J. Soc. Cosmet. Scientists Korea
Vol. 30, No. 2, September 2004, 147-151

전단응력 하에서 에멀젼 상 변이의 측정을 위한 전기 유변학적 연구

백승재†·이영진·남윤성·김진한·김한곤·강학희

태평양 기술연구원

Electro-rheological Measurements of Phase Inversion of Emulsions under Shear Flow

Seung Jae Baik†, Young-Jin Lee, Yoon Sung Nam, Chin Han Kim, Han Kon Kim, and Hak Hee Kang

Amore Pacific R&D Center, 314-1, Bora-ri, Giheung-eup, Yongin-si, Gyeonggi-do 449-729, Korea

요 약: 본 연구는 다양한 종류의 에멀젼에 전단응력을 가하며 그때 일어나는 에멀젼의 상 변이를 전기, 유변학적 특징을 통해 실시간으로 측정해 보는 것이다. 전기 전도도의 변화는 자체 제작한 JELLI$^{\text{TM}}$ (Joint Electro-rheometer for Liquid-Liquid Inversion) 칩을 이용하였으며, 동시에 유변물성측정장치(rheometer)를 이용하여 유변물성의 변화를 측정하였다. JELLI$^{\text{TM}}$ 칩과 인조 피부를 유변물성측정장치 사이에 장착하고 그 사이에 다양한 종류의 에멀젼을 얇게 발라준 후, 일정한 전단응력을 주며 시간에 따른 저항과 점도 값의 변화를 측정하였다. O/W 제형의 경우 시간에 따라 저항값이 커지는 경향을 보였으며 저항값은 내부 상이 많을수록 더 급격한 변화를 나타냈다. 이때의 점도 변화를 보면, 저항값의 변화가 클수록 점도의 변화도 큼을 볼 수 있었다. 이것은 내부 상의 파괴로 인해 외부의 힘에 저항하는 힘이 약해졌기 때문이라고 예상된다. 이런 결과를 이용하여 전단응력에 의한 에멀젼 상 변이 특성과 정도를 실시간, 정량적 비교할 수 있었다.

Abstract: This study aims at measuring electrical and rheological properties of cosmetic emulsions on the skin under shear flow. The effects of volume ratio and surfactants on structural changes of emulsions were examined by determining the changes of electrical resistance, viscosity, and morphology. As the ratio of the internal phase increased, the phase inversion occurred more quickly. The viscosity change was found to increase with increasing of the variation of electrical resistance of the emulsions. This phenomenon may be caused by decreased resistant force against the shear flow because of the breakdown of the internal phase. Surfactants also played a key role on phase transition of emulsions. It is likely that polymeric surfactants anchoring on the emulsion surface reinforced the interfacial mechanical strength. As the concentration of surfactants increased, the phase transition occurred more slowly. It has been demonstrated that the phase changes of emulsions under shear flow can be monitored on the real-time basis by using a JELLI$^{\text{TM}}$ chip system, a combination of conductiometry and rheometry. Our approach is expected to a useful experimental tool for predicting the phase transition of the cosmetic products during skin application.

Keywords: *emulsion, phase transition, rheology*

1. Introduction

Emulsions are thermodynamically unstable dispersions of deformable liquid droplets in a second liquid; hence, external stress can highly affect their physical degradation, which is driven by the reduction of the interfacial area between two phases. Emulsion separation is known to happen by a combination of four processes: creaming or sedimentation, flocculation, coalescence, and Ostwald ripening. The phase separation or inversion of emulsions may depend on the ratios of volume and/or viscosity between emulsion phases, size distribution of internal droplets, and interfacial properties of emulsions[1-3].

One interesting question is about structural changes of emulsions under high shear flow. This is very important for cosmetic products because it is highly relevant to the physical degradation of emulsions during the application on the skin. Here, in order to examine the response of emulsions against the external

---

† 주 저자 (e-mail: Baik75@amorepacific.com)

shear forces, we designed a new device, JELLI^{TM} (Joint Electro-rheometer for Liquid-Liquid Inversion) chip, for the measurement of electrical and rheological properties of emulsions under shear flow. By using this device, we investigated the effect of formulational factors on the changes in conductivities of oil-in-water (O/W) and water-in-oil (W/O) emulsions on the artificial skin during large deformation under shear flow.

