〈연구논문〉

# 전기 유변유체로서의 폴리아닐린 현탁액의 유변학적 특성

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# Rheological Characteristics of Polyaniline Suspension as an Electrorheological Fluid

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## 요 약

전기장 하에서 폴리아닐린/미네랄 오일 현탁액의 유변학적 특성에 관한 실험적인 연구를 큐엣 셀 형태의 레오미터를 사용하여 수행하였다. 폴리아닐린 현탁액은 전기장을 가해 줄 때 점도가 크게 상승하는 현상을 보였고 부피 분율과 전기장의 3/2승에 비례하는 동적 항복응력을 나타내었다. 작은 변형 진폭의 동적 상태 실험을 통하여 저장계수와 손실계수를 변형진폭, 변형의 구동 주파수 및 전기장의 함수로 나타내었다. 저장계수는 전기장을 증가시킬 때 증가하나 손실계수(5 wt%)는 약한 전기장 의 존성을 보였다. 낮은 응력을 가해 줄 때의 크립과 회복 곡선은 초기의 순간적인 변형 증가와 지연되는 변형 그리고 회복 불가능한 영구적 변형으로 구성되어진다. 탄성 한계 항복응력은 전기장의 세기가 증가함에 따라 증가하였다. 매우 작은 변형에서는 응력과 변형 사이의 선형적 관계를 보여 고체와 유사한 거동을 나타내었다.

**Abstract** - The rheological characteristics of polyaniline suspension in the mineral oil subjected to an electric field were studied experimentally using a Couette cell type rheometer. The polyaniline suspension shows dramatic increase in the viscosity on the application of the electric field. The dynamic yield stress of polyaniline suspension is linearly increased with volume fraction and $E^{3/2}$. The storage shear modulus and loss modulus have been measured using small amplitude forced oscillatory dynamic test as functions of strain amplitude, driving frequency, and the applied field strength. The storage modulus of polyaniline suspension increased with increasing applied field strength, but the loss modulus of dilute(5 wt%) suspension was slightly dependent upon the electric field strength. At low imposed shear stress, the creep and recovery curve comprises instantaneous strain, retardation strain, and permanent strain. The permanent strain is due to the viscous flow. The elastic limit stress increased with increasing of the electric field strength. At very small strain, linear dependence between the stress and strain was obtained as for a solid body.

**Keywords:** Electrorheology, polyaniline suspension, viscoelasticity, creep and recovery.

## 1. Introduction

Electrorheology is concerning with a phenomenon where rheological properties of fluids can be greatly modified by imposing the electric fields. Winslow[1] first noticed that viscosity of an oil suspension of silica gel particles can be greatly enhanced by the applied field and ascribed it to the field-induced aggregation of the suspended particles. This type of behavior has been thought to be applied as an instrumental device in the development of high-speed robotics, a real-time active damping device, or a host of automotive and hydraulic applications, while several important questions of fundamental nature remain unanswered.

Selecting an electrorheological(here after ER) fluid for a particular application requires the accurate knowledge of its dynamic mechanical behavior. In addition to the shear stresses, viscoelastic properties and solid-liquid transition of the electrorheological fluid are also important especially for the vibration damping application. Since most devices using ER suspensions are operated under the dynamic conditions, small amplitude oscillatory measurements are necessary from the practical point of view.

There are some problems to be solved for the real application of ER fluid, which include the temperature limitation. Most of ER particles require the addition of small quantities of water or other polar additives to improve the ER effect. Water based system has some critical problems such as increasing of current density and reducing of ER effect due to drying at high temperature(above 70°C). Recently, there were a few reports of water-free systems based on alumino-silicate particles[2] and semi-conducting poly(acenequinone radicals) particles[3]. 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.

In this study, in order to understand the physics governing the ER effect and to develop a semi-conducting polymer based ER fluid, experimental investigations were done for the steady shear and dynamic behaviors of a polyaniline suspension and the creep and recovery behavior of ER suspension was investigated under various constant stresses in the electric field as a continuing investigation of the previous report[4].

