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반도성 고분자 현탁액의 전기유변학적 거동과 계면편극화

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Electrorheological Behaviors and Interfacial Polarization of Semi-conductive Polymer-based Suspensions

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요 약

반도성 고분자인 폴리아닐린과 폴리파라페닐렌을 이용한 전기유변유체의 유변학적 및 전기적 특성을 고찰하였다. 이들 반도성 고분자 현탁액은 분산입자와 현탁매질의 전기전도도 차이로 인하여 직류 전기장 하에서 큰 점도 증가를 보였다. 전기유변효과로 기인한 동적 항복응력은 낮은 전기장 하에서는 전기장 제곱에의 의존성을 보였으나 높은 전기장 하에서는 전기장의 1승에 비례하는 거동을 나타내었다. 항복 응력은 분산입자의 전기전도도가 증가함에 따라 최대값을 보이다가 다시 감소하는 현상을 나타내었다. 직류 전기장 하에서의 이러한 항복 응력 거동은 전도도 효과에 의한 맥스웰-와그너 계면편극화로 설명되는 현탁액의 유전 특성과 관련됨을 발견하였다. 계면 편극화 효과가 전기유변현상에 미치는 영향에 대한 더 깊은 이해와 분산액의 침강 안정성 개선을 위하여, 전기유변효과의 조절이 가능할 뿐 아니라 현탁액의 콜로이드 안정성을 향상시킬 수 있는 여러 가지의 계면 활성제의 영향을 피력하였다.

Abstract— We have studied the rheological and electrical properties of two types of electrorheological (ER) fluids based on semi-conductive polymers (poly(p-phenylene) and polyaniline). These semi-conductive polymer-based suspensions showed a dramatic increase in viscosity on the application of the static electric field due to the large value of conductivity ratio between particle and medium. The dynamic yield stresses of these ER suspensions exhibited a quadratic dependence on electric field strength at low electric fields and a linear one for high fields. They showed a maximum and then decreased with increasing bulk conductivity of particles. These yield stress behaviors under the static electric field were found to be closely related to the dielectric properties, which is in accord with Maxwell-Wagner interfacial polarization induced by the conductivity effects. In order to achieve better understanding of interfacial polarization effect on ER response and to improve the stability of ER suspension, different kinds of surfactants were employed for controlling the ER activity as well as for enhancing the colloidal stability of suspensions.

Keywords: Electrorheology, Semiconductive polymer suspension, Interfacial polarization, Yield stress, Nonionic surfactant

1. Introduction

It is well known that rheological properties of a certain fluid can be modified by the imposition of the external (e. g. electric or magnetic) fields. Winslow[1] first noticed that viscosity of an oil suspension of silica gel particles can be greatly enhanced by the applied electric field and ascribed it to the field-induced aggregation of the suspended particles. This type of behavior has potential applicability as an instrumental device in the development of high-speed robotics, a real-time active damping device, a host of automotive, and hydraulic applications, while several important questions of fundamental nature remain unsolved. Most of electrorheoogical(ER) particles require the addition of small quantities of water or other polar additives to generate the ER effect. However, water-based systems have some critical problems such as large value of current density and degradation of ER effect due to the evaporation of aqueous layer at high temperature (above 70°C). Recently, there were a few reports of water-free systems based on alumino-silicate particles[2] and semi-

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conductive polymer particles[3-6]. The explanation for the activity of these water-free systems is essentially based on the presence of mobile charge carrier, which can move locally under the influence of an electric field. The ER fluid based on semi-conductive polymer is one of the novel, intrinsic ER systems since it has such advantages as wide working temperature range, reduced abrasion of device, good stability against sedimentation, and relatively low current density. The fact that conductivity of these polymers can be easily controlled is another advantage as an ER material. However, details of the relationship between the basic properties of constituents in ER fluid (e.g., conductivity and dielectric properties of polymer, concentration of surfactants) and its rheological behaviors should be extensively studied in order to achieve the enhanced ER activity with optimum electric and physical properties of these materials.

In this study, in order to understand the effect of several material parameters on the ER effect and to develop effective semi-conductive polymer-based ER fluids, an experimental investigation was done for the rheological and electrical behaviors of two kinds of semi-conductive polymer based suspensions.

