

Electrorheological Properties of Polyaniline Suspensions

Piyanoot Hiamtup,[†] Anuvat Sirivat,[†] Alexander M. Jamieson[‡]

[†]The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330 - Thailand

[‡]Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106 - USA

anuvat_s@chula.ac.th

ABSTRACT

Polyaniline (PANI) was synthesized via an oxidative coupling polymerization in acid condition and dedoped in ammonium hydroxide solution. Rheological properties of the PANI/silicone oil suspensions were investigated in the oscillatory shear mode to explore the effects of electric field strength, particle concentration, and host fluid viscosity on electrorheological (ER) characteristics. The PANI-based ER fluids exhibit unusual viscoelastic behaviors under an applied electric field and the ER response is enhanced with increasing electric field strength. The dynamic moduli, G' and G'' dramatically increase by 6 orders of magnitude when the electric field strength is increased up to 2 kV/mm. ER response increases with electric field strength, particle concentration and silicone oil viscosity. The sol-gel transition point is determined and found to occur about 50-200 V/mm for the system investigated.

Keywords: Electrorheological fluids, Conductive polymer, Polyaniline

*Corresponding author, email: anuvat_s@chula.ac.th

1. INTRODUCTION

Electrorheological (ER) suspensions, firstly studied extensively by Winslow (1949), can display dramatic changes in rheological properties under large applied electric field [1]. ER fluids is typically a suspension consisting of micron-sized polarizable particles dispersed in a non-conducting medium. The mismatches in conductivity and dielectric properties between the dispersed particles and the continuous medium phase induce polarization upon application of an electric field. Under the action of an electric field, the induced particle dipoles tend to attract the neighboring particles to one another and cause the particles to form fibril-like structures, which are aligned along the direction of the electric field, and that provides additional resistance against fluid motion [2]. A semiconducting polymer usually has a high polarizability, even in the absence of any activator. Many polyaniline (PANI) derivatives based upon modifications of oxidation state, dopant, and polymerization conditions have been studied and reported extensively. PANI has several advantages over other polymer particles such as density, conductivity control, and thermal and environmental stability. PANI can be easily polymerized by an oxidative polymerization at relatively low temperatures and can be doped from an insulating state to a conducting state by using simple protonic acids. This allows controlled variations in the particle dielectric constant and conductivity while keeping all other particle properties and suspension characteristic intact [3].

In this study, we shall report the synthesis and characterization of PANI. ER properties of PANI were investigated under the linear oscillatory deformation mode. We are interested in the effects of electric field strength, frequency, host oil viscosity, and particle concentration on the storage and loss modulus. Moreover, sol-gel transition points where the material theoretically changes from the liquid state to the solid state are determined.

2. EXPERIMENTAL

Materials. Aniline, C_6H_7N (AR grade, Merck) was vacuum-distilled and used as the monomer. Ammonium peroxydisulphate, $(NH_4)_2S_2O_8$ (AR grade, Merck) was used as the oxidant. 37 % of Hydrochloric acid, HCl (AR grade, Labscan); 25 % of ammonium solution, NH_4OH (Ar grade, Merck) and methanol, CH_3OH (AR grade, Labscan) were used as received. The host fluids, silicone oils (AR grade, Dow corning) with density 0.96 g/cm^3 and kinematic viscosities of 100 cSt and 500 cSt were vacuum-dried and stored in a desiccator prior to use.

Synthesis of PANI and sample preparation. PANI was synthesized via an oxidative coupling polymerization [4]. 20.4 g of distilled aniline was added to 250 ml of 1.5M HCl aqueous solution and the mixture was vigorously stirred and cooled to $0-5\text{ }^\circ\text{C}$ in a 3-necked round bottom flask. 250 ml of 1.5M HCl solution of 25.5 g $(NH_4)_2S_2O_8$ was then added dropwise into the flask within an hour. After all of the oxidant was added, the reaction mixture was left stirring at $0-5\text{ }^\circ\text{C}$ for 4 hours. The precipitated polyaniline was then washed with CH_3OH/H_2O mixture until the washing liquid was completely colorless. It was then dedoped by immersion in 3% NH_4OH , washed and dried at room temperature for 48 hours in vacuum before passing through a $38\text{ }\mu\text{m}$ sieve shaker to control the particle size and its distribution. The particles were then dispersed in silicone oil with an ultrasonicator for 30 minutes at $25\text{ }^\circ\text{C}$. The suspensions were then prepared at the volume fractions of 0.048 and 0.092. They were stored in a desiccator and redispersed ultrasonically before each experiment.

