CHAPTER VI
GELATION OF POLYTHIOPHENE ELECTRORHEOLOGICAL FLUID DRIVEN BY AN ELECTRIC FIELD

6.1 Abstract

Electrorheological properties under oscillatory shear of perchloric acid doped-poly(3-thiopheneacetic acid) PTAA/silicone oil suspension have been investigated. The effects of electric field strength, viscosity of silicone oil, and particle concentration were observed and determined. Upon the application of electric field, the PTAA-based ER fluid undergoes the transition from liquid-like to solid-like behavior in which its equilibrium rheological properties satisfy the sol-gel transition criteria. The critical electric field strength required for the sol to gel transition to occur, as determined by the frequency independent loss tangent, decreases with increasing particle concentration. The effect of oil viscosity is observed only at weak electric field strength. Using the sol-gel transition criteria, the viscoelastic scaling exponent n satisfying the sol-gel transition criteria varies between 0.05-0.83, corresponding to the fractal dimension value between 2.5 and 1.5.

KEYWORDS: Gelation, Polythiophene, Electrorheological fluid

6.2 Introduction

Electrorheological or ER fluids are typically composed of electrically polarizable particles dispersed in low-dielectric oil. It is generally accepted that the ER effect is the result of particle fibrillation forming strings oriented along the electric field direction. In the absence of electric field, ER fluids show the Newtonian behavior while on the application of an electric field, particles become polarized, and the local electric field is distorted. The migration of mobile charges to areas with greatest field concentration increases the polarizability of the particle and results in a larger dipole moment. These field-induced dipoles attract each another and cause the particles to form chains or fibrillated structures between two electrodes in the direction of electric field. These chains are held together by interparticle forces that have sufficient strength to inhibit fluid flow (Bonnecaze and Brady, 1992). The connectivity between the particles in the strings arises from their field-induced dipoles. The particles interaction greatly affects the viscoelastic behavior of ER fluids and resulting in an increase of the shear viscosity. In additional, if the developing structure possesses sufficient rigidity, the ER fluid is expected to exhibit a liquid-solid transition or a sol-gel transition.

The gelation usually happens when aggregation or branching of the solid matter takes place in a liquid. The gelation and aggregation are tightly linked to each other where systems undergo a liquid-to-solid transition, i.e. the formation of non-crystalline materials (an infinite molecule, a gel) from a solution or a dispersion. Rheology is a most sensitive tool to study the onset of network formation which eventually results in sample spanning connectivity at the gel point. Gelation is a critical phenomenon in which many physical quantities are expected to diverge near or at the critical point (gel point or sol-gel transition point). These properties can be expressed in power law forms and their exponents (critical exponents) are used to describe the phenomena.

There are several systems that exhibit the sol-gel transition: polymers under the influence of temperature (Hsu and Huang, 2000, Nystrom *et al.*, 1996, Shay *et al.*, 2001), polymer-surfactant complexes (Shay *et al.*, 2001), gelatin (Hsu and Jamieson, 1992), alumino silicates (Charoenpinijkarn *et al.*, 2001), and etc.

Here, we are interested in the equilibrium rheological properties of solutions of a conductive polymer, polythiophene, under the influence of electric field. It will be shown that, provided the electric field strength is sufficiently strong, the equilibrium rheological properties satisfy the sol-gel transition conditions where tan δ becomes independent of frequency (Chambon and Winter, 1987). The effects of particle conductivity, particle concentration, and surfactant on the gels and the gel strength will be reported here.

6.3 Experimental

6.3.1 Materials and ER Fluids Preparation

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer. Anhydrous ferric chloride, $FeCl_3$ (AR grade, Riedel-de Haen) was used as the oxidant. Chloroform, $CHCl_3$ (AR grade, Lab-Scan) and methanol, CH_3OH (AR grade, Lab-Scan) were dried over CaH_2 for 24 hours under the nitrogen atmosphere and then distilled. The perchloric acid dopant, $HClO_4$ (AR grade, AnalaR) was used as received. The dispersing phase was a silicone oil (AR grade, Dow corning) with the density 0.96 g/cm^3 and the kinematic viscosity of 100 and 500 cSt; it was vacuum-dried and stored in a desiccator prior to use. Polyoxyethylene sorbitanmonolaurate, Tween 20 (AR grade, Fluka), a nonionic surfactant was used as received.

As in our previous work, we use a system of poly(3-thiopheneacetic acid), PTAA which synthesized via the oxidative polymerization (Kim *et al.*, 1999). The PTAA particles have been treated with perchloric acid to have a highly controlled level of conductivity (Chen *et al.*, 2000). All the particles used in this study have essentially the same electrical conductivity, size distribution and shape (Chotpattananont *et al.*, 2004).

The electrorheological, ER, fluids were prepared by dispersing $HClO_4$ doped PTAA particles in the silicone oil and placed within an ultrasonicator for 30 minutes at 25 ± 0.1 °C. The prepared ER fluids were then stored in a dessiccator prior to use and redispersed again prior to each measurement.

