

CHAPTER IV

RESULTS AND DISCUSSION



4.1 Silica Characterizations

4.1.1 FTIR Spectroscopy

The FTIR spectra of two types of silica (s5631 and Hisil 927) are shown in Figure. 4.1 The spectra of two silica types shown have the same broad absorption peak at $\sim 1100 \text{ cm}^{-1}$ indicating the Si-o-Si bond (The Aldrich Library of FT-IR Spectrum. Vol.3, p. 4717).

4.1.2 Thermal Gravimetric Analysis

For silica dispersion ER fluid, the water adsorbed on the surface of silica plays an important role for the induced particle to be polarized in the electric field (Otsubo *et al.* 1991, 1992). From TGA thermograms (Appendix C), the amount of adsorbed water in each silica type were determined. The weight loss of silica at 40-50°C was attributed to the desorption of water. The amount of water in each silica is shown in Table 4.2.

Table 4.2 The amount of adsorbed water in s5631 and Hisil 927

Silica type	The amount of water (%wt)
S5631	0.10
Hisil 927	3.53

4.1.3 Scanning Electron Microscope

From previous studies on the ER fluids, the morphology and the size of the particle can affect the ER behavior (Yatsuzuka *et al.* 1995, Shaw *et al.* 1996 and Havelka *et al.* 1996). The SEM micrograph of silica s5631 particles shows their shapes to be irregular. The shapes of Hisil 927 particles appear to be round (see Appendix B).

4.1.4 Particle Size Analyzer

Particle size analyzer was used to determine size and size distribution of each silica type. The results show that the mean sizes of s5631 and Hisil 927 were 2.57 and 17.53 micron in diameters and the standard deviations of 2.21 and 14.38, respectively.

4.2 Polyaniline Characterizations

4.2.1 FTIR Spectroscopy

The FTIR spectra of the synthesized polyaniline are shown in Figure. 4.2 and the characteristic peaks of polyaniline are listed in Table 4.3. The absorption peak at 828 cm^{-1} indicates the type of substituted benzene in the polyaniline. Other peaks indicating other types of substituted benzene were not observed. Therefore, the FTIR spectrum gave an evidence for the formation of poly (*p*-aniline) which is a polyaniline emeraldine base. The absorption at 1162 cm^{-1} indicates an electronic band, which is associated with electrical conductivity in polyaniline (Palanlappan and Narayana, 1994).

Table 4.3 The summary of FTIR characteristic peaks of the synthesized polyaniline emeraldine base (Palanlappan and Narayana, 1994)

Peak locations (cm ⁻¹)	Functional groups
1587	C = C stretching of quinoid imine
1494	C = C stretching of benzenoid diamine
1302	C-N-C stretching of a secondary of aromatic amine benzenoid segments
1162	Vibration mode of quinoid segments
828	out of plane bending of para-substituted aromatic benzene ring

4.2.2 Ultraviolet-Visible Spectrometer (UV-VIS)

The optical properties of conductive polymer play an important role in changing molecular conformation, which can affect the electrical properties of a conductive polymer. Figure.4.3 shows the UV-Visible spectra of a solution of the synthesized polyaniline emeraldine base in NMP solvent. The absorption at 325 nm indicates the π - π^* transition electrons of the benzene ring delocalized onto nitrogen atoms of the amine in the benzenoid segments. The absorption at 625 nm indicates the excitation from the highest occupied molecular orbital (HOMO) of the benzenoid ring to the lowest unoccupied molecular orbital (LUMO) of the localized quinoid segments. The peak positions at 325 and 625 nm depend on the purification method and the level of purification of the synthesis (Laakso *et al.* 1994).

4.2.3 Thermogravimetric Analysis

The thermal stability of the polyaniline particles was studied. A three-step decomposition was detected from the TGA thermogram. The first step at 100°C corresponds to the loss of water in particles. The second step, which occurred between 500-700°C, corresponds to the loss of the counter anion of dopant and the low molecular weight oligomer. The last step, which occurred above 700°C is attributed to the decomposition of the backbone of the polyaniline. The TGA thermogram of the dope polyaniline with a Cl⁻ counter anion (appendix B), show only first two steps because the limited temperature range of the instrument.

4.2.4 Scanning Electron Microscope (SEM)

The shape of the polyaniline particles was observed using a scanning electron microscope. The shape was very irregular as shown in Appendix B, resulting from the fact that polyaniline can not rotate freely because of the chloride anions and imine located in the main chain (Choi *et al.*, 1997).

4.2.5 Particle Size Analyzer

Particle size analyzer was used to determine size and size distribution of polyaniline particles. The results show that the mean size of PAN particles was 19.74 micron in diameters and the standard deviations of 13.34.

4.3 Polyaniline-Coated Silica Characterizations

4.3.1 FTIR Spectroscopy

The FTIR spectra of the synthesized polyaniline-coated silica (S5631) are shown in Figure. 4.4 and the characteristic peaks of polyaniline-

coated silica are listed in Table 4.4. The absorption peak was the same as polyaniline except there is an absorption peak of the silica at 1100 cm^{-1} .

Table 4.4 The summary of FTIR characteristic peaks of the synthesized polyaniline-coated silica (S5631) (Palanlappan and Narayana 1994)

Peak locations (cm^{-1})	Functional groups
1587	C = C stretching of quinoid imine
1494	C = C stretching of benzenoid diamine
1302	C-N-C stretching of a secondary of aromatic amine for benzenoid segments
1162	Vibration mode of quinoid segments
1100	Si-O-Si bond (The Aldrich Library of FT-IR Spectrum. Vol.3, p. 4717).
828	out of plane bending of para-substituted aromatic benzene ring

4.3.2 Particle Size Analyzer

Particle size analyzer was used to determine size and size distribution of polyaniline-coated silica (S5631) particles. The results show that the mean size of PAN-coated silica (S5631) particles was 5.57 micron in diameters and the standard deviations of 6.61.

