

## Rheological properties of three component creams containing sorbitan monoesters as surfactants

Mirka Korhonen<sup>a,\*</sup>, Johanna Lehtonen<sup>b,c</sup>, Leena Hellen<sup>c</sup>, Jouni Hirvonen<sup>d</sup>,  
Jouko Yliruusi<sup>d</sup>

<sup>a</sup> Pharmaceutical Production, Orion Corporation Orion Pharma, P.O. Box 425, FIN-20101 Turku, Finland

<sup>b</sup> Pharmaceutical Development, Leiras Oy, P.O. Box 415, FIN-20101 Turku, Finland

<sup>c</sup> Pharmaceutical Development, Orion Corporation Orion Pharma, P.O. Box 425, FIN-20101 Turku, Finland

<sup>d</sup> Pharmaceutical Technology Division, Department of Pharmacy, University of Helsinki, P.O. Box 56, FIN-00014 Helsinki, Finland

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### Abstract

Creams from three components, surfactant, purified water and oil, were prepared. Comparable molar fractions of components were used in order to better understand the structural properties of the components used. The surfactants were sorbitan monoesters, sorbitan monolaurate, monopalmitate, monostearate and monooleate, which differed from each other in the length or structure of the hydrocarbon chain. The oils used were isopropylpalmitate and myristate, and they differed from each other in the length of the fatty acid chain. Rheological properties, droplet size distributions and types (either o/w or w/o) of the creams were studied. The rheological tests used were oscillation stress sweep test, creep recovery test and viscosity test. The modelling of the creep phase was based on the creep recovery test. Sorbitan monolaurate and monostearate formed w/o creams, sorbitan monopalmitate and monooleate o/w creams. It appeared that the double-bonded structure of the surfactant made the cream less elastic. Elasticity was increased due to lengthening of the alkyl chain of the surfactant and increased amount of surfactant. Also the lengthening of the fatty acid chain of the oil made the creams more elastic. The results of the rheological tests and droplet size distributions correlated well each other. According to the modelling of the creep phase, creams could be represented either with the Burger model or with the Maxwell model. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Rheology; Sorbitan monolaurate; Sorbitan monooleate; Sorbitan monopalmitate; Sorbitan monostearate; Viscoelastic

### 1. Introduction

To develop a cream, at least three components are needed; oil, water and surfactant. Surfactants possessing both polar and non-polar regions on the same molecule adsorb to the phase interfaces and decrease the interfacial free energy. Usually creams contain surfactants more than is required

\* Corresponding author. Tel.: +358-10-429-7509; fax: +358-10-429-7395

E-mail address: [mirka.korhonen@orionpharma.com](mailto:mirka.korhonen@orionpharma.com) (M. Korhonen).

to form monomolecular interfacial films. Excess amount of surfactant interacts with other components either at droplet interfaces or in the continuous phase to produce complex multiphase formulations (Eccleston, 1986). The characters and concentrations of surfactants are important factors affecting the structure and the rheological properties of creams (Barry and Saunders, 1971a,b; Barry and Eccleston, 1973a,b,c; Eccleston and Beattie, 1988; Virtanen et al., 1993; Kallioinen et al., 1994; Förster and Herrington, 1997; Korhonen et al., 2000, 2001).

The rheological properties of creams, in addition to character and concentration of the surfactant, are affected by the interfacial rheology of the surfactant film, volume fraction of the disperse phase, viscosity of disperse droplets, droplet size distribution as well as viscosity and chemical composition of the medium (Tadros, 1993). Determination of rheological properties—unrecoverable viscous, partly recoverable viscoelastic and recoverable elastic properties—gives reliable and versatile information about the structural properties of the cream. Viscoelastic properties are the most important rheological properties for creams, like for other semisolids. Analyses of viscoelastic materials are designed not to destroy the structure so that measurements can provide information on the intermolecular and interparticle forces in the material (Martin, 1993). As the measurements are made in the rheological ground state, the method of testing does not significantly alter the static structure of the material (Barry and Warburton, 1968).

The aim of the study was to investigate how the components used, the ratios of the components and the types (either o/w or w/o) of the creams formed influenced the structure and rheological properties of the creams.

## 2. Materials and methods

### 2.1. Materials

The surfactants used were non-ionic sorbitan fattyacid esters (Fluka, Switzerland), sorbitan monolaurate (Span<sup>®</sup> 20), sorbitan monopalmitate

(Span<sup>®</sup> 40), sorbitan monostearate (Span<sup>®</sup> 60) and sorbitan monooleate (Span<sup>®</sup> 80). Sorbitan monolaurate, monopalmitate and monostearate are saturated and sorbitan monooleate unsaturated sorbitan monoesters. Saturated sorbitan monoesters differ from each other in the length of the alkyl chain. Unsaturated sorbitan monooleate differs from sorbitan monostearate in the double-bond in the alkyl chain. The structures of sorbitan monoesters are presented in Fig. 1. The oils used were isopropylpalmitate and isopropylmyristate (Henkel KGAA, Germany), isopropylesters of palmitic acid and myristyl acid, respectively. The oils used differ in the length of the fatty acid chain; isopropylpalmitate has two carbons more in the alkyl chain.