2. Theoretical Backgrounds

The classical theory relating the dynamics of particles in ER suspension with its shear stress is electrostatic polarization model, which gives the stress proportional to $\varepsilon'_c\beta^2E_0^2$, where $\beta=(\varepsilon'_p-\varepsilon'_c)/(\varepsilon'_p+2\varepsilon'_c)$ is the relative permittivity, E_0 is the strength of external electric field. ε'_c and ε'_p denotes the dielectric constant of continuous medium and particles, respectively. Effects of the conductivity of particles and medium on ER response under d.c. electric field were considered by replacing the value of β with $(\sigma'_p-\sigma'_c)/(\sigma'_p+2\sigma'_c)$, where σ'_c and σ'_p denotes the conductivity of continuous medium and particles, respectively. However, these models cannot explain why the electric field dependence of the yield stress is often less than quadratic, especially in d.c. fields and why the ER activity passes through a maximum as the bulk conductance of the disperse phase is increased [3]. For low-frequency or d.c. electric fields, the role of mismatch in the conductivity of dispersed and continuous phase is dominant in the ER phenomena and this effect can be treated within a Maxwell-Wagner approach[7]. According to this mechanism, the induced polarization of the particles arises from the buildup of charge at the interface between the particle and the surrounding fluid. For the two phase systems having some particles of semi-conductive materials embedded in insulating medium, dielectric constant of suspension(ε') can be expressed as follows :

$$\varepsilon' = \varepsilon'_\infty \left(1+\frac{K}{1+\omega_2\tau_r^2}\right) \tag{1}$$

$$\text{where}\quad \varepsilon'_\infty = \varepsilon'_c\left(1+\frac{3\phi(\varepsilon'_p-\varepsilon'_c)}{2\varepsilon'_c+\varepsilon'_p}\right) \tag{2}$$

$$K=\frac{9\phi\varepsilon'_c}{2\varepsilon'_c+\varepsilon'_p} \tag{3}$$

$$\tau_r=\frac{\varepsilon'_0(2\varepsilon'_c+\varepsilon'_p)}{\sigma_p} \tag{4}$$

$$\tan\delta=\frac{K\omega\tau_r}{1+K+\omega_2\tau_r^2} \tag{5}$$

Here ω is the frequency of alternating field and τ_r is the relaxation time of the interfacial polarization. σ_p is the conductivity of the particle, ϕ is the volume fraction of suspension, and ε'_0 is the dielectric constant of free space. Eq. (4) shows that the relaxation time decreases as the conductivity of particle increases. Detailed explanation on the prediction using this model and dielectric properties of semi-conductive ER suspension was given in the next session.

3. Experimental

The ER fluids used in this study were suspensions of poly(p-phenylene) in a silicon oil and polyaniline particles in a mineral oil. The poly(p-phenylene) particles were synthesized using the method of Kovacic and Oziomek[8]. The density of dried poly(p-phenylene) was 1.22 g/cm^3 and the mean average particle diameter was 22 μm with broad distribution. The conductivity of poly(p-phenylene) particle was controlled by the oxidative doping method using $FeCl_3$ solutions. The relation between the concentration of $FeCl_3$ solution and the electrical conductivity of polymeric particles is given in Table 1. Viscosity, density and electrical conductivity of the silicone oil are 0.05 Pa · s, 0.96 g/cm^3, and 10^{-12} S/m, respectively.

The polyaniline particles were synthesized using the method of MacDiarmid et al.[9]. The number average particle diameter was about 32 μm with broad distribution. The density of dried polyaniline was 1.30 g/cm^3. Viscosity and density of a mineral oil used are 0.02 Pa · s and 0.84 g/cm^3, respectively. Three kinds of non-ionic surfactants (Span 20, 80, and 85 from Sigma Co.) were dissolved in mineral oil with specified weight percent before the preparation of

Table 1. Electrical conductivity of poly(p-phenylene) under different doping conditions