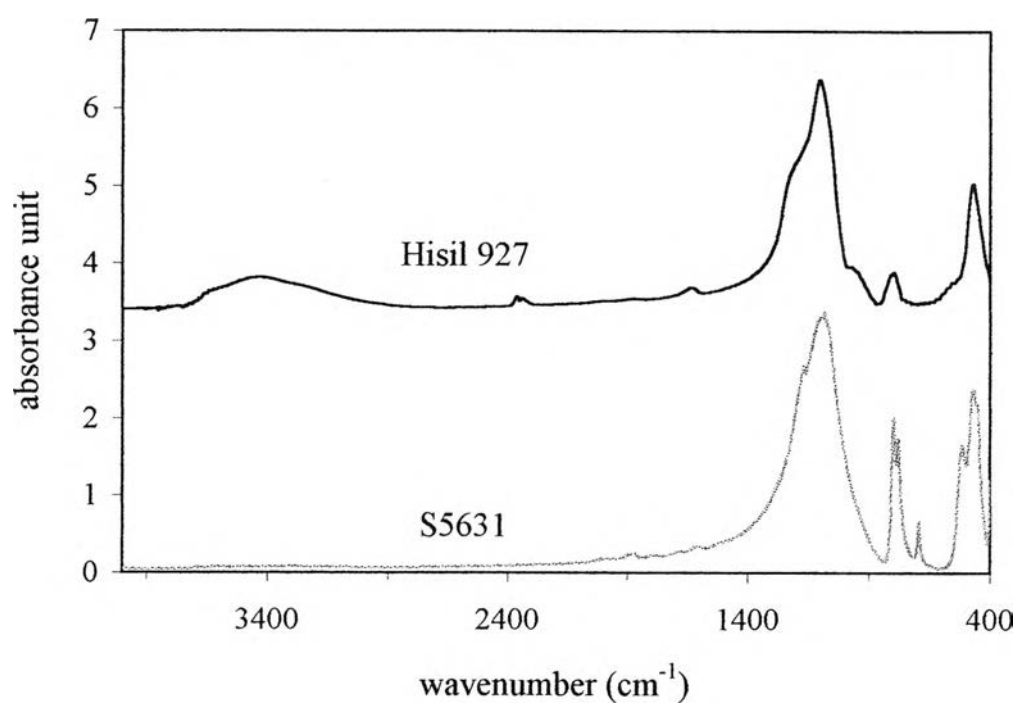


Figure 4.1 FTIR spectra of two different silica types: (a) Hisil 927, and (b) s5631.

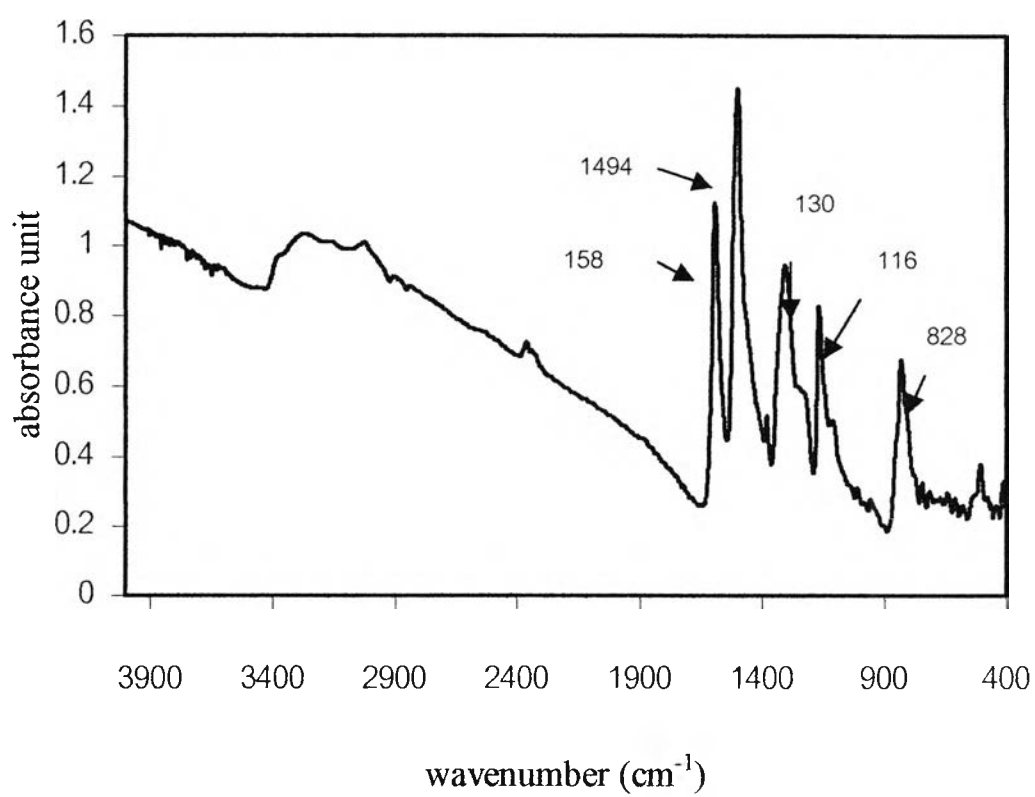


Figure 4.2 FTIR spectra of the synthesized polyaniline.

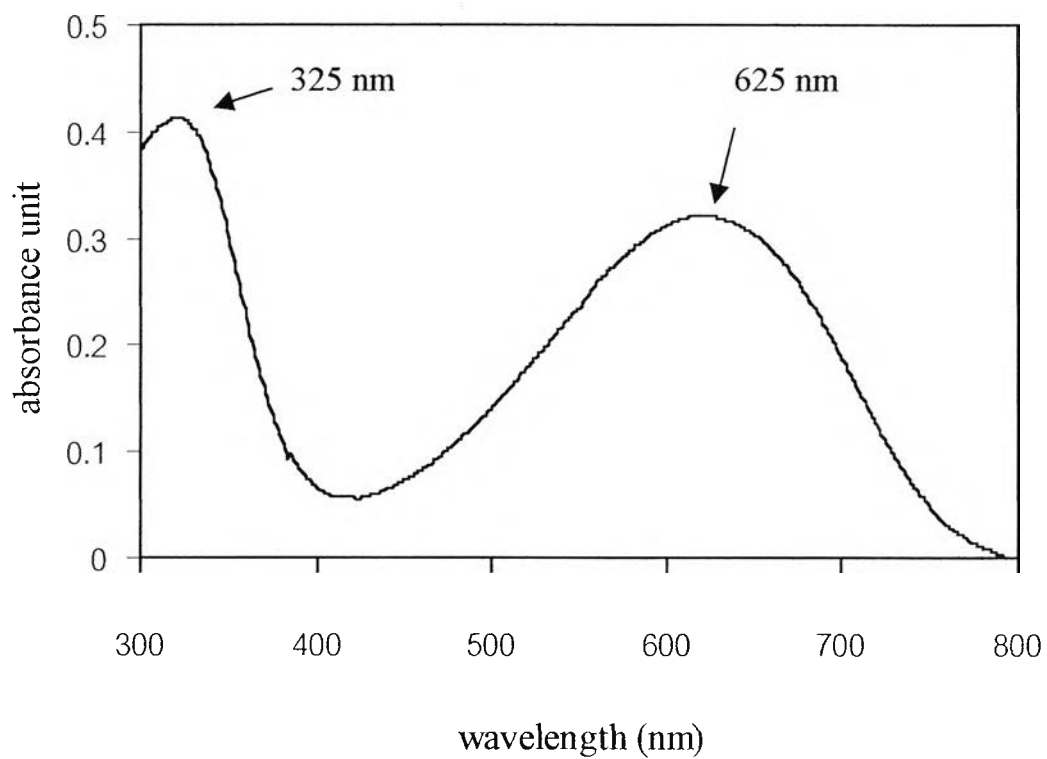


Figure 4.3 The UV-VIS spectra of the synthesized polyaniline particles.