### 2.2. Cream preparation

Creams were prepared in laboratory scale (batch size 100 g). Aq. purif. was added to the mixture of surfactant and oil at the temperature of 80 °C within 5 min, mixing at a speed of 230 rpm with a u-blade blender (RW 16 basic, Ika Labortechnik, Janke & Kunkel, Staufen, Germany). During the cooling phase the cream was continuously mixed (290 rpm) with two homogenization steps of 3 min (Ultra-Turrax, TP 18/10, Ika-Werk, Janke & Kunkel, Staufen, Germany). The adjusted capacity during the homogenization period was five (adjusted with Thyristor Regler TR50, Ika Labor-technik, Janke & Kunkel, Staufen, Germany).

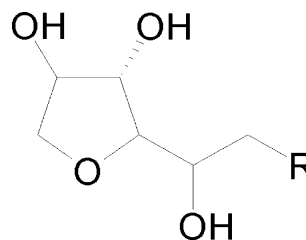


Fig. 1. Structures of sorbitan monoesters. R =  $-\text{OOC}(\text{C}_{11}\text{H}_{23})$  for sorbitan monolaurate (Span<sup>®</sup> 20),  $-\text{OOC}(\text{C}_{15}\text{H}_{31})$  for sorbitan monopalmitate (Span<sup>®</sup> 40),  $-\text{OOC}(\text{C}_{17}\text{H}_{35})$  for sorbitan monostearate (Span<sup>®</sup> 60) and  $-\text{OOC}(\text{C}_{17}\text{H}_{33})$  for sorbitan monooleate (Span<sup>®</sup> 80).

Mixing was continued until the temperature of the cream had dropped to 30 °C. All batches were prepared using the same manufacturing procedure. Two batches were prepared from each formulation.

### 2.3. Analytical methods

Conductivity measurement was used to determine the type (either o/w or w/o) of the cream. Conductivity was measured with a portable conductivity instrument (Mettler Check Mate 90, Mettler Toledo, Essex, USA). An ion-sensitive transistor was used. Conductivity determinations were made in triplicate for each batch.

Rheological properties were determined using a rheometer (StressTech, ReoLogica Instruments AB, Lund, Sweden, STRESS RHEOLOGIC Basic software, version 3.6) with the concentric cylinder system (diameter 15 mm). The temperature of the base plate was  $25.0 \pm 0.2$  °C. The tests performed were oscillation stress sweep test, creep recovery test and viscosity test. In the oscillation stress sweep test the stress was increased from 0.06 to 100 Pa and the frequency was kept constant (1 Hz). The linear viscoelastic region of each cream was determined with oscillation stress sweep test. In the linear viscoelastic region the ratio of stress and strain is a function of time alone (Kobayashi et al., 1982). In this study the end point of the linear viscoelastic region was determined as a stress when the storage modulus ( $G'$ ) value was dropped 10% from the linear level. In the creep recovery test the sample was exposed to the stress for 120 s and strain recovery was registered up to 360 s. The stress applied was chosen from the linear viscoelastic region of each cream determined in the oscillation stress sweep test. In the viscosity test the shear rate range was individual for each cream; measuring was started as the linear viscoelastic region ended and it was continued as far as the structure remained homogeneous. The shear rate regions used were selected due to the resisting abilities against the stresses applied. Both up-curves and down-curves were determined. All rheological determinations were made in triplicate for each batch using separate samples.

Droplet size distribution was determined with a light microscope (Olympus BX40F, Olympus Optical Ltd., Tokyo, Japan) using a magnitude of 600. A 10% suspension with the material of continuous phase was prepared and the measurements were performed immediately after sample preparation. The diameter was determined from 500 randomly chosen droplets of each batch.

## 3. Results and discussion

Seven formulations were prepared using four different sorbitan monoesters as surfactants (Table 1). One formulation was prepared with isopropylpalmitate and six formulations with isopropylmyristate as an oil phase. The formulations were selected based on comprehensive preliminary tests on each surfactant. More than 100 test formulations were prepared to find out the manufacturing method and composition areas to prepare creams with comparable molar fractions of components. The formulations can be divided into three formulation groups with the same molar fractions of components (Table 1). The formulations selected met the set criteria of short-term stable homogeneous creams remaining visually homogeneous for at least 2 days after cream preparation.

### 3.1. Types of creams

The types (either o/w or w/o) of creams prepared were determined with a conductivity test (Table 1). The results indicated that formulations containing sorbitan monolaurate (Span 20) or sorbitan monooleate (Span 80) formed w/o creams (formulations I–IV) and formulations containing sorbitan monopalmitate (Span 40) or sorbitan monostearate (Span 60) formed o/w creams (formulations V–VII). According to the supplier of surfactants, the HLB values of the sorbitan monolaurate and sorbitan monooleate batches used were 8.4 and 4.9 and of sorbitan monopalmitate and sorbitan monostearate batches 7.6 and 4.2, respectively. The HLB values of the surfactants did not explain the types of the creams formed. The unifying factor between these surfactant pairs is sorbitan

Table 1  
Formulations (g), conductivity values and types (either w/o or o/w) of creams ( $n = 6$ )