6.3.2 Oscillatory Shear Experiments

A fluids rheometer (Rheometrics, ARES) was used to measure various rheological properties. It is fitted with custom-built copper parallel plates fixture (diameter of 50 mm) attached to insulating plexiglass sheets. A DC voltage was applied with a DC power supply (Tektronic, PS280) and a custom-built DC power supply, which can deliver an electric field strength up to 2 kV/mm. A digital multimeter (Tektronic, CDM250) was used to monitor the voltage and current. To ensure a steady state ER response, the electric field was applied for 10 minutes to ensure formation of an equilibrium agglomerate structure before measurements were taken. Each measurement were carried out at a temperature of 25 ± 0.1 °C and repeated at least two or three times.

In our experiments, storage G' and loss G" moduli were measured as functions of frequency and electric field strength. Strain sweep tests were first carried out to determine the strain appropriate for both G' and G" to be in the linear viscoelastic regime. The appropriate strain was determined to be 0.1% for the electric field strengths of 2, 1, 0.5 kV/mm, 1% for the electric field strengths of 200, 100, 80 V/mm, and 10% for the electric field strengths of 50, 20, 10, 1, 0 V/mm. The deformation frequency was varied from 0.01 to 100 rad/s.

6.4 Results and Discussion

The mean PTAA particle diameter was determined to be approximately 30 μm with a standard deviation of ~ 8 μm. SEM monographs indicate the shapes of the undoped and doped PTAA particles are quite irregular (Chotpattananont *et al.*, 2004).

The effect of particle concentration and particle conductivity on the equilibrium electrorheological properties of the suspensions was investigated. Particle concentrations investigated were 5%, 10%, and 20% by weight (corresponding to volume fraction of 0.024, 0.048, and 0.092, respectively) at a specific electrical conductivity of 7.5×10^{-2} S/cm (HPT5, HPT10, and HPT20).

Figure 6.1 shows the dynamic mechanical properties of 20 wt% suspension of highly doped PTAA in 0.1 Pa.s silicone oil (HPT20/η0.1). The result shows that the dynamic moduli, G'(ω) and G"(ω), of the Poly (3-thiopheneacetic acid) suspensions increase dramatically by nearly 8-9 orders of magnitude as the electric field strength is increased through the range of 0-2 kV/mm. Without electric field, the suspension is fluid or exhibit liquid-like behavior in which G" is significantly larger than G' over the entire range of frequency. Basically, the dynamic mechanical behavior of the suspension at zero field should follow the liquid-like behavior:

$$G'(\omega) \propto \omega^2 \qquad G"(\omega) \propto \omega \qquad (6.1)$$

while the deviation from the above relations becomes more pronounced for the higher electric field strength (Li and Aoki, 1997). From Figure 6.1, the G' of this suspension does not show the expected ω^2 behavior at zero field strength. The deviation from the ideal ω^2 behavior in ER fluids has been reported. Chin et al. observed the deviation for high concentration of silica/silicone oil ER fluid (30 wt%). They suggested that the deviation is attributed to a weak water-bridging effect between silica particles and the presence of van der waals interaction. Moreover, the volume fraction might be too high, so the accessible frequencies were not low enough for G; to show the ω^2 relation (Chin and Winter, 2002). In our experiment, the fraction of PTAA particles was reduced to lower concentration 10 wt% (HPT10/η0.1) and 5 wt% (HPT5/η0.1). The overall behavior was similar, except that the dynamic moduli were smaller. The G' deviation from the ideal ω^2 behavior was still observed even at low particle concentration.

6.4.1 Effect of oil viscosity

Furthermore, the effect of silicone oil viscosity on the ER response of the suspensions was investigated. Figure 6.2 shows the dynamic mechanical properties of 20 wt% of highly doped PTAA in 0.5 Pa.s silicone oil (HPT20/η0.5). The dynamic moduli, G'(ω) and G"(ω), of the HPT20/η0.5 suspensions also increase with electric field strength. The magnitude of the dynamic moduli increase

dramatically by about 8 orders as the electric field strength is increased through the range of 0-2 kV/mm. However, as oil viscosity is increased, the suspension exhibits the fluid-like behavior at zero field, e.g. the dynamic moduli show the liquid-like behavior follow the Equation 6.1. This might be from the fact that as the oil viscosity is increased, the viscous response from the oil begins to dominate, and so the suspension becomes more fluid (Sakurai *et al.*, 1999).