Sample code	Type and concentration of dopant solution	Electrical conductivity (σ_p, S/m)
ppp-1	Undoped	1.0×10^{-10}
ppp-2	1.00M $FeCl_3$ aqueous solution	4.1×10^{-10}
ppp-3	0.05M $FeCl_3$ nitromethane solution	7.8×10^{-10}
ppp-4	0.10M $FeCl_3$ nitromethane solution	1.3×10^{-9}
ppp-5	0.25M $FeCl_3$ nitromethane solution	9.4×10^{-8}

Table 2. Properties of surfactants used in the polyaniline/mineral oil system

Commercial name	Chemical composition	Dielectric constant	Molecular weight
Span20	Sorbitan monolaurate	5.57	346
Span80	Sorbitan monolaurate	4.16	428
Span85	Sorbitan trioleate	3.37	956

polyaniline suspension. Properties and chemical compositions of Span series used are listed in Table 2.

To measure the steady shear behaviors of the ER suspension, the Couette cell type rheometer, PHYSICA universal measuring system was employed. The suspension under investigation is placed in the gap between the stationary outer measuring cup surrounded by the temperature controlling bath and rotating measuring bob. The diameter of the cup and bob was 27 mm and 25 mm, respectively (i.e. the gap was 1 mm). The electric field is applied by high voltage power supply (HVG5000) to the cylinder cup, where the outer cup is the positive electrode and the bob is grounded. The electric field of 1~4 kV/mm was employed. Dielectric constants of poly(p-phenylene) suspensions under well-dispersed quiescent state were measured using DEA 2970 dielectric analyzer (TA Instrument). The frequency range measured was in 10^0~10^5 Hz at room temperature.

4. Results and Discussion

4.1. Electric Field Dependence of Yield Stress for the ER Suspensions

In the absence of the electric field, ER suspensions behave like ordinary concentrated suspensions. When the external electric field was applied, they show the yield stress such as Bingham-plastic body. Experimental studies on the steady shear behaviors and dynamic yield stresses of ER suspensions were given elsewhere[4-5]. Dependence of the yield stress on the electric field for both polyaniline/mineral oil and poly(p-phenylene)/silicone oil suspension systems without any surfactant is given in Fig. 1.

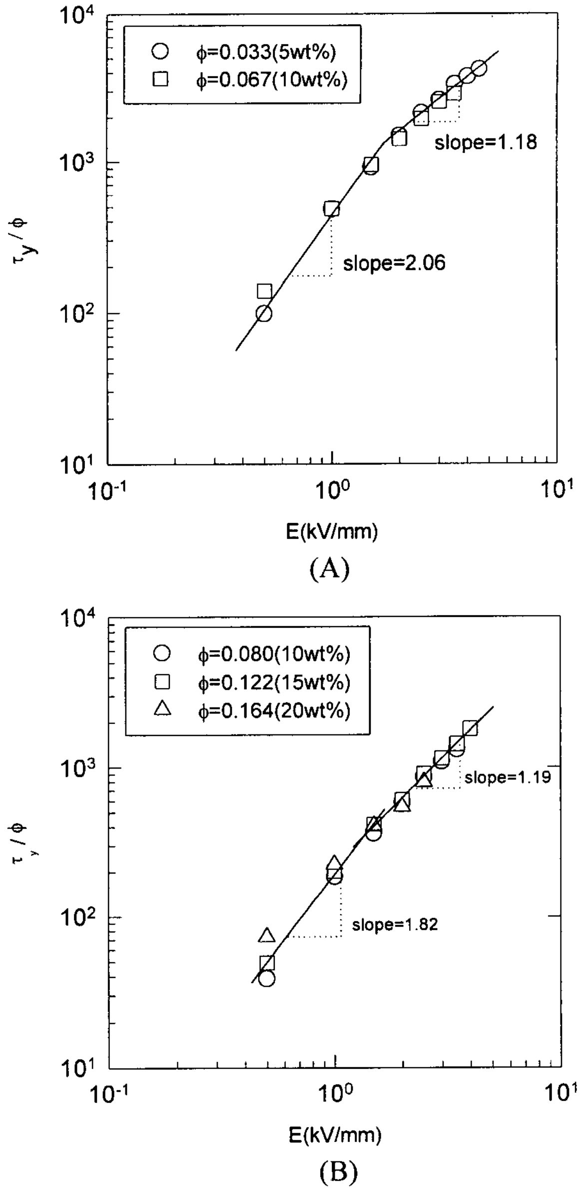

Fig. 1. Electric field strength dependency of yield stress(normalized by volume fraction, τ_y/ϕ); (A) polyaniline in mineral oil, ϕ= 0.033 and 0.067 and (B) poly(p-phenylene), ppp-1 in silicone oil, ϕ=0.080, 0.122, and 0.164.

