

# The Aging of Polymer-Stabilized Creams: A Rheological Viewpoint

*Five o/w creams were prepared using four natural oils and hydrocarbon-based mineral oil. Data showed the rheology of creams was related to the polarity of the oil used.*

**key words:** rheological parameters, flow, oscillation, polymeric emulsifier, ageing, natural oils, mineral oil, polarity index

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A series of five o/w creams were prepared, using a polymeric emulsifier and different emollients. The four natural oils used in a simple o/w formulation were olive (*Olea europaea*), avocado (*Persea gratissima*), peanut (*Arachis hypogaea*) and apricot kernel oil (*Prunus armeniaca*). The fifth oil was a hydrocarbon-based mineral oil (*Paraffinum liquidum*). The oils used feature different chemical compositions, polarities and iodine values. It was of interest to learn whether and to what extent these variables affect rheological profiles of the test creams, based on acrylates/C10-30 alkyl acrylate crosspolymer. It was also important to evaluate the changes that occur during aging of these products.

Rheological parameters (yield value, viscosity and hysteresis area) were followed for 10 months. Both continuous flow and dynamic tests were performed on 10-month old samples, in order to determine complete viscoelastic status. The data obtained revealed that the rheology of creams was related to the polarity of the oil used. The mineral oil-containing sample showed a different pattern of structure change during aging, falling behind in the rank order of creams as time progressed. All samples revealed a structure build-up during this observation period, indicating a long-term stability.

## Introduction

The rheological profile of a cosmetic product is one of its most important features, in both technical and esthetic terms. Rheological properties are often directly related to the product sensory attributes and to its performance<sup>1,2</sup>. The relationship between rheology and product stability, especially in the case of emulsions, has been recognized as an important parameter in product formulation<sup>3,4</sup>.

**Demand for natural cosmetics:** In recent years, cosmetic oils of plant origin have been reintroduced into the market, following consumers' demand for "natural" cosmetics. Known to be less occlusive than petroleum-derived emollients and with better safety record than their synthetic relatives, natural oils are increasingly used in all types of cosmetic and toiletry products. However, they are also known to be inconsistent in their chemical composition and to cause stability problems. It was of interest to compare the performance of different plant-derived oils with a mineral oil in a simple o/w cream base, using rheological parameters.

Two pairs of natural oils were chosen for this study: olive and avocado oil, as a relatively "polar pair" and peanut and apricot kernel oil, as a less polar pair. Their polarity indices (measured as the interfacial tension against water), together with other relevant parameters, are presented in **Table 26.1**.

The nominal value of polarity index for each oil differs, depending on the source of information.<sup>5,6,7</sup> However, it shows the same trend of decrease from a nonpolar mineral oil, to a relatively polar olive/avocado pair (**Table 26.1**). The oils also vary in their chemical composition and iodine value, with olive/avocado pair being significantly more stable. All five oils were within the same viscosity range, hence allowing the comparison of the effect of their structure on the cream rheological properties.

**Table 26.1. Characteristic parameters of selected oils**

Oil	Polarity Index (mN/m)	Iodine value <sup>8</sup>	Chemical structure <sup>8</sup>	Cosmetic uses <sup>9</sup>
Olive oil	16.9 <sup>5</sup> 14.7 <sup>6</sup>	84	C18: 84%	Skin care, sun protection, shaving aids
Avocado oil	18.3 <sup>5</sup> 11.5 <sup>6</sup>	84	C16 22% C18:1 62%	Skin care, hair conditioners, bath products, make up, face powders
Peanut oil	20.5 <sup>5</sup>	98	C18: 59% C18:2 23%	Skin cleansing, hand and body products
Apricot kernel oil	21.6 <sup>6</sup>	102	C16 44% C18:1 40% C18:2 11%	Skin care, bath oils, hair products
Mineral oil	38.3 <sup>5</sup> 32.8 <sup>7</sup>	–	Hydrocarbon mixture	Skin care, skin cleansing, make up removers

**Benefits of cold emulsification:** A polymeric emulsifier was chosen for the formulation of the test creams, mainly because it allows for a "cold" emulsification procedure and the avoidance of the heating/cooling stress. In addition, it was of interest to follow the rheology profiles of fresh and aging o/w creams stabilized with this relatively new class of emulsifiers, which are used in very low concentrations (0.1–0.5%)<sup>10</sup>.