The effect of oil viscosity on dynamic properties can be clearly observed in Figure 6.3. Figure 6.3a shows the plot of storage modulus G' as a function of frequency at various electric field strengths. The dependence of the G' on oil viscosity can be observed at the low to moderate electric field (0-100 V/mm). Under this range of field strengths, the G' shows a significant decrease as the oil viscosity becomes large. Unlike the loss modulus G", the dependence of the G" on oil viscosity can be observed at any particular field strengths. As the oil viscosity is increased, the value of G" increases due to the viscous response from the oil begins to dominate (Sakurai *et al.*, 1999). These results are in agreement with the results reported by Sakurai et al. (Sakurai *et al.*, 1999). They have suggested that the dependence of ER responses on oil viscosity can be interpreted in terms of a model based on the competition between the dipole-dipole electrostatic interaction (which acts to maintain neighboring particles together) and the shearing force due to the deformation of the matrix (which acts to separate the particles). B ased on the polarization model, the application of an electric field polarizes the particles creating induced dipole moments. The induced dipole moments leading to the electrostatic interaction between particles:

$$F_{elec} = \frac{3\pi p^2}{8\varepsilon_s r^4} \tag{6.2}$$

where ε_s is the dielectric constant of matrix, r is the distance between particles, and p = $(\pi/2)\varepsilon_s a^3[(\sigma_p-\sigma_s)/(\sigma_p+2\sigma_s)]E_o$, where a is radius of particle, E_o is the electric field strength, and σ_p, σ_s are the electrical conductivities of the particle and matrix, respectively. While the hydrodynamic force which is generated from the difference

between the velocity of the particle, v_p, and the ambient solvent velocity, v_s, can be written as

$$F_{shear} = 6\pi\eta a(v_s - v_p) \tag{6.3}$$

where η is the solvent viscosity.

If the electric field is weak and the viscosity is large so that the F_{shear} will dominate over F_{elec}, the storage modulus G' is expected to be decreased as the viscosity is further increased since the relatively weaker electrostatic interactions will be unable to form aggregates of any size. On the other hand, F_{elec} will dominate the particle interactions at the large electric field, and particle aggregates will form leading to increased flow resistance and thus the G'.

6.4.2 Sol-Gel Transition

From Figure 6.1 and Figure 6.2, it is clearly seen that the responses of G' and G" with the electric field pass through the typical features of a liquid-to-solid transition. Close inspection of these results indicates that the fluid systems appear to pass through a sol-to-gel transition at certain electric field strength, as evidenced by the fact that the storage modulus undergoes a particularly large increase, whereas the loss modulus lags behind. Moreover, at a high field strength, G' and G" each become essentially frequency independent with G' larger than G" ($\tan \delta < 1.0$) within a certain range of frequencies investigated.

Several theoretical analyses have been developed to express the frequency dependence of G' and G" at the gel point through the scaling exponent n (Chambon and Winter, 1987). Subsequent theories use the fractal scaling concept to relate the scaling exponent to the gel network structure. The early theory suggests that at the sol-gel transition point (Hsu and Jamieson, 1992):

$$G'(\omega) = A\omega^n \tag{6.4}$$

$$G''(\omega) = B\omega^n \tag{6.5}$$

and

$$\tan \delta = G''/G' = B/A = \tan (n\pi/2) \qquad (6.6)$$

The storage and the loss moduli share the same scaling exponent value, and tan δ becomes independent of frequency. These sol-gel transition conditions (Eqs. 6.4-6.6) are known as the Winter-Chambon criteria. Typically, a gelation process evolves with time and when the above conditions are satisfied, the material is said to be at the sol-gel transition point.

In our study, we found that the equilibrium electrorheological properties of some polythiophene systems satisfy the sol-gel criteria of Winter-Chambon as in Eqs. 6.4-6.6. The word 'equilibrium' refers to the steady state or long-time behavior, after cessation of the temporal gelation process which necessarily proceeds. We may note here that the gelation time of our systems is rather short and therefore G' and G'' cannot be measured in details in order to investigate the temporal gelation process.

Figure 6.4a shows the plots of loss tangent, tan δ, vs. frequency of 20 wt% suspension of highly doped PTAA in 0.1 Pa.s silicone oil (HPT20/η0.1) at various electric field strengths. The slope of tan δ is positive at zero and low electric field and turn to negative at higher field strength. It can be deduced that the tan δ does not show any distinct sol-gel transition in the experimental accessible frequency range, e.g. the Winter-Chambon criterion has been found not to hold for this suspension. The possible formation of water-bridges between the particles may cause sufficient connectivity for the suspension to show the solid behavior (Chin and Winter, 2002).

Unlike the 20 wt% suspension of highly doped PTAA in 0.5 Pa.s silicone oil (HPT20/η0.5) as presented in Figure 4b, the plots of tan δ vs. frequency at various electric field strengths. The slope of tan δ appears to change from negative to positive with increasing of electric field strength. The flat of tan d can be observed at a field strength of 20 V/mm which is identified as the sol-gel transition point, according to Winter (Chin and Winter, 2002).

