

## 폴리머와 계면활성제의 상호작용을 이용한 젤타입 제형의 제조

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(2007년 2월 23일 접수, 2007년 3월 5일 채택)

### Gel Type Formulation Utilizing Polymer-Surfactant Interaction

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(Received February 23, 2007; Accepted March 5, 2007)

**요 약:** 수용성 폴리머와 계면활성제의 상호작용을 레올로지와 표면 장력을 측정하여 연구하였다. 본 연구에 사용된 폴리머는 acrylates/C<sub>10-30</sub> alkyl acrylate crosspolymer (AC), ammonium acryloyldimethyltaurate/VP copolymer (AV)이다. 계면활성제는 PEG-40 hydrogenated castor oil (HC), polysorbate 60 (P60)이다. HC와 P60은 AC 폴리머 주위에서 마이셀을 형성하여 점도를 증가하였다. 그러나, HC는 P60보다 보다 높은 농도 범위에서 점도 증가 거동을 보였다. 같은 농도 범위에서 계면활성제들의 표면장력을 비교해보면, 표면장력이 AC/HC의 농도 증가에 따라 증가한 반면, AC/P60의 농도증가에 대해서는 거의 증가하지 않았다. 이런 결과는 AC/HC 사이의 마이셀이 강하게 조직화된 구조를 형성하기 때문으로 추정된다.

**Abstract:** The interaction between polymers and surfactants was investigated by means of rheological and surface tension measurements. The polymers used in this study were acrylates/C<sub>10-30</sub> alkyl acrylate crosspolymer (AC) and ammonium acryloyldimethyltaurate/VP copolymer (AV). And the surfactants were PEG-40 hydrogenated castor oil (HC) and polysorbate 60 (P60). HC and P60 made the micelles intervening between AC polymers, resulting in the increase of viscosity. However, HC showed a similar behavior over the wider range of surfactant concentration than P60. Regarding of surface tensions in the same range of surfactant concentration, AC/HC solution showed the area of increasing surface tension with surfactant concentration in contrast to the AC/P60 solution showing no increasing area. It is assumed that the micelles between AC/HC were formed so cooperatively and strongly that the surfactants located at the surface originally moved to the micelles.

**Keywords:** polymer-surfactant interaction, acrylates/C<sub>10-30</sub> alkyl acrylate crosspolymer, ammonium acryloyldimethyltaurate/VP copolymer, surface tension, rheological

### 1. Introduction

In gel type formulation the polymer plays an important role not only on stability but also rheological properties. The hydrophobically modified polymer in gel should interact with surfactant because the surfactant must be added for the solubilization of hydrophobic materials, e.g. fragrance.

The interaction between polymers and surfactants has

been studied and applied to the industry for several decades[1,2]. Nowadays polymers are synthesized with hydrophobic alkyl substitutes to increase the binding affinity to surfactant[3,4], and these systems are tested in industrial field as solubilizer or emulsifier[5,6]. The importance of polymer-surfactant system in personal care industry is that critical aggregation concentration (C.A.C) is at least 100 times than critical micellar concentration (C.M.C) [7-9]. That is, to the industry struggling to decrease the content of surfactant in personal care polymer-surfactant system can give a

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chance to decrease the amount of surfactant. Also, the polymer with hydrophobic substitutes can increase the viscosity of solution several times just by adding small content of surfactant[4]. In other words, surfactant can save the concentration of polymer to get a thickened solution giving decreased polymer texture.

This study investigated the interaction between polymer and surfactant with rheological and surface tension measurement i.e., rheological parameters and surface tension.

## 2. Experiment

### 2.1. Materials

The polymers used in this investigation are acrylate/C10-30 alkyl acrylate copolymer (AC, Noveon, USA), and ammonium acryloyldimethyltaurate/VP copolymer (AV, Clariant, USA). AC are neutralized with triethanolamine before being used. Surfactants are an anionic surfactant PEG-40 hydrogenated castor oil (HC, Nikkol, Japan) and an polysorbate 60 (P60, Uniqema, USA).

### 2.2. The Measurement of Rheological Properties

Viscosity was measured with Brookfield DV-E Viscometer, Spindle #4 at 25°C, 30 rpm, 1 min. For the measurement of yield stress and viscoelasticity Rheometer (Physica UDS 200 Plate & plate sensor, 25°C) was used. Yield stress was evaluated by Casson's equation[10] using viscosity data through  $0.01 \text{ s}^{-1}$  to  $1.00 \text{ s}^{-1}$  of shear rate.

