14] the lowest yield stress value (τ_γ) of sample E1 reveals the lowest level of elasticity in it (Table 3). Based on that fact, it was expected that E1 would be the most unstable sample. A possible reason for this kind of behavior lies in structural changes during aging of samples. Although rotational experiments provide information concerning the flow properties of a system such as yield value, thixotropy, and steady-flow curve, they are only a part of the complete rheological characterization. Dynamic oscillation testing is a much more powerful tool for revealing the secret of the microscopic structure of a viscoelastic material; therefore, it is more attractive and useful from a practical point of view.[15]

Parameters of oscillatory rheology: storage modulus (G'), loss modulus (G''), loss angle (δ), and damping factor ($\tan\delta$) are good indicators of viscoelastic properties of the samples and have been often used for characterization and prediction of the long-term stability.[16]

As presented in Table 5, values of G' and G'' for the fresh creams are the highest for sample E3 and the lowest for sample E1 during the entire observation period.

On account of that, high $\tan\delta$ value is considered a sign of domination of viscous over elastic behavior of the sample. It could be supposed that higher concentration of emulsifier in samples E2 and E3 resulted in interpenetration of polymeric chains at the droplet surface and more pronounced elastic behavior in the sample. Changes in parameters of oscillatory rheology were more pronounced in sample E1, especially for the G' value, which became lower (Table 5) than the G'' value after a 6-month period. The $\tan\delta$ value higher than 1 (Fig. 4) indicated domination of viscous over elastic properties.

In samples E2 and E3, the changes of aforementioned parameters were insignificant, and low $\tan\delta$ (lower than 0.3) indicated that formed gel structure in aqueous phase and polymer-oil interaction was sufficient to ensure elasticity of samples (Table 5, Figs. 4, 5) during oscillatory measurements. This is very interesting, since after a 6-month period sample E3 exhibited breaking of structure during continuous (rotational) measurements (Fig. 2).

When the emulsion has a noticeable yield stress it is stable, but further increase in the yield stress does not necessarily result in improvement of stability, since there is a variety of mechanisms that can be involved in the effect of polymeric emulsifier on emulsion stability.[17]

Dynamic (oscillation) testing is a tool for characterization of both viscosity and elasticity of the material without altering the structure, since it is conducted at very low shear rates (10^{-6}–$10^{-4}\,s^{-1}$). On the other hand, measuring range of rotational (continuous) measurement should correlate to the process with much higher shear rates. Chewing and coating should be evaluated in the range between 10 and $100\,s^{-1}$, while rubbing and spraying between 10^3 and $10^5\,s^{-1}$. At these higher shear rates where material starts to flow and the yield stress value is overcome, initial structure of the material is broken and it may or may not return to initial value.[8]

The main factor in structure formation is the interboundary interaction of the hydrophilic and lypophilic phases.[18] Polymeric emulsifier bonds to the emulsion's internal phase through several mechanisms: dipol-dipol interaction, hydrogen bonding, and hydrophobic interactions.[19] These interactions could be altered during the shearing process and could give an explanation for irregular flow in sample E3 with higher emulsifier concentration.

Table 5. Viscoelastic parameters G' and G'' at the frequency of 1 Hz, for test emulsion samples.

	G' (Pa)				G'' (Pa)			
Sample label	After 48 h	After 1 month	After 2 months	After 6 months	After 48 h	After 1 month	After 2 months	After 6 months
E1	225 ± 2.5	234 ± 3.3	77 ± 3.0	48 ± 2.9	103 ± 3.0	107 ± 4.1	71 ± 5.4	58 ± 5.5
E2	628 ± 3.0	566 ± 3.1	516 ± 3.8	484 ± 4.0	152 ± 3.2	147 ± 5.3	142 ± 6.0	127 ± 6.4
E3	673 ± 3.2	681 ± 3.9	653 ± 4.4	482 ± 3.8	141 ± 4.5	160 ± 5.5	149 ± 6.1	122 ± 5.8

