CHAPTER V

CRITICAL ELECTRIC FIELD STRENGTH FOR FREQUENCY RELAXATION PROCESS OF POLYANILINE/SILICONE OIL SUSPENSIONS

5.1 Abstract

Polyaniline (PANI) was synthesized via oxidative coupling polymerization in acid conditions and de-doped in ammonia solution. The electrorheological (ER) properties of the PANI/silicone oil suspensions were investigated in oscillatory shear, with particular focus on the high frequency region where a crossover in $G'(\omega)$ and $G''(\omega)$ signals the onset of a dissipative relaxation process, associated with motion of PANI partciels within the fibrillar structures generated by the electric field.. The relationship between the crossover frequency, ω_c, and the electric field strength (E) was investigated as a function of matrix viscosity and shear strain.. We find that ω_c increases with increase in field strength, and decreases with increase of matrix viscosity and strain amplitude, in qualitative agreement with a theoretical model which relates the relaxation mechanism to the competition between hydrodynamic and electrostatic forces between PANI particles within thick fibrillar structures. at the crossover point, the critical dimensionless parameter, the Mason number (Mn), varies with Peclet number (Pe) according to a scaling relation $Mn \sim Pe^{0.091}$.

5.2 Introduction

Electrorheological (ER) suspensions, first studied extensively by Winslow (1949), display dramatic changes in rheological properties due to the application of electric field (Klingenberg, 1993). A typical ER fluid is composed of micron-sized polarizable particles dispersed in a non-conducting medium. Under the action of the field, the particles form three dimensional fibrillar network structures, which are aligned along the direction of the electric field and generate additional resistance against fluid motion (Tao and Sun, 1991). With their adjustable viscosity, fast response, and reversible rheological behavior, ER fluids are regarded as smart materials, with potential for applications in active devices, which transform electric energy to mechanical energy (Choi *et al.*, 1998). Possible applications include clutches, breaks, shock absorbers, engine mounts, valves, flow pumps, and other variable control and servo devices (Jang *et al.*, 2001).

Experimental data for the dynamic response of ER fluids are limited relative to that of steady shear flow. A dimensionless parameter, the Mason number (Mn), has been widely used to describe the relative importance of hydrodynamic to electrostatic polarization forces, and has been shown to be useful to predict the ER suspension behavior in steady shear (Marshall *et al.*, 1989). In the case of oscillatory shear, relatively few studies have explored the influence of the forces acting on the polarisable particles (Klingenberg, 1993, Toor, 1993). Of particular interest here are molecular dynamics simulation studies (Klingenberg, 1993, Parthasarathy and Klingenberg, 1996) which found frequency scaling of the dynamic shear moduli analogous to the Mason number scaling of the steady shear response. Experimental measurements have reported frequency scaling of the shear moduli of ER fluids based on conducting polymers consistent with the theoretical prediction (Cho et al., 2004, Chotpattananont *et al.*, 2004). In this paper, we focus on a prediction of molecular dynamics simulations that the oscillatory shear moduli of an ER fluid exhibits a relaxation process traced to motion of the polarizable spheres within thick fibrillar clusters (Klingenberg , 1993).

In previous studies, the use of polyaniline (PANI), as well as other semiconducting polymers, as the dispersed phase in an ER fluid has been extensively

explored (Cho *et al.*, 2004, Kim *et al.*, 2001, Lin *et al.*, 2006, Hiamtup *et al.*, 2006), since such polymers typically have a high intrinsic polarizability, even in the absence of any activator. PANI in particular has several advantages over other polymer particles such as low density, ease of synthesis and conductivity control, and thermal and environmental stability (Jang *et al.*, 2001, Pinto *et al.*, 2000). In the linear viscoelastic regime, a PANI suspension typically shows a liquid to solid transition at a critical electric field strength, whose value depends on particle concentration and host fluid viscosity (Hiamtup *et al.*, 2006). Such behavior is consistent with the idea that there are two opposing forces which influence the assembly of the polarizable particles into fibrillar structures spanning the electrodes, viz. the electrostatic interparticle driving force for assembly, and the opposing hydrodynamic force associated with fluid motion (Sakurai *et al.*, 1999).