### 2.3. The Measurement of Surface Tension

Surface tension was measured with a Tensionmeter (KRUSS Co., K12 Tensionmeter, Du Noüy's ring method at 25°C). The ring is an alloy of platinum and iridium.

## 3. Result and Discussion

For the AC solution, from the Figure 1, with increasing concentration of HC there was an area of increasing viscosity and the viscosity reached to the maximum (about 3 times larger than that without surfactant) at the concentration of HC 0.1% (w/w) and maintained higher viscosity up to 0.5% and then decreased slowly to the ground viscosity (without

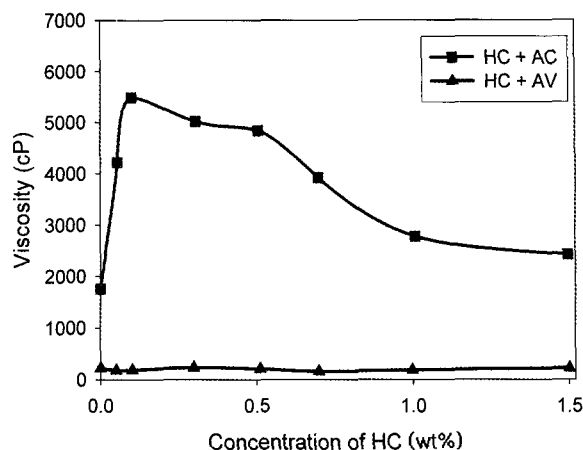


Figure 1. The changes of viscosity as the concentration of HC with various polymer increased.

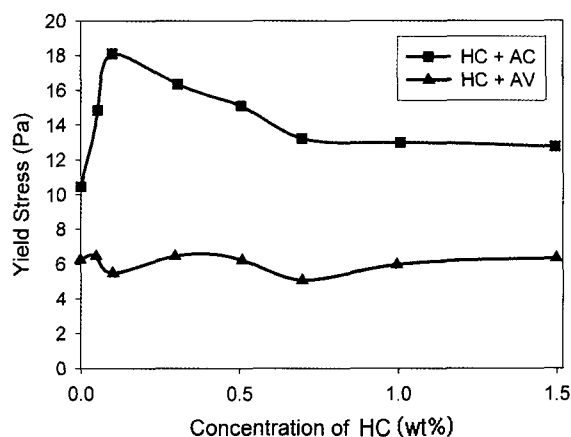


Figure 2. The changes of yield stress as the concentration of HC with various polymer increased.

surfactant). These properties mean that in this system there is interaction between surfactant and hydrophobically substituted hydrophilic polymer. That is, the area of steeply increasing viscosity means that HC micelles are being formed around substitutes between polymers. The area of decreasing viscosity means breaking of micelles between polymers but also means micelles forming on each polymer. On the contrast, for the AV having no hydrophobic substitutes there was no area of varying viscosity, i.e., no interaction between AV and HC. And the tendency of yield stress was the same (Figure 2).

For the same system Figure 3 shows the profile of surface tension. At the area of HC concentrations of micelle forming between polymers, surface tension

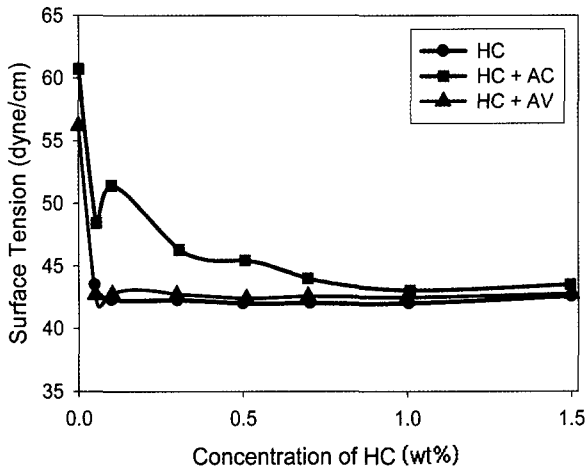


Figure 3. The changes of surface tension as the concentration of HC with various polymer increased.