2. Materials and Methods

JELLI^{TM} chip was made on 25 mm×75 mm×1 mm slide glass, which was Aluminum-sputtered by 500 nm thickness. Figure 1 shows the chip geometry and the gap size between the electrodes is 10 mm. Artificial skin was fixed on one side of junction tip, as in Figure 1, to make a similar situation as the cosmetics are applied on human skin. The junction tip with artificial skin and JELLI^{TM} chip were installed in rheometer (RMS800) as shown in Figure 2. FLUKE189 was used to measure the electrical resistance. All rheological experiments were carried out at frequency 50 $^{rad}/_{s}$, strain 6×10^{5}% during 5 min. The water-phase ratios of prepared oil-in-water (O/W) emulsions were 20%, 30%, 36%, and 80%.

Polysorbate 60, Sorbitan Sesquioleate, and poloxamer 407 were used to investigate the effect of surfactant on phase inversion. Three kinds of emulsions with fixed water ratio of 34.0% were made. All compositions except surfactants were same. To investigate the effect of surfactant concentration, emulsions containing polysorbate 60/Sorbitan Sesquioleate of 1.2%/0.4% and 2.4%/0.8% were prepared. An emulsion with poloxamer 1.6% was made to look into the effect of polymeric surfactant on phase inversion under shear flow. Table 1 summarized surfactants composition.

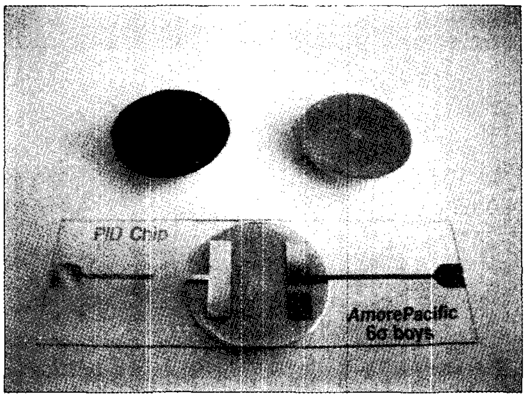


Figure 1. A photograph of JELLI^{TM} chip (below) and a junction tip coated with (above, left) and without (above, right) the artificial skin.

Table 1. Composition of Surfactants in Each Emulsion

Emulsion A	polysorbate 60 / Sorbitan Sesquioleate = 1.2% / 0.4%
Emulsion B	polysorbate 60 / Sorbitan Sesquioleate = 2.4% / 0.8%
Emulsion C	Poloxamer407 = 1.6%

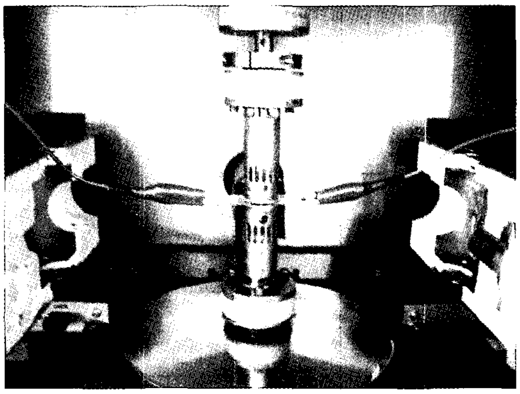
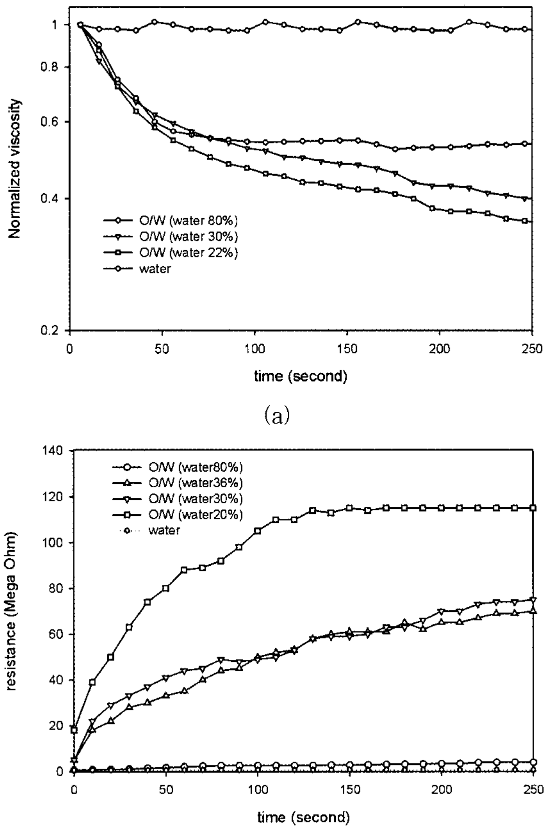


Figure 2. A photograph of a rheometer equipped with a JELLI^{TM} chip connected to a conductiometer.