## 2. Experimental

The ER fluid used in this study was suspension of anhydrous polyaniline particles in a mineral oil. The polyaniline particles were synthesized using the method of MacDiamid et al. [5]. The number average particle diameter was about 32 μm. Viscosity and density of a mineral oil used are 0.02 Pa · s and 0.84 g/cm$^3$ at 25°C, respectively.

To measure the steady shear and viscoelastic properties of the ER suspension, the Couette cell type rheometer was employed. The suspension under investigation is placed in the gap between the stationary outer measuring cup and rotating measuring bob. The Physica universal measuring system is equipped with TEZ 150E which is temperature control bath. 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, the outer cup is the positive electrode and the bob is grounded. The electric field of 0.5~4.5 kV/mm was employed. The steady shear and sinusoidal shear strain were applied to the ER fluid by driving the cylindrical bob. The viscoelastic

parameter($G'$, $G''$ and tanδ) were automatically measured.

The creep and recovery behaviors were also measured with the same geometry on a Physica rheometer. The strain is monitored as a function of time for the constant applied stress, and after a set time, its recovery is monitored. Prior to each measurement, the suspensions were sheared at $\dot{\gamma}=3.0\times10^2 s^{-1}$ for 60 s to give the initial conditioning, and electrified in a quiescent state for 120 s. Firstly, the suspensions undergoed a stationary condition during the 10 s. Subsequently the stress was applied at 10 s, maintained for 40 s, and suddenly removed. The time dependence of strain was measured in electric fields up to $E=3.0$ kV/mm. All the measurements were performed at 25°C.

## 3. Results AND Discussion

The steady shear and viscoelastic properties of the polyaniline based ER fluid has been reported elsewhere[4]. Hence we are going to just review some of them briefly.

In the absence of the electric field, ER suspensions behave like Newtonian fluid with viscosities of 0.035 Pa·s for 5 wt% and 0.057 Pa·s for 10 wt%. The flow curves become nonlinear as the electric field is applied. If moderate strength of electric fields are applied such as 0.5, 1.0 and 1.5 kV/mm, Bingham type rheological behavior are obtained. The dynamic yield stresses can be easily obtained by extrapolating to zero shear rate from the plateau stresses in the range of low shear rate ($\dot{\gamma}=0.1 s^{-1}$) in flow curve. Fig. 1 gives the dynamic yield stress normalized by volume fraction as a function of electric field imposed. All the points lie very close to a solid line with the slope of about 3/2. Thus, it may be concluded that the yield stress is linearly increased with volume fraction($\phi$) and $E^{3/2}$.
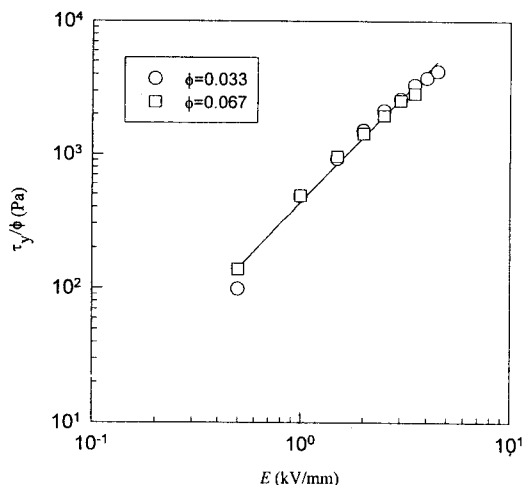


**Fig. 1.** Electric field strength dependency of yield stress (normalized by volume fraction) from low shear rate($\dot{\gamma}=0.1$) for 10 wt.%($\phi=0.067$) and 5 wt.%($\phi=0.033$).

The dependency of the yield stress on the electric field strength differs from $E^2$ dependency suggested by the polarization model.

