RHEOLOGICAL PROPERTIES OF OIL/WATER EMULSION AND OIL/LIQUID CRYSTAL/WATER SYSTEMS AND THEIR CONSUMER PERCEPTION IN HAIR CARE PRODUCTS

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Abstract

Liquid crystal known as a rheological barrier to coalescence of oil droplets, increases emulsion stability, water-holding capacity and promotes active material penetration to skin. Some investigation for its rheological characteristics have been reported but its relations to consumer perception have been rarely published.

In this study, oil/water emulsion and oil/liquid crystal/water systems were manufactured using the same composition of Behenyltrimethylammonium chloride/Cetostearyl alcohol/Lanolin oil, and rheological properties of each system were investigated with Cone and Plate rheometer. The formation of liquid crystalline phase was observed with polarized microscope and Differential Scanning Calorimeter. Continuous shear experiment, creep, yield and water holding capacity were measured for oil/water and oil/liquid crystal/water systems. The results were compared with sensory evaluations. Oil/liquid crystal/water system showed higher viscosity at the same shear rate, higher viscoelasticity and higher yield stress than oil/water system. These properties were expected to show good spreadability and excellent richness without waxiness in hair care products of creme type. This expectation was consistent with the results of sensory experiments. Water-holding capacity was evaluated by measuring residual water of specimens at specific temperature and relative humidity. Oil/liquid crystal/water system was proved to have higher ability to hold water in comparison with oil/water system. The results indicated that oil/liquid crystal/water system was of benefit to rheological properties creme type hair care products.

Key word : Liquid crystal, Rheological properties, Sensory evaluation

1. Introduction

In recent years the cosmetic industry has acknowledged the importance of rheological assessment of raw material as well as of the finished products. It is crucial that hair care product, besides possessing efficacies on hair, should have consumer acceptability that has an effect on consumer's buying preference. Thus, rheological properties in hair care products are very important. It was also found that liquid crystalline phase formed by complexation of long chain alcohol/surface active agent/water in emulsion plays a very significant role in rheological behavior of it. Some authors examined flow characteristics of emulsions of different concentrations of mixed emulsifiers through continuous shear experiment, creep test, oscillatory measurement and related them to internal gel network in system. Forster and Herrington concluded that good O/W crème should have shear thinning behavior, low yield stress and elastic behavior. (2)

In the present work, two systems, S_1 and S_2, of the same composition of Behenyltrimethyl ammonium chloride/Cetostearyl alcohol/Lanolin oil/water were prepared using different methods and continuous shear experiment, creep test, yield test and water-holding capacity were conducted over them. The formation of liquid crystal in system was examined using a polarizing microscope. Sensory assessments were evaluated with a panel of 10 members and the results were correlated with the rheological characteristics of S_1 and S_2.

2. Experimental

2.1 Material

Deionized water, Lanolin oil(Westbrook Lanolin Ltd.), BTAC(Behenyltrimethyl ammonium Chloride, BTAC 85%, IPA 15%)(Witco Ltd.), Cetostearyl alcohol(Henkel Ltd.) were used to prepare S_1 and S_2.

2.2. Preparation

S_1 and S_2 were prepared according to the general formula : Lanolin Oil 0.5 g, Cetostearyl alcohol 4 g, BTAC 3 g, deionized water 92.5 g.

S_1 : After Lanolin oil(0.5 g), Cetostearyl alcohol(4 g), and BTAC(3 g) were melted, the solution was poured into deionized water(92.5 g) at about 70^0C and mixed for 10 min using Homogenizer. The beaker and contents were cooled slowly.

S_2 : After Lanolin oil(0.5 g). Cetostearyl alcohol(4 g) were melted. the solution was poured into aqueous solution of BTAC(3 g)/deionized water(92.5 g) at about 85°C and mixed for 10 min using Homogenizer. The beaker and contents were cooled slowly.

2.3 POM(Polarized Optical Microscope) and DSC(Differential Scanning Calorimeter) Analysis

S_1 and S_2 were examined individually at room temperature at a magnification of x 400 using a polarizing microscope (Nikon).

Measurements of thermal properties of two systems were conducted using DSC. The Individual sample was sealed in silver cell and heated at the rate of 10 °C/min.