3. Results and Discussion

Figure 3 represents the electrical resistance (R) and viscosity (η) profiles of O/W emulsions spreaded on the artificial skin as a function of shear application time. The shear force had no effect on R, nearly zero, of pure water. As the application time increased, R of all the emulsion samples increased and reached to plateau values within 3~4 min. In addition, ΔR increased as lowering the water content. What causes the increase of the electrical resistance as a result of shear force application? Because the chemical compositions are assumed to remain unchanged, the only possibility is the structural changes of the emulsions, relevant to alteration of conductivities in the continuous phase.

Structural changes of emulsions can be expected from rheological data. Figure 3 shows that viscosities of the emulsions decreased as a function of the shear



(a)

(b)

Figure 3. Resistance (a) and viscosity (b) profiles of emulsions as a function of application time in various water ratios.

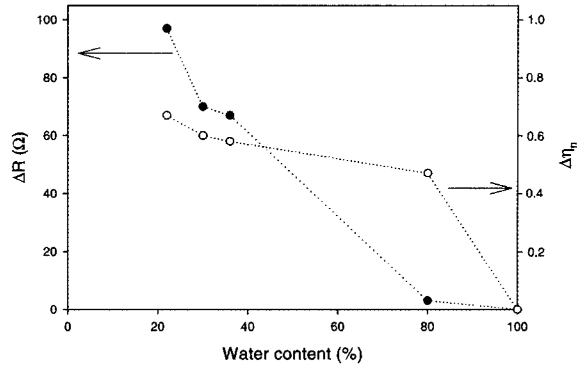
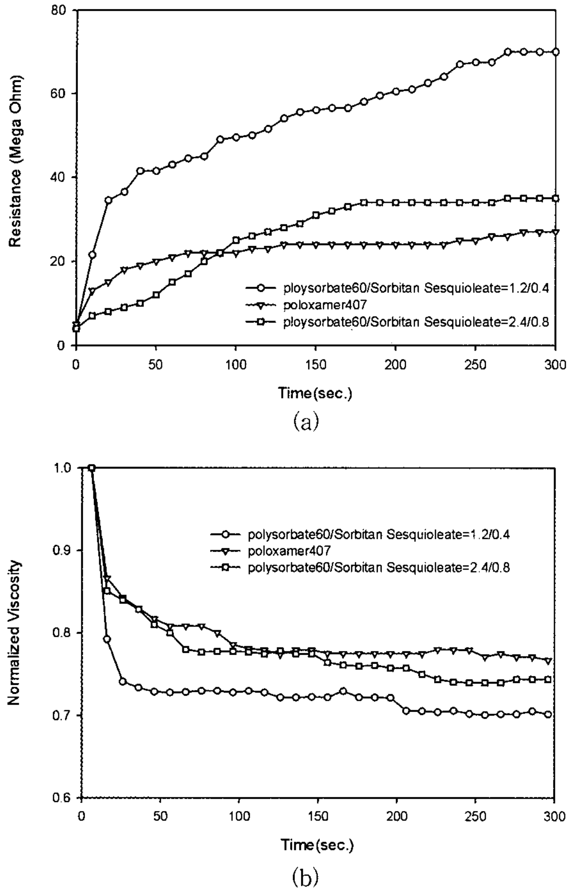


Figure 4. $\Delta\eta$ (normalized viscosity difference) and ΔR (resistance difference) as a function of water ratio.

application time. Interestingly, $\Delta\eta_n$ (normalized viscosity difference) was getting larger as lowering the water content in the emulsions. This tendency is very similar with that of ΔR, as described in Figure 4. These results imply that the changes of the responses to the applied shear stress were caused by phase transitions of emulsion, e.g., phase inversion, increases of droplet sizes, disordering or formation of new structures, etc. This kind of phase transitions can involve the breakdown and rearrangement of the interfaces of oil-rich and water-rich phases. One possible explanation for the increase of R and decrease of η of the O/W emulsions is the leakage of surface stabilizing materials and the following drainage of oil molecules to a continuous aqueous phase. Because the higher oil content of O/W emulsions produces the larger areas of interfaces to be covered with emulsifying agent, at the same concentration of surfactants, the emulsion having the higher oil concentration can be more liable to the external shear forces. In order to examine the effect of surfactants on the phase transition of emulsions, three sets of formulation having different kind and concentration of surfactants were prepared as listed in Table 1. The polysorbate 60/sorbitan sesquioleate system was selected because they have been the most widely utilized in cosmetic emulsion products. Figure 5 shows that the higher concentration of the surfactants produced the smaller changes of the electrical resistance and viscosity. This can be explained by the increased colloidal stability of the emulsions.