In this study, we focus particularly on the fact that, at higher frequencies, the storage and loss shear moduli of PANI ER suspensions exhibit a crossover which signals the onset of the relaxation mechanism predicted by molecular dynamics simulations (Klingenberg , 1993). We explorte the effect of the medium viscosity, the shearing amplitude as well as the electric field strength on the crossover frequency, ω_c, in the linear and nonlinear viscoelastic regimes. Dimensionless parameters, the critical Mason number (Mn) and Peclet number (Pe) associated with the onset of the transition are correlated according to a scaling relation.

5.3 Experimental

5.3.1 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. 38 % Hydrochloric acid, HCl (AR grade, Labscan); 25 % solution of ammonia, NH_4OH (Ar grade, Merck) and methanol, CH_3OH (AR grade, Labscan) were used as received. The base fluids, silicone oil (AR grade, Dow corning) with density 0.96 g/cm^3 and kinematic viscosity of 100 cSt were vacuum-dried and stored in a desiccator prior to use.

5.3.2 Polymerization Procedure

PANI was synthesized via an oxidative coupling polymerization according to the method of Cao *et al.* (1989). After the course of polymerization, the precipitate was then dedoped by immersion in 3% NH_4OH in order to adjust its conductivity, before being vacuum dried and passed through a 38 μm sieve shaker to control the particle size and its distribution.

To determine the electrical conductivity, PANI powder was pressed into disk pellets by a hydraulic press (diameter of 25 mm and ~0.2 mm thick). Electrical conductivity was measured using a custom-built four-point probe at 30 °C. The measurements were performed in the linear Ohmic regime where the specific conductivity values are independent of the applied DC voltage.

5.3.4 Preparation of ER Fluids

Prior to mixing in silicone oil, PANI powder was dried for 2 days at room temperature to remove moisture in a vacuum oven at room temperature. The particles were then dispersed in the silicone oil with an ultrasonicator for 30 minutes at 25 °C. The PANI suspensions were then prepared at volume fractions of 0.05. The suspensions were stored in a dessiccator and redispersed by ultrasonificator for a period of 10 minutes at 25 °C before each experiment

5.3.5 Rheological measurements

Dynamic rheological properties of the suspensions were investigated using a modified melt rheometer (ARES, Rheometric Scientific Inc.) with parallel plates (diameter of 50 mm) attached via insulating spacers to the transducer and motor. A DC electric field was applied across the gap between the plates by a function generator (GFG-8216A, Instek) and a high voltage amplifier (Model 609E-6, Trek). The electric field was applied for 10 minutes to obtain an equilibrium fibrillar or columnar structure before each measurement was taken. The experiments were carried out in the frequency sweep mode with frequency (ω) ranging from 0.1 to 100 rad/s at a temperature of 27 ± 1 °C to investigate the effect of electric field strength on G' and G". The applied field at which G' equals to G" at particular frequencies were reported as the critical values.

5.4 Results and Discussion

5.4.1 Electrorheological Properties and Liquid to Solid Transition of PANI/Silicone Systems

The effects of the silicone oil viscosity and the strain amplitude, on ω_c and E_c were investigated for PANI suspensions prepared at volume fractions of 0.05 in silicone oils of three different viscosities; 100, 500, 1000 cSt; the systems are coded as PANI/100, PANI/500, and PANI/1000, respectively. The PANI particle mean diameter, as determined by a particle size analyzer, is 23.5 ± 2.37 μm and particle conductivity is 2.93×10^{-9} S/cm. A PANI of low conductivity was chosen in order to be able to investigate ER behavior at high electric field strength without current leakage in the system.