Formulation	Sorbitan monolau- rate Span 20	Sorbitan monopalmi- tate Span 40	Sorbitan monostea- rate Span 60	Sorbitan monoole- ate Span 80	Isopropyl- palmitate	Isopropyl- myristate	Aq. purif	Conductivity ( $\mu\text{s} \pm \text{S.D.}$ )	Type
I <sup>a</sup>	3.7	—	—	—	9.8	—	86.5	$0.0 \pm 0.0$	w/o
II <sup>a</sup>	3.7	—	—	—	—	9.0	87.3	$0.0 \pm 0.0$	w/o
III <sup>b</sup>	2.4	—	—	—	—	7.1	90.5	$0.0 \pm 0.0$	w/o
IV <sup>b</sup>	—	—	—	3.0	—	7.0	90.0	$0.0 \pm 0.0$	w/o
V <sup>c</sup>	—	6.9	—	—	—	20.0	73.1	$51.1 \pm 2.6$	o/w
VI <sup>a</sup>	—	—	4.6	—	—	8.9	86.5	$164.4 \pm 5.9$	o/w
VII <sup>c</sup>	—	—	7.3	—	—	19.9	72.8	$120.0 \pm 9.1$	o/w

From each formulation two batches were manufactured. Formulation groups based on the same molar fractions of surfactant and oil.

<sup>a</sup> Surfactant 0.011 mol, oil 0.033 mol.

<sup>b</sup> Surfactant 0.007 mol, oil 0.026 mol.

<sup>c</sup> Surfactant 0.017 mol, oil 0.074 mol.

monolaurate and monooleate being liquids and sorbitan monopalmitate and monostearate solids at room temperature. According to Yoshioka et al. (1994) sorbitan monopalmitate and sorbitan monostearate have higher phase transition temperatures ( $T_c$ ) than sorbitan monolaurate and sorbitan monooleate. At 25 °C the molecules of sorbitan monopalmitate and monostearate are in the ordered gel state, but those of sorbitan monolaurate and sorbitan monooleate are in the disordered liquid–crystalline state (Yoshioka et al., 1994). Also in other studies differences were observed between sorbitan monoesters according to their physical characters (Yoshioka and Florence, 1994; Peltonen and Yliruusi, 2000; Peltonen et al., 2001a,b).

### 3.2. Rheological properties

#### 3.2.1. W/o creams

W/o creams, creams which contained sorbitan monolaurate or sorbitan monooleate as surfactant (formulations I–IV), had wide linear viscoelastic regions (Table 2). According to crossing over point values, elastic properties were dominant up to high stress values at the expense of viscous properties (Table 2). Wide linear viscoelastic regions and great crossing over point values are signs of the ability of structures to resist external stresses to a greater extent. Also the minimal loss tangent ( $\tan \delta$ ) values in the linear viscoelastic region

showed that the elastic properties were clearly more dominant than the viscous ones (Table 3). It has been noticed that the storage modulus increases with increasing volume fraction of the dispersed phase (Pal, 1999). Due to the volume fraction of the dispersed phase (86.5–90.5%), w/o creams can be considered high internal phase emulsions (HIPRE). In HIPRE emulsions the volume fraction of the dispersed phase of cream exceeds the maximum packing volume fraction where the droplets just touch each other (Pal, 1999).

Among w/o creams, formulation I containing sorbitan monolaurate as surfactant and isopropylpalmitate as oil had the lowest loss tangent ( $\tan \delta$ ) values and the greatest storage modulus ( $G'$ ) value (Table 3). Also the linear viscoelastic region of formulation I was the widest (Table 2). Formulation I differed from formulation II only in the oil component used (Table 1). The isopropylpalmitate used in formulation I has two carbons more in the fatty acid chain than the isopropylmyristate used in formulation II. The longer hydrocarbon chain of oil made formulation I more elastic (Tables 2 and 3). Also the viscosity of the isopropylpalmitate is slightly greater than that of isopropylmyristate ( $5\text{--}10 \times 10^{-3}$  vs.  $5\text{--}7 \times 10^{-3}$  Pa s) (Kibbe, 2000).

In formulation II the concentration of surfactant, sorbitan monolaurate, was higher (3.7 vs. 2.4%) than in formulation III (Table 1). Increasing concentration of surfactant has been noticed to increase the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) values of creams (Förster and Herrington, 1997). An increase in consistency can be seen also in this study (Tables 2 and 3). The influence of double-bonded structure of surfactant can be seen with formulations III and IV. The unsaturated double-bonded structure of sorbitan monooleate in formulation IV made the cream less consistent than the saturated structure of sorbitan monolaurate in formulation III. It has been noticed that an unsaturated double-bonded structure may loosen the packing of the surfactant at the interfaces (Carlotti et al., 1995). For example, unsaturated double-bonded sorbitan monooleate has a larger molecular area and lower collapse pressure than its saturated counterpart sorbitan monostearate (Peltonen and Yliruusi, 2000).

Table 2

End-point values of the linear viscoelastic regions and crossing over point ( $G' = G''$ ) values in the oscillation stress sweep test ( $n = 6$ )

Formulation	End point of the linear viscoelastic region (Pa)	Crossing over point (Pa)
I	$39.4 \pm 9.5$	$42.1 \pm 8.8$
II	$25.9 \pm 6.8$	$30.7 \pm 6.0$
III	$14.5 \pm 2.4$	$20.0 \pm 2.8$
IV	$8.1 \pm 1.1$	$13.1 \pm 1.7$
V	$0.7 \pm 0.2$	$2.6 \pm 0.8$
VI	$0.7 \pm 0.1$	$2.7 \pm 0.7$
VII	$33.9 \pm 15.1$	$53.7 \pm 24.8$

Formulations I–IV were w/o creams, formulations V–VII o/w creams.