When the electric field is applied, ER suspension is no longer a viscous fluid but a viscoelastic material. In the range of 0.1~1.0% strain, we found that $G'$ and $G''$ are approximately constant irrespective of the strain amplitude. However, as the magnitude of strain amplitude increases, both moduli considerably decreases. The effect is stronger for the higher ER suspension concentration. The storage shear modulus undergoes more drastic changes thus reflecting a brittle fracture of the structure under mechanical loading. For very small strains, Jordan et al. [6] found that $G'$ was substantially greater than $G''$, indicating that strings remained essentially intact. And they also found that the response of $G'$ was flat, indicating that up to 4% strain the material was in the linear viscoelastic region. But in our result, we were clearly in the nonlinear region as the modulus decreases with increasing strain even for very

small strain of 1% or more at driving frequency of 1.0 rad/s and 2.0 kV/mm. This limiting strain would correspond to the break-up of chain linkages and can be viewed as a yield point of the material. Recently, Koyama et al.[7] reported two step yield strain for polyaniline/silicone oil suspension. In their experiment, smaller yield strain at ca. 1% was obtained in addition to the

larger value of ca. 50%. This reported value of smaller yield strain was in agreement with our result.

The driving frequency sweep test was performed in the linear region of deformation, i.e., under conditions of extremely low deformation amplitude, which do not disrupt the internal structure obtained by the electric field. Fig. 2(a) shows the storage shear modulus of a polyaniline suspension of 10 wt% as a function of driving frequency $\omega$ for frequency range of $10^{-1}\sim$ $10^{2}$ rad/s at small strain amplitude of 0.004. The general shapes of the curves are similar; the storage shear modulus obtain the plateau behaviors over a wide range($\omega=10^{-1}\sim10^{2}$ rad/s) of driving frequency which is the characteristics of solidified electrorheological fluids[8]. But the storage modulus monotonously decreases with driving frequency above $\omega=10^{2}$ rad/s. If experiments were performed at this range of driving frequency, the storage and loss moduli would be not constant with variation of strain amplitude(non-linear viscoelastic region). These non-linear threshold frequencies increase with increasing the electric field strength. At these large frequency, the decrease in the storage shear modulus indicates the break-up of the chain structure induced by the electric field. Fig. 2(b) gives the measured loss modulus at the same condition. The response of loss modulus with frequency even at linear region can not be characterized by a single relaxation time. Recently Ahn and Klingenberg's simulations[9] suggested that when polydispersity of the particles increased, relaxation is significantly broadened and loss modulus would have many small peaks of relaxation time while the storage shear modulus was nearly constant at linear viscoelastic region. Our polyaniline particles have a broad distribution with large polydispersity, which may be responsible for the
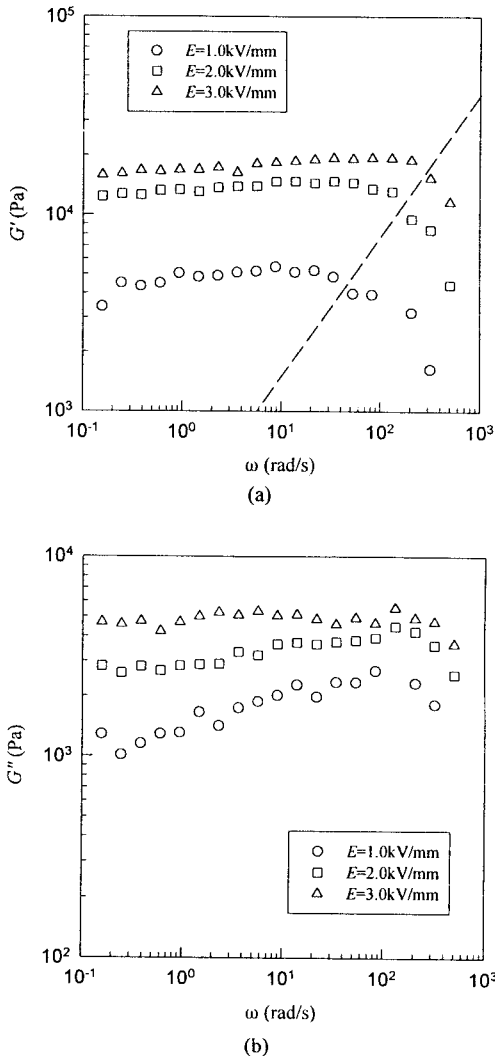


