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Rheological properties of creams with four different surfactant combinations - effect of storage time and conditions

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Abstract

Changes in the rheological properties of four o/w cream formulations differing in the combination of surfactants were studied. The non-ionic surfactants used were soybean derivatives, polyethylene glycol 10 and 25 soya sterol, and sorbitol derivatives, sorbitan monooleate and trioleate. Combinations of the soybean and sorbitol derivatives were used. The rheological properties were tested during a 28-day storage period at three different storage conditions (cold, room temperature and accelerated conditions). In addition to dynamic and static rheological tests, droplet size distributions and conductivities of the creams were also determined. The consistency of the creams containing polyethylene glycol 10 soya sterol decreased during storage. Despite the greatest decreases in consistency, the creams containing polyethylene glycol 10 soya sterol exhibited the most viscoelastic structures with linear viscoelastic behaviour. Storing the creams for 28 days in the three different storage conditions made the differences in the consistency of the formulations smaller. All three storage conditions were involved when the conditions of the most viscoelastic cream of each formulation was specified. In the case of linearly viscoelastically behaving creams containing polyethylene glycol 10 soya sterol, all the rheological tests correlated with the droplet size distributions and the conductivity tests.

Keywords: Dynamic rheological tests; Rheology of creams; Static rheologicl tests; Storage conditions; Storage time; Surfactants

1. Introduction

As soon as a cream has been manufactured, time- and temperature-dependent separation processes occur (Rieger, 1986). As thermodynamically unstable systems creams have a tendency to revert back to the original two-phase system with a minimum interfacial area (Block, 1989).

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Changes in the rheological properties of creams represent important early warnings of impending failure of the product (Rieger, 1991).

Surfactants make the forming of the cream structure possible, and are mainly responsible for the stability of the structure during the storage period. Like rheological properties of the continuous phase, also viscosity in the interfaces affects the stability of a cream (Elworthy and Florence, 1969). In o/w creams, surfactants have to have a degree of hydrophilicity to confer an enthalpic stabilizing force, and a degree of hydrophobicity to secure adsorption at the interface (Attwood and Florence, 1983). Usually a combination of surfactants is used to complement the properties of each other. The effectiveness of the surfactant combination is affected, for example, by the structural interaction between single surfactants, complementary hydrophilic-lipophilic balance, orientation of molecules at the interface of phases and the suitability of the surfactant combination to the whole cream formulation (Korhonen et al., 2000).

The rheological linear viscoelastic behaviour of a cream can be determined by dynamic and static methods (Barnes et al., 1989). These methods give detailed information about the structural properties and structural changes of a cream. Dynamic rheological tests have been presented in an earlier study (Korhonen et al., 2000). Static rheological tests are either creep tests at a constant stress or relaxation tests at a constant strain (Barnes et al., 1989). Time-dependent strain response is known as a creep curve (Davis, 1969a). In the creep test, a cream is exposed to a certain stress which is then kept constant. The creep curve of pharmaceutical semisolids can be split up into three separate regions: the instantaneous elastic region representing elastical stretching of primary structural bonds, the curved viscoelastic region representing orientation of crystals or droplets due to breaking and reforming of secondary bonds and the viscous flow (Davis, 1974). All bonds do not break and reform at the same rate, and a wide range of retardation times will exist. The retardation time is defined as a ratio of viscosity to elasticity (Barry and Warburton, 1968). The size, shape and number of the droplets, for example, affect the retardation time (Warburton and Barry, 1968). The strain response to removal of stress is known as a recovery curve (Davis, 1969a). The instantaneous elastic region and the viscoelastic region recover totally and in part, respectively (Barry and Eccleston, 1973). The viscous region does not recover (Davis, 1969a).

Although the complete creep recovery tests may take hours, also shorter times, minutes and even seconds, have been used (Ceulemans et al., 1999; Pal, 1999a,b; Romero et al., 2000).

