



Dependance of viscoelastic properties of two emulsion formulations on preparation process

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Abstract: Rheological properties are crucial for cosmetic formulations, determining product's properties during production and application. O/W emulsions (pH 6.86–7.10) were prepared with decyl-oleate as internal phase. A-formulations contained K-stearate, while N-formulations contained polyglyceryl-stearate and -behenate as principal emulsifiers. The formulations were prepared by adding the water to the oil phase (NA and AA) or vice versa (NB and AB). Oscillatory measurements were performed on Haake RheoStress using double gap cylinder. In amplitude sweep at low stresses all samples behaved as viscoelastic solids. With increasing stress, phase angles increased to $>80^\circ$. Crossover of storage and loss moduli for AA happened at nine times higher stress compared to the other formulations, forming lamellar crystalline gel network. Linear viscoelastic region showed that AA was much more stable. Frequency sweep showed NA and AB to be liquid-like. In NB and AA decrease in complex viscosity indicates better spreadability. Stability of phase angles and storage and loss moduli indicate more elastic behavior. New nonionic emulsifier was more independent of processing, unlike anionic emulsifier. However, AA formulation gives much better feel properties, needed in cosmetic formulations.

INTRODUCTION

One of the major groups of topical formulations are emulsions, consisting of two immiscible liquid phases (water and oil) in which one phase is dispersed in the other and stabilized by emulsifier. Emulsions are thermodynamically metastable systems. They are exposed to physical, chemical and microbiological influences during manufacture, transport, storage and use that can induce changes in the emulsion. Very different emulsion structures can be achieved depending on the emulsifiers used and their concentration. Also, the production process affects the end product, since different droplet sizes and droplet size distributions can be achieved. This all affects not only microstructure and

stability of an emulsion, but also macrostructure and how the product appeals to the consumer.

Studies of rheological properties are crucial for liquid and semisolid pharmaceutical and cosmetic formulations, because they determine product's properties during production and application. However, rheological studies for regulatory purposes are used only to a certain degree, remaining at the level of viscosity determination (Podczeck, 2007). Studies of viscoelastic characteristics have great potential in development and optimization of stability as well as sensory properties of topical formulations (Adeyeye, Jain, Ghorab *et al.*, 2002; Ibanescu, Danu, Nanu *et al.*, 2010; Moravkova and Filip, 2013).

Emulsions show, like all real materials, viscoelastic flow characteristics, displaying both viscous (liquid-like) and elastic (solid-like) behavior (Đaković, 2006; Podczeczek, 2007). These characteristics are studied using oscillatory measurements (rotor of the rheometer goes back and forth at an angular frequency and amplitude or oscillates).

In an ideal elastic material, deformation is proportional to the load, and the force (shear stress, τ) is greatest at maximum deformation. The stress and strain curves will be in phase (phase angle (δ) equals 0°) for a sinusoidal load (Fig. 1(a)) (Brummer, 2006).

In an ideal viscous material, there is proportionality of shear stress and shear rate, *i.e.* maximum shear rates correspond to maximum forces. There is a phase lag of 90° between shear rate and the strain (Fig. 1(c)) (Brummer, 2006).

Between these extremes lie viscoelastic materials. Here, the phase angle or lag of shear stress (τ) and the strain (γ) of the material is between the extreme values ($0^\circ > \delta > 90^\circ$) (Fig. 1(b)), depending on the nature of the material, *i.e.* is it more elastic or viscous.

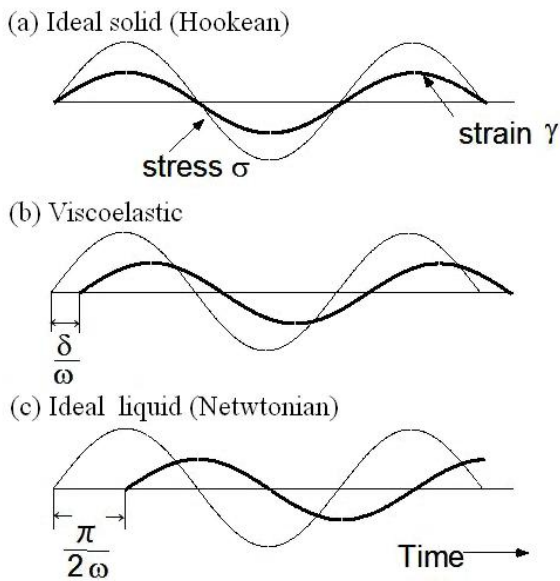


Figure 1: Relationship between applied stress and strain of the material and phase angle for (a) ideally elastic (solid) material, (b) viscoelastic and (c) ideally viscous (liquid) material.