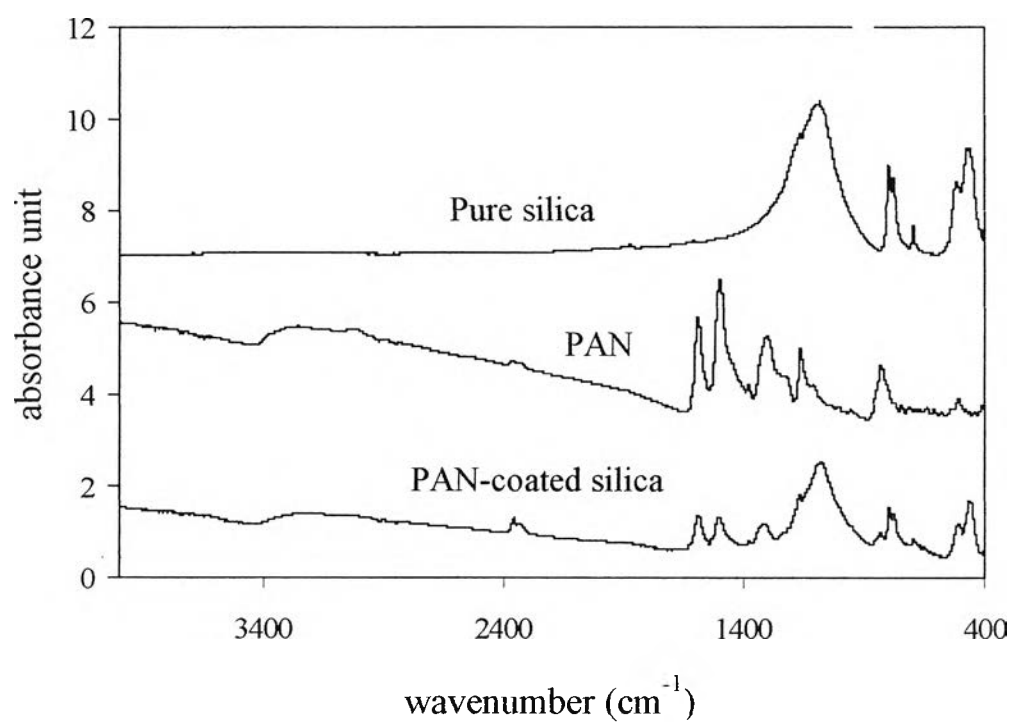


Figure 4.4 FTIR spectra of: (a) pure silica; (b) polyaniline; and (c) polyaniline-coated silica.

4.4 Rheological Measurements of Silicone Oil

The medium or liquid phase used in the electrorheological fluids should be a Newtonian fluid; i.e. its viscosity does not depend on shear rate (Choi *et al.*, 1997b). Thus, the changes in viscosity or other rheological properties upon applying an electric field are due to the formation of chain-like or fibrillar structures in the suspension.

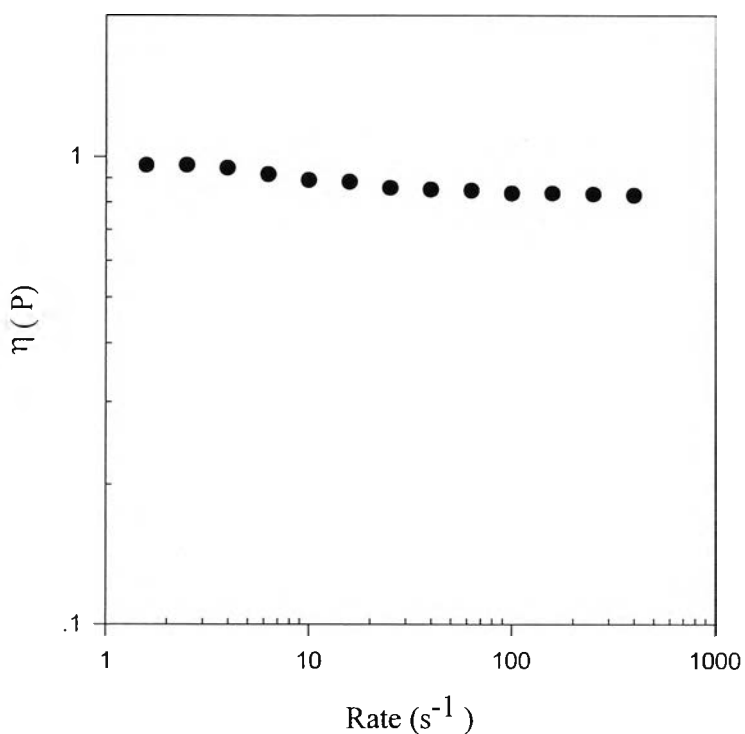


Figure 4.5 Viscosity dependence of shear rate of silicone oil.

From the steady state rate sweep test shown in Figure 4.10, the viscosity of the silicone oil, which is used as a medium for all ER fluid samples in this work, changes with shear rate. We can infer that this silicone oil behaves essentially like a Newtonian fluid.

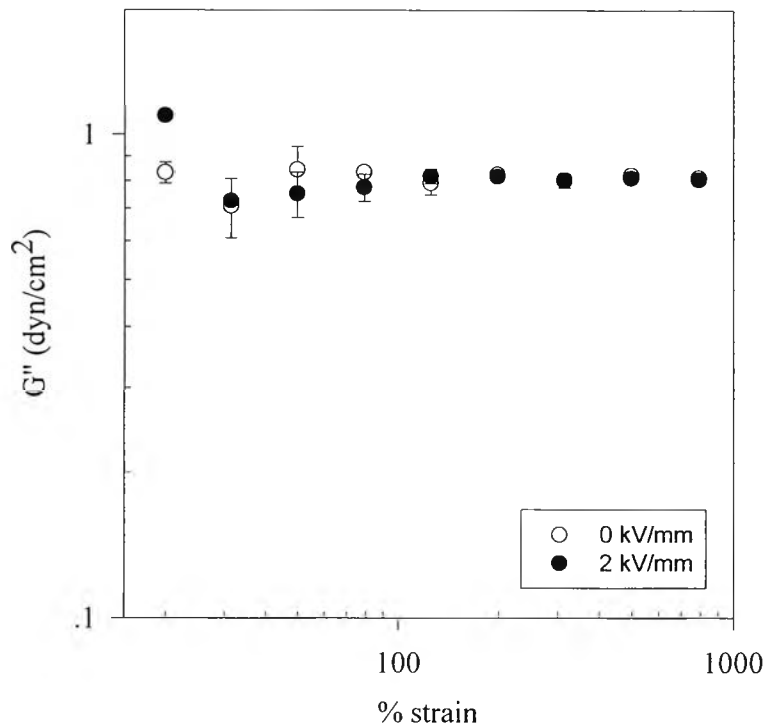


Figure 4.6 The strain dependence of the loss modulus of silicone oil.