The yield stresses of both suspensions were proportional to the particulate volume fraction. At low electric field, dependence of the yield stress on the electric field strength was nearly quadratic. However, under strong electric field, dependence on the electric field strength was reduced to nearly unity. The bulk polarization model cannot readily explain these experimental results. This non-uniform dependence on the electric field strength is typical behavior of electrorheological phenomena induced by the conductivity effects. In this case, the yield stress is mainly determined by the ratio of the conductivity of particles to that of the medium and by the distance between the fibrillated particles which is the characteristics of ER suspension. According to the conduction model on electrorheology concerning this mechanism[10, 11], quadratic dependence on the electric field strength at low field and linear dependence at high electric field strength can be well explained. However, the coincidence between the experimental results and theoretical consideration relevant to the dependence of electric field strength, were only valid for low and intermediate volume fraction of suspension(ϕ~0.12). For the poly(p-phenylene)/silicone oil suspension system with ϕ=0.164(20 wt%), normalized yield stress did not show the quadratic dependence on electric field even at low electric field strength, probably due to the complicated particle-to-particle interaction in the dense suspension.

4.2. Dielectric Evidence of ER Behaviors in terms of Interfacial Polarization

Several experimental results suggested that there is no simple relationship between ER effect and the magnitude of the dielectric constant of dispersed particles[12]. As an example, ferroelectric materials with very high dielectric constant (e.g., $BaTiO_3$~1,600) do not show ER response without adsorbed water layer. Khusid and Acrivos[13] theoretically examined the effects of conductivity and interfacial polarization on the electric field-induced aggregation in ER fluid and clarified the condition for effective ER response. They proposed that in d.c.electric fields, the interparticle force should be determined by the interfacial polarization, where the effects of conductivity are dominant only at low electric field. This is in accord with the conduction model[10,11], which gives the quadratic dependence of conductivity ratio on interparticle force at low electric field and very weak dependence at high field. Therefore, dielectric behaviors due to the interfacial polarization process are very important in the conductivity effects of semi-conductive polymer-based ER suspensions[5]. For the successful design of ER fluids composed of semi-conductive polymers, we should understand the effects of structural and compositional factors which control the interfacial polarization behaviors of ER suspension. In this part, the effects of particle conductivity (doping level) on the dielectric behaviors of interfacial polarization were investigated for the poly(p-phenylene) suspensions doped with different concentrations of $FeCl_3$ solution.

We have treated the ER suspensions of several volume fractions in the previous chapter. However, for the development of high-performance ER fluids based on the semi-conductive polymers, decisive factors on the design of concentrated ER suspension would be most important. Therefore, we only focused on the ER behaviors and dielectric characteristics of poly(p-phenylene) suspensions with ϕ=0.164 (20 wt%) and the less concentrated system is beyond the scope of the present study.

Dielectric behavior of our suspension is significantly affected by increasing the electrical conductivity of dispersed poly(p-phenylene) particle. For 20 wt% suspensions (from ppp-1 through ppp-5) and continuous medium, dielectric constants were measured as a function of the frequency (f) of the electric field (Fig. 2(A)).