The parameters of viscoelastic materials are usually frequency dependent. Elastic component of a material is described by storage modulus (G'), while the viscous component is described by loss modulus (G''). They are related to phase angle as follows:

$$\tan \delta = \frac{G''}{G'} \quad (1)$$

$$G^* = \frac{\tau}{\gamma} = G' + iG'' \quad (2)$$

G^* is complex modulus which is a measure of material's overall resistance to deformation and $i = \sqrt{-1}$.

Complex dynamic viscosity can be calculated:

$$\eta^* = \frac{G^*}{i\omega} = \frac{G''}{\omega} - \frac{G'}{\omega} \quad (3)$$

ω is angular frequency (Brummer, 2006).

Viscoelastic properties are studied using dynamic oscillatory measurements, which are done without destroying material's structure. These measurements include oscillatory amplitude sweep, in which frequency is kept constant and the amplitude of deformation changes, *i.e.* the strain increases. In oscillatory frequency sweep the amplitude is kept constant and the frequency changes.

The aim was to study viscoelastic properties of O/W emulsions prepared in two different manners using either nonionic or anionic emulsifier system.

EXPERIMENTAL

Preparation of emulsion formulations

Decyl oleate, cetostearyl alcohol, glyceryl monostearate and stearic acid were obtained from Caesar & Loretz GmbH, Germany. Propylparaben and methylparaben were obtained from Sigma-Aldrich Inc., USA. TEGO[®] Care PBS 6 (polyglyceryl stearate and behenate) was kindly provided by FC Franken-Kosmetik-Handel GmbH & Co.KC, Germany and Evonik Industries AG, Germany. These chemicals were used as received. Potassium hydroxyde was from Kemika Zagreb, Croatia, and was of p.a. quality. Deionized water was produced on Milli-Q Water Purification System (Millipore Corporation, USA).

Four formulations of O/W emulsions were prepared with composition shown in Table I. Formulations NA and NB contained nonionic principal emulsifier (TEGO[®] Care PBS 6), while formulations AA and AB contained anionic principal emulsifier (potassium stearate).

Table I: Composition of the formulations

Excipient	NA and NB	AA and AB
A		
Decyl oleate	25.5%	25.5%
Stearic acid	-	3.0%
TEGO [®] Care PBS 6	3.0%	-
Cetostearyl alcohol	0.5%	0.5%
Gliceryl monostearate	0.5%	0.5%
Propylparaben	0.05%	0.05%
B		
Disodium-EDTA	0.1%	0.1%
Potassium hydroxyde	-	0.12%
Methylparaben	0.3%	0.3%
Deionized water q.s. ad	100.0%	100.0%

The formulations were prepared by heating the oil phase (A) and the water phase (B) to 80°C separately (until clear), and then mixed in two manners:

1. by adding the water phase (B) to the oil phase (A), resulting in phase inversion as the formulation is stirred (200 rpm) and cooled to room temperature (NA and AA formulations)
2. by adding the oil phase (A) to the water phase (B) and stirring (200 rpm) until the mixture is cooled to room temperature, which is the standard way of preparing stearate creams (NB and AB formulations).

pH measurements

The pH of the formulations was measured directly using Orion Star A211 (ThermoScientific, USA).

Oscillatory measurements

Oscillatory measurements were performed on Haake RheoStress (ThermoScientific, USA) using double gap sensory geometry with 5.100 mm gap.

Amplitude sweep was carried out during 100 s, with τ ranging from 0.01 through 1000.0 Pa at frequency of 1.000 Hz at 23°C.