Continuous stress (flow) tests were employed on the freshly made (one day old) and aged (three and 10 month old) samples. To get a more comprehensive picture of the rheological status of the test samples, dynamic (oscillatory) tests were also performed on the aged creams. Our aim was to determine whether and to what extent oil polarity affects the consistency of the polymer-stabilized creams and to follow these changes during storage.

## Materials

Acrylates/C10-30 alkyl acrylate crosspolymer<sup>a</sup> was used as a primary emulsifier to make a series of o/w creams by cold emulsification. This polymeric resin belongs to a family of copolymers of acrylic acid, with minor levels of long chain (C10–C30) alkyl acrylate co-monomers, crosslinked with a polyalkenyl ether.<sup>10</sup> Four natural oils have been employed: olive oil<sup>b</sup>, Avocado oil<sup>c</sup>, peanut oil<sup>c</sup>, and apricot kernel oil<sup>c</sup>, alongside with a hydrocarbon-based mineral oil<sup>d</sup>. The viscosity of the five oils was in the range of 59–65 mPa, as measured by Brookfield LTV viscometer, spindle 1, at the room temperature. Triethanolamine (TEA, Sigma, UK) was used as a neutralizing agent, and preserved purified water as an external phase of the creams.

The composition of test samples is presented in **Table 26.2**.

Ingredient	% w/w
Acrylates/C10-30 alkyl acrylate crosspolymer	0.4
Oil	20.0
Triethanolamine (10% aqueous solution)	6.0
Preservative (in a propylene glycol solution)	1.0
Purified water	72.6

<sup>a</sup> Pemulen TR-1Ç BFGoodrich, Cleveland, Ohio

<sup>b</sup> Fisons, UK

<sup>c</sup> SNOI International, USA

<sup>d</sup> Fisher Scientific, UK

<sup>e</sup> Carri-Med CSL<sup>2</sup> 500, TA Instruments, UK

## Emulsion Preparation Method

A “direct method”<sup>10</sup> was used in the production of the test samples. The emulsion was obtained by dispersing a polymeric emulsifier in the mixture of water and propylene glycol-based preservative at the room temperature, by means of an overhead stirrer. After a 20-minute stirring period, the oil phase was added and the stirring continued for another 30 minutes. The acidic dispersion obtained was then neutralized with triethanolamine 10% w/w aqueous solution to the pH value of approximately 6.0. A resulting o/w cream was packed in an opaque container and tightly closed.

## Rheological Studies

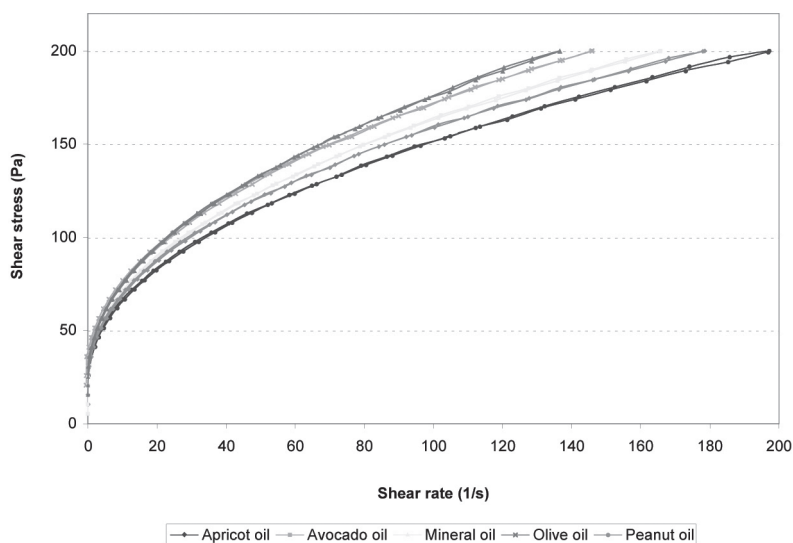
A controlled-stress rheometer<sup>c</sup> with a cone-and-plate measuring system was used in all the experiments. Continuous flow tests were performed by increasing a shear stress from 0–200 Pa and decreasing it back to 0, each stage taking one minute. Five runs were carried out on each sample, with the coefficient of variation less than 15%.