The effect of particle concentration on sol-gel transition has been further investigated, by suspend the PTAA particles in 0.5 Pa.s silicone oil as different concentration: 5%, 10%, and 20% by weight (HPT5/η0.5, HPT10/η0.5, and HPT20/η0.5, respectively). The general pattern of behavior is the same for all systems. Thus we do not show the results of those systems but summarize their properties in Table 6.2. For HPT10/η0.5, the slope of tan δ becomes frequency independent at electric field strength about 40 V/mm. However, the frequency independence of tan δ for HPT5/η0.5 system appears at a higher electric field strength, i.e. 50 V/mm.

The experimentally obtained scaling exponents for our polythiophene suspensions are shown in Table 6.2. Our experimental values of n in our systems are in the range of 0.83 to 1.47, depending on particle concentration, particle conductivity, and electric field strength. From Table 6.2, the power law exponent n' decreases and approaches 0 as electric field strength is increased while the power law exponent of G" shows frequency independent at higher field strength. This may be resulted from the characteristic of the suspension where the fibrillar structure is sensitive and easily disrupted at high frequency since it is like a physically crosslink system. Moreover, we have found that the values of n' and n" are quite close at a critical field strength which is identified as the gelation point, according to Winter. This result is consistent to the result obtained from the analysis of the frequency independent of tan δ values. Taking the HPT20/h0.5 system for example, the values of n' and n" are quite close at field strength of 20 V/mm indicating that the gel point should be occurred at this field strength.

The values of the power exponent, n from Eq. 6.4 and Eq. 6.5, can be interpreted physically from several theoretical models and it has been found to be in the range of $0 < n < 1$ depending on the type of the system. The simple analogy and effective medium theory predicts n to be 0.5, as for the regular and nonfractal resistor-capacitor linear response (Nystrom et al., 1995). On the basis of the percolation approach, the Rouse model, assuming no hydrodynamic interaction between polymeric clusters, it predicts a value of n = 0.67 (Nystrom et al., 1996, Martin et al., 1988). In the electrical analogy, a suggested isomorphism between the

complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors results in a unique value of n equal to 0.72.

Several oscillatory shear studies have been undertaken to observe the values of power law exponent, n. The values of n in the whole range $0 < n < 1$ on various gelling systems have been reported such as poly(vinyl alcohol) (n = 0.45-0.65) (Kjoniksen and Nystrom, 1996), polyurethanes (n = 0.69) (Durand *et al.*, 1987), polyester (n = 0.69) (Rubinstein *et al.*, 1989), tetraethoxysilane (n = 0.66) (Hodgson and Amis, 1990), gelatin (n = 0.69) (Hsu and Jamieson, 1992), epoxy resins (n = 0.70) (Martin *et al.*, 1988). There are other observations of n which cannot be described by the above models. The value of n has been observed to be equal to 0.5 at gel point for stoichiometrically balanced gelling systems of poly(dimethylsiloxane) (Winter and Chambon, 1986), polyurethane (Chambon *et al.*, 1986), and poly(ethylene oxide) (Muller *et al.*, 1991). Moreover, value of n in the range of $0.5 < n < 1$ have been reported at gel point for a stoichiometrically imbalanced poly(dimethylsiloxane) gel with cross-linker deficiency (Chambon and Winter, 1987).

The values of n in the range of $0 < n < 0.5$ have also been observed; examples include thermoplastic elastomer polypropylene (n = 0.13) (Lin *et al.*, 1991), polystyrene (n = 0.2–0.5) (Antonietti *et al.*, 1989), poly(dimethylsiloxane) (n = 0.2-0.3) (Scanlan and Winter, 1991), ethyl(hydroxyethyl)cellulose/CTAB mixture (n = 0.38-0.43) (Nystrom *et al.*, 1995), ethyl(hydroxyethyl) cellulose/SDS mixture (n = 0.24-0.41) (Nystrom *et al.*, 1995).

The scaling exponent, n, can be related to the mass fractal dimension, d_f. Muthukumar elaborated on a theoretical model (Muthukumar, 1985), based on the assumption that variations in the strand length between crosslinking points of the gel network giving rise to changes of the excluded volume interactions. When the hydrodynamic interaction is completely screened out and the excluded volume effect is dominant, n changes from 1 to 3/5 and d_f varies from 1 to 3. From his theory, the scaling exponent can be expressed in terms of d and d_f as

$$n = d / (d_f + 2) \tag{6.7}$$

where d denotes the space dimension.

It has been suggested that the sol-gel transition is not a pure percolation process, but a combination of percolation and either partial or fully extent screening depending on the nature of the chemical system. It has been shown that if the excluded volume effect is screened out the n may decrease (Nystrom *et al.*, 1995, Kjoniksen and Nystrom, 1996)

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \tag{8}$$

All values of the scaling exponent for $0 < n < 1$ are possible for a fractal in the realizable domain $1 \leq d_f \leq 3$.