This study is a continuation of an earlier study where the rheological properties of four o/w cream formulations were examined during two days after cream manufacture (Korhonen et al., 2000). The aim of this study was to examine the influence of storage time and storage conditions on the rheological properties of the creams. The most elastic structures are presumed to maintain the structural stability and resistance to external forces longer.

2. Materials and methods

2.1. Materials

Formulations of different combinations of surfactants were studied. The surfactants used were polyethylene glycol 10 soya sterol (Generol® 122 N E 10 D, Henkel KGaA, Germany), polyethylene glycol 25 soya sterol (Generol® 122 N E 25 D, Henkel KGaA, Germany), sorbitan monooleate (Kosteran® -O/1, Ph. Eur., Dr. W. Kolb AG, Germany) and sorbitan trioleate (Kosteran® -O/3, Ph. Eur., Dr. W. Kolb AG, Germany). Polyethylene glycol 10 and 25 soya sterols have 10 and 25 moles of ethylene oxide on average (Wenninger and McEwen, 1993). Sorbitan monooleate and trioleate are monoesters and triesters of oleic acid and hexitol anhydrides (Wenninger and McEwen, 1993). The soybean and sorbitol derivatives used are non-ionic surfactants. The combinations of the surfactants used and the HLB values of these combinations are given in Table 1. Other ingredients of the formulations were caprylic triglyceride, isopropyl palmitate and cetostearyl alcohol 8%, glycerin (85%)

12%, methylparaben and propylparaben 0.1% and 0.02%, respectively and Aq. Purif. ad 100%. For each formulation, two batches of 3 kg were prepared.

The creams studied are identified as formulations I-IV. Polyethylene glycol 10 soya sterol and polyethylene glycol 25 soya sterol are referred to in Section 3 as PEG 10 soya sterol and PEG 25 soya sterol, respectively.

2.2. Analytical methods

Rheological properties were determined using a rheometer (StressTech, ReoLogica Instruments AB, Lund, Sweden, Stress RheoLogic Basic software, version 2.2) with parallel plate system. The temperature of the base plate was 25.0°C ± 0.1°C. In the oscillation stress sweep test the stress was increased from 0.03 Pa to 300 Pa in 40 logarithmic steps and the frequency was kept constant (1 Hz). The linear viscoelastic region of each cream was determined with the oscillation stress sweep test. In the linear viscoelastic region the stress to strain ratio was a function of time alone. In the oscillation frequency sweep test the frequency was increased from 0.01 Hz to 30 Hz in 16 steps and the stress was kept constant (1 Pa). In the creep test the sample was exposed to a 1 Pa stress (σ) for 30 s and the strain (γ) was registered. In the recovery test, after removal of the stress applied, the strain recovery was registered for 60 s. The change of the strain value was measured at zero stress. The compliance (J) is the deformation measured (strain, γ) divided by the stress (σ) applied, $J(t) = \gamma(t)/\sigma$. The creep compliance and recovery compliance are referred to in Section 3 as J_c and J_r, respectively. The very short creep tests were chosen for timesaving reasons. Also the knowledge that the results are used only for comparison affected the choice of time parameters (30 s).

Droplet sizes were determined using a light microscope (Olympus BX40F, Olympus Optical Ltd., Tokyo, Japan). A 10% water suspension was prepared and the measurement was performed immediately after sample preparation. The diameter was determined from randomly chosen droplets. Conductivity was measured with a portable conductivity instrument (Mettler Check Mate 90, Mettler Toledo, Essex, USA). An ion-sensitive transistor was used.

2.3. Stability study

The stabilities of the creams were examined during a 28-day period in three different conditions. Measurements were made during the first two days after cream manufacture (0-sample) and 14 and 28 days after cream manufacture. Room temperature conditions (25°C, relative humidity 60%) were used when the influence of storage time was examined. The influence of storage conditions was examined only after the 28-day storage. The storage conditions studied were cold (5°C), room temperature (25°C, relative humidity 60%) and accelerated conditions (40°C, relative humidity 75%).