Table 3

Loss tangent ( $\tan \delta$ ), storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex modulus ( $G^*$ ) and complex viscosity ( $\eta^*$ ) values from the linear viscoelastic region of each formulation in the oscillation stress sweep test ( $n = 6$ )

Formulation	$\tan \delta$	$G'$ (Pa)	$G''$ (Pa)	$G^*$ (Pa)	$\eta^*$ (Pa s)
I	$0.014 \pm 0.001$	$303.4 \pm 3.7$	$4.1 \pm 0.2$	$303.4 \pm 3.7$	$48.3 \pm 0.6$
II	$0.014 \pm 0.001$	$273.2 \pm 5.5$	$3.8 \pm 0.2$	$273.2 \pm 5.5$	$43.5 \pm 0.9$
III	$0.016 \pm 0.001$	$212.1 \pm 9.5$	$3.5 \pm 0.1$	$212.2 \pm 9.5$	$33.8 \pm 1.5$
IV	$0.029 \pm 0.002$	$157.2 \pm 5.3$	$4.6 \pm 0.3$	$157.3 \pm 5.3$	$25.0 \pm 0.8$
V	$0.454 \pm 0.020$	$224.4 \pm 34.8$	$102.1 \pm 18.4$	$246.5 \pm 39.2$	$39.2 \pm 6.2$
VI	$0.206 \pm 0.006$	$96.8 \pm 19.4$	$19.9 \pm 4.3$	$98.8 \pm 19.9$	$15.7 \pm 3.2$
VII	$0.232 \pm 0.003$	$2050.1 \pm 192.0$	$475.0 \pm 42.0$	$2104.4 \pm 196.4$	$334.9 \pm 31.3$

Formulations I–IV were w/o creams, formulations V–VII o/w creams.

The results of the creep recovery test supported the results of the oscillation stress sweep test. In w/o creams, compliance reached a certain value ( $0.0035$ – $0.0115$  1/Pa) instantaneously after stress application (Fig. 2a). The increase in compliance during stress application was minimal in creams containing sorbitan monolaurate. With these creams the recovery was total after stress application. In formulation IV containing sorbitan monooleate as surfactant there was increasing compliance with viscoelastic and viscous regions (Fig. 2a). The recovery part of the curve showed unrecoverable viscous changes in the structure.

In the viscosity test, w/o creams behaved thixotropically (Fig. 2b). The creams were thixotropic and shear-thickening, dilatant. According to Martin (1993), dilatant systems are deflocculated and ordinarily contain more than 50% by volume of the solid dispersed phase. Formulations I and II, where the only difference was the oil used, had similar flow curves. Formulations III and IV had greater thixotropical hysteresis loops than formulations I and II. Up-curves of formulations III and IV indicated shear-thickening, down-curves slightly shear-thinning properties. With formulation IV the up-curves and down-curves intersected, implying that the shearing cycle itself caused some structural build-up (Eccleston and Beattie, 1988).

### 3.2.2. O/w creams

O/w creams had more viscous properties, greater loss tangent ( $\tan \delta$ ) values, than w/o creams (Table 3). However, also each o/w cream

had a linear viscoelastic region (Table 2). The only o/w cream, which had a wide linear viscoelastic region was formulation VII containing sorbitan monostearate as surfactant. Among all the creams studied, formulation VII had clearly the greatest storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta^*$ ) values in the linear viscoelastic region (Table 3). However, great loss tangent ( $\tan \delta$ ) values show more dominant viscous properties in formulation VII than in w/o creams. In formulation VII the volume of inner phase was small (19.9%), unlike the amount of surfactant (7.3%) (Table 1). The influence of surfactant concentration on the rheological properties of creams can be seen in formulations VII and VI, both containing sorbitan monostearate as surfactant (Table 1). An increase of over 50% in the amount of surfactant made formulation VII clearly more elastic than formulation VI (Tables 2 and 3). A greater amount of surfactant made also the conductivity of the cream smaller and bound more water in the lamellar water (Table 1).

Formulations VII and V had the same molar fractions of surfactant and oil (Table 1). However, formulation VII containing sorbitan monostearate had a clearly more elastic structure than formulation V containing sorbitan monopalmitate (Tables 2 and 3). The alkyl chain of sorbitan monostearate is two carbons longer than that of sorbitan monopalmitate. Up to a certain limit the length of the hydrocarbon chain of a surfactant makes the structure of the cream more consistent (Barry and Eccleston, 1973b). Sorbitan monoesters derive