The scaling exponents observed link the gelation with the spanning cluster structure and reflect the different interaction forces present in the system. For arbitrarily aggregating system that forms a non-ordered structure, the equation where the screening of the excluded volume effects is assumed, Eq. 6.8 is expected to be valid and appropriate for our system. By using Eq. 6.8 and inserting the values of n = 0.05-0.83, we thus arrive at d_f = 2.5-1.5. From Table 6.2, it can be deduced that the mass fractal dimension value increases with increasing the field strength but it is almost particle concentration independent.

6.5 Conclusions

In this study, we have investigated the equilibrium rheological properties of suspensions of a conductive polymer, polythiophene, under the influence of electric field. The results show that the PTAA suspension exhibits viscoelastic behavior and a transition from fluid-like to solid-like behavior as the field strength is increased. The dependence of the G' on oil viscosity can be observed at the low to moderate electric field (0-100 V/mm). Unlike the loss modulus G", the dependence of the G"

on oil viscosity can be observed at any particular field strengths, G" increased with increasing oil viscosity. Furthermore, it is observed that the equilibrium rheological properties of our PTAA suspensions satisfy the sol-gel transition Winter-Chambon criterion, in which tan δ becomes independent of frequency, when the sufficiently strong electric field strength is applied. The electric field strength for the transition has been found to decrease with increasing particle concentration. Moreover, the values of the power law exponent, n, are located in the range 0.05-0.83 depends on electric field strength. Finally, the fractal dimension value between 1.5 and 2.5 and it found to increase with the electric field strength.

6.6 Acknowledgements

6.7 References

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Table 6.1 Properties of $HClO_4$ doped PTAA suspensions in silicone oil and electrical conductivity values of PTAA pellets

System	Particle concentration (% wt.)	Viscosity of silicone oil (Pa.s)
HPT5/η0.1	5	0.1
HPT10/η0.1	10	0.1
HPT20/η0.1	20	0.1
HPT5/η0.5	5	0.5
HPT10/η0.5	10	0.5
HPT20/η0.5	20	0.5

Table 6.2 Viscoelastic properties of $HClO_4$ doped PTAA suspensions in silicone oil at temperature of 25 $^{\circ}$C

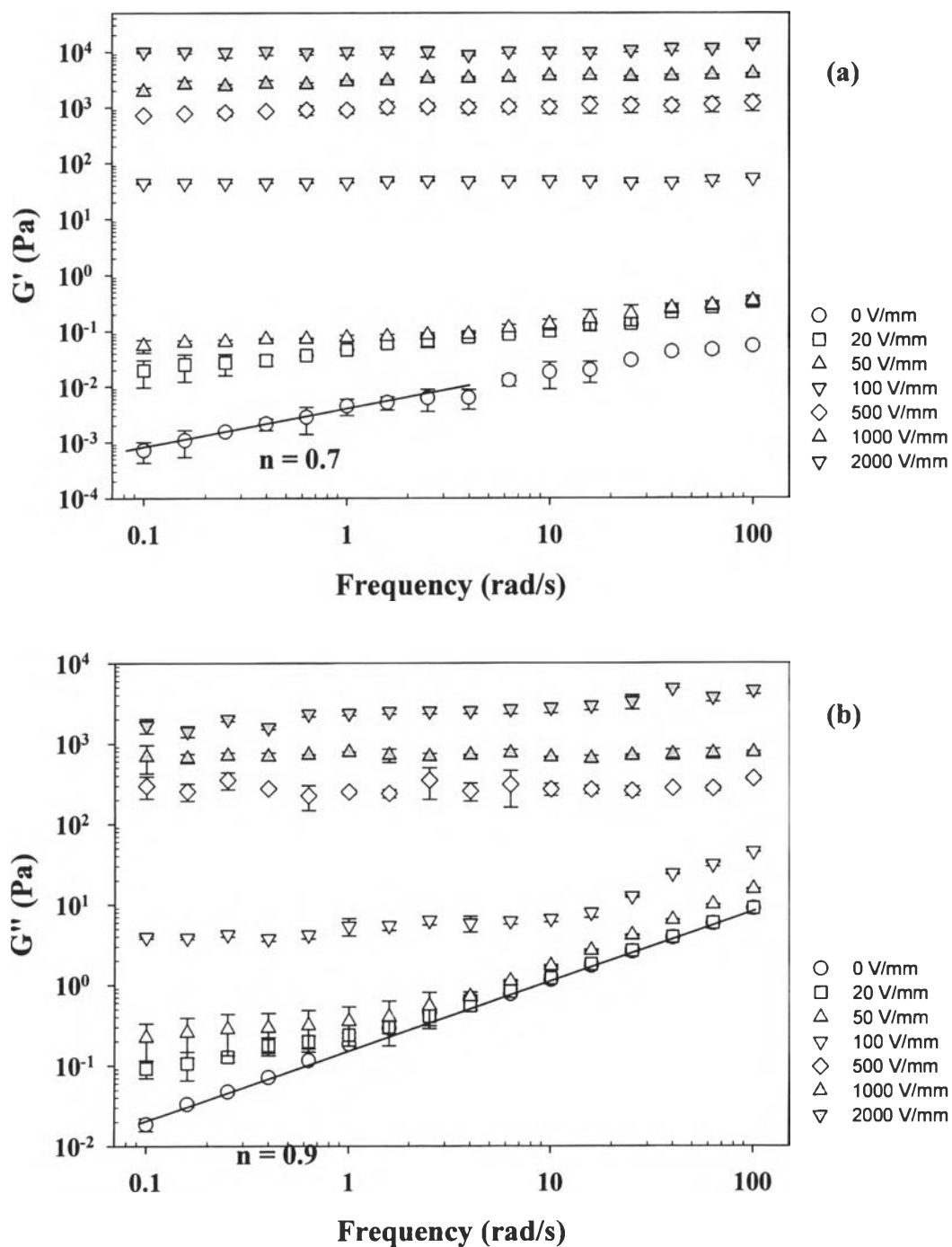| System	E_{gel} (V/mm)	n'	n"	n_{avg}	d_f
HPT5/η0.5	0	1.95	0.99	-	-
	20	1.87	0.98	-	-
	50	*0.84*	*0.82*	*0.83*	*1.54*
	100	0.13	0.55	-	-
	500	0.08	0.42	-	-
	1000	0.09	0.31	-	-
	2000	0.04	0.11	-	-
HPT10/η0.5	0	1.83	0.99	-	-
	20	1.52	0.99	-	-
	40	*0.92*	*0.92*	*0.92*	*1.39*
	50	0.84	0.84	-	-
	100	0.17	0.55	-	-
	500	0.06	0.42	-	-
	1000	0.08	0.31	-	-
	2000	0.05	0.11	-	-
HPT20/η0.5	0	1.72	0.99	-	-
	20	*0.98*	*0.99*	*0.98*	*1.28*
	50	0.12	0.43	-	-
	100	0.04	0.25	-	-
	500	0.07	0.30	-	-
	1000	0.08	0.26	-	-
	2000	0.01	0.09	-	-