Analytical techniques. The synthesized PANI was characterized by FTIR, UV-Vis, and XRD techniques. Size and morphology of the particles were observed by a particle size analyzer and SEM. TGA was also carried out to investigate the thermal stability of PANI. The microstructure evolution of PANI suspension under an applied electric field was observed by a video camera attached to an optical microscope.

Rheological measurements. Rheological properties of the suspensions were investigated by using a fluid rheometer (ARES, Rheometric Scientific Inc.) with custom-built copper parallel plates geometry (diameter of 25 mm) attached to insulating spacers where they connect to a transducer or motor. The electric field for rheological measurement was applied by a high voltage power supply (Source Meter 2410, Keithley). The intensity of voltage could be precisely controlled in the range of 0-1 kV, corresponding to the electric field strength of E between 0-2 kV/mm. An electric field was initially applied for 10 minutes to obtain an equilibrium chain-like, or columnar structure before each measurement was taken. The samples were firstly checked for viscoelastic linearity by the strain sweep mode tests. The resulting stress was decomposed into an in-phase and out-of-phase contribution, the storage and loss moduli, G' and G'' . The experiments were carried out under the frequency sweep mode ranging from 0.1 to 100 rad/s in order to

investigate the effect of electric field strength on G' and G'' for the suspensions. All experiments were carried out at the temperature of 25 ± 1 °C and repeated at least two or three times at each applied electric field strength to ensure the reproducibility.

3. RESULTS AND DISCUSSION

Characterization of PANI. FT-IR spectrum obtained from PANI base shows typical five characteristic peaks at 826, 1163, 1307, 1495, and 1584 cm^{-1} . These peaks are attributed to the out-of-plane bending vibration of C-H on para-disubstituted rings, characteristic vibrational mode of N= quinoid segment =N, stretching vibration of C-N, stretching vibration of N-benzoid segment -N, and stretching vibration of N= quinoid segment =N, respectively [5]. UV-Vis absorption spectrum of PANI in NMP shows two absorption peaks. One with maxima at 326 nm attributed to two different transitions, which are the π - π^* transition and the transition from low-lying orbitals to the π_b orbital [6]. The other with maxima at 635 nm attributed to the excitation from HOMO (highest occupied molecular orbital, π_b) of the free benzenoid part to LUMO (lowest occupied molecular orbital, π_q) of the localized quinoid ring and two surrounding imine nitrogen atoms [6]. XRD pattern of PANI shows only a broad peak at $2\theta = 19.5^\circ$ indicating a typical amorphous polymer. TGA thermograms of PANI show two steps weight losses. For the first-step weight loss, occurs at temperature between 49.6 and 100 °C; it can be attributed to the loss of moisture or other solvents. After the initial weight loss, emeraldine base shows a slower weight loss, which may be assigned to the loss of low molecular-weight oligomer. A significant weight loss occurs at 490 °C, where PANI chains begin to decompose [7]. The shape of PANI particles and their surface are irregular. The mean diameter of PANI particles was found to be 23.51 μm with the standard deviation of 2.37 μm .

Electrorheological Properties of PANI / Silicone Suspension.

The effects of particle concentration and host fluid viscosity on the electrorheological properties of the suspensions were investigated. Particle concentrations investigated were at volume fraction of 0.024 and 0.048 at a specific conductivity of order 10^{-8} S/cm and silicone oil viscosity was varied at 100 and 500 cSt. The samples are coded as PANI024/100, PANI024/500, PANI048/100, PANI048/500, the number after PANI is volume fraction of particle which is followed by viscosity of silicone oil.

Effect of electric field strength and particle concentration

Figure 1a and 1b show the effects of electric field strength and particle concentration to storage and loss moduli of the suspension. Figure 2a and 2b show the characteristic value of G' and G'' , obtained at $\omega = 0.1$ rad/s. Without the electric field, the particles were randomly dispersed in the suspension under the influence of the Brownian force. The system showed a liquid-like behavior in which G'' was larger than G' . Under the action of an electric field, the particles formed and developed strings spanning the electrodes, and the suspension became solid-like. The interfacial polarization of charge carriers migrating in the bulk and at the particle surface plays the main role in this process [8]. Higher electric field strength induces a higher dipole moment and causes particle chains to pull themselves together tighter due to the greater electrostatic force and form thicker chains [9]. These thicker and stronger particle chains result in high rigidity as can

be represented by the dramatically increasing in both G' and G'' with electric field strength [10]. $[G'(\omega = 0.1)]$ and $[G''(\omega = 0.1)]$ increased about 6 orders of magnitude when the electric field was applied up to 2 kV/mm. In comparison with the higher concentration suspension (PANI048), the moduli of PANI02448 are lower about 1 order of magnitude. This may reflect the fact that the higher particle concentration results in a denser particle structure organized in the electric field with a higher flow resistance [11].