The dynamic moduli, G' and G", were measured in the frequency range 1-100 rad/s. In an ER system, in the absence of a field, the particles are randomly dispersed in suspension in the absence of an electric field and the dynamic moduli generally exhibit liquid-like behavior such that G" is significantly larger than G' over the entire frequency range. On application of a field, the particles form strings or columns spanning the gap between the electrodes, as a result of interfacial polarization due to migration of charge carriers in the PANI particle (Block et al., 1990). As the electric field strength increases to a critical value, the ER fluid passes through a liquid-to-solid transformation. Two characteristic transition points can be identified rheologically: the first is the sol-gel transition, characterized by the appearance of identical power law frequency scaling of the storage and loss moduli (Chin and Winter, 2002), and, subsequently, the solid-liquid transition associated with the crossover where G' becomes larger than G", the latter coinciding with the visible appearance of fibrillar structures (Hiamtup et al., 2006, Chin and Winter, 2002).

Figure 5.1 shows the change in G'(ω) and G"(ω) of the PANI/500 suspension as the applied filed strength is increased. Evidently at the lowest deformation frequencies, G' is greater than G", indicative that the polarization-induced fibrillar structures have formed, i.e we are beyond the liquid-solid transition.

Of more interest in this study is the fact that, at higher frequencies, indicated by arrows, we observe a G'-G" crossover, where G" becomes larger than G', characteristic of the onset of the relaxation process identified in the molecular dynamics simulations (Klingenberg, 1993). It can be seen in Figure 5.1 that the crossover frequency, ω_c, increases at higher field strength, e.g.. E_c = 850 V/mm for ω_c = 100 rad/s as compared with E_c = 310 V/mm for ω_c = 1 rad/s.

5.4.2 Effect of the host fluid viscosity and the strain amplitude

Figure 5.2 shows the correlation between critical electric field strength and crossover frequency for various PANI/silicone oil suspensions having different host viscosities. Included are data for PANI/100, PANI/500, and PANI/1000, all measured at a strain γ = 2%, as well as PANI/500 measured at γ = 1% and γ = 5%. Figure 5.2 further illustrates that higher critical electric field strength, E_c, correlates with a higher crossover frequency, ω_c, and further indicates that increased matrix viscosity leads to a higher E_c at fixed ω_c, but a lower ω_c at fixed E_c. Finally, Figure 5.2 suggests that increase strain amplitude increases E_c at fixed ω_c, and increases ω_c at fixed E_c. The correlation between log Ec and logγ is further detailed in Figure 5.3, which indicates a power law relationship. Figure 5.3 further indicates that at fixed E_c, ω_c decreases with increase of strain amplitude.

These results are qualitatively consistent with the theoretical model that assumes the relaxation mechanism depends on the competition between hydrodynamic and polarization forces between particles within thick fibrillar columns (Klingenberg, 1993). Thus we may deduce that the onset of the relaxation process, correlates to the condition where the two opposing forces, i.e. the shear force, F_{shear}, and the electrostatic force, F_{elec}, are in balance. In such a case we may use an argument proposed by Sakurai et al. (Sakurai et al., 1999) to relate the critical field strength to the crossover frequency, strain amplitude, matrix viscosity and particle conductivity. Specifically, since

$$F_{shear} = 6\pi\eta\omega_c\gamma a^2 \qquad (1)$$

where a is the (assumed spherical) particle radius, and

$$F_{elec} = \frac{3\pi p^2}{8\varepsilon_s r^4} \qquad (2)$$

where p is the induced dipole moment, which, in the presence of a dc field may be written as:

$$p = \frac{\pi}{2}\varepsilon_s a^3 \left(\frac{\sigma_p - \sigma_s}{\sigma_p + 2\sigma_s} \right) E = \frac{\pi}{2}\varepsilon_s a^3 \beta E \tag{3}$$

where σ_p and σ_s are the electrical conductivities of PANI particles and matrix, respectively,. Equating eqs. (1) and (2), Sakurai et al., obtained:

$$E_{crit} = \frac{32}{\pi} \sqrt{\frac{\omega_c \gamma_0 \eta_s}{\varepsilon_s \beta^2}} \tag{4}$$