Frequency sweep was carried out at $\tau = 1.0$ Pa with changing frequency from 10.0 to 0.01 Hz at 23°C.

All results were processed using software HAAKE RheoWin (ThermoScientific, USA).

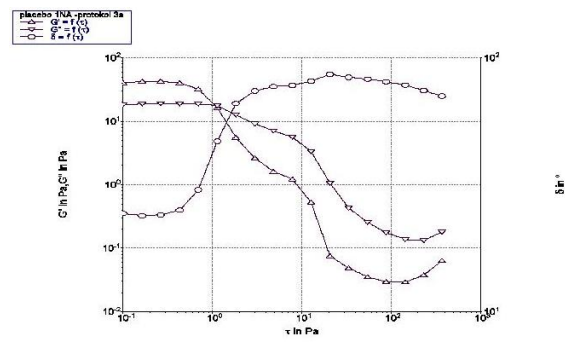
RESULTS AND DISCUSION

The results of pH measurements of emulsion formulations are shown in Table II.

Table II: Measured pH values of the formulations

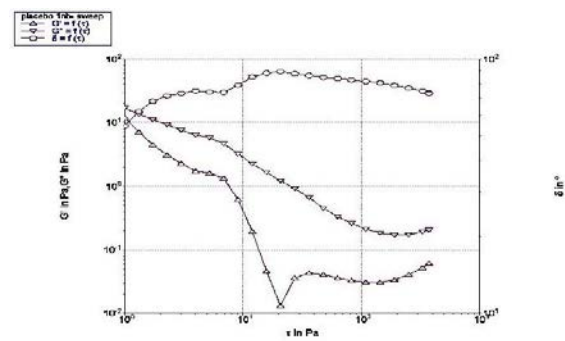
Formulation	pH value
NA	6.91
NB	6.86
AA	6.90
AB	7.10

The results were all very near pH 7, thus the adjustment of pH was deemed unnecessary.



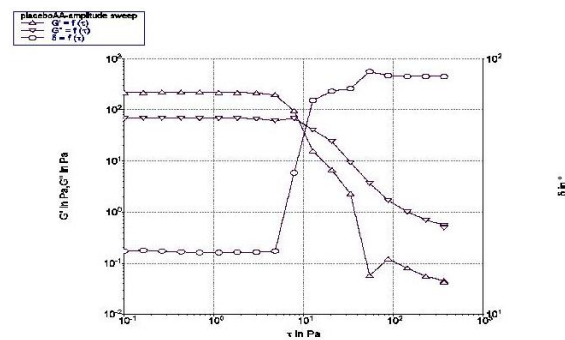
HAAKE RheoWin 4.30.0030

(a)



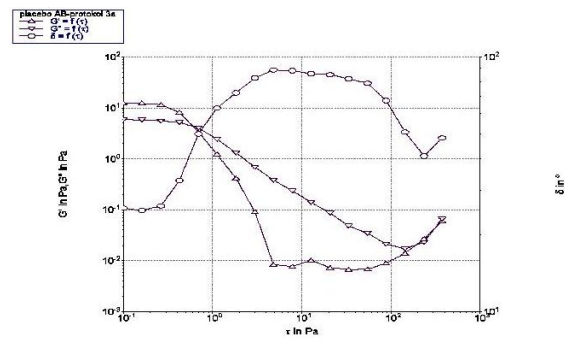
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(b)



HAAKE RheoWin 4.30.0030

(c)



HAAKE RheoWin 4.30.0030

(d)

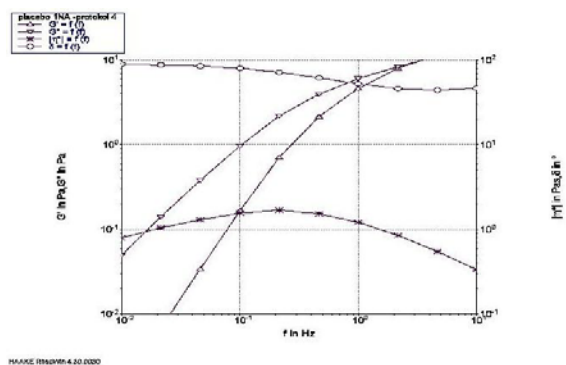
Figure 2: Amplitude sweep for formulations NA (a), NB (b), AA (c), AB (d). The storage modulus ($\Delta - G'$), loss modulus ($\nabla - G''$) and phase angle ($\circ - \delta$) are functions of shear stress (τ).

