

Study on the Evaluation of Stability of Gel Structured Cosmetics

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SUMMARY

The stability of gel structured emulsion and the effect of polyols on it have been studied by rheological property and interfacial tension.

In this paper, three types of gel structured emulsions were prepared by using three polyols respectively (glycerine for sample 1, 1.3 BG for sample 2, PG for sample 3). And both complex modulus (G^*) and loss angle [$\delta = \tan^{-1}(G''/G')$] of samples were investigated against oscillating shear stress and frequency (ω). The results show sample 1 is most highly consistent with oscillating shear stress. And the results were compared with those of accelerated tests concerning storage stability of gel structured emulsion. To correlate consistency of rheological property with storage stability, interfacial tension from which adsorption efficiency of surfactant (Octyldodecyl Ether) could be known was measured. Sample 1 showed the largest value of $[dy/d\ln C_{\text{conc. of surfactant}}]$ in Gibbs equation.

In summary, the prediction of stability could be correctly made by the consistency of rheological property (G^* , γ) of gel structured emulsion against oscillating shear stress and it could be supported by measuring interfacial tension. And polyol affected the value of $[dy/d\ln C_{\text{conc. of surfactant}}]$, consequently affected the stability.

INTRODUCTION

In present, gel structured emulsion which is microemulsion or liquid crystalline gel is very useful in cleansing cosmetics⁽¹⁾ and the evaluation of its stability is essential to commercialization. But stability test made mainly by accelerated tests based on temperature or centrifugation cannot be guaranteed because accelerated tests have the inherent danger of their submitting emulsion to conditions that far exceed any that it will experience in its real life time⁽²⁾. Therefore it is necessary to find proper stability index of emulsion in its real-time conditions⁽³⁾.

In case of emulsion, any change to structure directly results in change of rheological behavior⁽³⁾. So accurate measurement of rheological properties is essential to prediction of stability of emulsion. There are three representative tests measuring rheological properties of emulsion⁽⁴⁾. One is flow test. The relation between shear rate and shear stress can be known from the test. Flow test is usually adopted to get thixotropy diagram, viscosity and yield stress value^(5, 7, 8). Another is oscillation test. Storage modulus and loss modulus are main variables. The former means how elastic an emulsion system is and the latter means how viscous the emulsion is. And loss angle is related to a ratio of G'' to G' [$\delta = \tan^{-1}(G''/G')$]. Oscillation test is a useful method to investigate viscoelasticity of emulsion without breaking structure of emulsion. The third is creep test. Creep test is useful for characterizing viscoelastic property of emulsion mathematically in that emulsion system of which creep curve follows Berger model can be analyzed into 4 components(J_0, J_1, η_0, η_1)⁽⁴⁾.

In this paper, to get the stability index of gel structured emulsion in real-time condition, we performed accelerated test and oscillation test. And interfacial tension measurement was executed to correlate consistency of rheological property with the results of accelerated test. We use Gibbs equation by which amount of surfactant molecules absorbed at interface can be quantitatively calculated^(2, 6) to know the effect of polyol on gel structured emulsion.

EXPERIMENTAL

Materials

Octyldodecyl Ether(EOD 25JJ) was from Nihon Emulsion. For simplicity, only Trioctanoin(TIO) was from Nissin Oil Mills as oil. And we use deionized water. Glycerin(98%) was from LG Chem. Ltd., 1,3-BG was from Daicel and PG was from Yukong.

Preparation

Formulations are as follows ;

Table.1 Formulations selected in this paper

Sample number	Water phase		Oil phase	
#1	Water 7%	Glycerin(98%)17%	TIO 60%	EOD 25JJ 16%
#2	Water 7%	1,3-BG 17%	TIO 60%	EOD 25JJ 16%
#3	Water 7%	PG 17%	TIO 60%	EOD 25JJ 16%

Water phase and oil phase were both heated to 80°C and then we added oil phase to water phase. Finally, we made emulsions using homomixer(model M) from TK Ltd. and cooled emulsions to 28°C by water circulating bath.