In Figure 4.6, the loss modulus is shown in a strain sweep experiment at the frequency of 1 rad/s, and is found to be independent of strain amplitude, i.e. it shows linear viscoelastic behavior. In this experiment, only the loss modulus is shown because the storage modulus was too small to measure, the silicone oil is a viscous fluid but has no elasticity. As evident in Figure 4.6, the loss moduli at 0 and 2 kV/mm electric field strengths are indistinguishable, and are independent of the strain.

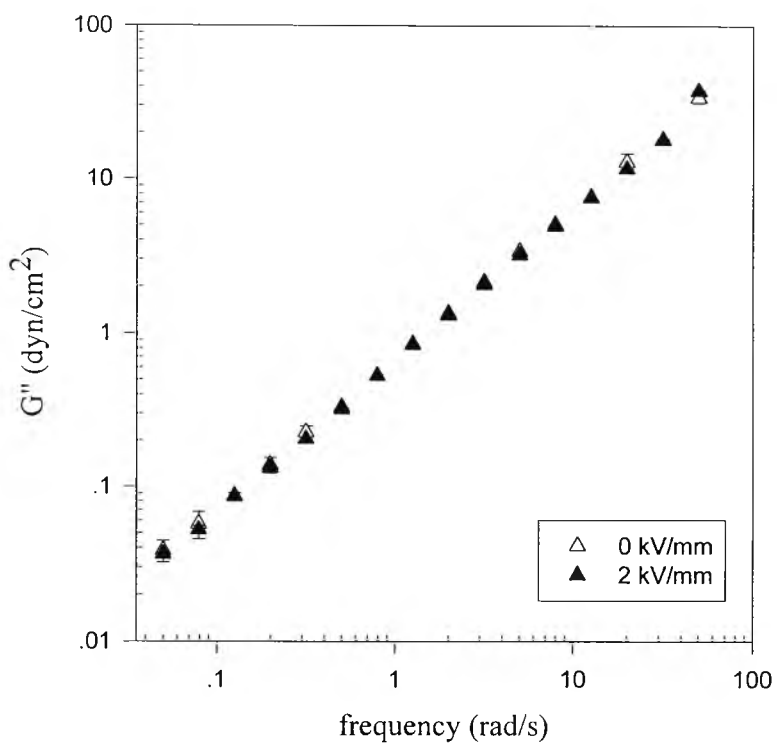


Figure 4.7 The loss modulus dependence on frequency of silicone oil.

Figure 4.7 shows G'' of silicone oil at the 0 and 2 kV/mm electric field strengths vs. frequency at 600 % strain. The dependence of the loss modulus on frequency in the absence and the presence of electric field are compared. The loss modulus of silicone oil increases linearly with increasing frequency (slope ~ 1) in zero electric field. With an applied electric field to silicone oil, the loss modulus does not change. Therefore, the electric field has no influence on the loss modulus of the silicone oil.

4.5 ER Measurements of Silica (s5631) Suspensions

4.5.1 Effect of Strain Amplitude

Figure 4.8 represents a plot of the loss modulus (G'') versus % strain at a frequency of 1 rad/s at electric field strengths of 0 and 2 kV/mm for 20 %wt silica in silicone oil system. This measurement was conducted to determine the linear viscoelastic region of the strain for the frequency sweep experiment. At zero electric field, G'' was independent on strain amplitude, but with the electric field strength of 2 kV/mm, G'' exhibited a linear plateau for only small % strain (<10%). Above a critical strain of 10 %, G'' decreases with increasing % strain. Additional strain sweep results for other ER fluid samples based on silica s5631 are shown in Appendix D.

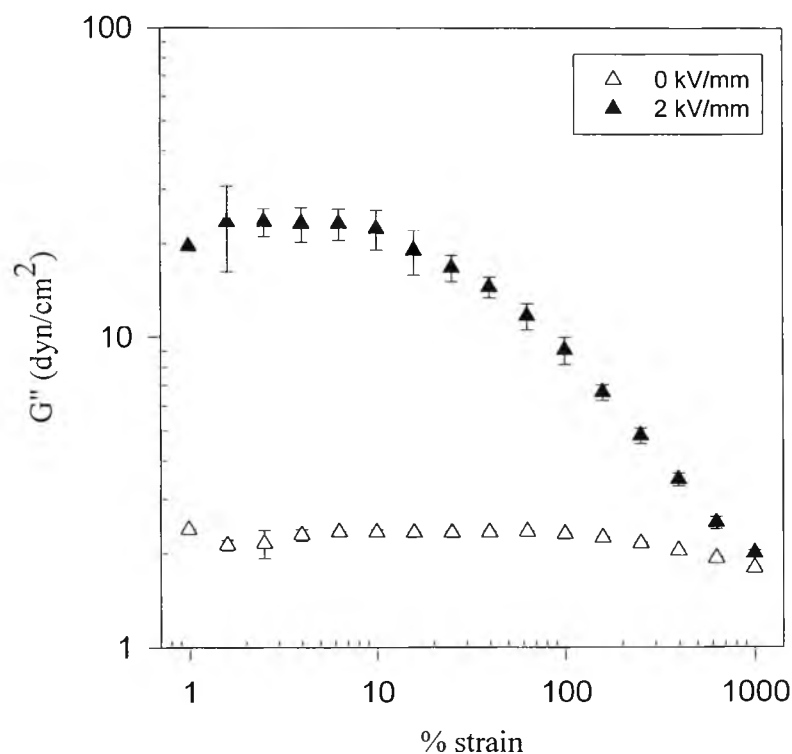


Figure 4.8 Strain sweep test of the 20%wt silica s5631 suspension at 0 and 2 kV/mm electric field strength.

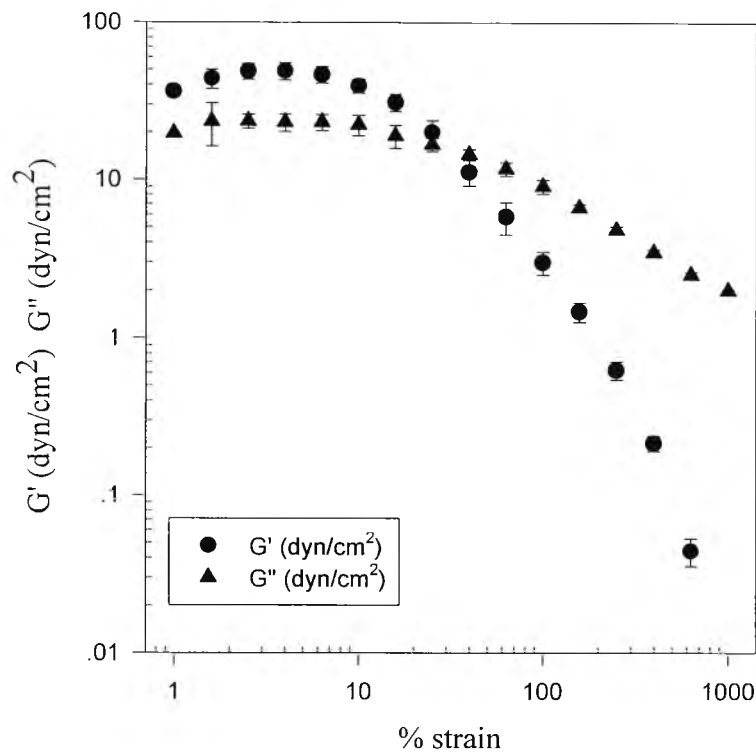


Figure 4.9 G' and G'' dependence on % strain of 20%wt silica (S5631) suspension at the electric field strength of 2 kV/mm.