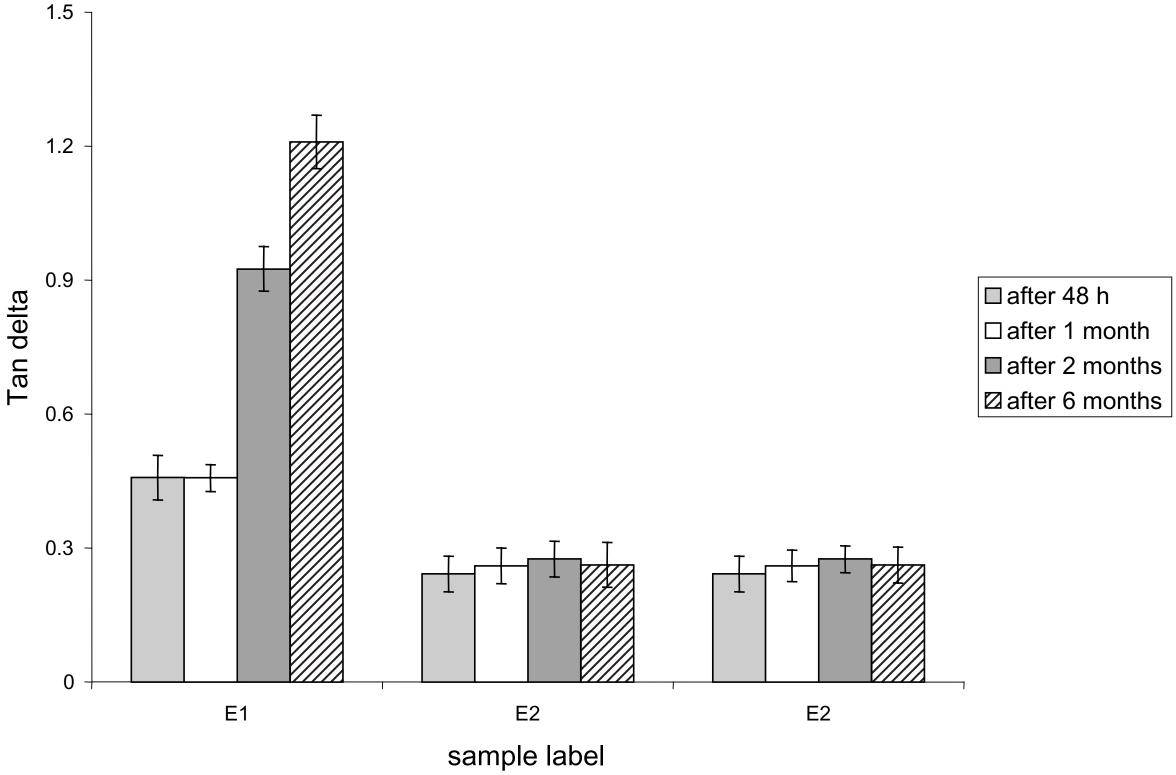

Figure 4. Tan delta values of tested emulsion samples.