Table 1
Concentrations (%) of individual surfactants in the formulations and HLB values of the surfactant combinations

Surfactant	Formulation			
	I	II	III	IV
Polyethylene Glycol 10 Soya Sterol	12	12		
Polyethylene Glycol 25 Soya Sterol			12	12
Sorbitan Monooleate	8		8	
Sorbitan Trioleate		8		8
HLB-value of the combination	9.2	8.2	12.3	11.4

Table 2
Influence of storage time on the storage modulus (G′) values in the oscillation stress sweep test

Storaging time	Formulation			
	F I	F II	F III	F IV
0-sample	319.3 ± 11.7	946.6 ± 28.4	59.9 ± 15.5	112.5 ± 16.6
14 days	273.8 ± 25.2	635.8 ± 24.3	42.8 ± 3.3	91.3 ± 21.3
28 days	224.3 ± 11.7	596.3 ± 27.0	42.0 ± 5.2	96.1 ± 33.6

In the 0-sample measurement point of formulation III $n = 9$, otherwise $n = 6$. Means ± standard deviations are presented.

3. Results and discussion

3.1. Dynamic rheological tests

3.1.1. Oscillation stress sweep

During the 28-day storage period at room temperature, the most consistent cream of each formulation was the 0-sample cream (Table 2), which is a sign of instability of these creams. The drop of the storage modulus (G′) was the greatest in formulation II which contained PEG 10 soya sterol and sorbitan trioleate. However, despite the greatest elasticity loss, formulation II was still clearly the most elastic cream after the 28-day storage period. Creams containing PEG 25 soya sterol (formulations III and IV) had clearly smaller storage modulus values than creams containing PEG 10 soya sterol (formulations I and II). Sorbitan trioleate, included in formulations II and IV, made the creams more elastic than sorbitan monooleate, included in formulations I and III (Table 2).

The less elastic behaviour of creams containing PEG 25 soya sterol can be seen also from the loss tangent values (Fig. 1). Loss tangent (tan δ) is the ratio of loss modulus (G'', characterises the viscous behaviour of the material) and storage modulus (G′, characterises the elastic behaviour of the material) (Kobayashi et al., 1982; Rieger, 1991; Gasperlin et al., 1997). The higher the loss tangent is, the less elastic is the material. However, each formulation behaved predominantly elastically as, according to Gasperlin et al. (1998), values of tan $\sigma < 1$ characterize a predominant elastic behaviour and values of tan $\delta > 1$ indicate a prevailing viscous behaviour. For all formulations, the tan δ values were clearly below 1 (Fig. 1).

Storing the creams for 28 days in three different storage conditions made the differences in the elasticities of the formulations smaller. The most viscoelastic creams of PEG 10 soya sterol (formulations I and II) were quite as elastic when comparing the highest storage modulus values irrespective of storage conditions (Fig. 2). Most creams have a specific maximum temperature (T_{max}) until which the consistency increases (Barry and Eccleston, 1973). In formulation II, T_{max} was probably between 25°C and 40°C, because the most elastic structure after the 28-day storage period was observed in creams stored at room temperature. Formulation I was clearly the most elastic after the 28-day storage period in cold irrespective of storage time and conditions. In formulation I, the decrease of elasticity with growing storage temperature can be a result of a temperature-dependent breakdown in the structure responsible for the viscoelastic properties (Davis, 1969b). The creams containing PEG 10 soya sterol behaved linearly viscoelastically irrespective of storage time and conditions. In the linear viscoelastic area the stress to strain ratio is a function of time alone (Kobayashi et al., 1982). Of the creams containing PEG 25 soya sterol (formulations III and IV), the only cream behaving linearly viscoelastically was formulation III stored for 28 days at accelerated conditions. Despite that, formulation III had the most elastic structure after the 28-day storage in cold (Fig. 2). In formulation IV (containing PEG 25 soya sterol and sorbitan trioleate), the increase in consistency with increasing storage temperature may be due to the increased Brownian movement in the system (Barry and Saunders, 1970) (Fig. 2). This is believed to form new linkages and to strengthen the cream network when bringing free ends of strands into contact with the main meshwork (Barry and Saunders, 1970).