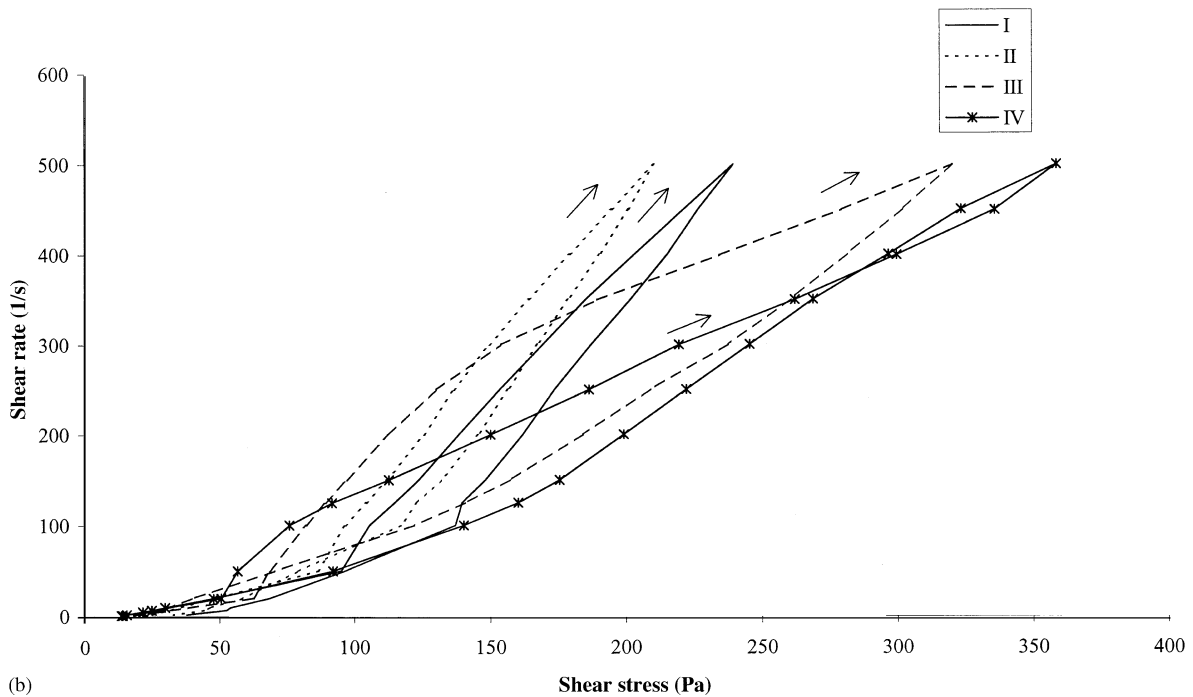
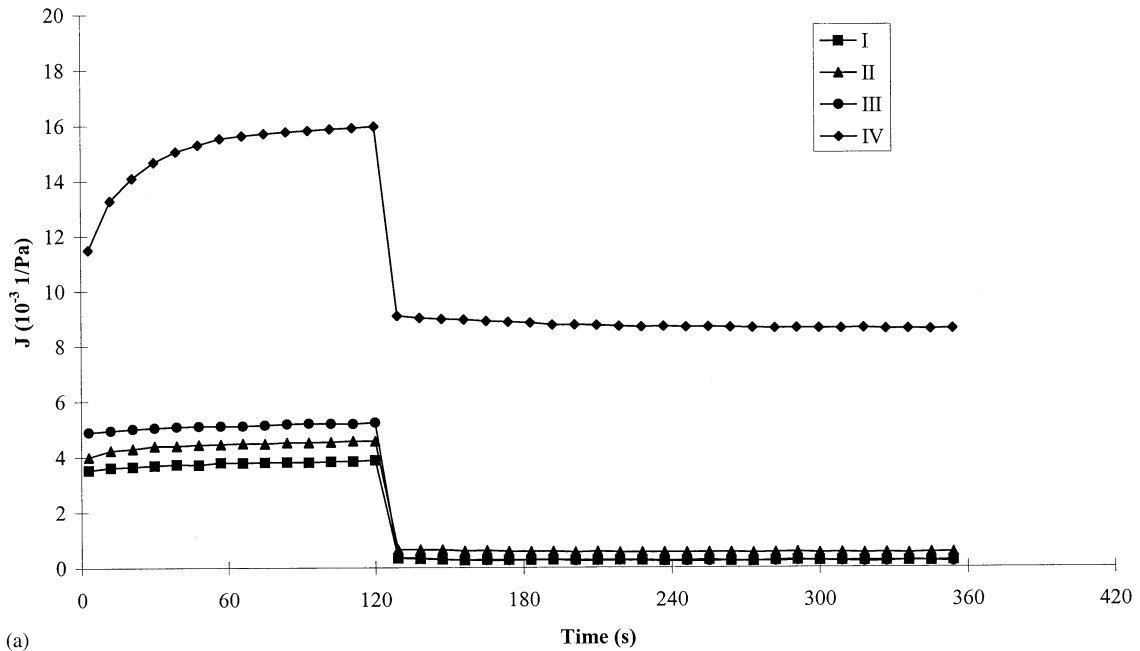


Fig. 2. (a) Results of creep recovery test of w/o creams ( $n = 6$ ). Standard deviations ( $\pm$ S.D.) were  $< 0.3 \times 10^{-3}$  1/Pa for formulation I,  $< 0.6 \times 10^{-3}$  1/Pa for formulation II,  $< 0.4 \times 10^{-3}$  1/Pa for formulation III and  $< 0.01$  1/Pa for formulation IV. The stress applied was 2 Pa. (b) Results of viscosity test of w/o creams ( $n = 6$ ). Standard deviations ( $\pm$ S.D.) were  $< 4.1$  Pa for formulation I,  $< 4.5$  Pa for formulation II,  $< 14.5$  Pa for formulation III and  $< 50.1$  Pa for formulation IV. The shear rate measurement range was 1–500 1/s.