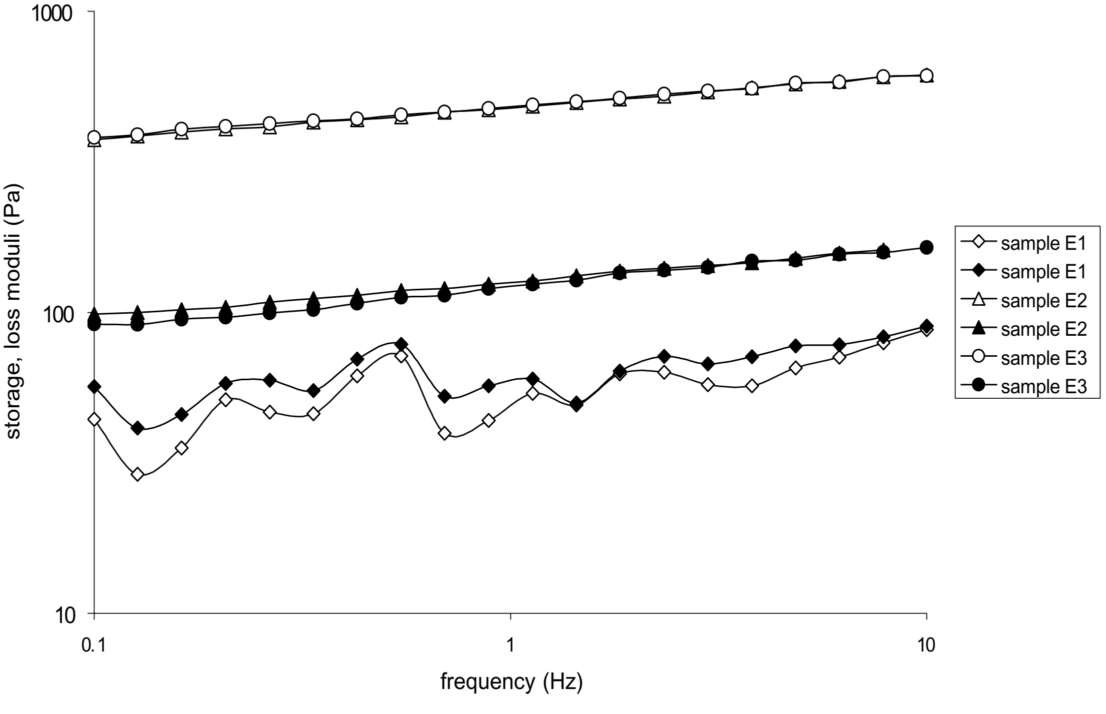

Figure 5. The storage G′ modulus (open symbols) and loss G″ modulus (filled symbols) of the test emulsion samples, 6 months after preparation.

Microscopic images of fresh samples (magnification 400 times) provide an overview of droplet structure and size (Figs. 6–8).

It was noticeable that the droplet size was related to emulsifier concentration, i.e., the sample with the greatest amount of emulsifier had the smallest droplet size. Emulsifier formed a layer around the oil drops, already observed in emulsions stabilized with polymeric emulsifier.[7]

Mean droplet diameter and standard deviation were calculated using the software program provided with the equipment. The results are presented in Table 6.

The mean droplet diameter of all samples, during the period of observation, ranged from 4.5 to 11.7 µm (Table 5), which could be considered a sign of possible long-term stability and good esthetic characteristics important for pharmaceutical and cosmetic use. In systems stabilized by polymeric emulsifier, the mean droplet diameter of dispersed phase can widely vary in range. For instance, emulsions prepared with Pemulen®TR-1 polymeric emulsifier were physically stabile during a long period of time, although their mean droplet diameter was in the range of 1–2 mm. However, these emulsions were not esthetically acceptable since they had droplets of oil phase on the surface; emulsions with internal phase droplets in the range of 1–5 µm are stabile, white, and with no separation of phase observed.[19]

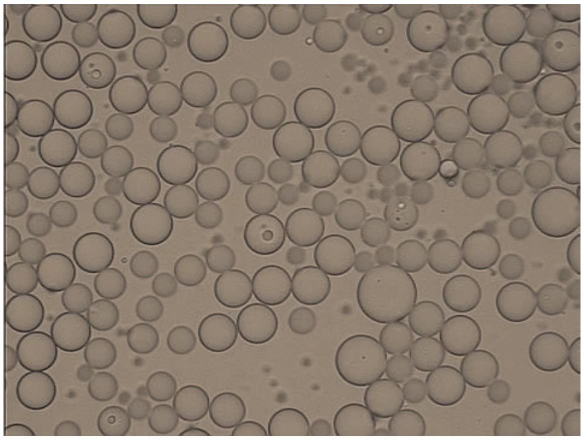

Figure 6. Microscopic image of sample E1 (magnification 400 times), 48 hours after preparation.

With an exception of sample E1, which exhibited insignificant increase of droplet size during longer storage compared with fresh samples, the mean droplet diameter in all the other samples had the same trend of diminution within the testing period. This finding could be an indicator of the greatest structural changes in this sample and it was confirmed by oscillatory rheological measurements.