The HLB values of the surfactant combinations presented in Table 1 correlated directly with the viscoelasticities of the creams irrespective of storage time and conditions; the smaller the HLB value the more viscoelastic was the cream.

3.1.2. Oscillation frequency sweep

Creams containing PEG 10 soya sterol (formulations I and II) had high storage modulus values even at the lowest frequencies (Fig. 3a). The curves of creams containing PEG 25 soya sterol (formulations III and IV) were differently shaped with continuously increasing storage modulus values as the frequency increased (Fig. 3a).

The creams containing PEG 10 soya sterol (formulations I and II) can be considered almost perfectly elastic, because the storage modulus (G′) values changed rather slowly as the frequency was increased (Ferry, 1980). In the creams containing PEG 10 soya sterol and in those containing PEG 25 soya sterol the oscillation frequency sweep test did not show any differences between creams containing sorbitan monooleate and those containing sorbitan trioleate (Fig. 3a). The storage modulus curves were equal with formulations I and II and formulations III and IV. Also the loss tangent (G''/G') values were equal, depending only on the soybean derivative (Fig. 3b); the smaller the value of tan δ, the more rubberly or elastomeric was the behaviour.

3.2. Static rheological tests — creep recovery

The results of the creep recovery tests supported those of the dynamic tests with all formulations despite the fact that the 1 Pa stress used was not in the linear viscoelastic area of formulations III and IV. Despite the knowledge that the creep recovery tests of formulations III and IV were not in the linear viscoelastic region the tests were performed and the results are shown for comparison.

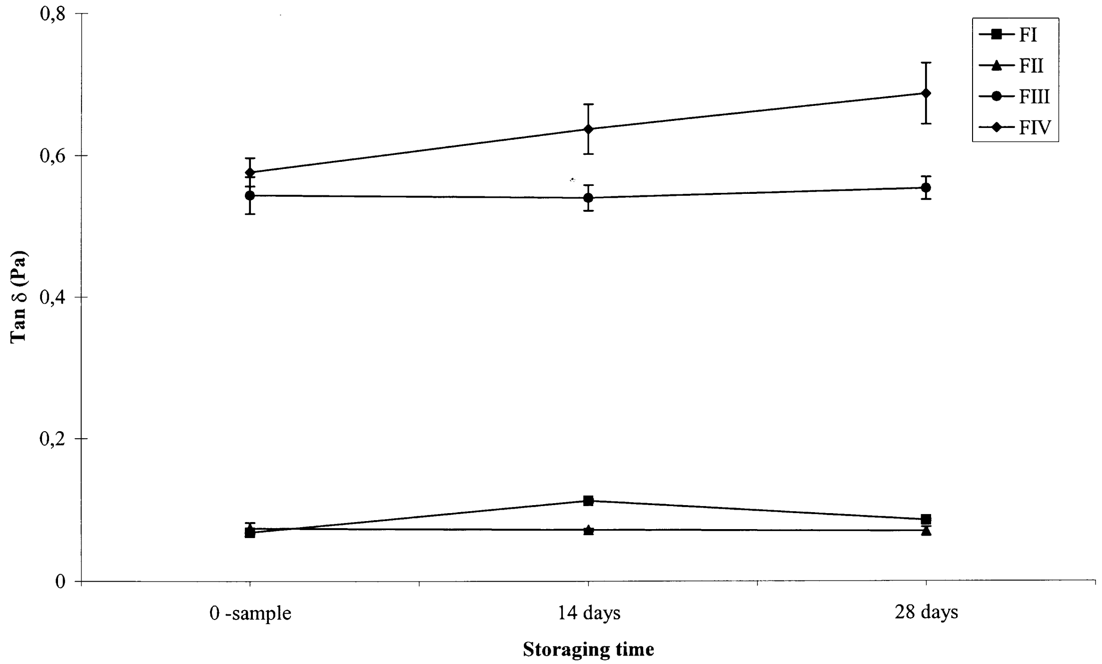

Fig. 1. Influence of storage time on the tan δ (G''/G') values in the oscillation stress sweep test. In the 0-sample measurement point of formulation III $n = 9$, otherwise $n = 6$. Error bars around the measurement values present standard deviations (± sd) for each value.