Method of rheological property measurements

We used Rheo-Stress 100 from Haake as rheometer to carry out oscillation test. Temperature is controlled by Peltier Plate Temperature Controller Base. We performed oscillation test at 25°C and temperature control accuracy is $\pm 0.2^\circ\text{C}$. We used 35mm diameter cone with angle 1 degree made of brass with Armoloy and solvent trap for cone/plate measurement.

Method of interfacial tension measurement

Water/polyol/surfactant solutions of different concentration were prepared and allowed to equilibrate at 25°C for 24 hours. Processor Tensiometer K12 from KRÜSS was used for interfacial tension measurements with a Platinum-Iridium ring in a temperature-controlled double jacket glass at $25.0 \pm 0.1^\circ\text{C}$.

RESULTS

Accelerated test

Samples were placed in 45°C chamber, 25°C chamber and cycling chamber. Similar results were got from three types of chamber conditions, but among those accelerated conditions, storage durability difference in 45°C chamber was the most evident(Fig.1). So we presented the results of only 45°C chamber. The results are in following table.

Table.2 Results obtained from 45°C chamber

Sample number	3 days	7 days	28 days
#1	O	O	O
#2	O	X	-
#3	X	-	-

(O : stable, X : phase separation occurred)

Oscillation test

A. Stress sweep

The results are given in Fig.2. Sample #1 is consistent with 100Pa and sample #2 is consistent with 9Pa. But sample #3 is not consistent with oscillating shear stress($\omega 1\text{s}^{-1}$).

B. Frequency sweep

The results are given in Fig.3. All elastic moduli of sample #1, #2 and #3 continuously increase with increasing frequency.

Interfacial tension measurement

The results are given in Fig.4. The value of $d\gamma/d\ln C_{\text{conc. of surfactant}}$ of surfactant at the concentration of Octyldodecyl Ether between 10^{-5} mol/liter and 10^{-3} mol/liter is calculated for sample #1 and #3. The larger became the slope, the more surfactant molecules moved to interface according to Gibbs equation^(2, 6). In case of sample #2, interfacial tension decreases continuously with increasing concentration, so it is meaningless to compare sample #2 with other samples in that range.

Table.3 $d\gamma/d\ln C_{\text{conc. of surfactant}}$ value calculated

Sample number	$d\gamma/d\ln C_{\text{conc. of surfactant}}$	Units
#1	12	(mN · Liter)/(m · mol)
#3	7	(mN · Liter)/(m · mol)

DISCUSSION AND CONCLUSION

In 45°C chamber, sample #1 lasted longer than sample #2 and #3. For sample #1 in stress sweep, G^* and δ are consistent with shear stress by 10 times higher than that of sample #2. From these results, strength of structure of sample #1 is far stronger than that of sample #2. Though sample #3 has higher elasticity than that of sample #2, sample #3 shows inconsistency with shear stress, which means inner structure is very unstable. In viscoelastic fluid, Deborah number ($D = \text{Relaxation time} / \text{Experiment time}$) is the index of viscoelasticity. Generally if Deborah number is larger than 1, we say the system is elastic, if smaller than 1, then viscous⁽⁵⁾. With increasing experimental time (in oscillation test, experimental time is $1/\omega$), Deborah number increases by definition. That is to say, elastic part is to increase at faster rate than viscous part is with increasing frequency. Really in Fig.3, increment of elastic modulus (G') is greater than that of viscous modulus (G''). From this fact, we can guarantee the reliability of rheological data obtained.

From the comparison of results obtained from rheological property measurement with those of accelerated test, it can be known that in gel structured emulsion formulated by table.1, the strength of structure is directly related to the stability of emulsion⁽³⁾. The

obtained results show that rheological behaviors of emulsions investigated clearly correspond with the stability of emulsions (i.e. sample 2 and sample 3 of which rheological behaviors were not so consistent experienced phase separation after around 1 week at 45°C chamber).

Then, there remains a question that what the reason of the fact that substitution of polyol affects emulsion stability is. The results in 'Interfacial tension measurement' gives an answer. That is, Octyldodecyl Ether molecules in Glycerin/water solution tend to move to interface rather than exist in bulk solution. This tendency of Octyldodecyl Ether molecules moving to interface is stronger when Octyldodecyl Ether molecules is in Glycerin/water solution than in 1,3-BG/water solution or PG/water solution. So it can be known that there exist more Octyldodecyl Ether molecules at interfaces of sample #1 than at those of sample #2 or those of sample #3.