Fig. 2. Storage shear(a) and loss(b) moduli as a function of oscillatory frequency of 10 wt.% polyaniline suspension at strain amplitude of 0.004 with different electric field strengths.
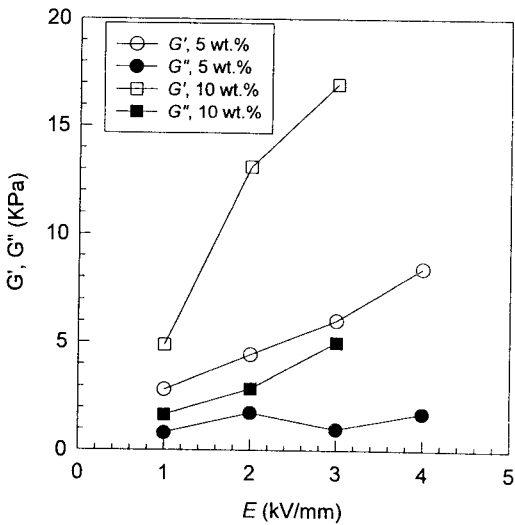
**Fig. 3.** Electric field dependency of the storage and loss moduli for 5 wt.% and 10 wt.% polyaniline suspensions with ω=1.5 rad/s and γ=0.004.
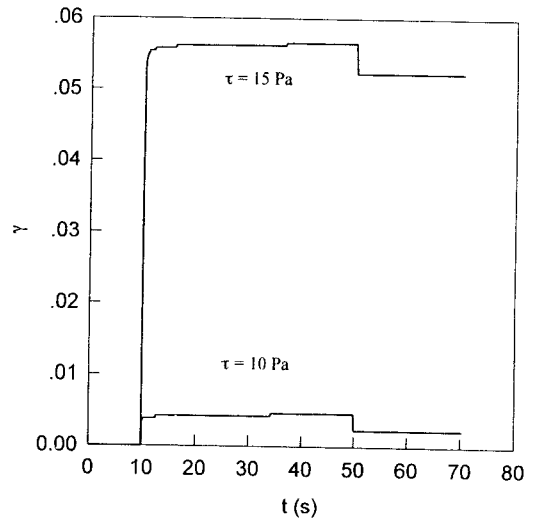


**Fig. 5.** Creep and recovery curves of 10 and 15 Pa for 10 wt.% polyaniline suspension in an electric field of 1.0 kV/mm.
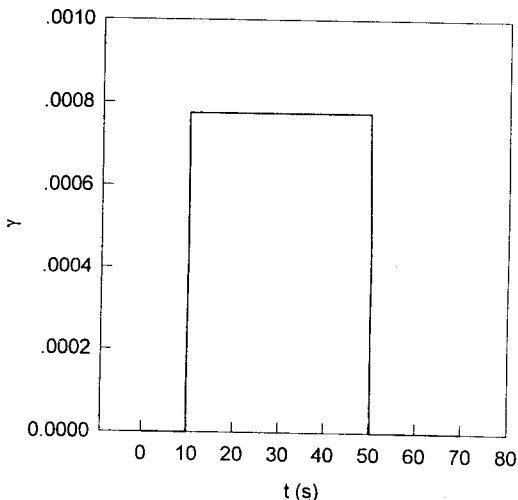


**Fig. 4.** Creep and recovery curve of 5 Pa for 10 wt.% polyaniline suspension in an electric field of 1.0 kV/mm.

fluctuation of loss modulus. Fig. 3 shows the dynamic properties as a function of applied electric field strength. The storage moduli for 5 wt.% and 10 wt.% polyaniline suspensions increased with increasing applied field strength. As mentioned above, the loss modulus for 5 wt.%

suspension shows slight dependency on the electric field strength. However, for 10 wt.%, it continuously increased with increasing field strength.

Fig. 4 shows the creep and recovery curves at imposed shear stress of 5 Pa for 10 wt.% polyaniline suspension in electric field of 1.0 kV/mm. From Fig. 1, the yield stress at $E$=1.0 kV/mm is determined as 28.40 Pa under the steady shear test. The suspension behaves like an elastic solid. After removal of imposed stress, the strain was perfectly recovered. Without the electric field, the shear strain linearly increases with constant rate at same imposed stress(5 Pa).