2.4 Measurement of Rheological Properties

The examination of rheological properties of two samples were made using Cone and Plate Rheometer(Physica) at 30 °C which was assumed to be hair temperature.

- Continuous shear experiment : The samples were continuously sheared from 0.0 to 100 sec⁻¹
- Yield stress : Shear rate of samples were measured with increasing shear stress from 1 to 100 Pa.
- Creep test : Constant shear stress(10 Pa) was imposed on the samples at zero time. being maintained constant. growth of strain was measured.

2.5 Measurement of Approximate Water-holding Capacity

To compare water-holding capacities of S_1 and S_2 which are associated with aqueous phase entrapped in liquid crystal. the tests were performed as described.

Test 1 : 1 g of S_1 and S_2 was put into a pan maintained at 70°C and at relative humidity of 60%. Residual mass was measured in every 10 min.

Test 2 : Tress of 2 g was treated with S_1 and S_2 for 5 min carefully at room temperature and washed with flowing deionized water during 30 sec and towel dried. Then. each tress was put in the room at constant temperature(25°C) and constant relative humidity(RH 60%). of which mass was measured by micro balance(Mettler) every 60 min for 9 hours. Test was performed for 15 tresses and the results were averaged. Water holding ratio was calculated. defined as.

Approximate water-holding ratio

$$= \frac{\text{(weight of residual water within tress)}}{\text{(total weight of water entrapped within tress)}}$$

where weight of residual water within tresses = initial weight of wet tress - weight of tress

at specific time, total weight of water entrapped within tress = initial weight of wet tress equilibrium weight of tress

2.6 Sensory Evaluation

Evaluations were made by panelists (five men and five women) who evaluated their perceptions (richness, spreadability, elasiticity, total preference) using their own personal experience criteria.

3. Results and Discussion

Preparation, POM and DSC analysis

After 7days storage at 25 °C, S_1 and S_2 were observed with a polarizing microscope. Although compositions of S_1 and S_2 were exactly same, they showed totally different appearance on microscope. Roughly circular masses surrounding oil droplets and acicular phases were visible in S_1 but not were visible in S_2. Between crossed polars, the circular masses those were visible in S_1 were strongly anisotropic, generally with a maltes cross- that is, they showed the optical properties of a uniaxial crystal. In contrast to this, nothing could be seen in S_2 between crossed polars. Thus S_1 was named oil/liquid crystal/water system and S_2 was named oil/water system owing to these results of microscopical observation. Concerned with long chain alcohol type, liquid crystals are formed at low surfactant concentration. This is due to closer packing allowed when the repulsion between polarized head groups of surfactant is reduced by strong interaction of alkyl chains(4). Liquid crystals have been reported to form below the surfactant c.m.c., at high water concentrations, in ternary systems containing alcohol amphiphiles(5).

In the preparation of S_1, solution of Lanolin oil, Cetostearyl alcohol and BTAC was poured into an aqueous phase at 70 °C, was mechanically mixed, and then was cooled slowly while still being mixed. As soon as temperature cools down, molten Cetostearyl alcohol and BTAC start to diffuse from oil phase, while being penetrated by water, to form highly viscous liquid crystals. In the preparation of S_2, solution of Lanolin oil and Cetostearyl alcohol was poured into an aqueous BTAC solution at 85 °C, was mechanically mixed, and then was cooled slowly while still being mixed. As temperature cools down, molten Cetostearyl alcohol starts to diffuse from oil phase and most part of molten alcohol dissolved into aqueous BTAC solution to form isotropic solution. This was considered to be due to concentration of BTAC above its c.m.c. in aqueous phase.