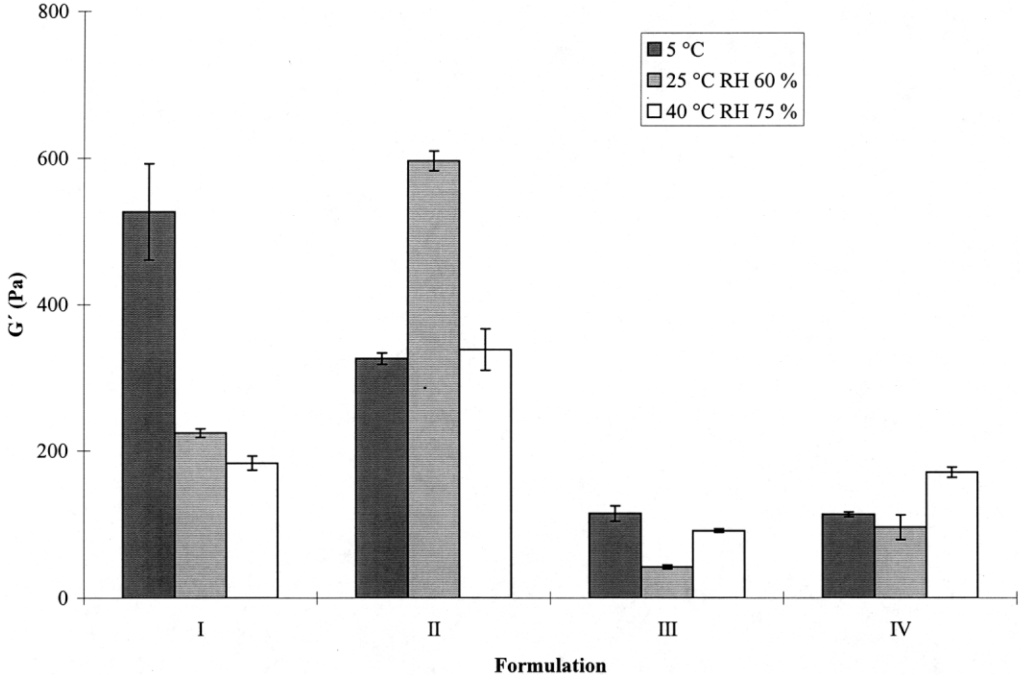

Fig. 2. Storage modulus (G') values after 28-day storage in three different storage conditions in the oscillation stress sweep test. In all formulations $n = 6$. Error bars around the measurement values present standard deviations (± sd) for each value.

Creams containing PEG 10 soya sterol did not show any clear evidence of viscoelastic behaviour (Fig. 4). Practically the creams studied behaved almost like Hookean solids with the strain proportional to the stress applied; on removal of the stress there was a complete recovery (Davis, 1969a). The instantaneous compliances of creams containing PEG 10 soya sterol (formulations I and II) were below one tenth of those containing PEG 25 soya sterol (formulations III and IV). In creams containing PEG 25 soya sterol there was a clear time-dependent retarded elastic region, a viscoelastic region and also a viscous region. The great consistency difference between the creams containing PEG 10 soya sterol and those containing PEG 25 soya sterol can be seen in addition to the compliance difference also from the great unrecoverable viscous flows of creams containing PEG 25 soya sterol (Fig. 4).