The storage and loss moduli as a function of the strain amplitude are plotted in Figure 4.9. In the linear viscoelastic region, the storage modulus is larger than the loss modulus, and the reverse trend is observed outside the linear region. This can be explained by the elasticity of the ER fluid, which is known to be determined by the formation of particle chain structures in an imposed electric field. These fibrillar structures of the suspended silica particles are known to span the gap between the electrodes. Shear deformation distorts the fibril structure. Above a certain degree of deformation, the structure is broken down, and the elasticity of the ER fluid abruptly decreases (Cho *et al.*, 1998).

4.5.2 Transient Response

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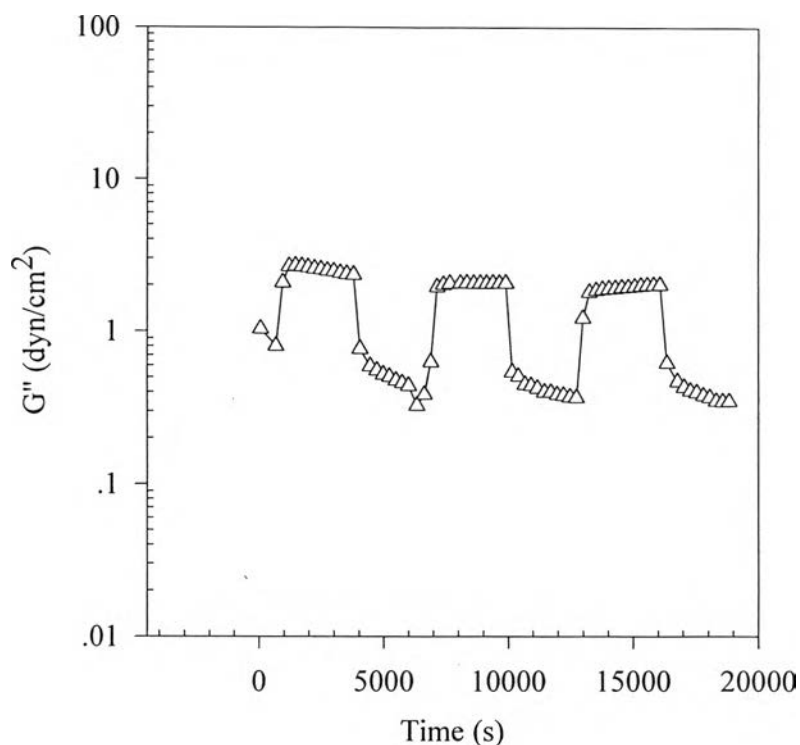


Figure 4.10 G'' dependence of the 20% wt silica (s5631) suspension at electric field strength of 2 kV/mm and 600% strain.

Figure 4.10 shows the G'' response to an electric step field of 2 kV/mm of 20%wt silica (s5631) suspension in the time sweep mode at a frequency of 1 rad/s and 600 % strain. An electric field of 2 kV/mm was repeatedly applied and released. For this ER fluid, the response time to equilibration with the external electric field is around 100 s. When the external electric field is applied, the loss modulus increases and obtains its equilibrium value in 100 s. Also, when the electric field is released, the sample recovers almost completely. For subsequent application of the electric fields, the sample shows almost the same response pattern. The time required for ER fluids to respond to a step change of electric fields has been reported to be of the order of 1 ms, while a fully stable structure in a static suspension is found

through microscopic observation to form on a time scale of seconds or minutes (Otsubo et al., 1992).

4.5.3 Effect of Electric Field Strength: Linear Viscoelastic Region

In order to obtain the well-defined initial condition and reproducible data, all of the ER samples were redispersed before each measurement. An electric field was applied for 5 min in order to obtain an equilibrium structure. All measurements were performed at $25 \pm 1^\circ\text{C}$. The frequency was varied from 0.05-100 rad/s. We chose a strain of 50% for 5 and 10%wt silica suspensions and 5% strain for 20 and 40%wt for the frequency sweep measurement, and investigated the rheological behavior as a function of the frequency, electric field strength and particle concentration.

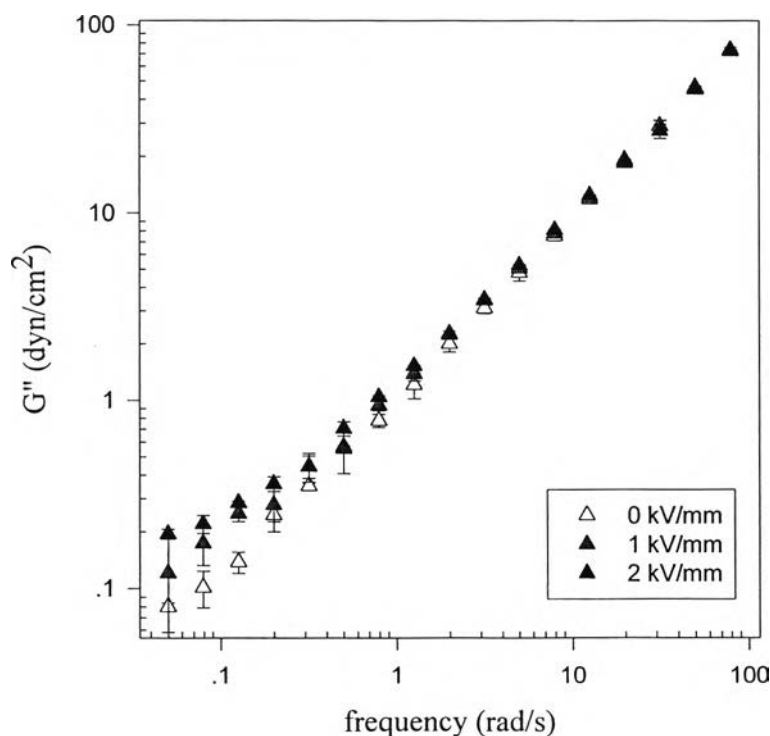


Figure 4.11a G'' dependence of 5 %wt silica (s5631) suspension for various electric fields at 50% strain.