where ω_χ is the crossover frequency, γ_0 is the strain amplitude, η_s is the suspension viscosity, and ε_s is the dielectric constant of the medium. Thus, eq. (4) predicts that $E_c \propto \omega_c^{1/2}$ at fixed γ_0 and η, and $E_c \propto \gamma_0^{1/2}$ at fixed ω_c and η. In comparison, the experimental data in Figures 5.2 and 5.3 indicate that indeed $E_c \propto \omega^\alpha$ and $E_c \propto \gamma_0^\beta$, but that α varies between 0.19-0.32, and β varies between 0.51-0.74 amongst various host fluid viscosities tested. The origin of the discrepancies is not clear. One possibility relates to the fact that eq. (4) pertains to a suspension of monodisperse speres, whereas the PANI suspension has particles of irregular shapes and a broad particle size distribution. Also, eq. (4) considers only pairwise interactions between particles, and ignores multi-particle interactions (Hiamtup et al., 2006) the case of the dependence on shear strain is that the experiments extend from the linear to the nonlinear viscoelastic regime.

5.4.3 Dimensionless group analysis

Under action of the electric field, an ER suspension experiences several inter-particle forces; the electrostatic force, the Brownian force, the short-range repulsion, the hydrodynamic interaction, as well as other colloidal forces. Dimensionless groups arising from such forces are commonly used to describe and interpret suspension behavior in terms of the relative importance of competing contributions (Parthasarathy and Klingenberg, 1996).

For steady shear flow, the relative importance of the viscous to the electrostatic polarization forces is described by the Mason number (Marshall et al., 1989),

$$Mn = \frac{\eta_s \gamma}{2\varepsilon_0 \varepsilon_c \beta^2 E_0^2} \qquad (5)$$

The relative importance of viscous to thermal forces is described by the Peclet number [Melrose, 1992],

$$Pe = \frac{3\pi a^3 \eta_s \gamma}{k_B T} \qquad (6)$$

where η_s is the medium viscosity, γ is shear rate, ε_0 = 8.85 pF/m^2 and ε_c = 2.4 pF/m^2 are the dielectric constant of medium and particle, respectively. The relative conductivity, β, approximately equals to 1 as σ_1 = 7.7 x 10^{-15} S/cm (Chotpattananont et al., 2004) and σ_2 = 2.93 x 10^{-9} S/cm are the conductivity values of medium and particle, respectively, k_B = 1.38x10^7 PaA^{o3}K^{-1} is the Boltzmann constant, and T = 300 K is absolute temperature in Kelvin.

In order to make equations 5 and 6 applicable for an oscillatory shear flow, the dynamic viscosity is required to transform the equations into appropriate forms; viz. $\eta'(\omega) = G''(\omega)/\omega$ and $\gamma = \omega \gamma$. Thus, equation 5 becomes,

$$Mn = \frac{G_s''(\omega)\gamma_0}{2\varepsilon_0 \varepsilon_c \beta^2 E_0^2} \qquad (7)$$

and equation 6 becomes,

$$Pe = \frac{3\pi d^3 G_s''(\omega)\gamma_0}{k_B T} \qquad (8)$$

where d = 23.5 μm is the particle diameter.

Figure 5.3 show the plot of the critical dimensionless parameter Mn versus Pe, at the crossover frequency for the PANI/silicone oil suspensions at various viscosities, shear frequencies and strain amplitudes. It is evident that the data points for all system approximately collapse into a single function of the dimensionless parameter Pe, where the scaling relation of the dependence is $Mn = 0.04832(Pe)^{0.091}$.

Alternatively, we tested the scaling relation between Mn and Pe using the modified Sakurai definitions of Mn and Pe defined as

$$Mn_{Sakurai} = \frac{4d^6 \varepsilon_m G_s''(\omega)\gamma_0}{p^2} \tag{9}$$

$$Pe_{Sakurai} = \frac{3\pi d^3 G_s''(\omega)\gamma_0}{4k_B T} \tag{10}$$

where p is the magnitude of dipole induced as Maxwell-Wagner type-polarization,

$p = \frac{\pi}{2}\varepsilon_s (d/2)^3 \beta E_o$. According to their derivation, electrostatic force is defined as

$F_{elec} = 3\pi \cdot p^2 / 8\varepsilon_s d^4$, the maximum value of hydrodynamic force acting to pull each

particle apart is $F_{shear} = 6\pi\omega\gamma_0\eta(d/2)^2$, and thermal force is defined as

$F_{thermal} = k_B T/(d/2)$ (Marshall *et al.*, 1989). The correlation obtained

is $y = 100.68x^{0.091}$. Noting that only isothermal data were obtained in these

experiments, the scaling exponent 0.091 nevertheless indicates that the Mason

number as defined in eq. (7), is not quite a universal constant at the crossover.