Figure 6.1 Storage and loss moduli of 20% wt. $HClO_4$ highly doped polythiophene/0.1 Pa.s silicone oil suspension (HPT20/η0.1) at 25 ± 0.1 °C: **(a)** storage moduli G'; **(b)** loss moduli G".
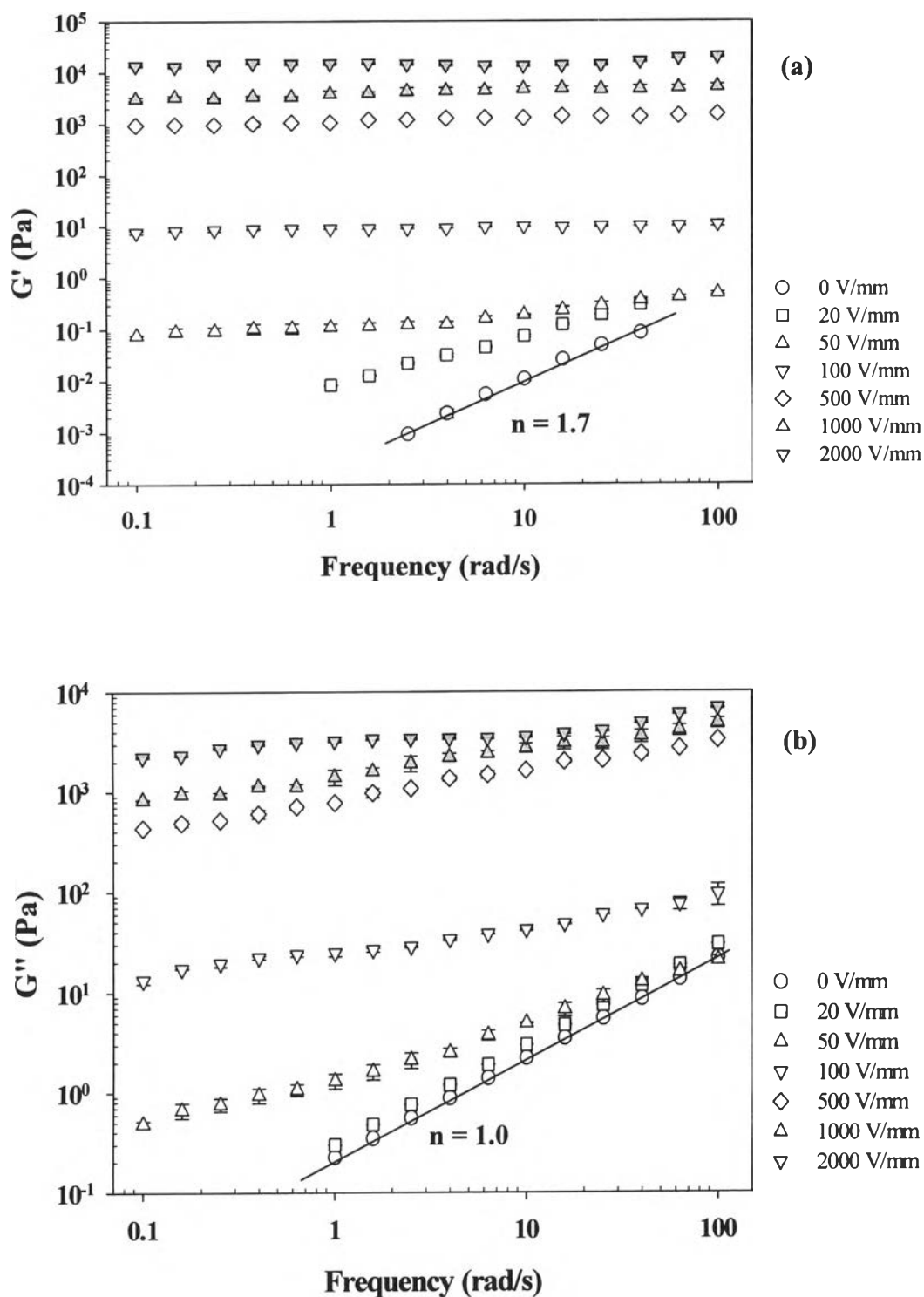
Figure 6.2 Storage and loss moduli of 20% wt. $HClO_4$ highly doped