Formation of liquid crystal in S_1 and S_2 was also examined with DSC after 7 days storage at 25 °C. It is well known that liquid crystal formed from the interaction of long chain alcohol, surfactant and water maintains its structure to well above the melting point of long chain alcohol,

Strong endothermic peak of liquid crystal was shown in S_1 at about 90 °C (Fig.1) which is well above melting point of Cetostearyl alcohol. However no endothermic peak at about 90 °C was found in S_2(Fig.2).
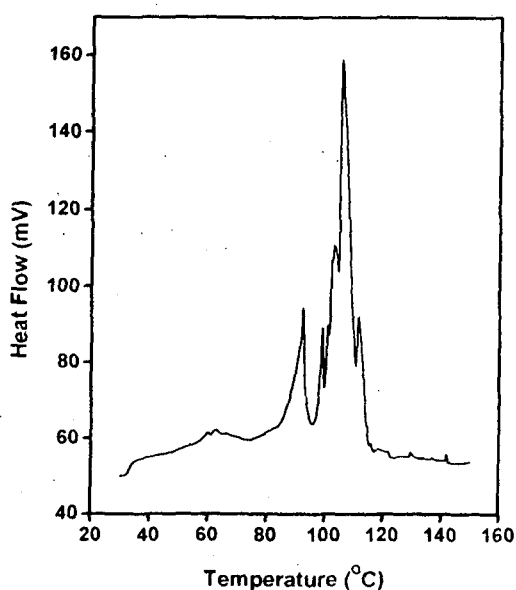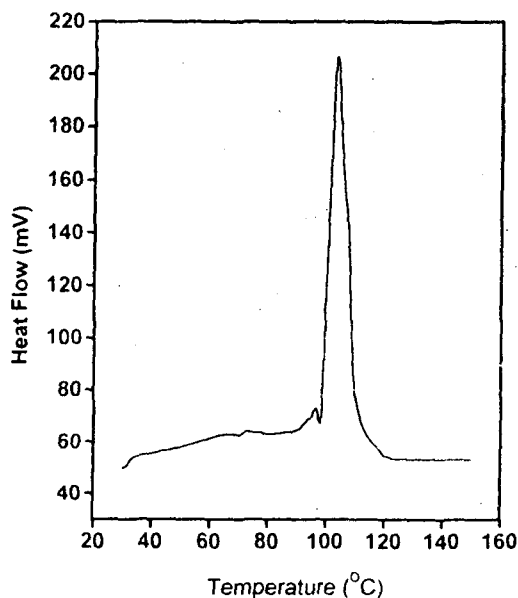

Fig. 1. Thermogram of S_1

Fig. 2. Thermogram of S_2

Measurement of rheological properties

continuous shear experiment. Flow curves for S_1 and S_2 were in the form of hysteresis loop (Fig. 3). The hysteresis loop was caused by the breakdown of structure due to shearing, and the area of the loop was related both to the amount of energy required to break down the network structure and to the amount of entrapped aqueous phase freed when the structure fractured. Each value of energy needed to break down the structure for S_1 and S_2 was 1.85kJ/m³ and 1.26 kJ/m³, which means that S_1 has more internal network and entrapped aqueous phase than S_2. Viscosities of S_1 and S_2 depending on shear rate were obtained for up curve and down curve (Fig.4). Viscosity in S_1 was higher than in S_2 at the same shear rate.

2. *Yield stress* : Yield stress corresponding to the transition from elastic to plastic deformation was examined with increasing shear stress. A lotion or cream with a higher yield value will flow more slowly, giving the impression of 'body' and 'richness'. Yield stress of S_1 and S_2 was about 80 Pa and 40 Pa in the test (Fig. 5).