Oscillatory (dynamic) measurements were performed over a frequency range of 0.1–10 Hz. In the case of cream samples, the standard frequency sweep procedure with a fixed torque value was not applicable, as it produced poor wave forms and inconsistent results. Therefore, in our procedure, the deformation of the sample was kept at the fixed level of  $10^{-3}$  radians, which corresponded with a 2.8% strain, leaving the rheometer to adjust the torque accordingly. Three repeat oscillatory runs were performed on each sample. Both flow and dynamic measurements were carried out at 20°C.

The first measurement was performed on 24-hour-old samples, which were then stored at the room temperature ( $20 \pm 2^\circ\text{C}$ ) for another two tests in a three- and 10-month period, respectively.

## Results

The flow data of the fresh samples are shown in **Figure 26.1** and **Table 26.3**. Lower values for shear rate under the same shear stress indicate a higher viscosity for the sample. It is evident that the mineral oil cream exhibits the highest viscosity, followed by the olive, avocado, apricot kernel and peanut oil cream, respectively (**Figure 26.1**).



**Figure 26.1.** Flow curves for the fresh creams (after 1 day.)

**Table 26.3. Flow parameters (yield value  $\tau_y$ , viscosity  $\eta$  and hysteresis area H) after 1 day, 3 months and 10 months of storage**

Sample	After 1 day			After 3 months			After 10 months		
	$\tau_y$ (Pa)	$\eta$ at 200 Pa (mPa s)	H (P/s)	$\tau_y$ (Pa)	$\eta$ at 200 Pa (mPa s)	H (P/s)	$\tau_y$ (Pa)	$\eta$ at 200 Pa (mPa s)	H (P/s)
Olive oil cream	20.53	1360	53.9	20.51	1400	248.5	25.63	3010	513.5
Avocado oil cream	20.55	1205	31.65	20.51	1240	236.7	25.67	1880	265.0
Peanut oil cream	20.53	1010	62.27	15.40	1080	270.3	20.51	1530	648.1
Apricot kernel oil cream	20.54	1120	27.65	15.42	1150	201.6	20.54	1490	384.7
Mineral oil cream	20.50	1460	23.58	15.38	1275	64.58	20.53	1570	493.6

**Elasticity levels:** All the samples possess yield stress value  $\tau_y$  (Table 26.3), indicating that their networks exhibit a resistance to an external force before they start flowing (plastic behavior). In the previous study<sup>12</sup>, we found a good correlation between yield values and elastic parameters of semisolids. Based on those findings, the almost identical yield values of the cream samples reveal the same level of elasticity in all fresh samples, regardless of the oil used.

It is noticeable from Figure 26.1 that the up and down parts of flow curves do not overlap completely, creating a hysteresis loop area, which is commonly used as a measure of thixotropy. The olive oil cream has shown considerably larger thixotropy at this stage (Table 26.3), indicating the presence of structures that are more susceptible to breakdown under shear than the other samples.

**Aging data:** After three months of storage, the mineral oil cream fell in the rank order of viscosity (Figure 26.2), followed by a further fall after 10 months (Figure 26.3 and Table 26.3). This result indicates different types of structural changes during aging, compared with the natural oil creams. The latter followed the same pattern throughout the observation period, with the olive/avocado oil pair having higher viscosity and yield stress values than the peanut/apricot kernel oil pair (Table 26.3). The general increase in viscosity upon storage in all the samples, however, shows a favorable internal structuring and indicates a long-term stability of the test samples<sup>1,3</sup>. An increase in the level of thixotropy was also apparent (Table 26.3), showing a prominent time-dependent flow behavior.