Effect of host fluid viscosity

Figure 3a, 3b, and 2b show the effect of silicone oil viscosity on the ER response of the suspensions. These figures show that the strongest dependency of moduli on the oil viscosity occurs at weak electric field (0 – 20 V/mm) and the dependency becomes less distinct and almost independent eventually as electric field strength increases. This behavior can be explained as there are two important forces contributing to rheological behavior of the suspension: electrostatic interparticle force and hydrodynamic force. According to Maxwell-Wagner type-polarization, the electric field will induce in an isolated sphere particle of radius a with a dipole of magnitude p :

$$p = \frac{\pi}{2} \epsilon_s a^3 \left(\frac{\sigma_p - \sigma_s}{\sigma_p + 2\sigma_s} \right) E_0 \quad (1)$$

where E_0 is the electric field strength, and σ_p , σ_s are the electrical conductivities of the particle and matrix, respectively [12]. The magnitude of the force between two particles aligned with the electric field and with a center-center separation of r is

$$F_{elec} = \frac{3\pi \cdot p^2}{8\epsilon_s r^4} \quad (2)$$

whereas in oscillatory shear, the maximum value of hydrodynamic force acting to pull two particle apart is [13]

$$F_{shear} = 6\pi\omega\gamma_0\eta a^2. \quad (3)$$

Under weak electric field, the hydrodynamic force is dominant and moduli of the suspensions increase as host fluid viscosity increases. In case of large electric field, a larger contribution from the interparticle electrostatic force is expected. Storage modulus depends primarily on the number of particle strings, corresponding to particle concentration.

As compared these results with molecular dynamics computer simulations of ER fluid under oscillatory shear, the moduli were only functions of the dimensionless frequency $\omega^* = (16\eta\omega)/(\epsilon_s\beta^2 E_0^2)$. Storage modulus will increase with increasing oil viscosity since the hydrodynamic forces are larger and the chains undergo larger deformations [1].

ER response can be determined from $\Delta G'$ value, which is calculated by subtraction $G'(\omega=0.1)$ with no electric field from $G'(\omega=0.1)$ with applied electric field. The

data suggested that ER response can be enhanced with increasing electric field strength: $\Delta G'$ increased from 0 to 1287.65 Pa as E field was varied from 0 to 2000 V/mm, respectively for PANI024/100. For the effect of particle concentration, $\Delta G'$ was 1287.65 and 2445.81 at E = 2000 V/mm for PANI024/100 and PANI048/100, respectively. For the effect of host oil viscosity, $\Delta G'$ was 2445.81 and 3728.09 at E = 2000 V/mm for PANI024/100 and PANI024/500, respectively.

Sol-gel transition

From the observations in Figure 1, 2, and 3, it is clear that the ER fluid passes through a sol-gel transition as the electric field increases. At the sol to gel point, theory and experiment [14-15] indicate that the frequency dependence of G' and G'' each exhibit identical power law dependence on frequency, i.e. that $G' = A\omega^{n'}$ and $G'' = B\omega^{n''}$, with $n' = n''$, and where A and B are related to the material strength factor of the gel, S, by

$$S = G' \omega^{n'} \Gamma(1-n)^{-1} \cos(n\pi/2) \quad (4)$$

$$S = (A^2 + B^2)^{1/2} \Gamma(n) \cdot \sin(n\pi/2) \quad (5)$$

The sol-gel transition point of an ER fluid can therefore be determined, in principle, by plotting the viscoelastic exponents, n' and n'' as a function of field strength, and observing a crossover where $n' = n'' = n$ [14-15]. That such an analysis works for ER fluids was demonstrated recently by Chin et al. [16] From figure 3b, both n' and n'' decrease toward to zero as the electric field is increased. For PANI048/100, the crossover occurs at E = 100 V/mm with the value of $n = 0.07$. The material strength factor of gel can then be determined and the values are shown in Table 1.

Microscopic observation

Figure 4a and 4b show changes in microstructure of dilute PANI suspension. Upon application of electric field, the fibril-like particle structure could be observed.