Specifically, from the fitted relation in Figure 3, $Mn = 0.04832(Pe)^{0.091}$, we deduce:

$$[G''(\omega)\gamma_0]^{0.909} = 0.101(2\varepsilon_0\varepsilon_c\beta^2 E_o^2) \tag{11}$$

A similar result but with a different prefactor follows for the definition of Mn in eq. (9). Again the deviation of Mn from a universal constant may be traced to a variety of factors mentioned above in connection with deviations from eq. (4).

5.5 Conclusions

Polyaniline (PANI) was synthesized via oxidative coupling polymerization in acid conditions and de-doped in 3% NH_4OH. The ER properties of PANI/silicone oil suspensions were investigated with a particular focus on the crossover in storage and loss shear moduli which signals the onset of a high frequency relaxation process associated with the motion of PANI particles within the fibrillar columns poroduced

by the applied field. The relationship between the critical electric field strength (E_c) and the deformation frequency (ω_c) at the crossover point was investigated as a function of medium viscosity, shearing amplitude, and shearing frequency. Qualitatively consistent with a theoretical model, which relates the relaxation process to competition between hydrodynamic and electrostatic forces between polarizable particles within the fibrillar columns, the value of E_c increases with increase in each of these three system variables. Quantitative deviations from the theory are found however, manifested as deviations in the scaling exponent of the dependences of Ec on shearing frequency and strain amplitude from the predicted values of 0.5 and 1.0, respectively. The dimensionless parameters, Mason number (Mn) and Peclet number (Pe), of the suspension at the critical point were also studied. Data plotted as Mn versus Pe, for all systems approximately collapse into a single function of the form $Mn = 0.00897(Pe)^{0.091}$. This indicates the Mason number is not a universal constant at the crossover point, but that there is an approximate universal scaling between the viscous stress and the electrostatic polarization stress.

5.6 Acknowledgements

5.7 References

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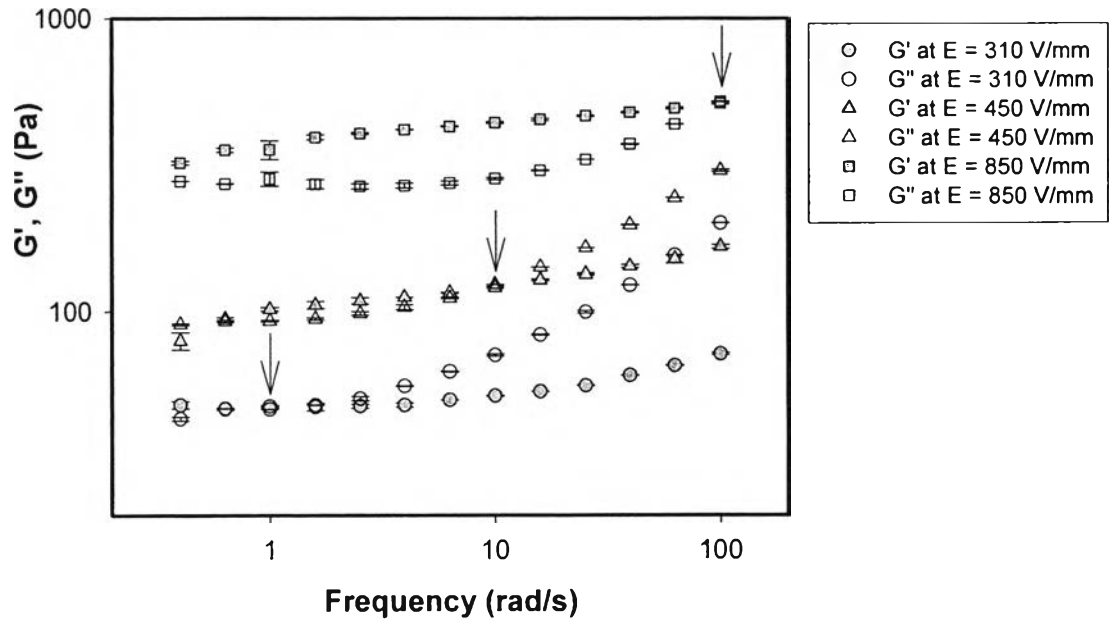Toor, W. (1993) Structure formation in electrorheological fluids. J. Colloid Interf. Sci., 156, 335.