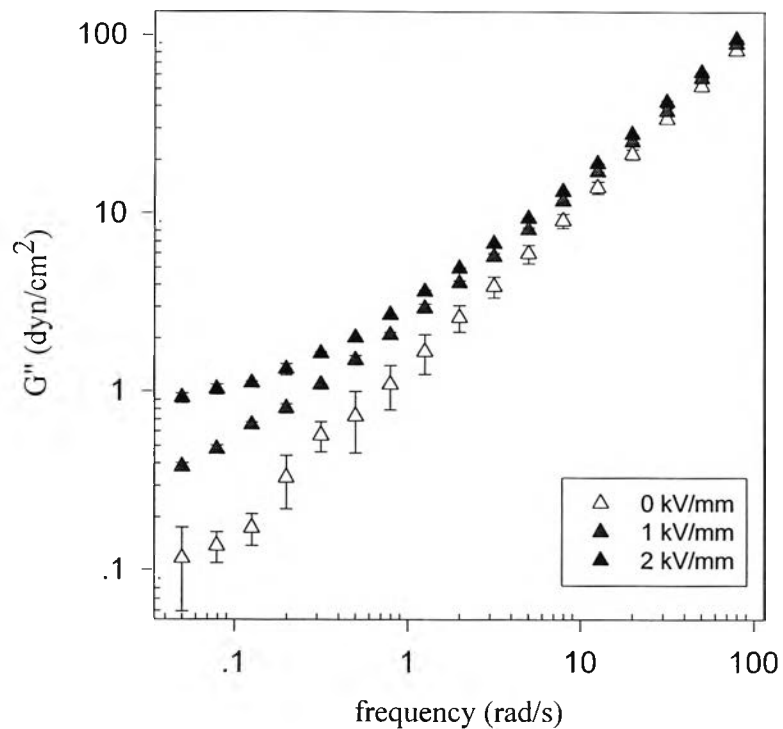


Figure 4.11b G'' dependence of 10%wt silica (s5631) suspension for various electric fields at 50% strain.

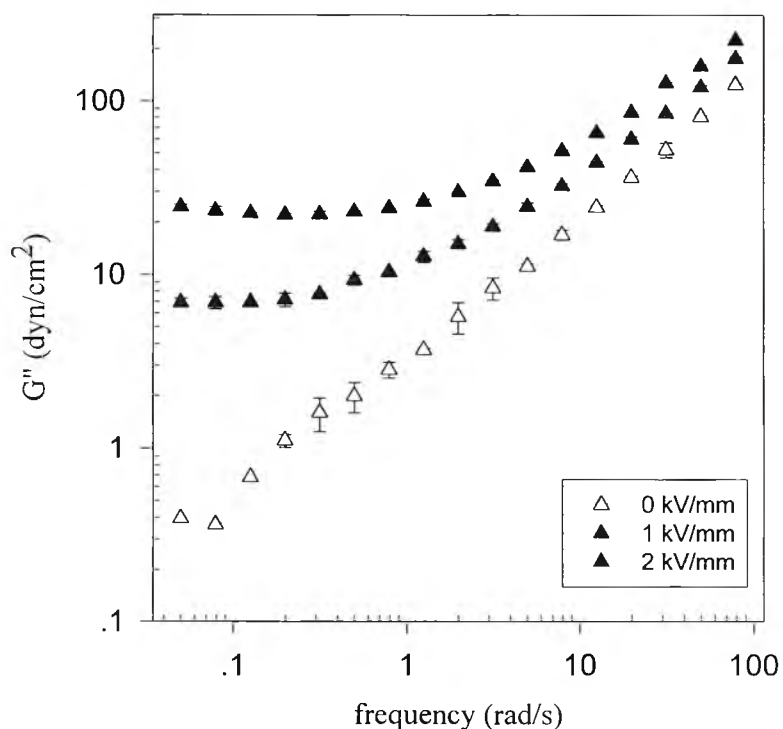


Figure 4.11c G'' dependence of 20%wt silica (s5631) suspension for various electric fields at 5% strain.

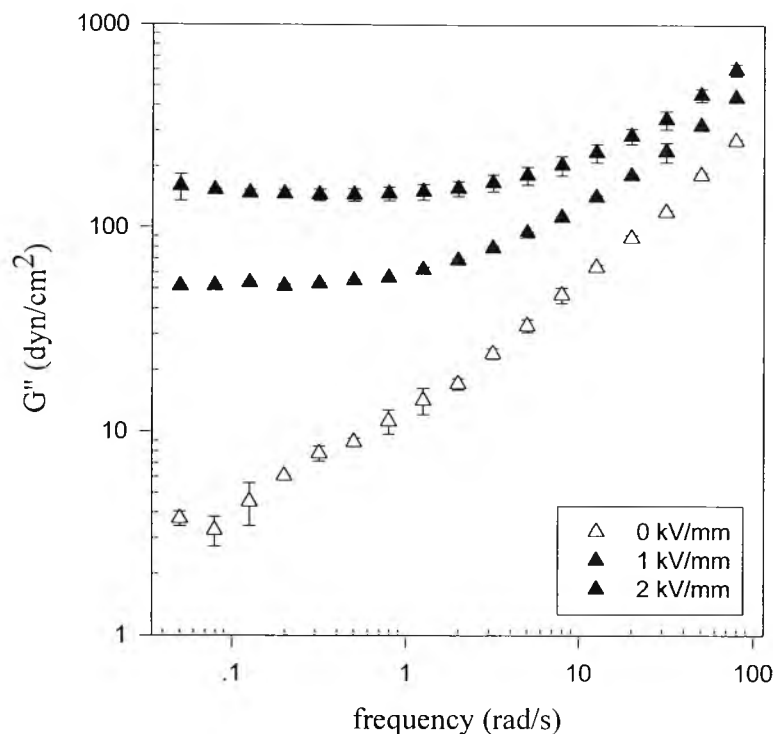


Figure 4.11d G'' dependence of 40% wt silica (s5631) suspension for various electric fields at 5% strain.

Figure 4.11a, b, c, and d show the results of a frequency sweep test of 5, 10, 20, and 40 %wt silica (s5631) particles, respectively, in 100 cSt silicone oil at various electric field strengths. The loss modulus (G'') was measured as a function of frequency. Under zero electric field, G'' increases linearly with frequency with a scaling exponent equal to 1. In the presence of the electric field, G'' increases with increasing electric field strength because the electric field strengthens the electrostatic force at the contact area of neighboring particles. If the electrostatic force between adjoining particles in a particle chain is increased, the strength of the chain structures is enhanced, resulting in a greater ER effect (Yatsuzuka *et al.*, 1995). As the applied electric field increases from 0 to 2 kV/mm, G'' at $\omega = 0.001$ rad/s increases from 0.12 to 0.78, 21.30, and 154.82 dyn/cm² for 5, 10, 20, and 40% wt silica (S5631)

suspensions, respectively. Therefore, increase of the particle concentration increases the loss modulus value. At low frequency, the increase in G'' with the applying electric field is more pronounced than at high frequency. It can be seen that G'' of 20, and 40 %wt silica (S5631) exhibits a low-frequency plateau in the presence of the electric field due to the formation of the chain-like or fibrillar structure. For 5, and 10% wt silica (S5631) suspensions, there is no plateau, because of the small number of the chains are formed, or only short separated chains are formed, or chains are attached to only one electrode. The width of the plateau also depends on the electric field strength and the particle concentration, Figure 4.11c shows the G'' exhibiting the plateaus at 1 and 2 kV/mm electric field strength, but the plateau at 1 kV/mm is narrower than at 2 kV/mm electric field strength. On comparing the data of Figure 4.11c and d at the same electric field strength, the plateau of the higher particle concentrations is wider than for the lower concentration. It can be concluded that the ER sample has a greater resistance to flow when the electric field strength and particle concentration are greater. However, at high frequency, G'' becomes similar to that without an electric field; i.e. the ER effect diminishes. The presence of the electrostatic field does not affect the rheological property of the sample in the high frequency regime because it depends on the structure of subfibrillar elements (individual particles).