By these results, it can be known that the position and amount of surfactant molecules moving to interface depend on polyols, which affects the stability of our gel structured emulsion system. Also, the prediction of stability could be correctly made by the consistency of rheological property (G^* , G' , G'' , δ) of gel structured emulsion against oscillating shear stress and it could be backed up by measuring interfacial tension.

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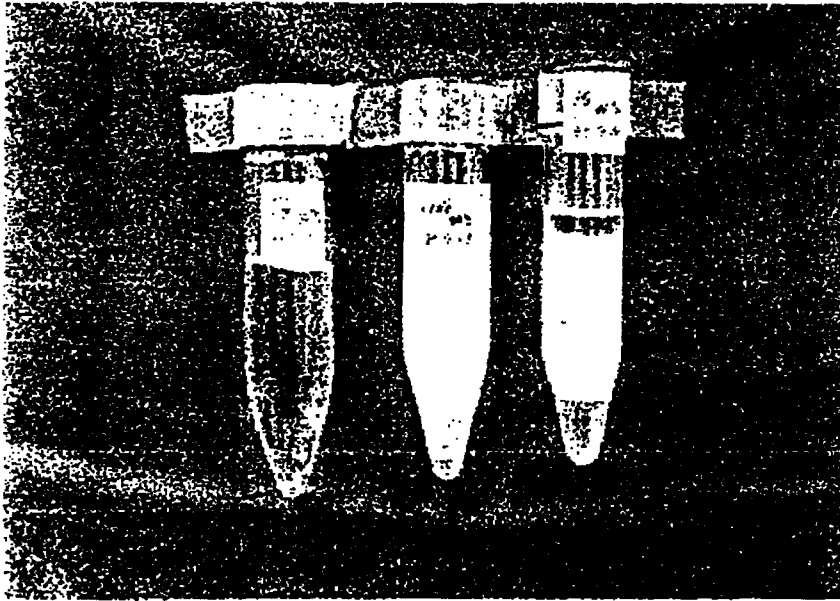


Fig 1 : Samples at 45°C chamber after week 1
 (left : #1, center : #2, right : #3)

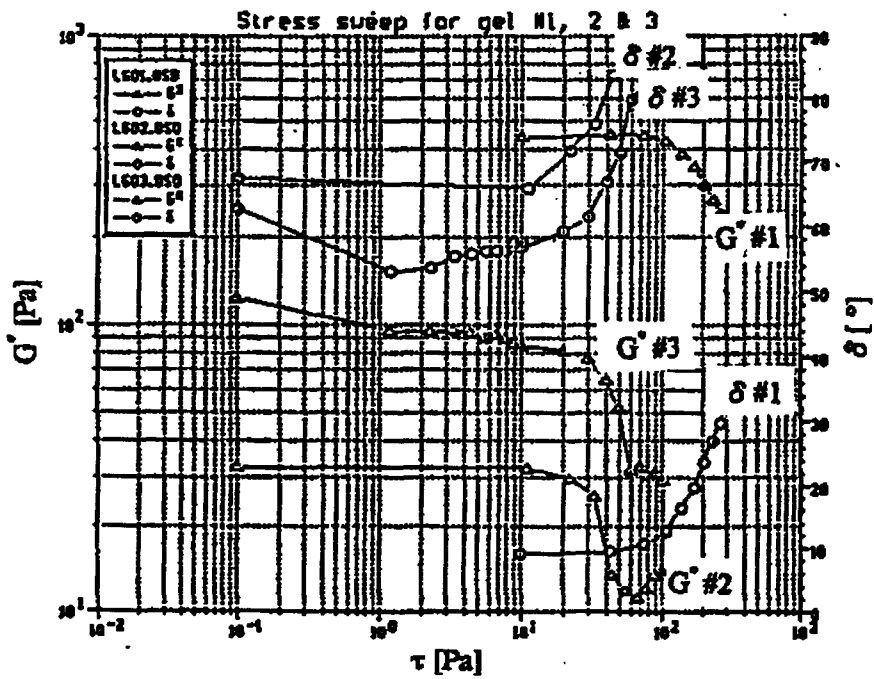


Fig 2 : Stress sweep curve ($\omega = 1s^{-1}$)
 (left ordinate : complex modules G^* in PA, right ordinate : loss angle δ in degree)