3. *Creep test*: One of the simplest methods for studying viscoelastic behavior is the creep test, in which a stress is suddenly imposed on a sample at zero time and then maintained constant. The creep curves were obtained for S_1 and S_2, which were shown in Fig. 6. The model proposed to represent the behavior is a Maxwell unit in series with a number of Kelvin units. A-B represents an instantaneous elastic component and is associated with a residual Hookean spring. C-D is the region of viscous flow and is associated with the residual Newtonian dashpot. B-C is the region where the flow is viscoelastic, and the model representation consists of a number of Kelvin units connected in series. Analysis of creep curves was performed diagrammatically here. The instantaneous elastic deformation (A-B) represented bonds being stretched elastically, and thus the Hookean spring simulated the elasticity of the gel network of S_1 and S_2. The extension of the Kelvin units (B-C) represented that part of the structure in which secondary bonds were breaking and reforming during a test. Thus, in comparison with creep curves of S_1 and S_2, it could be considered that gel network of S_1 has more elasticity than that of S_2.
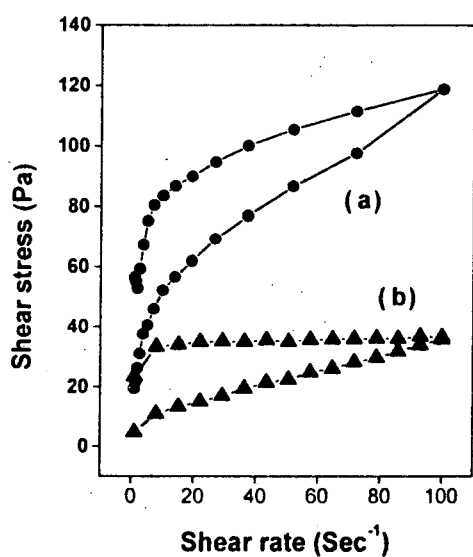

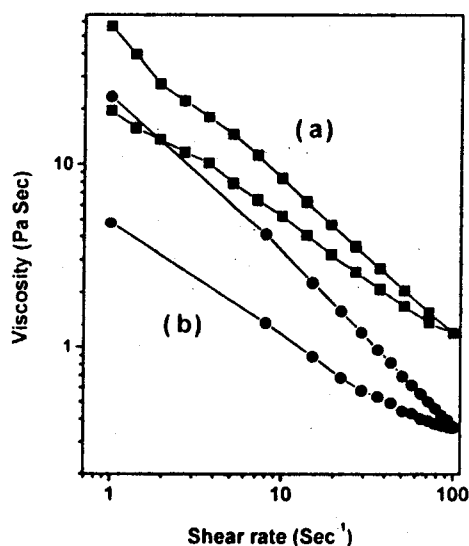Fig. 3. Shear rate Hysterisis Curve
(a) S_1 and (b) S_2

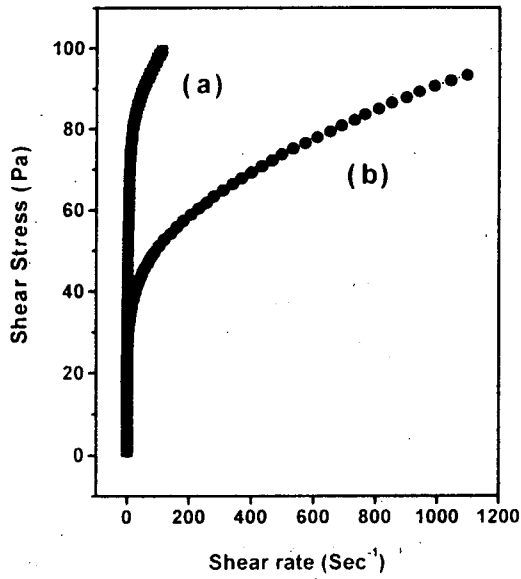Fig. 4. Viscosity VS Shear rate
(a) S_1 and (b) S_2