Many materials, especially semisolids, possess rheological properties of both solids and liquids, i.e., viscoelasticity. Dynamic (oscillatory) studies provide information on both elastic and viscous components of creams and other semisolid products. The behavior of the sample is expressed in terms of a storage (elastic) modulus, which is a measure of energy stored and recovered per cycle of deformation, and a loss (viscous) modulus, which reflects the energy lost per cycle<sup>13</sup>. Figures 26.4 and 26.5 show the viscous and elastic moduli of the test creams, respectively.

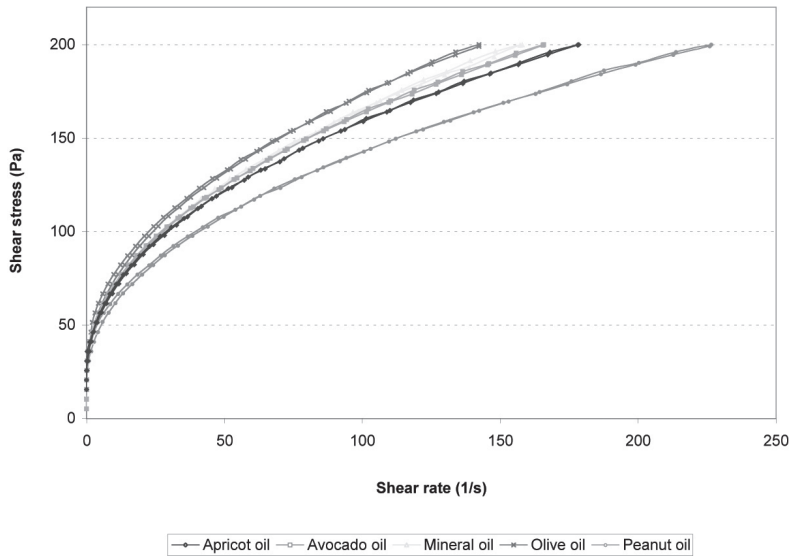


Figure 26.2. Flow curves for the 3-month old creams.

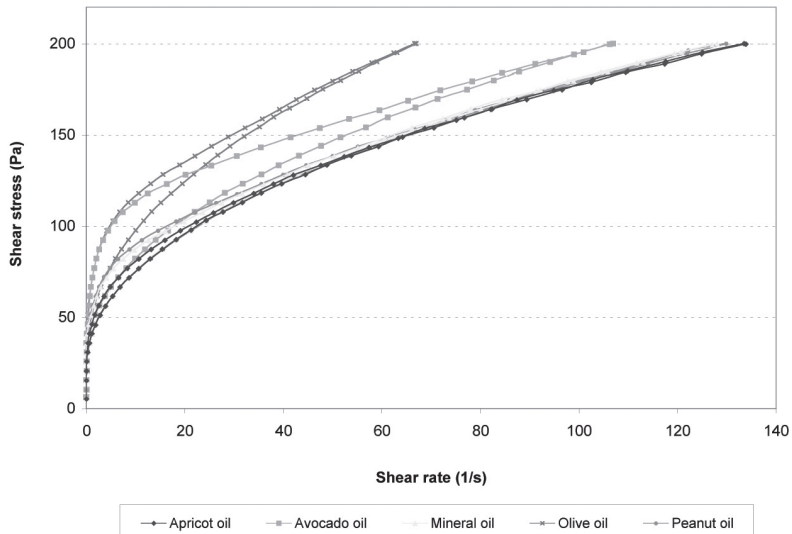


Figure 26.3. Flow curves for the 10-month old creams.

The information gained from oscillatory studies complemented the flow data in terms of behavioral patterns for the cream pairs. Both viscous and elastic moduli for the olive/avocado oil pair were higher than the corresponding values for the peanut/apricot kernel oil creams (**Figures 26.4 and 26.5**).