Oscillatory amplitude sweep showed (Fig. 2) that all samples behaved as elastic solids at low shear stress (0.1 Pa), since $G' > G''$. With increasing stress, the internal structure breaks down. The region of stable structure (linear viscoelastic region or LVER) differed. LVER for sample NA ended at $\tau = 0.7$ Pa, and for NB sample at $\tau = 0.43$ Pa, indicating somewhat more stable structure in NA sample, compared to NB. In sample AB the structure broke down at 0.26 Pa, while in AA the structure this happened at 4.83 Pa. This shows very large dependence on production processing in this type of formulation.

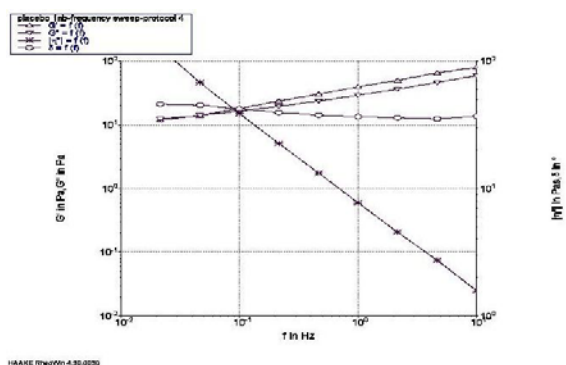
As the internal structure broke down at higher stress values, the crossover of storage (G') and loss (G'') moduli occurred, and formulations became more viscous than elastic, *i.e.* more liquid-like. This happened for all but one sample on low shear stresses ($\tau_{NA} = 1.080$ Pa, $\tau_{NB} = 1.349$ Pa, $\tau_{AB} = 0.620$ Pa). Sample AA had crossover at $\tau_{AA} = 9.220$ Pa. Crossover at lower stress levels indicates easier spreadability of lotions on skin (Ibanescu, Danu, Nanu *et al.*, 2010), which might be the case with formulations NA, NB and AB. On the other hand, sample AA displayed more stable and resilient structure, thus harder spreadability, but richer feel (Ibanescu, Danu, Nanu *et al.*, 2010).

In all samples, phase angle (δ) rose with increasing shear stress, but at low end of τ was the smallest for AA sample. As structures of formulations broke down (beyond LVER) phase angles increased to $>85^\circ$, also consistent with samples becoming liquid-like.

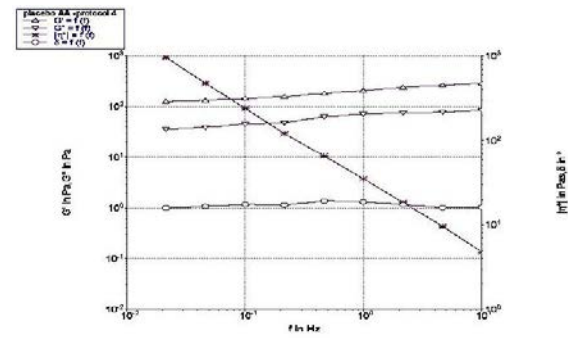
LVER, G' , G'' and δ values indicate much more stable structure in formulation AA compared to the classic emulsions and formation of lamellar crystalline gel network phase in this sample.