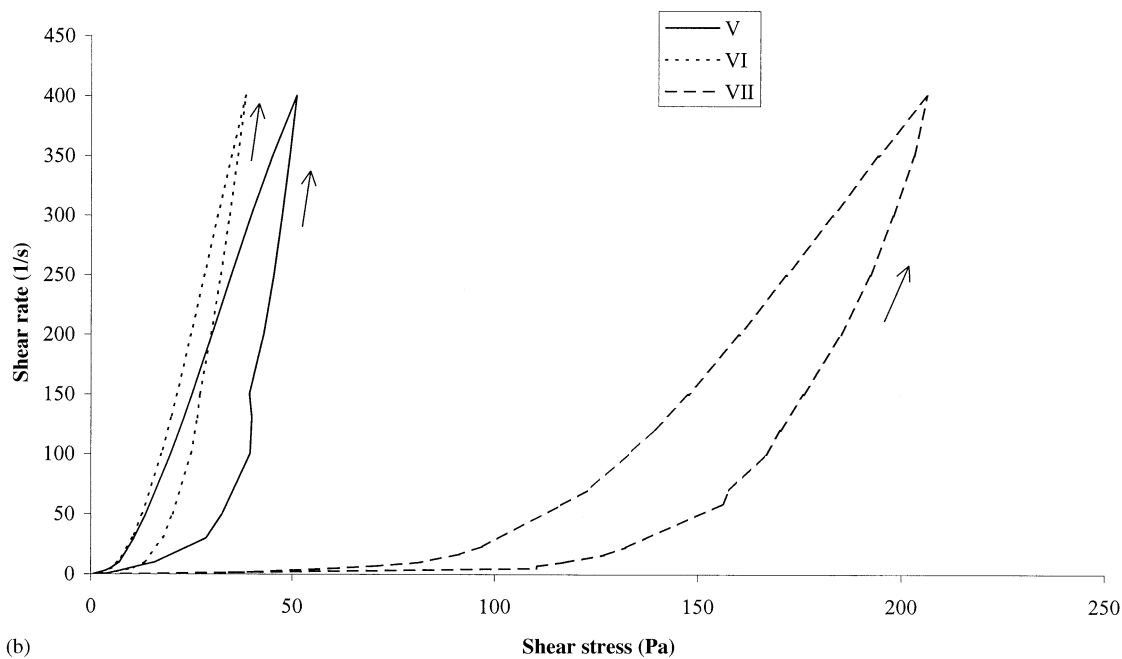
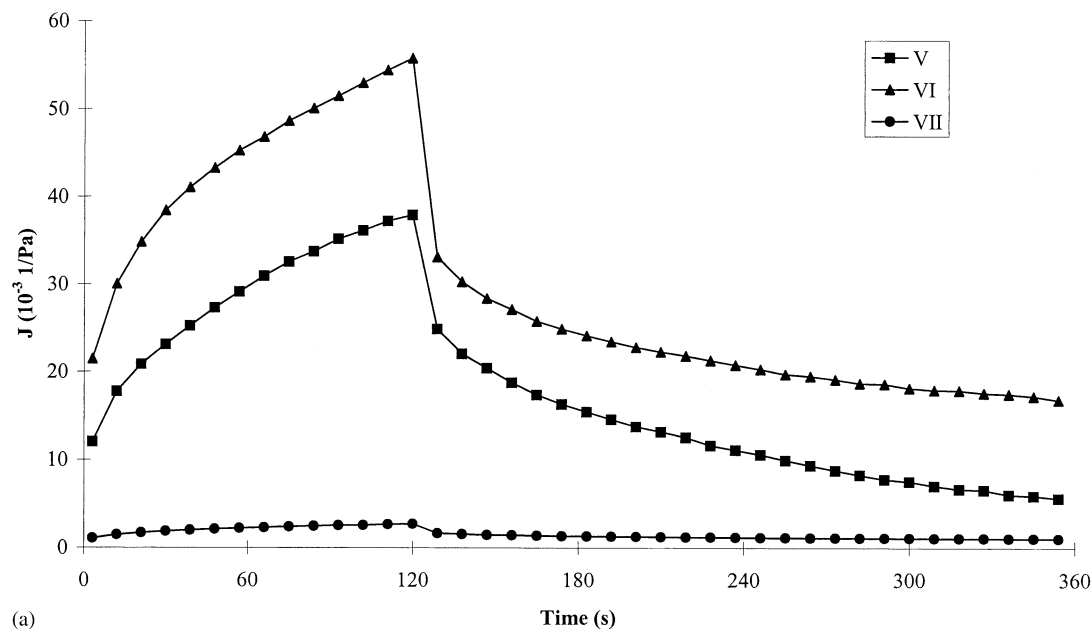


Fig. 3. (a) Results of creep recovery test of o/w creams ( $n=6$ ). Standard deviations ( $\pm$ S.D.) were  $<2.1 \times 10^{-2}$  1/Pa for formulation V,  $<1.4 \times 10^{-2}$  1/Pa for formulation VI and  $<1.0 \times 10^{-3}$  1/Pa for formulation VII. In formulations V and VI the stress applied was 0.3 Pa, in formulation VII 5 Pa. (b) Results of viscosity test of o/w creams ( $n=6$ ). Standard deviations ( $\pm$ S.D.) were  $<2.6$  Pa for formulation V,  $<1.4$  Pa for formulation VI and  $<18.7$  Pa for formulation VII. In formulations V and VI the shear rate measurement range was 0.1–400 1/s and in formulation VII it was 1–400 1/s.