Figure 5.1 Frequency dependence of the shear moduli of PANI/500 suspension at various electric field strengths, measured at strain amplitude of 2%, temperature of 27 ± 1 °C, and gap = 0.2 mm.
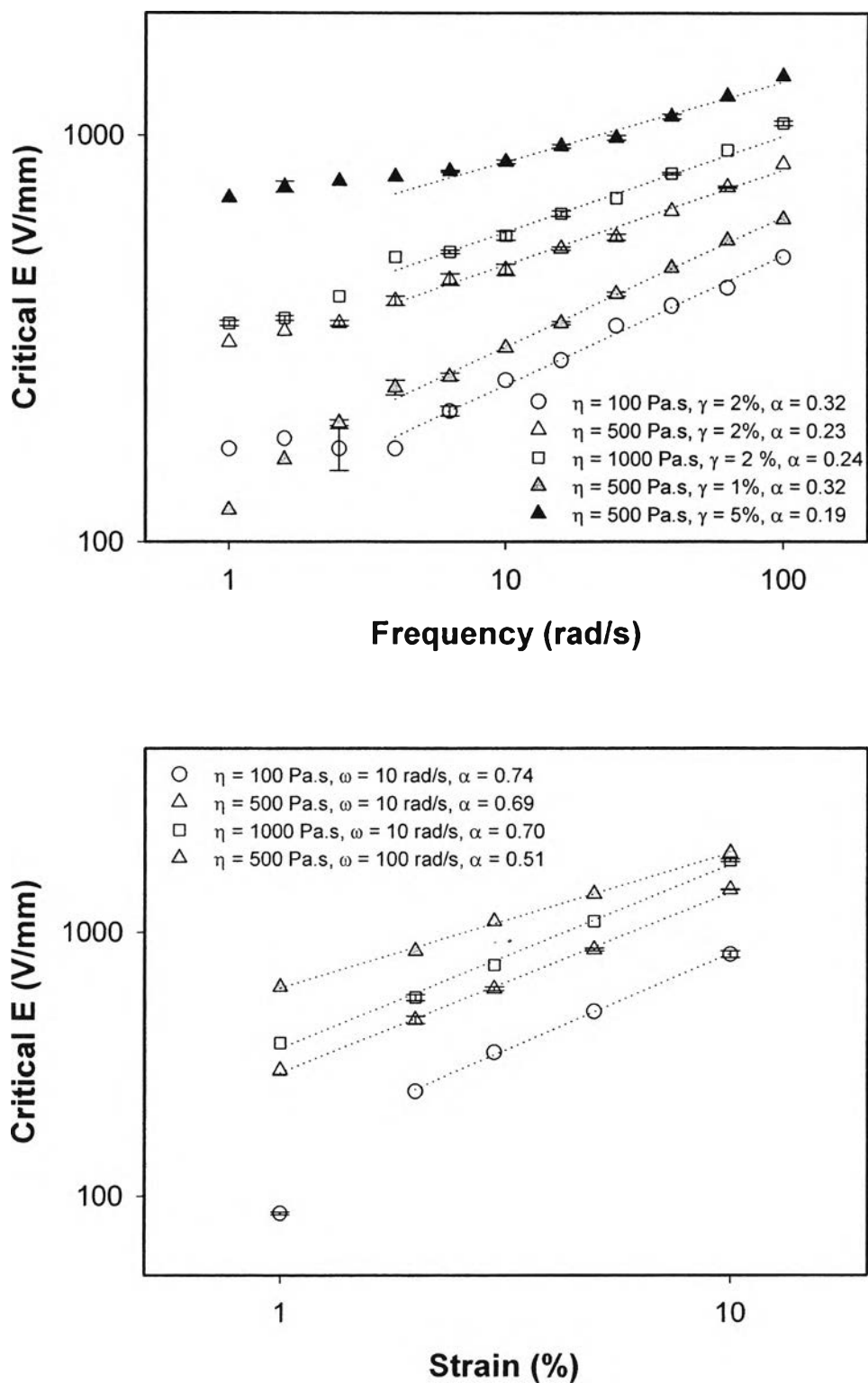