For comparative study of this parameter during testing period, with regard to fresh samples, student *t*-test was selected with significance level of 0.05. Results of the test suggested that the changes of mean droplet diameter were statistically significant ($p < 0.05$) for all the samples during the period of observation. However, this finding could not be used as the only relevant parameter when testing of stability of formulations was concerned. The insignificant increase in mean droplet diameter for sample E1 (Table 6) could be related to the decrease in elasticity of the external gel-phase (Table 5, Fig. 4) in emulsion samples. An emulsion system with the

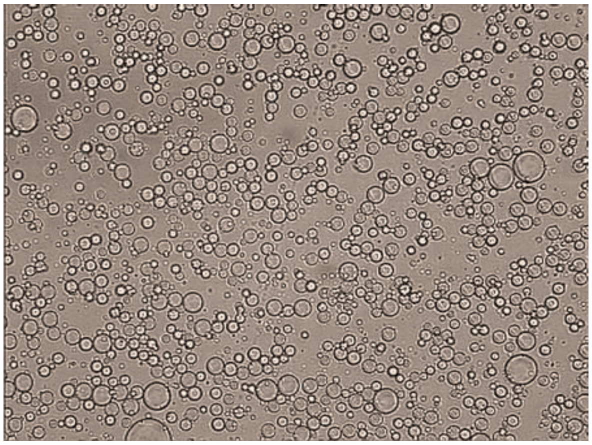

Figure 7. Microscopic image of sample E2 (magnification 400 times), 48 hours after preparation.

Figure 8. Microscopic image of sample E3 (magnification 400 times), 48 hours after preparation.

Table 6. Drop size analysis of test emulsion samples ($N = 500$).

	Mean droplet diameter ± standard deviation (μm)			
Sample	After 48 h	After 1 month	After 2 months	After 6 months
E1	11.582 ± 4.6545	11.393 ± 5.1236	9.439 ± 4.6400	11.749 ± 4.3778
E2	8.888 ± 2.1992	8.025 ± 2.1278	7.617 ± 1.9437	5.4281 ± 2.1714
E3	6.290 ± 2.7577	6.771 ± 1.326	5.690 ± 1.6588	4.4575 ± 1.5952

same content of internal phase develops higher yield stresses, apparent viscosities, and viscoelasticity as droplet size decreases.[12] On the other hand, these characteristics are related to sample stability.[8,13]

CONCLUSION

In this study model emulsions containing the same amount (30% m/m) of internal (oil) phase and polymeric emulsifier at three concentration levels (1, 3, 5% m/m) were prepared. Obtained results have shown that all samples exhibited nonNewtonian plastic flow without significant thixotropy in both fresh and aged states, except for the sample containing 5% of polymeric emulsifier in which breaking of the structure was observed after a 6-month period. Rheological measurement along with droplet size analysis revealed that increasing yields stress values accompanied with decreasing mean drop diameter were related to increasing emulsifier concentration. After a 6-month storage period the sample containing 1% m/m of polymeric emulsifier had more pronounced viscosity than elasticity, while parameters of oscillatory rheology in samples containing 3 i.e., 5% m/m changed insignificantly.

These results suggest that 1% m/m of emulsifier was sufficient for preparation of macroscopically stabile samples within the testing period, by means of phase separation, with consistency varying from semisolid (for fresh samples) to body lotion (after 6 months). Emulsions containing polymeric emulsifier in concentrations of 5% m/m demonstrated stability in oscillatory rheological measurements during the entire testing period, whereas during rotational measurements, i.e., during application process, this emulsion demonstrated instability.

High concentration of emulsifier also affected the skin feel in a way that the consistency of "cream-gels" systems, stabilized by polymeric emulsifier, was disturbed.

It was demonstrated that 3% m/m of polymeric emulsifier was sufficient for preparation of esthetically acceptable emulsion by means of organoleptic parameters and with good physicochemical stability by means of applied measuring techniques. High yield stress values (flow tests) and favorable $\tan\delta$ values (oscillatory studies) both indicated good internal structuring and long-term stability of this sample.

Microscopic analysis findings indicated that the mean drop diameter of all the samples during storage time was less than 15 μm. Different changes of mean droplet diameters could be taken as an indicator of emulsion stability only along with results of rotational and oscillatory rheometry.

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