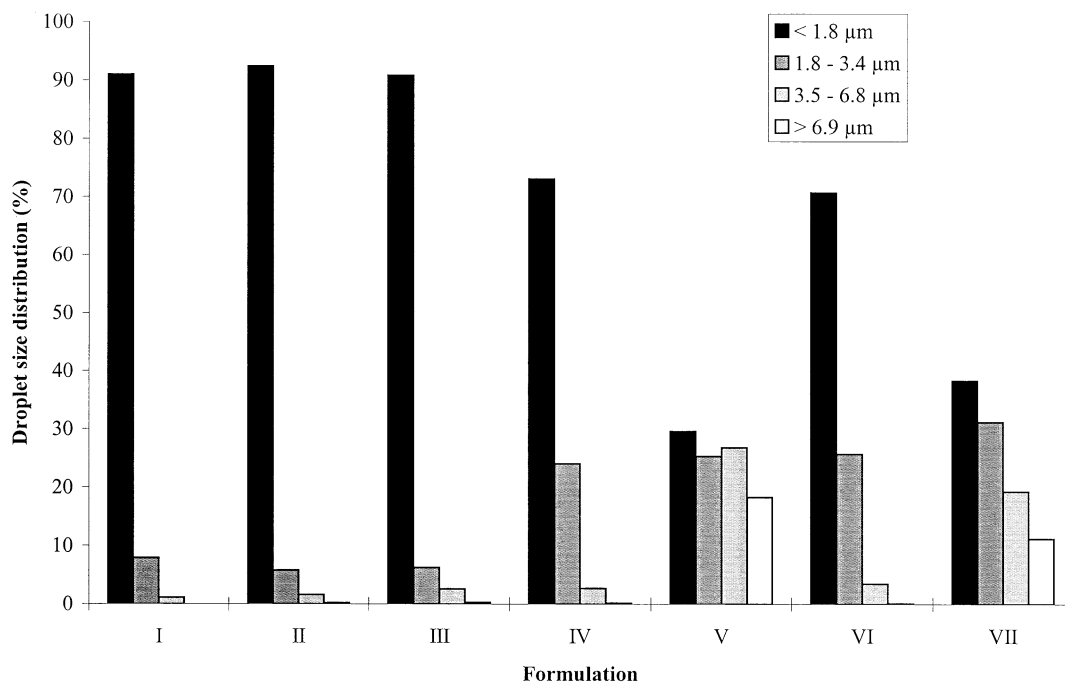


Fig. 4. Droplet size distributions (%) of formulations ( $n = 1000$ ; 500 droplets per batch in duplicate).

the surface activity primarily from the alkyl group (Peltonen and Yliruusi, 2000).

Formulation VI containing sorbitan monostearate formed an o/w cream. However, formulation II, which contained the same molar fractions of surfactant and oil, formed a w/o cream. Sorbitan monostearate is a more lipophilic surfactant than the sorbitan monolaurate used in formulation II (HLB values 4.2 vs. 8.4). Sorbitan monolaurate had enough of both hydrophilic properties to bind a large amount of water in the inner phase and lipophilic properties to make the oil a continuous phase.

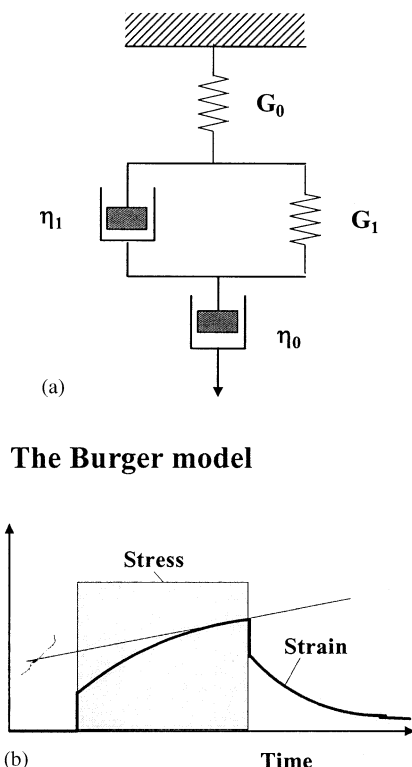
The results of creep recovery test supported the results of oscillation stress sweep test. As could be predicted from the results of oscillation stress sweep test, formulation VII containing sorbitan monostearate had the smallest compliance values, indicating the stiffest elastic and viscous structure (Fig. 3a). Formulations V and VI containing sorbitan monopalmitate and sorbitan monostearate had recoverable elastic, partly recoverable viscoelastic and unrecoverable viscous properties. In formulation VI, compliance grew the most

during the creep test, which could also be predicted from the results of oscillation stress sweep test (Table 3).