In order to examine the effect of a polymeric emulsifier on ΔR and $\Delta\eta$, poloxamer 407 was added as an emulsion stabilizer instead of polysorbate 60/sorbitan sesquioleate system. At the same concentration of surfactant (1.6% w/w), ΔR and $\Delta\eta$ obviously decreased when poloxamer 407 was used, compared with those of emulsion A. Even the values of emulsion C were smaller than those of emulsion B, where two-fold amount of low MW surfactants were used. This is presumably due to the mechanically stabilized interfaces created by entangled polymer networking.

The structural development of the emulsions on the skin under the application of shear forces was visualized by using confocal laser scanning microscopy. By adding a water-soluble fluorescent dye, FITC, into an aqueous phase, we could discern two phases, oil-rich and water-rich phases. At the initial condition, all O/W emulsion samples were seen as green-colored homogenous solutions because the droplet size was too small to observe. However, the emulsions were clearly imaged after the application of shear forces as a result



(a)

(b)

Figure 5. Resistance (a) and viscosity (b) profiles of emulsions as a function of application time in various surfactants systems.

of increase of droplet sizes. This formation of larger droplets in emulsion C might be caused by flocculation between water droplets deformed by shear forces. The CLSM observation demonstrated phase inversion of emulsion A from O/W to W/O was happened on the skin by shear forces. The continuous phase of emulsion A was changed from a water rich phase (bright green color) to an oil-rich phase (dark area) after the application of shear forces. Emulsion B also showed same phase inversion as in emulsion A. By contrast, the emulsion C still maintained a water-rich phase as a continuous one. These results are well consistent with those of ΔR and $\Delta\eta$, as shown in Figure 5. Relatively larger ΔR and $\Delta\eta$ of emulsion A can be explained by the phase inversion. Surfactant with low HLB value (sorbitan aesquioleate) could cause this complete inversion from O/W to W/O. Simple flocculation without phase inversion induced relatively smaller ΔR and $\Delta\eta$.

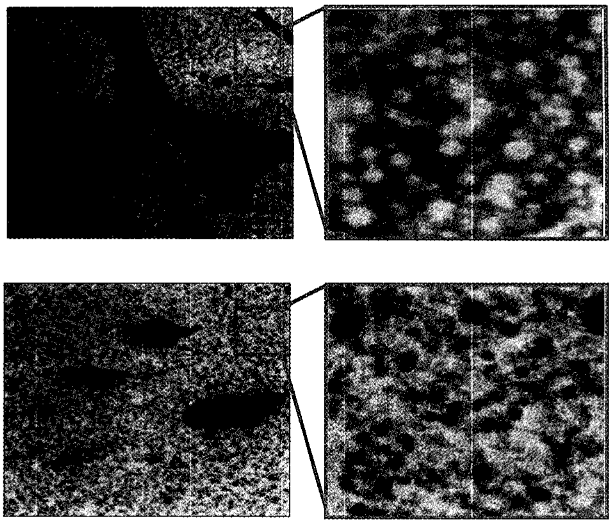


Figure 6. CLSM image of emulsion after shear flow. The upper image shows emulsion A and the bottom image shows emulsion C (× 400 magnitude).

4. Conclusions

In this study, the electrical resistance and rheological attributes of cosmetic emulsions on the skin under steady shear flow were investigated as a function of emulsion compositions by using a simultaneous real-time monitoring system. The electrical resistance increased as a function of time and jumped up to the infinite value as the internal oil phase was over 60%. The resistance showed more dramatic increase as increasing the oil/water ratio. On the contrary, it increased slowly as the emulsion had the weaker interfacial surface. In addition, the viscosity also decreased as increasing the oil content. This might be due to the weakened resistant forces against the shear flow as a result of the breakdown of the internal phases. These results suggest that the JELLI^{TM} system can be utilized as a powerful tool not only in investigating the phase behavior of cosmetic emulsions under shear flow but also sensory properties of cosmetic emulsions during skin application.

References

1. R. Pal, A novel method to correlate emulsion

viscosity data, *Colloids and Surfaces A.*, **137**, 275 (1998).

2. H. M. Lee, J. W. Lee, and O. O. Park, Rheology and dynamics of water-in-oil emulsions under steady and dynamic shear flow, *J. Colloid Interface Sci.*, **185**, 297 (1997).
3. T. G. Mason, New fundamental concepts in emulsion rheology, *Curr. Opin. Colloid Interface Sci.*, **4**, 231 (1999).