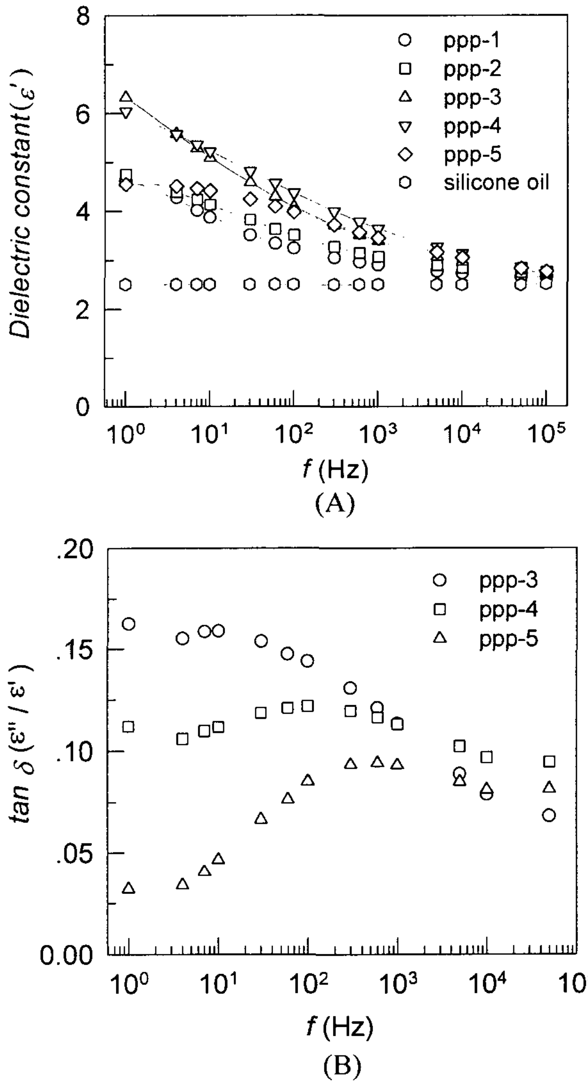

Fig. 2. Dielectric spectra as function of electric field frequency; (A) dielectric constant of silicone oil and 20 wt% ppp suspensions (ϕ=0.164) and (B) dielectric loss tanδ of ppp-3, 4, and 5.

Within the frequency range measured, the dielectric constants of all the suspensions (ε') were greater than that of the medium (silicone oil, $\varepsilon'_c=2.5$, independent of f). Enhancement of suspensions in ε' was clearly distinguished at low frequency region (<10 Hz), which explained the effects of interfacial polarization. As the conductivity of particle increases, ε' of suspensions at the same frequency regime increased first and then showed a maximum with intermediate conductivity. The reason is that a facilitated interfacial polarization occurs when the conductivity ratio between particle and medium is increased. However, when the conductivity of particle was further increased as high as 9.4×10^{-8} S/m (in the case of ppp-5), ε' decreased again. In this case, conduction between the particles prevents the buildup of charge at interface and correspondingly hinders the polarization. For all samples, ε' was gradually reduced with increasing frequency (f), therefore this reduction gives less rigorous dependence on conductivity. This infers that ER activity in the high frequency alternating field would be less dependent upon the conductivity. As a result, the conductivity of particle that shows a maximum dielectric constant was found to be in the regime of an intermediate level of $FeCl_3$-doping. Dependence of dielectric loss $\tan\delta$ ($\varepsilon''/\varepsilon'$) on the frequency is given in Fig. 2(B) for the samples of which relaxation peaks are located in the frequency range measured. The peaks of dielectric loss tangent corresponding to different particle conductivity in each suspension appeared at approximately 10^3, 2×10^2, and 10 Hz for ppp-5, ppp-4, and ppp-3, respectively. To elucidate the role of interfacial polarization for semi-conductive polymer suspension in the condition that σ_p/σ_c exceeds $\varepsilon'_p/\varepsilon'_c$ significantly (in case of ppp-3, ppp-4, and ppp-5, where σ_p/σ_c has sufficiently large value), the predicted values of $\tan\delta$ using Eq. (1) to (5) based on the Maxwell-Wagner interfacial polarization are given in Fig. 3. These results showed some discrepancy with the experimental results, since the relaxation peaks for higher σ_p/σ_c were shifted to higher frequency, probably due to the another complications such as a double layer polarization, which was not included in the Maxwell-Wagner model. However, relaxation time of experimental results ($\tau_r=1/2\pi f_c$, where f_c is the frequency measured at the maximum $\tan\delta$) were distributed within 10^{-2}~10^{-4} s, and these results were in accordance with the predicted value using Eq. (4) in that the relaxation time is in inverse relation with the conductivity of particle[5].