In the viscosity test, o/w creams behaved thixotropically (Fig. 3b). The creams were thixotropic and shear-thinning, pseudoplastic. At rest this kind of structure confers some rigidity on the system but, as the flow starts, the structure begins to break down and viscosity decreases (Martin, 1993). Viscoelastic and shear thinning properties and the presence of a yield value, are optimal properties for creams (Förster and Herington, 1997); creams remain consistent during storage and are easy to apply. The greatest yield value, about 100 Pa, was found in formulation VII. Thixotropic properties are particularly strong in flocculated systems (Barnes, 1994).

### 3.3. Droplet size distribution

In all formulations the droplet size fraction < 1.8 μm was the greatest (Fig. 4). In w/o cream formulations I–III the variation of droplet diameter was small. In formulations IV and VI the



**The Burger model**

Fig. 5. (a) Burger spring-dashpot model. (b) Strain curve according to the Burger model.

variation was greater and in o/w cream formulations V and VII the greatest. Droplet size is known to be a very important variable in emulsion rheology (Barnes, 1994). There was a clear correlation between droplet size distribution and viscoelastic properties. Creams with the smallest droplets, i.e. creams containing sorbitan monolaurate, behaved elastically ( $\tan \delta$  values in the linear viscoelastic region were below 0.016). Formulations IV and VI, in which the droplets were

greater on average, were slightly more viscously behaving ( $\tan \delta$  values in the linear viscoelastic region were 0.029 and 0.206). The greatest mean droplet sizes and the widest droplet size distributions were in cream formulations V and VII which had the most dominant viscous properties ( $\tan \delta$  values in the linear viscoelastic region were 0.454 and 0.232).

In w/o creams the volume of inner phase was so great, 86.5–90.5%, that the droplets of the inner phase had to be small or the droplets had to have a wide size distribution. Usually the width of the droplet size distribution and droplet deformability decreases with droplets size (Barnes, 1994). The 90% inner phase volume requires polydispersity. HIPRE creams, in which the amount of inner phase is even more than 90%, have to be multiple emulsions in which the outer phase itself is microemulsion. A part of the inner phase has to be a part of this microemulsion.

### 3.4. Modelling of creep phase

Creep phases were modelled using the Burger model (Fig. 5a and b). The model consists of two springs and two dashpots and can be described by the mathematical equation:

$$\gamma(t) = \frac{\nu\tau_0}{\eta_0} \cdot t + \frac{\nu\tau_0}{G_0} + \frac{\nu\tau_0}{G_1} [1 - e^{-t/\lambda_1}] \quad (1)$$

where  $\gamma(t)$ , strain;  $\tau_0$ , applied stress;  $G_0$  and  $G_1$ , shear moduli;  $\eta_0$  and  $\eta_1$ , viscosity coefficient;  $\lambda_1 = \eta_1/G_1$ , relaxation time.

According to the behavior in the creep phase, the formulations could be classified into three groups, formulations I–III, formulation IV and

Table 4

Calculated numeric values for creep phase parameters based on the Burger model

Formulation	$\tau_0$ (Pa)	$G_0$ (N m <sup>-1</sup> )	$\eta_0$ (10 <sup>3</sup> ) (Pa s)	$G_1$ (N m <sup>-1</sup> )	$\eta_1$ (Pa s)
I	2.0	286	240	–	–
II	2.0	238	300	5000	250
III	2.0	213	240	–	–
IV	2.0	111	40	400	60
V	0.3	100	8	200	14
VI	0.3	50	4	50	4
VII	5.0	1000	160	1333	80

formulations V–VII. The calculated numeric values are presented in Table 4.

W/o cream formulations I–III were rubbery systems with an extensive elastic strain and some non-recoverable viscous strain. Formulations I and III could be satisfactorily represented by the simpler Maxwell model consisting of one spring and one dashpot. Formulation II exhibited mainly the same properties as formulations I and III, although a very small exponential increase in the creep phase was observed. In practice all three formulations were almost ideal elastic Hookean solids. In the w/o cream formulation IV there was a small residual viscosity.

O/w cream formulations V–VI were viscoelastic systems with some instantaneous elastic strain followed by a viscoelastic strain which increased with time under stress. The relaxation was slow. Formulation VII had clearly the greatest instantaneous elastic strain followed by a viscoelastic strain. In o/w creams some non-recoverable viscous flow was also observed.

#### 4. Conclusions

The applicability of four different sorbitan monoester surfactants were studied. Different rheological tests gave quite a comprehensive picture of the structural properties of the creams studied. The rheological tests used were oscillation stress sweep test, creep recovery test and viscosity test. Creep phase was satisfactorily modelled by the Burger model or by the Maxwell model.

Sorbitan monolaurate (Span<sup>®</sup> 20) and sorbitan monooleate (Span<sup>®</sup> 80) formed w/o creams, sorbitan monopalmitate (Span<sup>®</sup> 40) and sorbitan monostearate (Span<sup>®</sup> 60) o/w creams. The physical character of surfactants affected the types of creams formed. The greater elasticity of creams containing sorbitan monolaurate compared with those containing sorbitan monooleate can be explained by the unsaturated structure of sorbitan monooleate. Sorbitan monostearate has two carbons more in the alkyl chain than sorbitan monopalmitate. Due to the longer alkyl chain, sorbitan monostearate formed a more elastic structure in the cream than sorbitan monopalmitate.

The influence of the amount of surfactant was seen with the creams containing sorbitan monostearate. An increased amount of surfactant made the cream more elastic.

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