Fig. 5 shows the creep and recovery curves at imposed stresses of 10 and 15 Pa for the same suspension in the same electric field strength. The creep and recovery curves comprise instantaneous strain, retardation strain, and permanent strain. The permanent strain is due to viscous flow and not recovered. In these implied stresses(10 and 15 Pa), this ER fluid behaves as a viscoelastic fluid. The suspension is expected
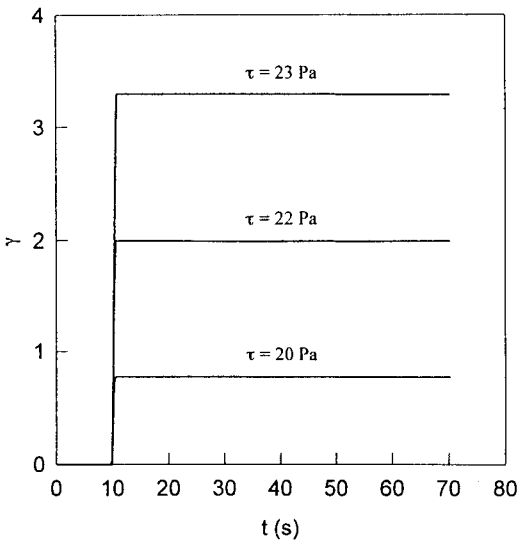
**Fig. 6**. Creep and recovery curves of 20, 22, and 23 Pa for 10 wt.% polyaniline suspension in an electric field of 1.0 kV/mm.
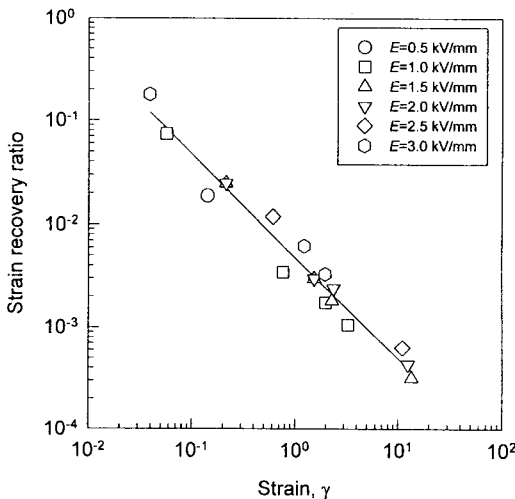


**Fig. 7**. Strain recovery as a function of strain for 10 wt.% polyaniline suspension with different electric field strengths.

to behave as an elastic solid below the elastic limit yield stress. So the elastic limit yield stress could be determined in the range between 5 and 10 Pa with $E$=1.0 kV/mm. The ER fluid behaves as viscoelastic fluid in the range of solid to liquid transition. In the linear

viscoelasticity, the instantaneous elastic strains on application and removal of stress are equal, but the instantaneous recovery in Fig. 7 is considerably small as increase of implied stress and strain. In electric fields the rheological response of suspension are markedly nonlinear in this region. But as small as imposed stress and strain, instantaneous recovery is very similar to instantaneous elastic strain.

Fig. 6 shows the creep and recovery behavior at imposed stresses of 20, 22, and 23 Pa in an electric field of 1.0 kV/mm. When the stress was imposed, the suspensions rapidly reached the equilibrium without continuous strain, and showed no elastic recovery when the stress was released. Although the retarded strain and viscous flow are negligibly small compared with the instantaneous strain in creep curve, the strain is not recovered after the removal of stress. Except in the limit of zero time the behavior of this suspension is plastic. The rheology of suspensions in electric fields can be expressed by a combination of elasticity, viscosity, and plasticity. When the stress approaches the dynamic yield stress which is determined from the steady shear test, the plastic tendency becomes striking. As a result, the ratio of instantaneous recovery to total strain decreases with increasing imposed stress.