4.CONCLUSION

PANI particles were synthesized via an oxidative polymerization. The ER properties of the PANI / silicone oil suspension were investigated by examining the effects of electric field strength, particle concentration, and silicone oil viscosity on dynamic moduli, G' and G'' . The results show that the ER response can be enhanced with increasing electric field strength, particle concentration, and also host oil viscosity. The effect of oil viscosity was strong at low electric field strength but became weaker as field strength continuously increased. The sol to gel transition were then determined and found to occur about E = 50-200 V/mm.

5.REFERENCES

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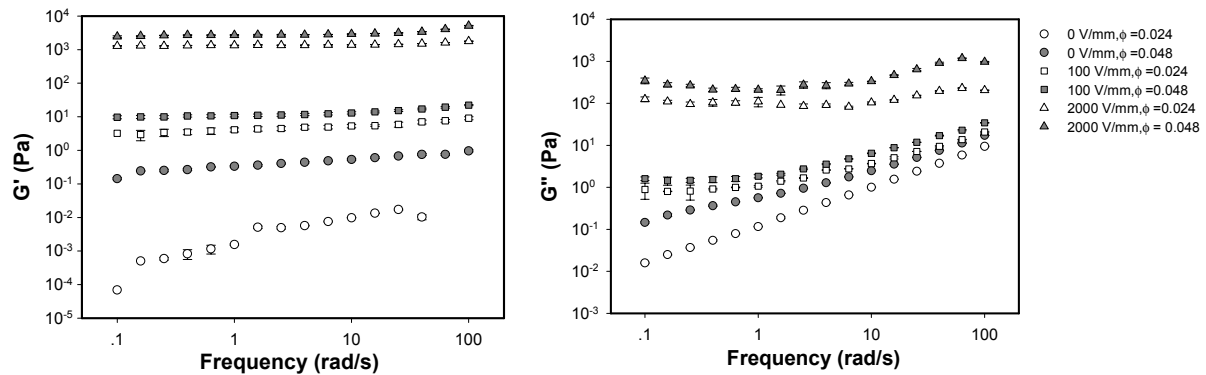


Figure 1 Frequency dependence of PANI /Silicone oil suspension: **(a)** storage modulus, G' ; **(b)** loss modulus, G'' , at temperature of 25 ± 1 °C, silicone oil viscosity = 100 cSt. Gap = 0.303-0.496 mm, strain 0.2-700%: white symbols are for PANI024; gray symbols for PANI048.

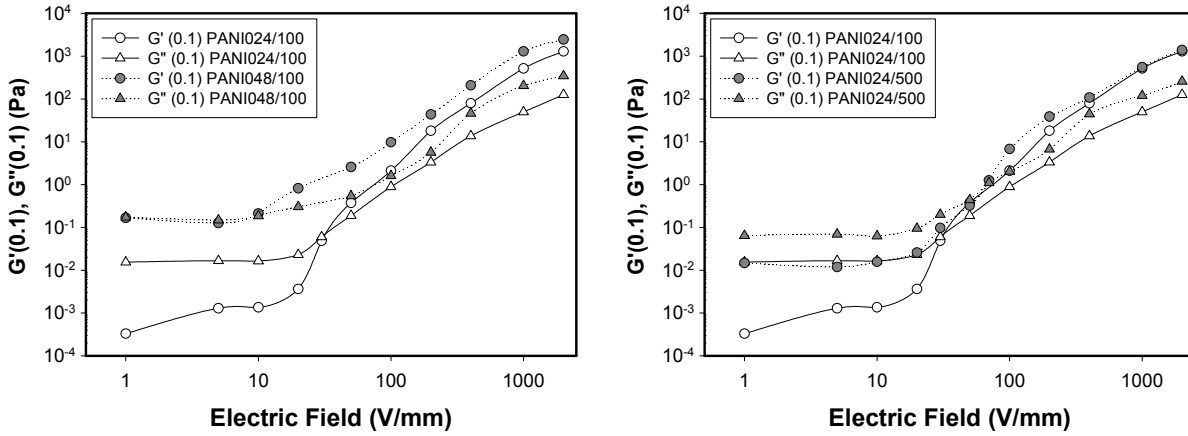


Figure 2 Characteristic values of G' and G'' at frequency 0.1 rad/s: **(a)** effect of particle concentration, white symbols for PANI024; gray symbols are for PANI048; **(b)** effect of silicone oil viscosity, white symbols are for $\eta = 100$ cSt; gray symbols are for $\eta = 500$ cSt.