The dynamic yield stresses of poly(p-phenylene) suspension as a function of conductivity of dispersed poly(p-phenylene) were illustrated in Fig. 4(A). Although the current density of this ER suspension showed a monotonous increase with the conductivity of the particle, the locus of ε' at low frequency (f =1 Hz), representing the interfacial polarization effect arisen from the conductivity mismatch was in good agreement with those of the dynamic yield stresses for semi-conductive poly(p-phenylene) suspensions (Fig. 4(B)). The value of optimum conductivity of particle showing maximum yield stress was about 10^{-9} S/m, where the interfacial polarization due to the conductivity effect was maximized, as seen in Fig. 2 (A).

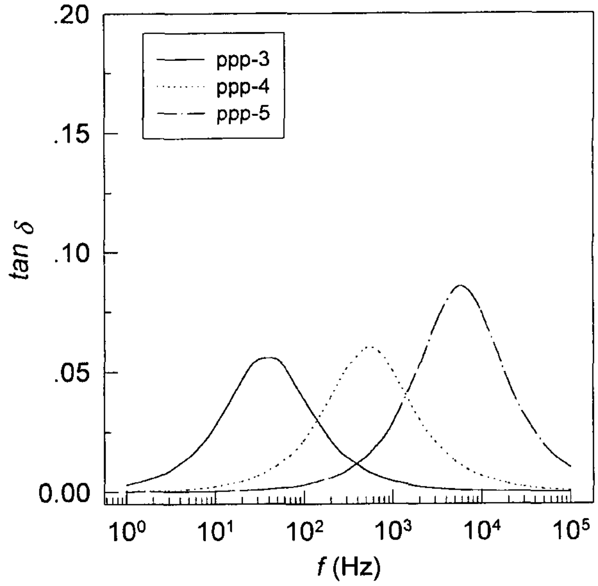

Fig. 3. Dielectric loss tan δ as a function of frequency which is predicted by Eq.(1-5) for several values of particle conductivity (ppp-3,4,5 specified in Table 1).

4.3. Effects of Surfactant on the ER Response and Colloidal Stability

We considered the surfactant effects in the ER response. Actually, the main objective of surfactant addition is to promote the sedimentation stability of ER fluid. Furthermore, the presence of small amount of the surfactant molecules can also enhance the ER effect[5,6,14]. Therefore, tuning of the properties of the dispersing medium with surfactant is another effective technique for improving ER response as well as controlling the properties of particle. Kim and Klingenberg[14] explained that yield stresses of inorganic alumina/silicone oil ER suspensions were increased by surfactant-enhanced interfacial polarization until the critical concentration where the surfactants adsorbed on the monolayer of particle surface. The role of several nonionic surfactants (Span) on