The strain recovery ratio is defined as,

$$\text{strain recovery ratio} = \frac{\gamma_{max} - \gamma_{final}}{\gamma_{max}} \qquad (1)$$

where $\gamma_{max}$ is the maximum strain during stress imposed, and $\gamma_{final}$ is the final strain during the recovery. This strain recovery ratio can be used as a measure of energy storage. Applying the electric field, the suspension are elastic at very small strain and viscous at large strain. To clarify the relation between the rheology and chain deformation process, the strain recovery ratio
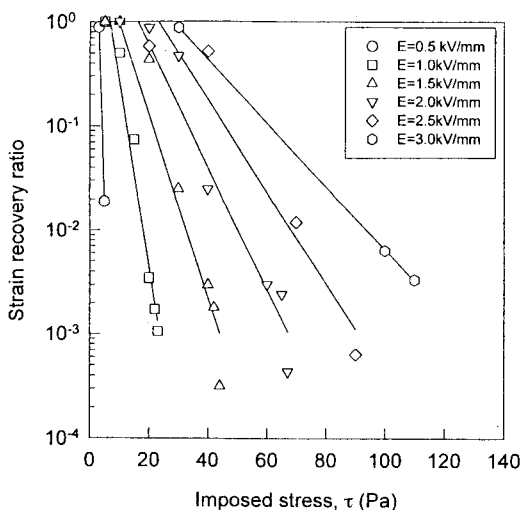
**Fig. 8**. Strain recovery as a function of imposed stress for 10 wt.% polyaniline suspension with different electric field strengths.



**Fig. 9**. Shear stress vs. shear strain at small deformation for 10 wt.% polyaniline suspension with different electric field strengths.

was examined as a function of maximum strain, imposed stress and the electric field strength. Fig. 7 shows the strain recovery ratio as a function of maximum strain for polyaniline suspension. Irrespective of field strength, the plots for each system have the same slope. The strain recovery ratio decrease with increasing final strain. Of course, the suspension shows no recovery above the yield point.

Fig. 8 shows the strain recovery ratio as a function of imposed stress with different field strength. The elastic limit stress, i.e. the strain recovery ratio equal to 1.0, increased with increasing of electric field strength. In optical observations, more crosslinked chain structure was developed as increase of electric field strength.

The shear stress vs. shear strain behavior of polyaniline suspension as a function of the field strength is given in Fig. 9. The stress and strain data have been extracted from the creep experiment. A general feature of the curves is an increase in shear stress with in-
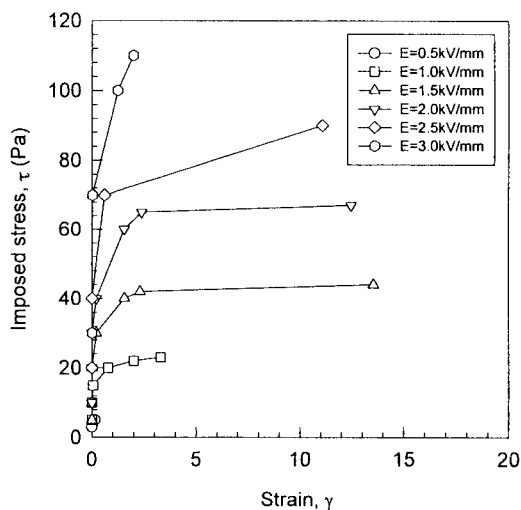
creasing strain. At very small strain, linear relation between the stress and strain showed solid-like behavior. There was no upper yield stress.

## 4. Conclusion

The rheological properties of an electrorheological fluid which consists of polyaniline and mineral oil were examined in the wide range of electric fields. The dynamic yield stress was found to be proportional to $\phi E^{3/2}$, where $\phi$ is the volume fraction of polyaniline particle and $E$ is the strength of electric field imposed. The storage shear and loss moduli were measured at strain amplitude of 0.004 in the linear viscoelastic region as functions of driving frequency and electric field strength. At small strain, the fluid responds elastically and its dynamic mechanical behavior is dominantly described by the storage shear modulus. The storage shear modulus is approximately constant with driving frequency of

$10^{-1} \sim 10^2$ rad/s. The nonlinear viscoelasticity is observed with not only increasing strain amplitude but also increasing driving frequency. At low stresses, the creep and recovery curve comprises instantaneous strain, retardation strain, and permanent strain. The permanent strain is due to viscous flow and not recovered. The elastic limit stress increased with increasing of electric field strength. At very small strain, linear dependency between the stress and strain showed solid-like behavior. At constant electric field, the strain recovery ratio decreased with increasing the stress imposed. Thus it can be noted that when the stress approach the yield stress, the plastic tendency becomes striking.

## Acknowledgment

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