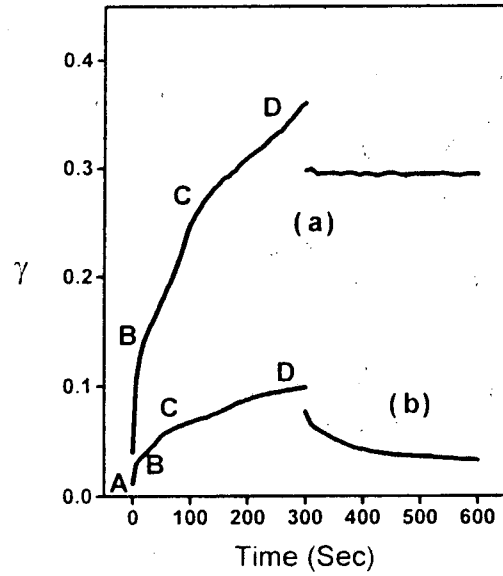Fig. 5. Yield Stress Curve

(a) S_1 and (b) S_2

Fig. 6. Creep Test Curve

(a) S_1 and (b) S_2

Measurement Of approximate water-holding capacity : Tests were conducted as described previously and results are shown in Fig. 7. 8. S_1 exhibited greater water-holding capacity than S_2 in each measurement, associated with aqueous phase entrapped in liquid crystal. Fully dried residue of S_1 and S_2 measured firstly, was the same, proving that two systems had the same concentration of water. In the first stage, water-holding ratios of S_1 and S_2 were similar owing to free water, but, as free water phase evaporated, difference between in S_1 and S_2 began to increase.
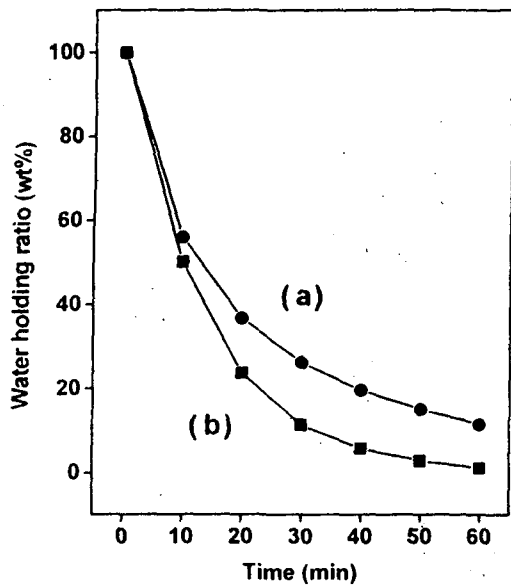
Fig. 7. Waterholding Ratio in Test 1
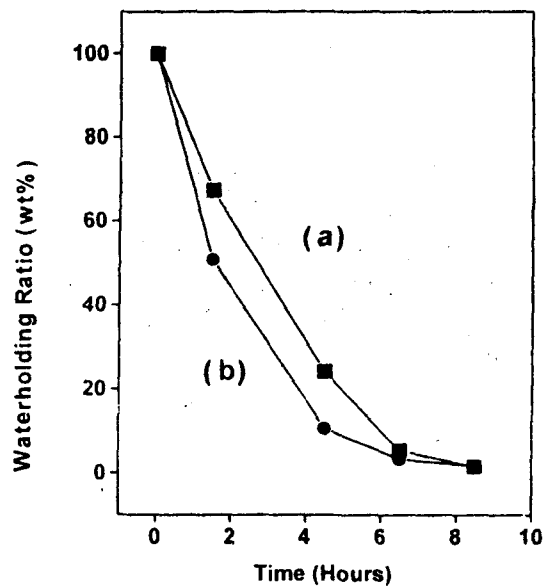
(a) S_1 and (b) S_2

Fig. 8. Waterholding Ratio in Test 2

(a) S_1 and (b) S_2

Sensory evaluation

Using half head test, a panel of 10 members was required to evaluate richness, spreadability, elasticity and total preference by rubbing S_1 and S_2 into wet hair tress. The result was represented in Table 1.

Table 1. Result of Sensory Evaluation

	No. of person who chose S_1	No. of person who chose S_2
Richness	10	0
Spreadability	8	2
Elasticity	9	1
Total preference	9	1

Overwhelmingly, panelists chose S_1 in terms of richness, spreadability and elasticity. Richness may be related to the continuous shear experiment and yield stress test, where S_1 showed larger internal structure was built in and higher yield stress. Elasticity may be associated

with creep test, where S_1 showed higher elasticity. Even though material of lower viscosity at the same shear stress could flow easily on a *plane surface* rheologically, S_1 was chosen concerned with spreadability. There can be some debate, however, remembering that hair tress is not a plane surface, S_2 with lower yield stress and viscosity flows not only alongside hair fibers but also easily flows down into the beneath layers of hair tress due to lower yield stress and viscosity. However, S_1 with higher yield stress and viscosity can travel farther on hair tress with the same amount of sample. From this fact, it may be deduced that S_1 was assessed to have a good spreadability. Panelists of 10 members were asked to assess total preference using their own criteria. 9 of 10 persons preferred S_1. From the results of sensory evaluation, it could be concluded that the oil/liquid crystal/water system was of benefit to rheological properties creme type hair care products.

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