3.3. Droplet size distribution

At the 0-sample measurement point, the most common droplet diameter was < 1.7 μm for creams which contained sorbitan trioleate (formulations II and IV) and 1.7–6.8 μm for those containing sorbitan monooleate (formulations I and III) (Table 3). Although the droplet sizes grew as a function of storage time with all the formulations, the most common droplet diameter fraction changed with storage time and different storage conditions only in formulation IV which contained PEG 25 soya sterol and sorbitan trioleate. The most common droplet diameter fraction changed from < 1.7 μm of the 0-sample to 1.7–6.8 μm.

The droplet size distributions supported best the rheological tests in the case of the most viscoelastic creams containing PEG 10 soya sterol

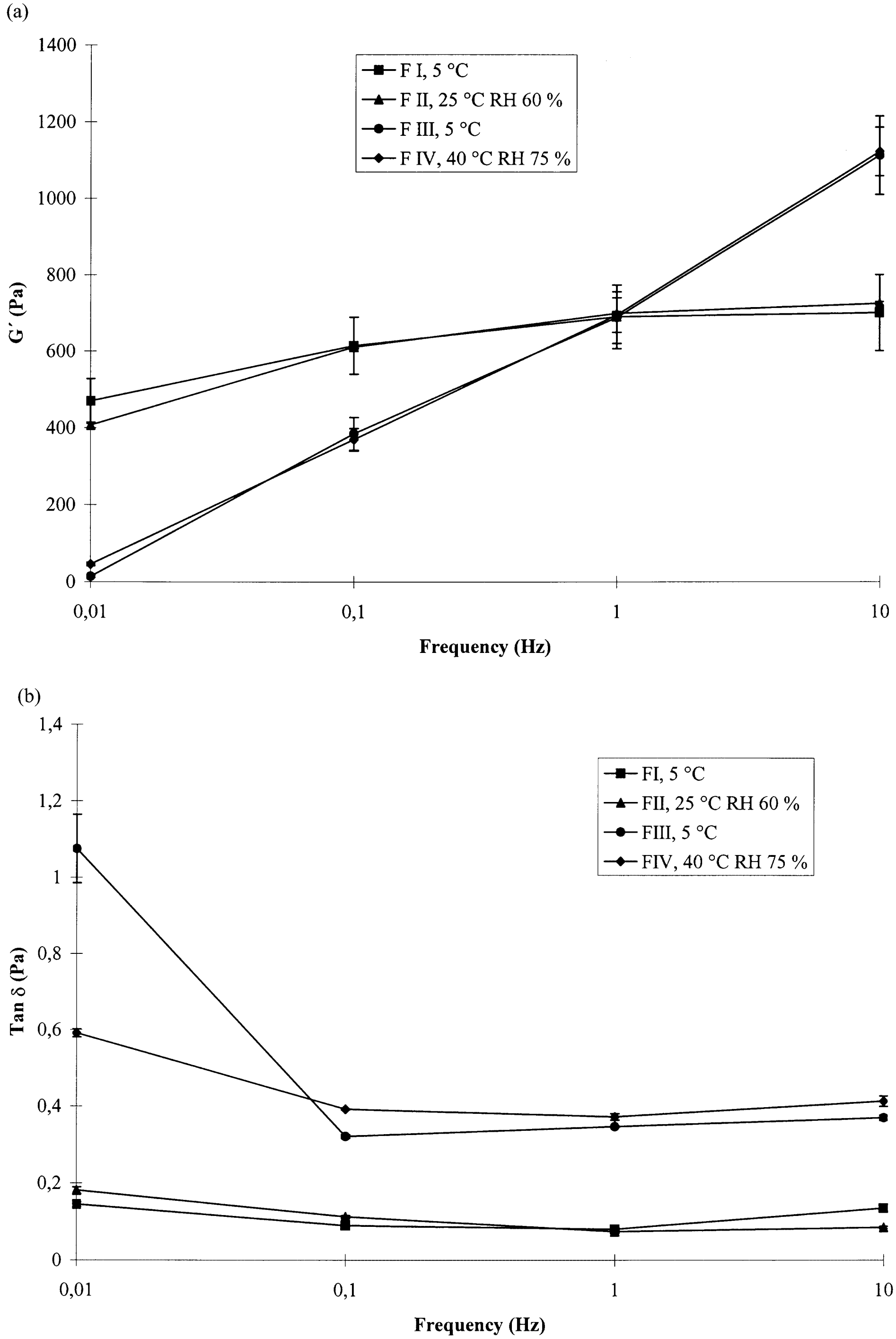

Fig. 3. (a) Storage modulus (G') values of the most viscoelastic creams of each formulation after 28-days of storage in the oscillation frequency sweep test. In all formulations $n = 6$. Error bars around the measurement values present standard deviations (± sd) for each value. (b) Tan δ (G''/G') values of the most viscoelastic creams of each formulation after 28-days of storage in the oscillation frequency sweep test. In all formulations $n = 6$. Error bars around the measurement values present standard deviations (± sd) for each value.

and sorbitan trioleate (formulation II); the smaller the droplets, the more consistent were the creams. In formulation II, also the droplet size distribution was the least dependent on the storage conditions. The droplet size distributions supported the rheological tests better in creams which contained PEG 10 soya sterol (formulations I and II) than in those containing PEG 25 soya sterol (formulations III and IV).

The stability of creams is traditionally evaluated by determining the droplet size distribution and changes in it. Droplet size distribution is not, however, the only and most important explaining factor when considering the rheological properties of creams. Creams are complex polydispersed multiple-phase systems composed of additional phases to oil-and-water (Eccleston, 1990). The basic rheology-determining parameters of a cream are the continuous phase rheology and the nature of the droplets (size distribution, deformability, internal viscosity, concentration and nature of particle-particle interaction) (Barnes, 1994).

3.4. Conductivity

The conductivity values of the creams increased during the 28-day storage time, mostly during the first 14 days (Table 4). In creams which contained PEG 10 soya sterol (formulations I and II) the conductivity test supported directly those of the rheological tests; with increasing conductivity of the creams the consistency of the creams decreased. In formulation III, which contained PEG 25 soya sterol and sorbitan monooleate, the smallest conductivity value was in a cream which behaved linearly viscoelastically in the oscillation stress sweep test (stored for 28 days at accelerated conditions). This shows that the linearly viscoelastically behaving cream had less free water and a more organized structure than the other creams.

The conductivity test is a rapid method for determining the stability of creams based on changes in the physical characters. The conductivity test supported the observation that when the amount of free water is reduced, the consistency