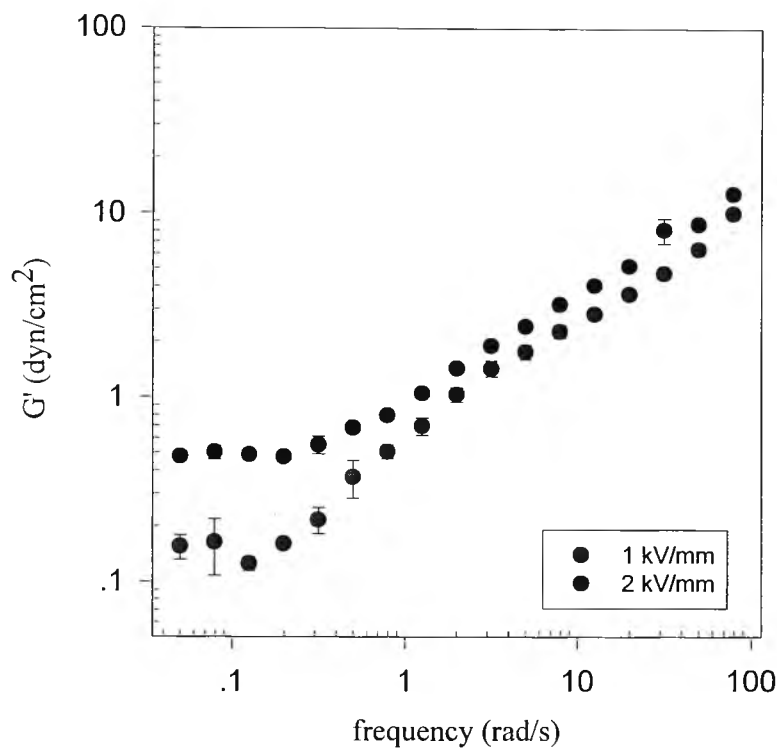


Figure 4.12a G' dependence of 10% wt silica (S5631) suspension at various electric field strengths at 50% strain.

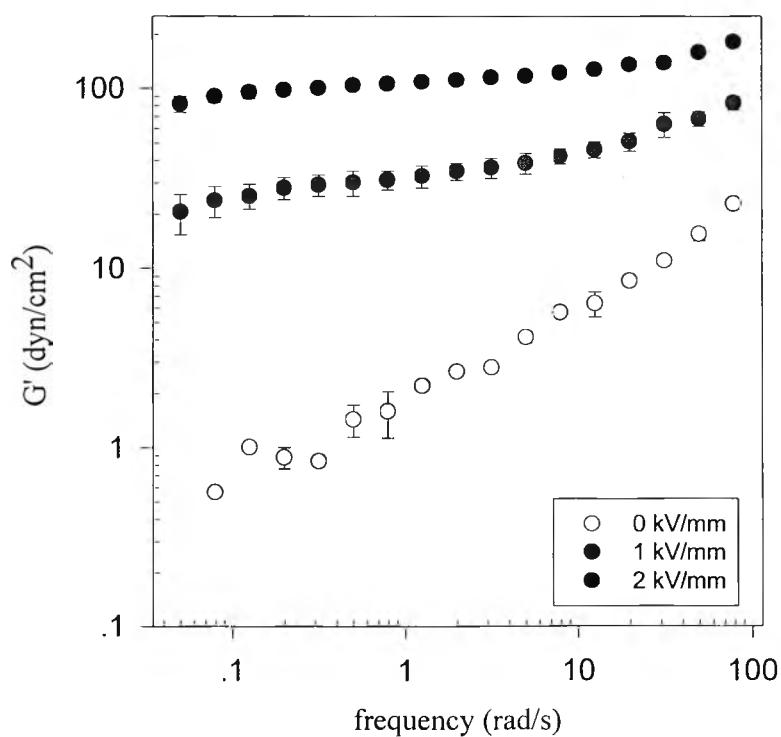


Figure 4.12b G' dependence of 20% wt silica (S5631) suspension at various electric field strengths at 5% strain.

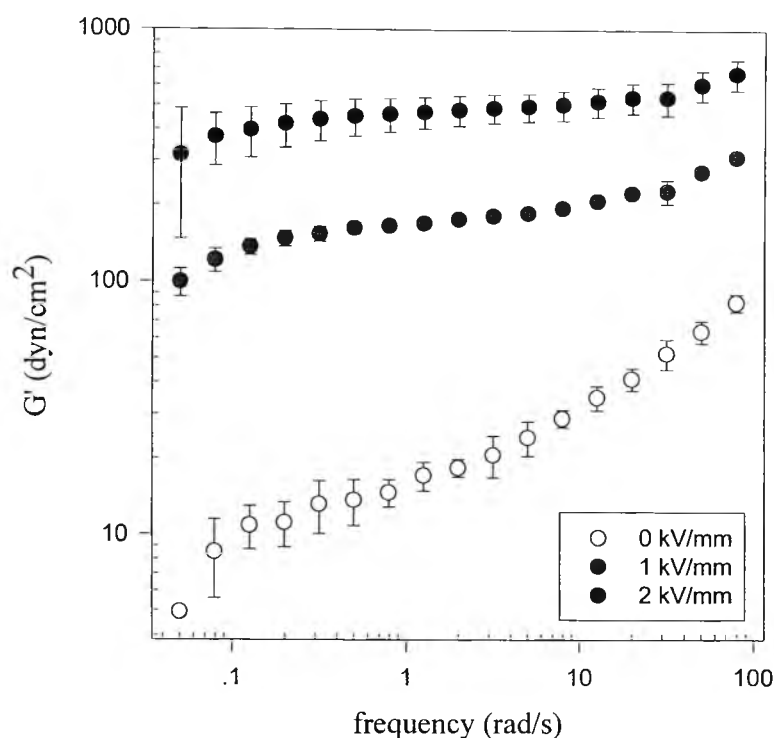


Figure 4.12c G' dependence of 40% wt silica (S5631) suspension at various electric field strengths at 5% strain.