polythiophene/0.5 Pa.s silicone oil suspension (HPT20/η0.5) at 25 ± 0.1 °C: **(a)** storage moduli G'; **(b)** loss moduli G".
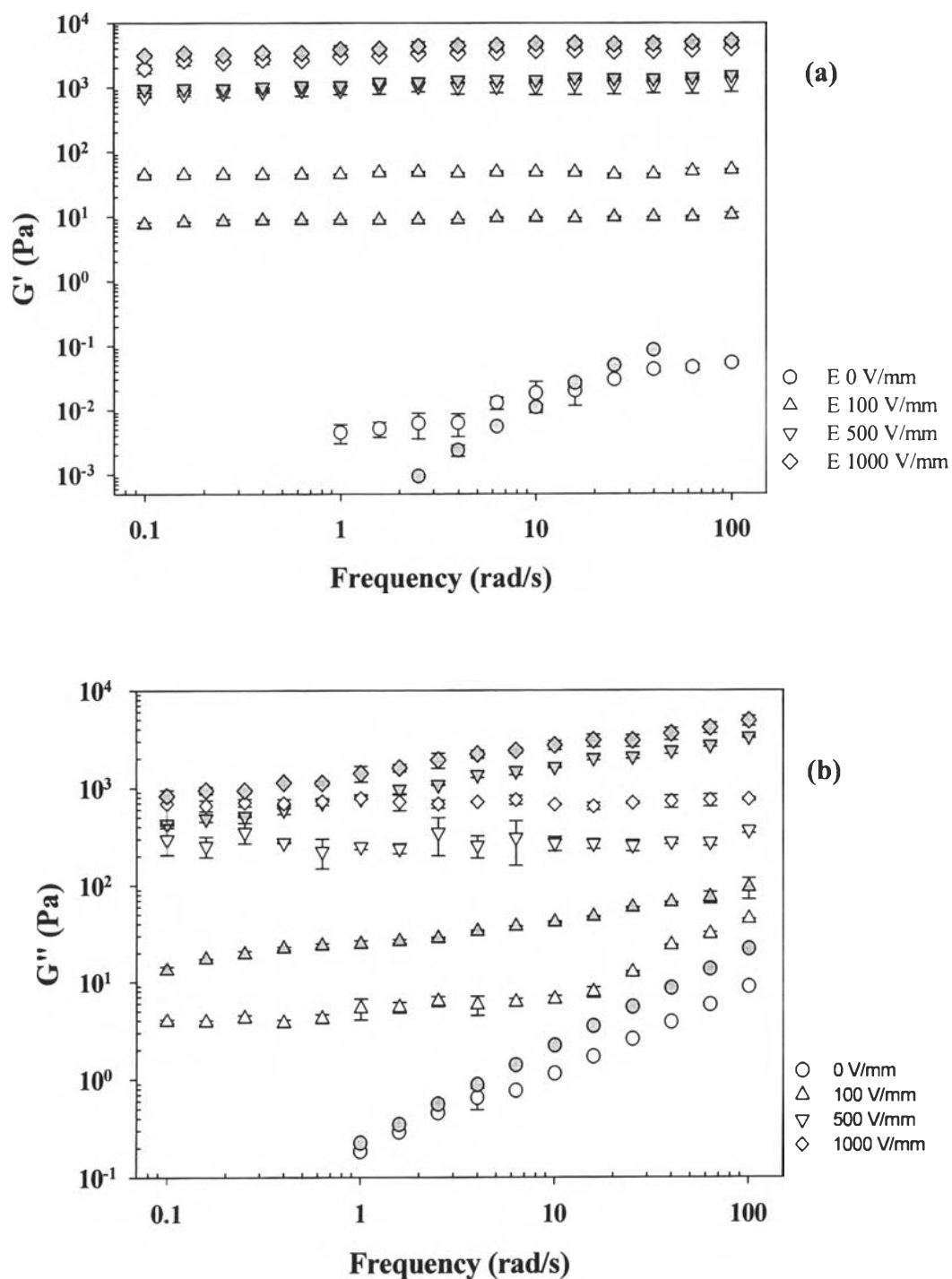
Figure 6.3 Storage and loss moduli of 20% wt. HClO$_4$ highly doped polythiophene/silicone oil suspension at 25 ± 0.1 °C: **(a)** storage moduli