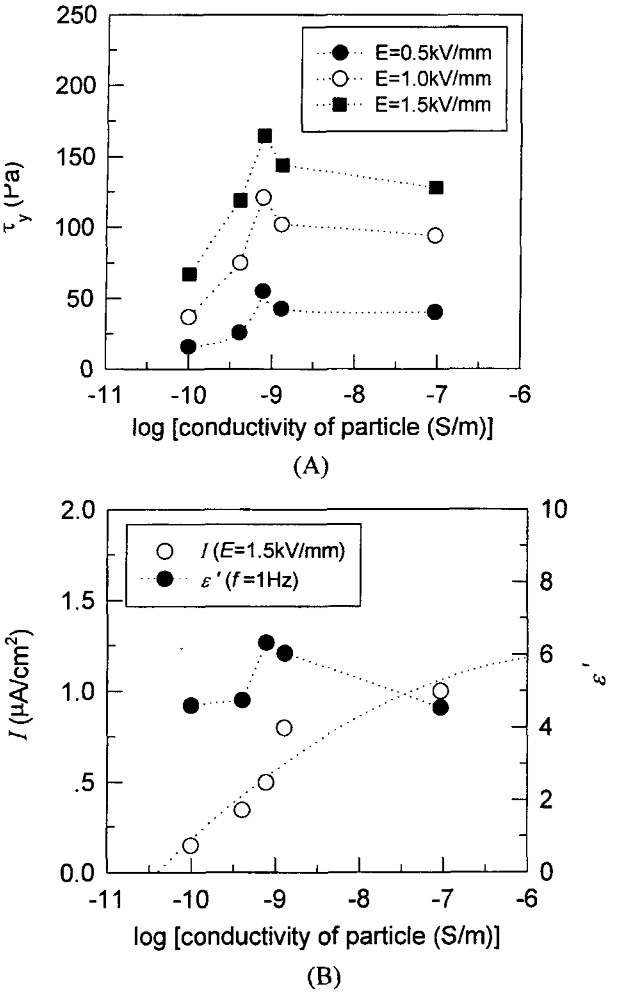

Fig. 4. (A) Dynamic yield stresses for poly(p-phenylene) suspension (ϕ=0.164) as a function of the conductivity of particle and (B) dielectric constant (ε' at f=1 Hz) and current density (I) of poly(p-phenylene) suspension (ϕ=0.164) as a function of the conductivity of particle.

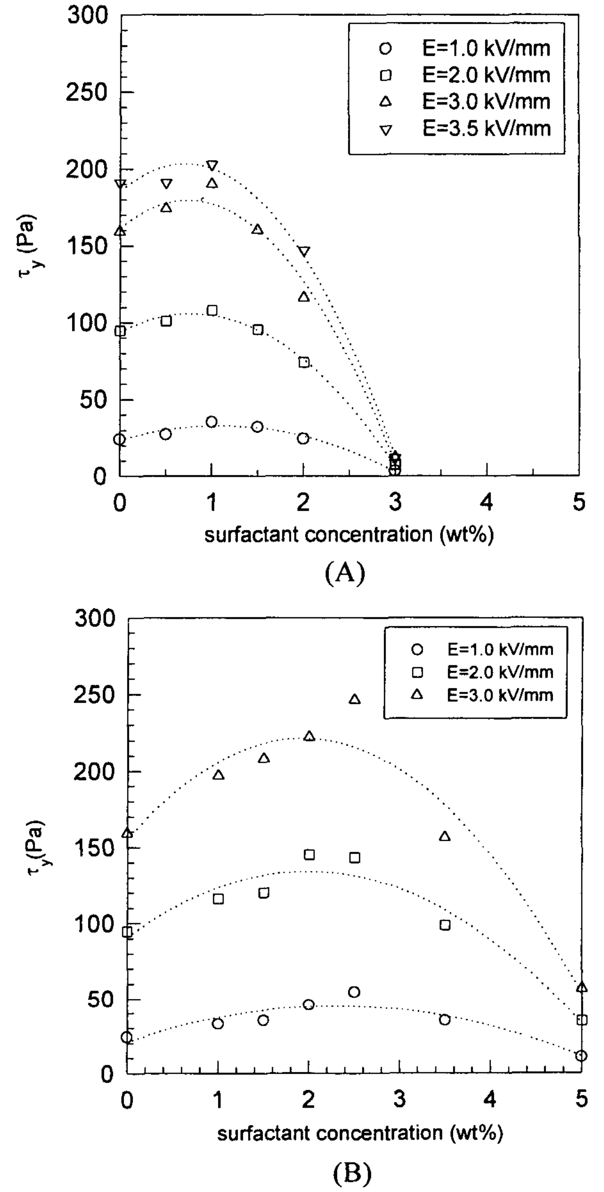

Fig. 5. Dynamic yield stress of 10 wt% polyaniline suspension as a functin of the concentration of surfactants (A) Span80 and (B) Span85.

the adsorption phenomena, ER response, and stability of polyaniline suspension was explained in another paper by the same authors[6]. The dynamic yield stress of polyaniline/mineral oil system was initially increased with the concentration of Span (irrespective of their chemical structures), passed through a maximum, and then exhibited monotonic decrease. The surfactant concentration, which gave rise to maximum yield stress, was not sensitive to the applied electric field strength, but dependent upon the type of surfactant. The concentration for maximum ER activity coincided with the saturation concentration in the adsorption isotherm[6].