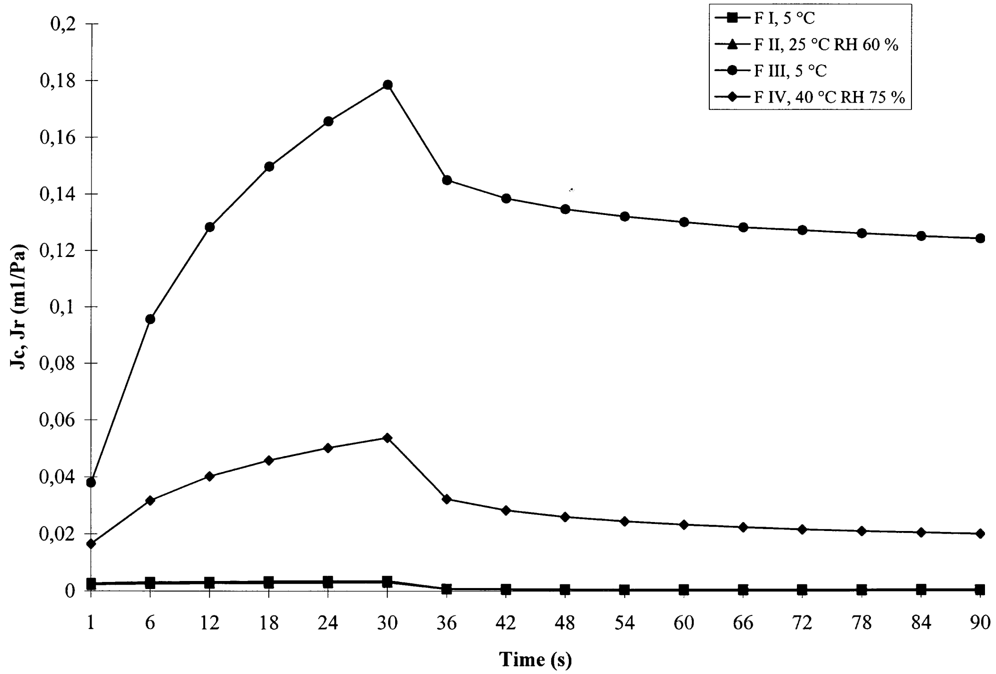

Fig. 4. *Jc* and *Jr* values of the most viscoelastic creams of each formulation after 28-days of storage in the creep recovery test. In all formulations $n = 6$. Standard deviations (± sd) for each measurement were < 0.001 for formulation I, < 0.002 for formulation II, < 0.04 for formulation III and < 0.01 for formulation IV.

Table 3
Droplet size distribution (μm) as a function of storage time and storage conditions (%)

Storaging time and condition	Diameter of droplets μm	Formulation			
		I	II	III	IV
0-sample	<1.7	32	**73**	33	**62**
	1.7–6.8	**65**	26	**67**	38
	>6.8	3	1	0	0
14 days 25°C RH 60%	<1.7	28	**70**	30	44
	1.7–6.8	**68**	28	**70**	**56**
	>6.8	4	2	0	0
28 days 25°C RH 60%	<1.7	25	**56**	28	45
	1.7–6.8	**77**	42	**72**	**55**
	>6.8	5	1	0	0
28 days 5°C	<1.7	32	**57**	35	44
	1.7–6.8	**63**	42	**65**	**56**
	>6.8	5	1	0	0
28 days 40°C RH 75%	<1.7	21	**58**	26	31
	1.7–6.8	**74**	41	**73**	**68**
	>6.8	5	1	1	1

In the 0-sample measurement point of formulation III $n = 600$, otherwise $n = 400$.

increases (Eccleston and Beattie, 1988). It has been suggested that the later the conductivity starts to rise and the smaller the rise is, the more stable the cream is going to be (Virtanen et al., 1993). The smallest changes in conductivity during the storage were observed in creams which contained sorbitan monooleate (formulations I and III).

4. Conclusions

The consistency of the creams decreased during storage, which is a sign of instability. Polyethylene glycol 10 soya sterol and sorbitan trioleate made the creams more elastic than polyethylene glycol 25 soya sterol and sorbitan monooleate. During the 28-day storage period the elasticity decreased the most in creams containing polyethylene glycol 10 soya sterol. Although the elasticity loss was the greatest, these creams were clearly more consistent after the 28-day storage period than those containing polyethylene glycol 25 soya sterol. The creams containing polyethylene glycol 10 soya sterol were linearly viscoelastically behaving creams. Storing the creams for 28 days in three different storage conditions levelled off the consistency differences of the formulations. With creams containing polyethylene glycol 10 soya sterol the dynamic and static rheological tests supported the droplet size distribution and conductivity tests. The HLB values of the surfactant combinations correlated directly with the viscoelasticities of the creams irrespective of storage time and conditions; the smaller the HLB value, the more viscoelastic was the cream.

Table 4
Conductivity values (μ*S*) as a function of storage time and storage conditions

Storaging time and conditon	Formulation			
	I	II	III	IV
0-sample	12.3	19.3	36.9	30.7
14 days, 25°C, RH 60%	13.7	28.3	38.6	36.9
28 days, 25°C, RH 60%	13.9	28.5	38.4	37.3
28 days, 5°C	11.0	44.9	42.8	35.6
28 days, 40°C, RH 75%	20.1	43.6	28.1	30.9

In the 0-sample measurement point of formulation III $n = 3$, otherwise $n = 2$.

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