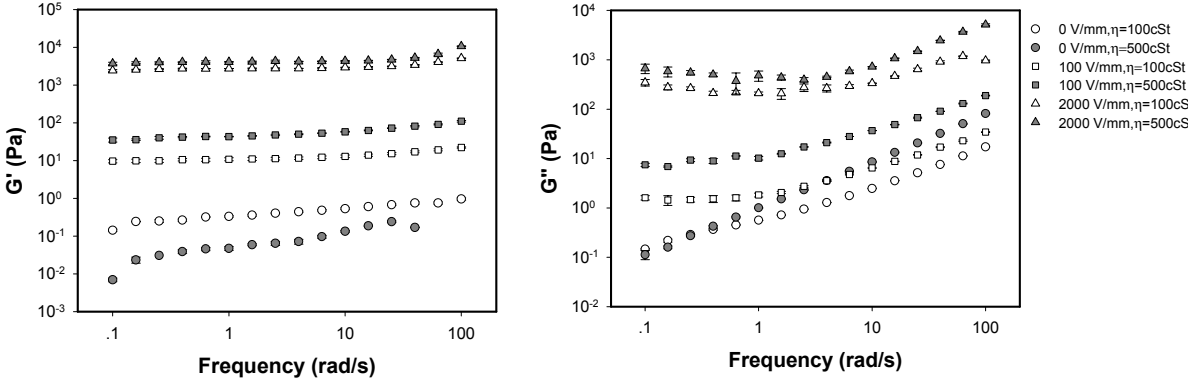


Figure 3 Frequency dependence of PANI /Silicone oil suspension: **(a)** storage modulus, G' ; **(b)** loss modulus, G'' , at temperature of 25 ± 1 °C, particle volume fraction = 0.048. Gap = 0.307-0.505 mm, strain 0.2-20%: white symbols are for $\eta = 100$ cSt; gray symbols are for $\eta = 500$ cSt.

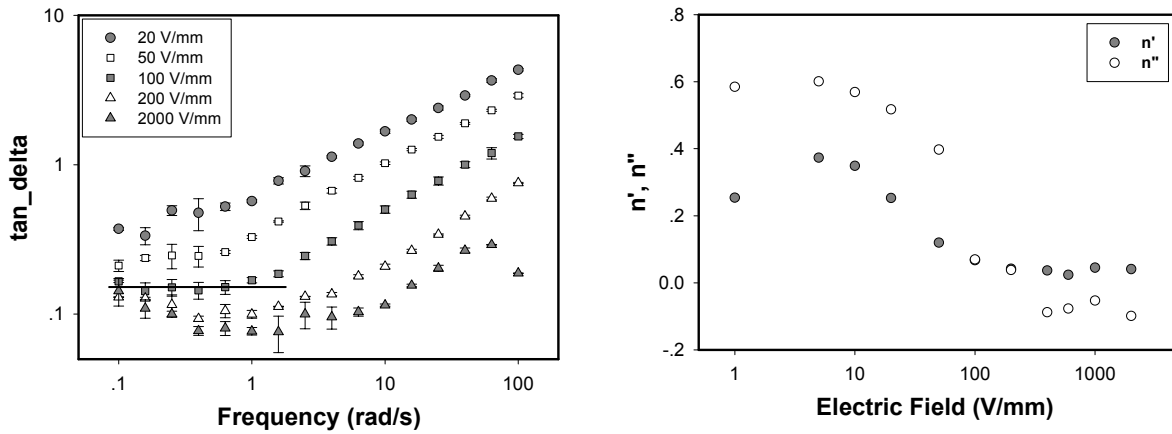


Figure 4 PANI /Silicone oil suspension at particle volume fraction = 0.048, silicone oil viscosity = 100 cSt, and temperature of 25 ± 1 °C: **(a)** frequency dependence of \tan_{δ} at various electric field strength; **(b)** the scaling exponents n' and n'' vs. electric field strength.

Table 1 Viscoelastic properties of PANI suspensions in silicone oil at temperature of 25 ± 1 °C.

System	E (V/mm)	$\tan \delta$	n'	n''	n avg	A,B (y intercept)	S (Pa.s ⁿ)
PANI024/100	100	0.30	0.15	0.13	0.14	3.93, 1.03	0.10
PANI024/500	200	0.20	0.087	0.10	0.094	5.94, 9.53	1.23
PANI048/100	100	0.15	0.067	0.069	0.068	10.92, 1.67	0.29
	200	0.11	0.042	0.038	0.040	47.52, 5.48	2.27
PANI048/500	50	1.05	0.41	0.44	0.43	3.84, .42	0.14

Figure 4 Microstructure formation of 1.6 % vol PANI / silicone suspension: **(a)** without electric field under; **(b)** with E = 1000 V/mm.