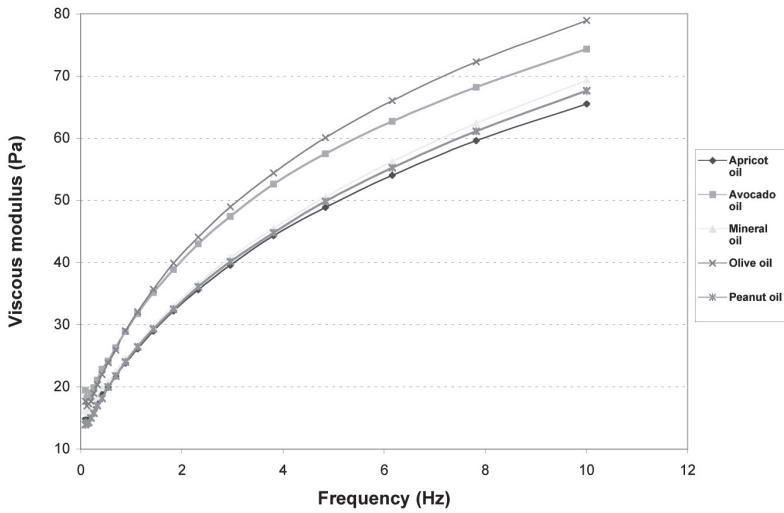


Figure 26.4. Viscous (loss) moduli for the 10-month old creams.

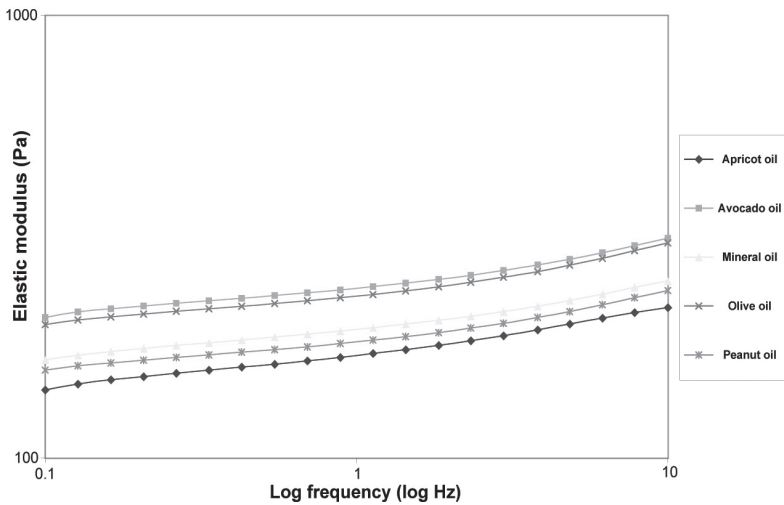


Figure 26.5. Elastic (storage) moduli for the 10-month old creams

A stable network structure: **Figure 26.6** shows the values of parameter  $\tan \delta$  over a frequency range studied.  $\tan \delta$  is the ratio between viscous and elastic moduli and is commonly taken as a measure of the overall viscoelasticity of the sample<sup>13</sup>, with the lower  $\tan \delta$  showing higher elasticity. Unlike corresponding polyacrylic acid gels studied previously<sup>12</sup>, which show relatively constant  $\tan \delta$  values throughout the frequency range used, the cream samples exhibit an increase in this parameter at higher frequencies, indicating a fall in network elasticity under rapidly oscillating

forces (Figure 26.6). A departure from the high-frequency pattern in  $\tan \delta$  values is evident in the case of mineral oil cream, confirming an assumption on the structural differences made on the basis of flow data. Generally, however,  $\tan \delta$  values of all test samples are relatively high (between 0.1–0.3), revealing a dominance of elastic over viscous properties and indicating a stable network structure.