(a)

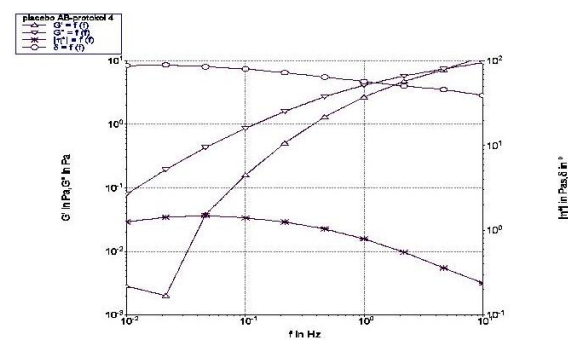


(b)



HAAKE RheoWin 4.30.0200

(c)



HAAKE RheoWin 4.30.0200

(d)

Figure 3: Frequency sweep for formulations NA (a), NB (b), AA (c), AB (d). The storage modulus ($\Delta - G'$), loss modulus ($\nabla - G''$), phase angle ($\circ - \delta$) and complex viscosity ($* - \eta^*$) are functions of frequency (f).

Oscillatory frequency sweep showed (Fig. 3) that sample NA behaved as a viscoelastic liquid, since $\delta \sim 80^\circ$, $G'' > G'$, with crossover at high frequency (6.514 Hz), and complex viscosity (η^*) decreased at the frequency region of the crossover of moduli. Sample NB, on the other hand, showed more elastic behavior compared to NA, since $\delta \sim 40^\circ$, at low frequency $G'' > G'$, but crossover happened at 0.04554 Hz, and at higher frequencies $G' > G''$. As the frequency increased complex viscosity fell logarithmically.

AA sample behaved as a viscoelastic solid. Its phase angle was constant at $\delta \sim 17^\circ$, $G' > G''$. The values of storage and loss moduli, without crossover in the studied frequency region, were higher than for sample NB, as well as complex viscosity, indicating more stable gel structure. Complex viscosity logarithmically fell. Since at rest complex viscosity was high, and phase angle was stable and low, it implies rich feel or texture of the cream (Ibanescu, Danu, Nanu *et al.*, 2010).

AB sample behaved as a liquid, since its phase angle was $\delta \sim 80 - 90^\circ$, $G'' > G'$, with crossover at frequency of 5.052 Hz. The complex viscosity (η^*) decreased at the frequencies of the crossover of moduli.

CONCLUSION

The differences in viscoelastic properties of nonionic (N) formulations were not as pronounced as in anionic (A) formulations with regard to the preparation process. Nonionic emulsifier used in N formulations is new one, designed for low viscosity cosmetic preparations. It is much more independent of processing compared to the much older anionic stearate emulsifier. On the other hand, AA sample obtained with phase inversion gave much better feel properties, very needed in cosmetic formulations.

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Summary/Sažetak

Reološke osobine su ključne za kozmetičke formulacije, budući da određuju osobine proizvoda tokom njegove proizvodnje i aplikacije. U/V emulzije (pH 6.86–7.10) su pripremljene sa decil-oleatom kao unutrašnjom fazom. A-formulacije su sadržavale K-stearat, a N-formulacije poligliceril-stearat i –behenat, kao glavne emulgatore. Formulacije su pripremljene dodajući vodu u masnu fazu (NA i AA) ili obrnuto (NB i AB). Oscilatorna mjerenja su izvršena na Haake RheoStress korištenjem cilindra sa duplim zazorom. Pri promjeni amplitude, kod niskih napona smicanja svi uzorci su se ponašali kao viskoelastična čvrsta tijela. Povećanjem napona smicanja, fazni uglovi su se povećali do >80°. Križanje modula elastičnosti i viskoznosti za AA se desilo pri devet puta većem naponu smicanja u poređenju sa ostalim formulacijama, te formira lamelarnu kristalnu gel mrežu. Linearni viskoelastični region je pokazao AA kao mnogo stabilniju. Promjena frekvencije je pokazala da su NA i AB slične tečnostima. Kod NB i AA smanjenje kompleksnog viskoziteta indicira bolju razmazivost. Stabilnost faznog ugla i moduli elastičnosti i viskoznosti ukazuju na više elastično ponašanje. Novi neionski emulgator je bio više neovisan o metodi izrade za razliku od anionskog emulgatora. Međutim, AA formulacija daje mnogo bolje osjetne osobine potrebne u kozmetičkim formulacijama.