We treated here rather dilute polyaniline suspension (10 wt%) with various surfactants since the evaluation of colloidal stability of concentrated suspension was difficult. The experimental results were given in Fig. 5 for the cases of Span80 and Span85. Below the optimal threshold concentration, the ER activity was enhanced by the increased interfacial polarization induced by the adsorbed surfactant molecules. Above the threshold concentration of surfactant, where the excess amount of surfactant molecules was dissolved in the medium, phase separation of surfactant-rich phase induced the non-linear conduction so that ER activity was degraded.

We also measured the ER suspension stability via the sedimentation ratio test in order to decide the best one of the surfactants (Span20, Span80, and Span85). Although the Span 80 could provide the the best colloidal stability

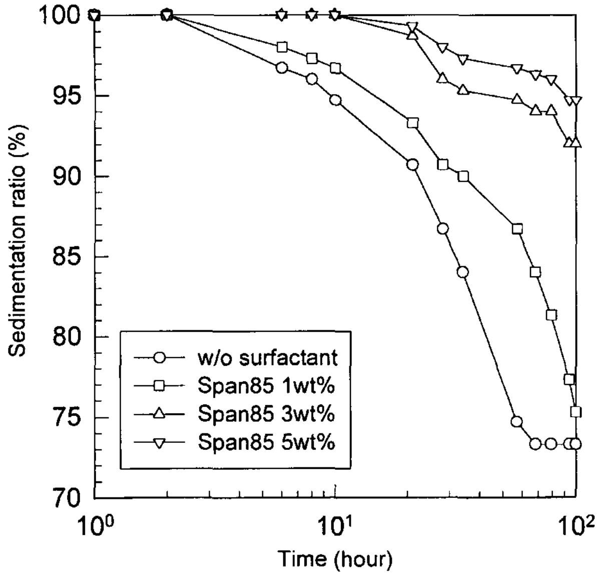

Fig. 6. Sedimentation ratio as a function of the settling time for 10 wt% polyaniline in mineral oil suspension containing Span85.

for very tiny particles in the dilute suspension (1 wt%) used for UV transmittance test, Span85 most effectively prevented the aggregation of relatively large polyaniline particles (mean diameter: 32 μm). In Fig. 6, the sedimentation ratio is plotted as a function of the settling time for the various concentrations of Span85. The pronounced stabilizing effect induced by Span85, especially for a concentrated suspension can be explained as follows: First, the settling velocity is increased by the particle flocculation in a highly concentrated system, where the gravitational force is dominant. In these circumstances, the sedimentation ratio is relevant only to the particle packing density. Second, the bulkiness of absorbed surfactant molecules becomes a decisive factor in the concentrated suspension. The absorbed surfactant molecules enhance the stability due to the steric hindrance. Span85, with the longest tail part among the surfactants used in this study, induced the stabilizing effect most effectively for the ER effective particle phase.

5. Conclusion and Remarks

The rheological and electrical properties of semi-conductive polymer based ER fluids were examined in the wide range of electric fields. The non-uniform dependence of dynamic yield stress on the electric field strength can be explained in terms of the conduction model. The electrical properties of ER fluids can be explained by the interfacial polarization phenomena. The dynamic yield stress showed a maximum, and then decreased with an increase in conductivity of the particle. The optimum conductivity of the particle was found to be $O(10^{-9})$S/m, when the conductivity of the medium was 10^{-12}S/m. This could be explained by the Maxwell-Wagner interfacial polarization which covered the conductivity effects of ER response. The facilitated interfacial polarization also gave rise to the increase in the dynamic yield stress of the ER suspension containing the appropriate concentration of non-ionic surfactants (Span20, 80, and 85). The threshold concentration of each surfactant showing the maximum yield stress were not sensitive to the electric field strength, but were dependent upon the type of surfactant. Span85 was shown to be the most effective surfactant for the phase stability of concentrated polyaniline suspension, although it was not so effective for tiny small particle as Span80. This is due to the fact that Span85, having the longest tail part of the surfactants used here, induces the most effective hindrance to the aggregation of large particles.

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