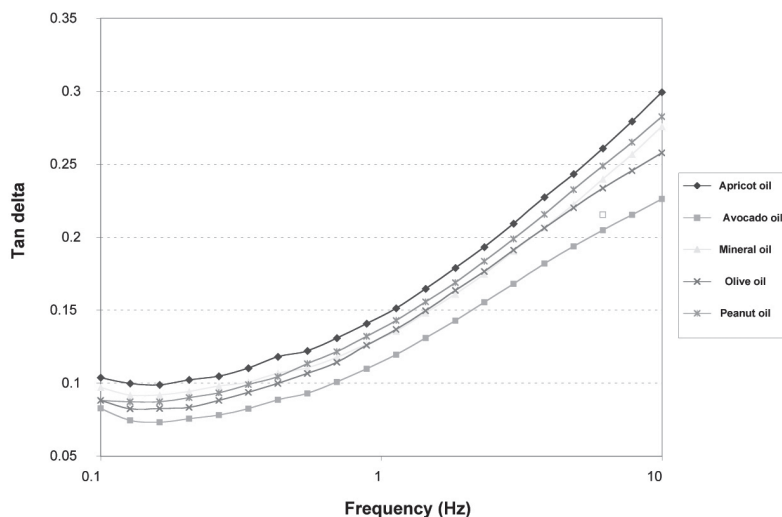


Figure 26.6.  $\tan \delta$  values for the 10-month old creams.

## Discussion

When first introduced in the early 1990s, polymeric emulsifiers (associative thickeners) showed a great promise for emulsion formulation. Being hydrophobically modified water-soluble polymers, they have no HLB and PIT constraints of conventional emulsifiers. They have been proven to act as primary emulsifiers and even to structure the continuous phase of the emulsion more consistently than lamellar gel or liquid crystalline phases<sup>4</sup>. “Steric stabilization” was identified as a main stabilizing mechanism, with the hydrophobic tails of these molecules being adsorbed at the oil/water interface and the hydrophilic portions swelling in water and forming microgels around the oil droplets<sup>11</sup>. Exceptional emulsion stability and triggered release upon application are claimed to be distinct advantages<sup>4,10–11</sup>. It was recognized, however, that certain oils need a co-emulsifier to stay dispersed in a polymer-stabilized emulsion and that oil polarity may play an important part in it<sup>10,14–15</sup>.

**Interboundary interaction:** The composition and polarity of the oil phase is known to have a large influence on the design, properties and stability of cosmetic emulsions<sup>14,16</sup>. The main factor in structure formation is the interboundary interaction of the hydrophilic and lipophilic phase<sup>16,17</sup>. The lipids differing mostly in terms of emulsion preparation are “easy-to-process” paraffin oils on the one hand and



the “problematic” triglycerides, in particular vegetable oils<sup>17</sup>, on the other. The strength of the interboundary interaction may correlate with the polarity of the oils<sup>14,16,17</sup>. The mechanism of this interaction is complex and particular to the oil/emulsifier system used.

In the case of polymeric emulsifier, it is known that it must bond to the emulsion's internal phase through dipole-dipole interactions, hydrogen bonding and hydrophobic interactions<sup>4</sup>. It is the balance of these forces that determines the overall interfacial interaction, which in turn has an impact on the rheological properties of the sample, as shown in this study. It was revealed by both flow (**Figures 26.1–26.3**) and oscillatory tests (**Figure 26.6**) that the changes in internal structuring during aging for the mineral oil cream differ from the natural oil creams. It is reasonable to assume that the balance of forces acting at the mineral oil/polymer interface varies from that present in the natural oil/polymer boundary. Among the natural oils used in the study, there was a distinct difference in rheological properties between a “polar” olive/avocado oil pair and a less polar peanut/apricot kernel pair. It is possible that polar interactions play more important roles in the structure build-up than hydrophobic interactions in the case of polymer-stabilized creams.

**Examining elastic properties:** Rheological profile of all test samples was characterized by plastic flow with thixotropy. Yield stress value is widely considered the most reliable indicator of the stability in a mixture, in fact “the best and only realistic approach” in many cases<sup>3</sup>. The presence of relatively high yield values in all test samples throughout the observation period (**Table 26.3**) is taken as an indicator of high emulsion stability. This study provided further support to the statement that yield value is directly related to elastic properties of the sample<sup>12</sup>. Both yield stress and elastic moduli values for olive and avocado oil creams were found to be higher than for the three remaining samples (**Table 26.3** and **Figure 26.4**).