Figure 5.2 The dependence of critical electric field strength on:(a) frequency; and (b) strain amplitude of various PANI suspensions having different silicone oil viscosities, measured at temperature of 27 ± 1 °C, gap = 0.2 mm.
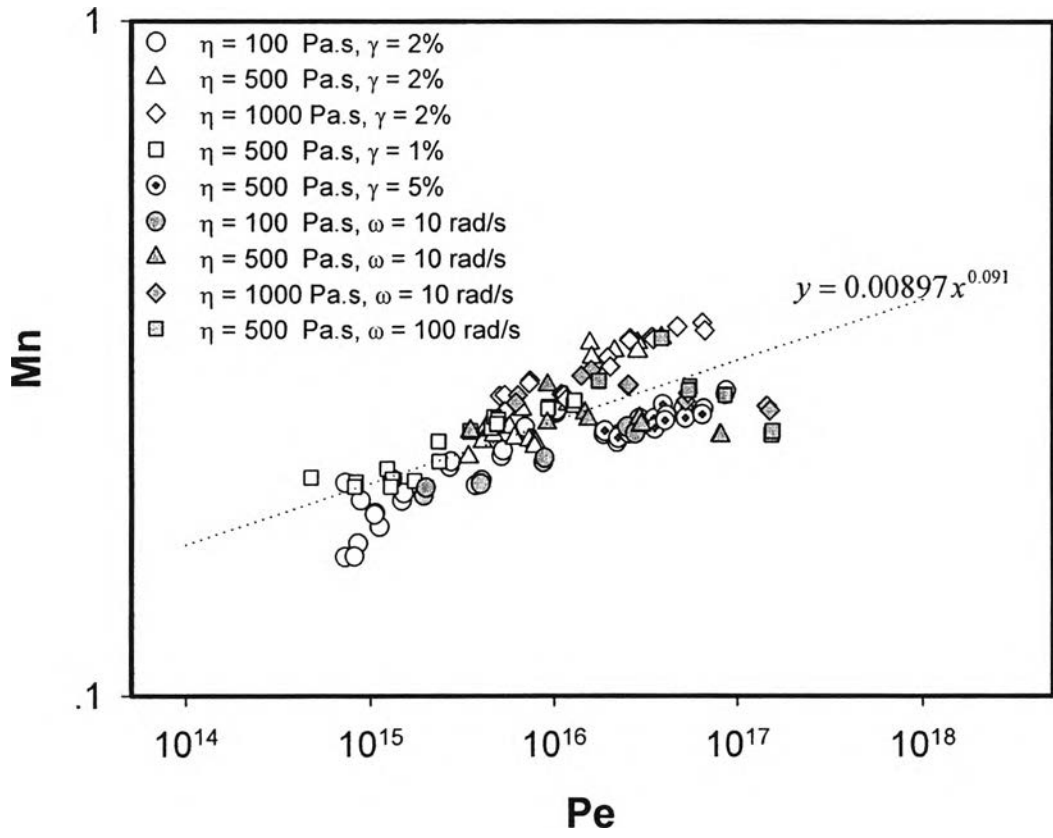
Figure 5.3 The dimensionless parameters Mn versus Pe of PANI suspensions of different silicone oil viscosities.