G'; **(b)** loss moduli G". White symbols are for 0.1 Pa.s oil and filled symbols are for 0.5 Pa.s oil.
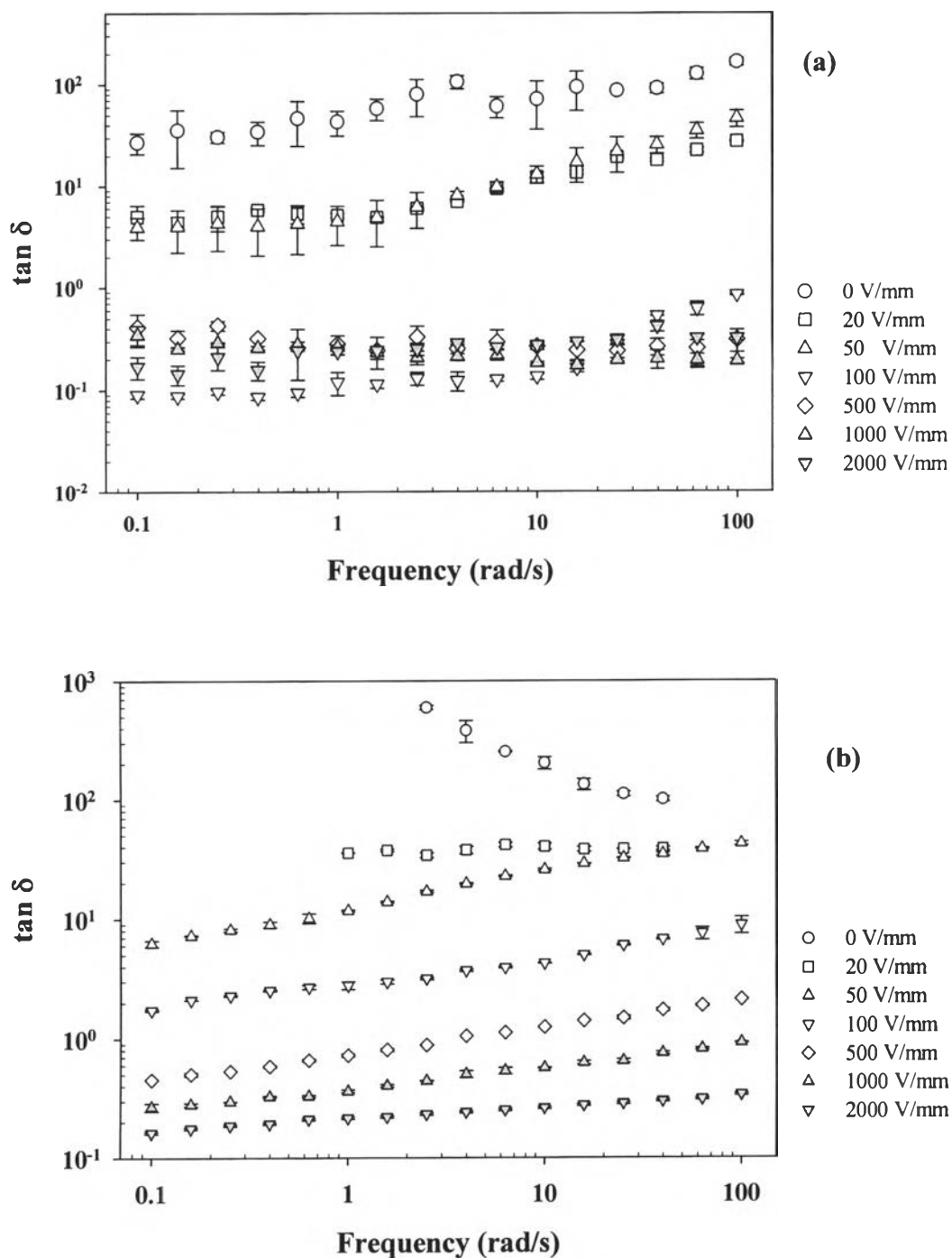
Figure 6.4 tan δ vs. frequency of HClO₄ doped polythiophene/silicone oil suspensions as various electric field strengths: **(a)** HPT20/η0.1 and **(b)** HPT20/η0.5.