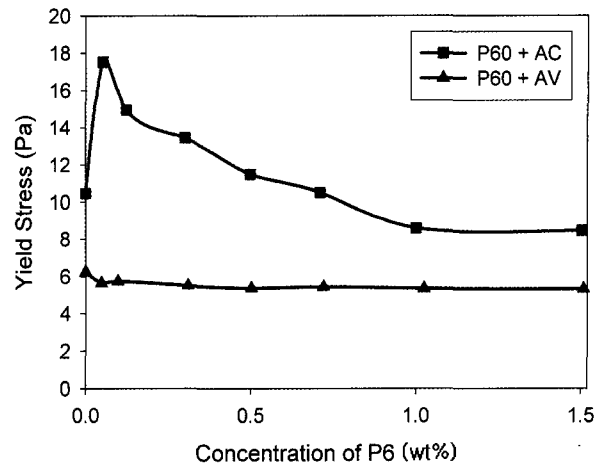


Figure 5. The changes of yield stress according to increase of the concentration of P60 with various polymer.

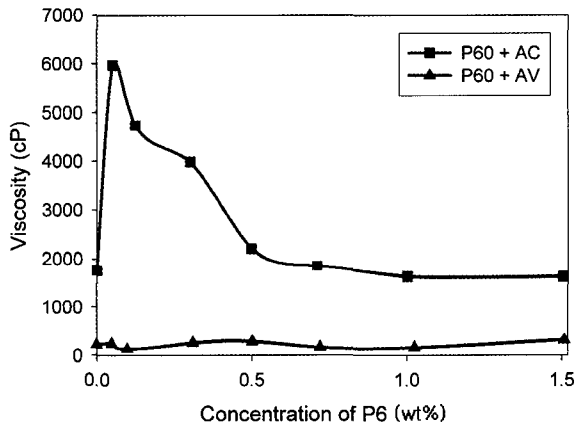


Figure 4. The changes of viscosity according to increase of the concentration of P60 with various polymer.

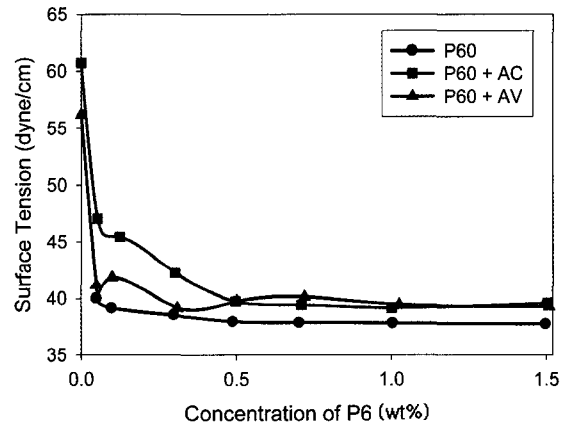


Figure 6. The changes of surface tension according to increase of the concentration of P60 with various polymer.

firstly decreased and then abruptly increased. At the HC concentration of maximum viscosity the surface tension also showed the maximum. And then surface tension was decreased slowly to the same that of surfactant only solution without polymer. Therefore it is suggested that at the area of increasing surface tension polymer and surfactant are interacting so cooperatively that the surfactants originally located at the surface moved to the aggregates up to the maximum. On the contrast, for there was no interaction between AV and HC, surface tension of solution with increasing HC was almost same with or without the presence of AV.

For the same polymer, we investigated the interaction with P60. It was somewhat different in that

with increasing P60 concentration the viscosity and the yield stress showed maximum at lower concentration (0.05%) than that of HC and the maximum value was higher by ca. 500 cP (Figure 4, 5). However, it was immediately decreased after the maximum. The decreasing slope was steeper than that of HC. The concentration needed to be original viscosity without surfactant was more than ca. 1.0% for HC but less than 1.0% for P60. It was assumed to be related with the HLB of surfactants.

Surface tension with increasing P60 was slowly decreased without increasing area (Figure 6). It was suggested that P60 micelle formation between polymers has lower cooperativity than HC micelle formation.

Also, P60 has no interaction with AV so there was

no viscosity change and no surface tension change with surfactant concentration.

#### 4. Conclusion

Surfactants interacted with only hydrophobically substituted polymer, AC not with AV and this interaction made micelles intervening between polymers, resulting viscosity increasing. P60 having lower HLB showed the maximum viscosity at lower concentration than HC but HC showed cooperative binding bringing about increasing of surface tension and long lasting of high viscosity. It is expected that AC/HC complex forms a safe gel having a high viscosity.

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