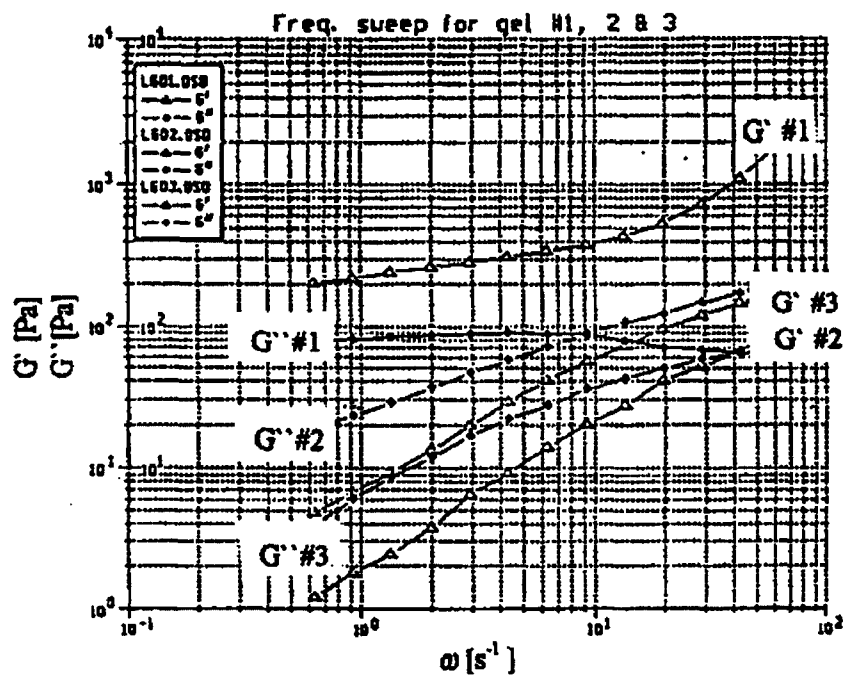


Fig 3 : Frequency dweep curve

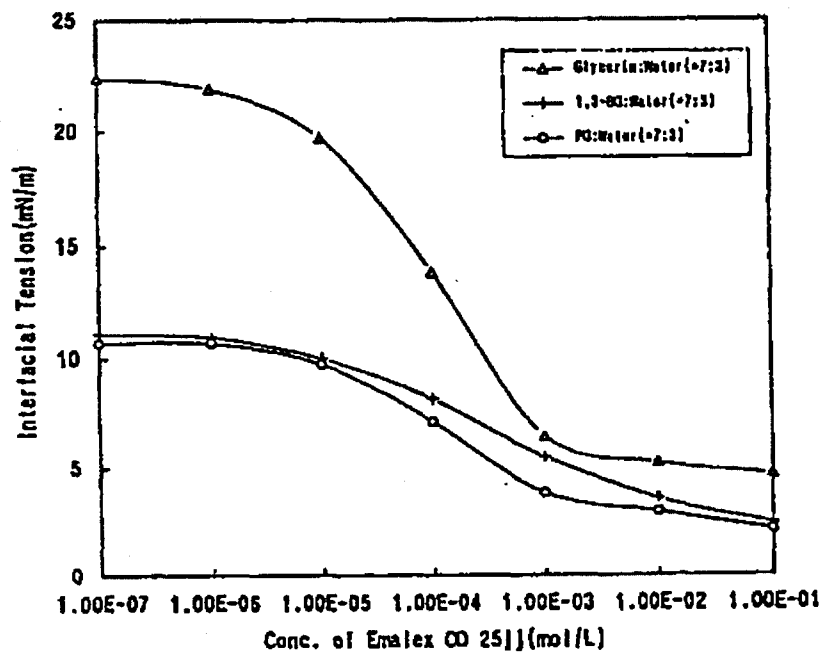


Fig 4 : Interfacial tension curve