An increase in thixotropy with aging was found to be a prominent trend in this study. Thixotropy (a time-dependent and recoverable sheer thinning) is a favorable rheological property, which offers not only a technical storage stability benefit, but also increases consumer appeal<sup>6</sup>. Aging induced increase in viscosity and thixotropy in these emulsion systems is based on the formation of additional inter- and intramolecular bonds, some of which break reversibly under shear.

## Conclusion

The results obtained in this study showed the chemical composition and the polarity of the oil play a significant role in the structure of polymer-stabilized emulsions. A nonpolar mineral oil caused a different pattern of aging-induced structural changes in a cream sample, compared with the more polar natural oils (olive, avocado, peanut and apricot kernel) when studied by rheological parameters.

All cream samples revealed plastic flow with thixotropy in both fresh and aged states. High yield values derived from flow tests and favorable  $\tan \delta$  values from oscillatory studies both indicate good internal structuring and a long-term stability.

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**References**

1. PE Miner, "Emulsion Rheology: Creams and Lotions." In: D Laba (ed.), *Rheological Properties of Cosmetics & Toiletries*, Marcel Dekker 313–369 (1993)
2. GH Dahms, "The impact of the emulsion structure on adsorption and release of actives on skin." In: *Emulsions: Technology, Structures, Ingredients, Formulations*, Verlag für chemische Industrie, H. Ziolkowsky GmbH, Augsburg 15–24 (1998)
3. CD Vaughan, "Predicting Stability in Rheologically Modified Systems." In: D Laba (ed.), *Rheological properties of Cosmetics & Toiletries*, Marcel Dekker 371–401 (1993)
4. RY Lochhead, *Emulsions, Cosmet & Toiletries* 109 93–103 (1994)
5. KF De Polo, *A Short Textbook of Cosmetology*, Verlag für chemische Industrie, H. Ziolkowsky GmbH, Augsburg 149–166 (1998)
6. ICI Surfactants, *Emulsifiers for oil-in-water Emulsions Brochure* 41-1E (1996)
7. U Zeidler, *The Tactile Properties of Cosmetic Oils*, Henkel—Referate 29, 91–96 (1993)
8. AJ O'Lenick and DC Steinberg, *Primary Ingredients*, Hansotech Inc. (1998)
9. M M Rieger, *Cosmetic Use of Selected Natural Fats and Oils*, *Cosmet & Toiletries* 114 33–40 (1999)
10. Lubrizol, *Noveon Consumer Specialities*, TDS-114, 2002 (available from [www.personalcare.noveon.com/literature/techdata.asp#pemulen](http://www.personalcare.noveon.com/literature/techdata.asp#pemulen))
11. K Schrader and A Domsch, *Cosmetology—Theory and Practice Vol III*, Verlag für chemische Industrie, H. Ziolkowsky GmbH, Augsburg 117–118 (2005)
12. S Tamburic and DQM Craig, *Rheological Evaluation of Polyacrylic Acid Hydrogels*, *Pharmazie* 1 107–109 (1995)
13. JD Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York (1970)
14. T Dietz, *Basic Properties of Cosmetic Oils and their Relevance to Emulsion Preparations*, *SÖWF Journal* 125 2–9 (1999)
15. M-F Bobin, V Michel, E Journet and M-C Martini, *Study of formulation and stability of emulsions with polymeric emulsifiers*, 2nd World Congress on Emulsions, Bordeaux, 1 1-175 (1997)
16. A Taleb and I Eros, *Rheological Studies of creams. III. Effect of lipophilic phase consistency*, *Acta Pharm Hung* 66 77–81 (1996)
17. P Hameyer and A Bungard, "The Viscosity Behaviour of w/o Emulsions with a High Dispersed Phase Content." In: *Emulsions: Technology, Structures, Ingredients, Formulations*, Verlag für chemische Industrie, H. Ziolkowsky GmbH, Augsburg 234–248 (1998)