Figure 4.12a, b, and c show the storage modulus (G') dependence of 10,20,40% wt silica (S5631) suspensions at various electric field strength. The storage modulus of 5% wt silica (S5631) was too small to measure in the absence and the presence of electric field, and G' of 10% wt suspension also cannot be measured under no electric field. All of the Figures show that the storage modulus increases with the electric field strength under linear viscoelastic conditions, i.e. they became more elastic. Generally, the storage modulus increases with the driving frequency as typical polymeric material does. G' at the frequency of 0.001 rad/s increase from 0.47 to 83.78, and 324.63 dyn/cm² for 10, 20, and 40% wt silica (S5631) suspensions respectively at the electric field of 2 kV/mm. For 10% wt suspension, G' has a plateau only at low frequency and then increases with increasing frequency. The storage modulus of 20 and 40% wt suspensions seems to depend only

weakly on frequency in the presence of the electric field but is strongly electric field dependent.

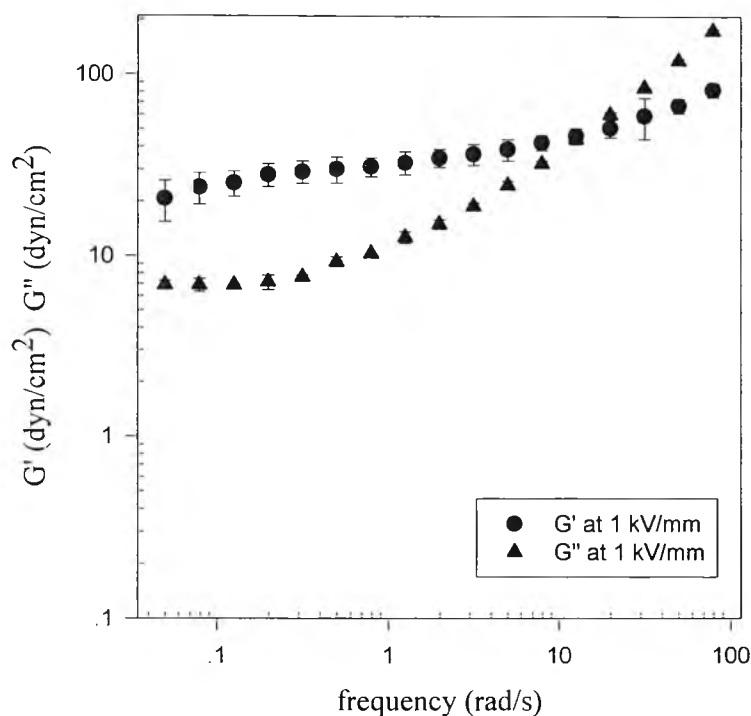


Figure 4.13a G' and G'' of 20% wt silica (s5631) suspension as a function of frequency at electric field of 1 kV/mm.

At zero electric field, ER samples behave as a viscous fluid for which the G'' was much higher than G' over the entire range of frequency. With an applied electric field to the sample, based on previous studies in the literature, the chain-like or fibrillated structure is formed in the suspension. The formation of the particle chains increased the resistance of fluid motion, which can be represented by G'' , and also increases elasticity, represented by G' . Comparing the magnitude of the storage and the loss moduli of 10% wt silica (S5631) at the same electric field strength (i.e. comparing Figure 4.11b with Figure 4.12a), G' is lower than G'' for the entire range of frequency. This may be due to the fact that the chains do not completely span across the gap but form separated short chains or are attached to only one electrode. Upon

increasing the particle concentration to 20% wt, it can be seen in Figure 4.13a that in the presence of 1 kV/mm electric field, G' becomes higher than that of G'' at low frequency (< 10). At the critical frequency, G' and G'' crossover each other. At this point, there is a transition from a solid-like response to a liquid-like response. At higher frequency, brownian motion of subfibrillar elements (individual particles) dominates, which means the viscous behavior is more dominant. When comparing between 1 and 2 kV/mm electric field strengths, the crossover points of G' and G'' are 50, and 10 rad/s at $E = 2$, and 1 kV/mm, respectively due to the stronger electrostatic force between the particles in the chains. It was also observed that there was a transition from solid-like to a liquid-like state of the 40% wt silica (S5631) suspension at the frequency of 30 rad/s under the 1 kV/mm electric field strength. For the electric field of 2 kV/mm, the storage modulus is higher than the loss modulus at all frequency .

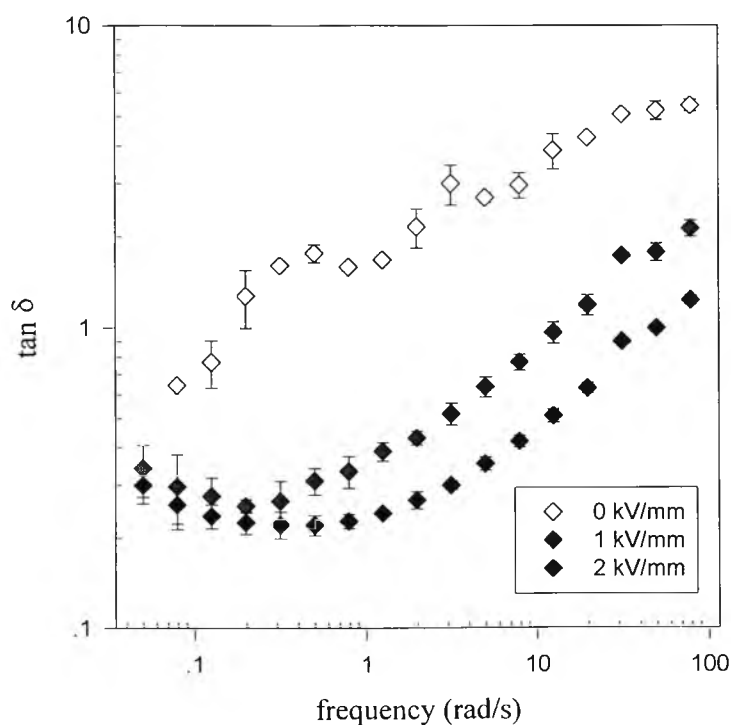


Figure 4.13b Tan δ of 20% wt silica (S5631) suspension as a function of frequency at 50% strain at various electric field strengths.

The variation of $\tan \delta$ as a function of frequency at the 1 and 2 kV/mm electric field strengths for the 20% wt silica (S5631) suspension at 50% strain is shown in Figure 4.13b. The tangent of the phase angle δ , $\tan \delta$, is the ratio of the out-of-phase to in-phase component: $\tan \delta \equiv G''(\omega)/G'(\omega)$. As electric field strength is increases, $\tan \delta$ decreases. This ratio demonstrates that at high electric field strength and low frequencies the storage modulus (G') dominates, i.e. the response is predominantly elastic. Similar behavior of $\tan \delta$ to that shown for 20%wt silica (S5631) in figure 4.13b is seen for the 40% wt at the same experimental conditions (Appendix D). However, the $\tan \delta$ of 40% wt suspension is lower than that of 20% wt suspension at the same electric field strength.

4.5.4 Effect of Particle Concentrations: Linear Viscoelastic Region

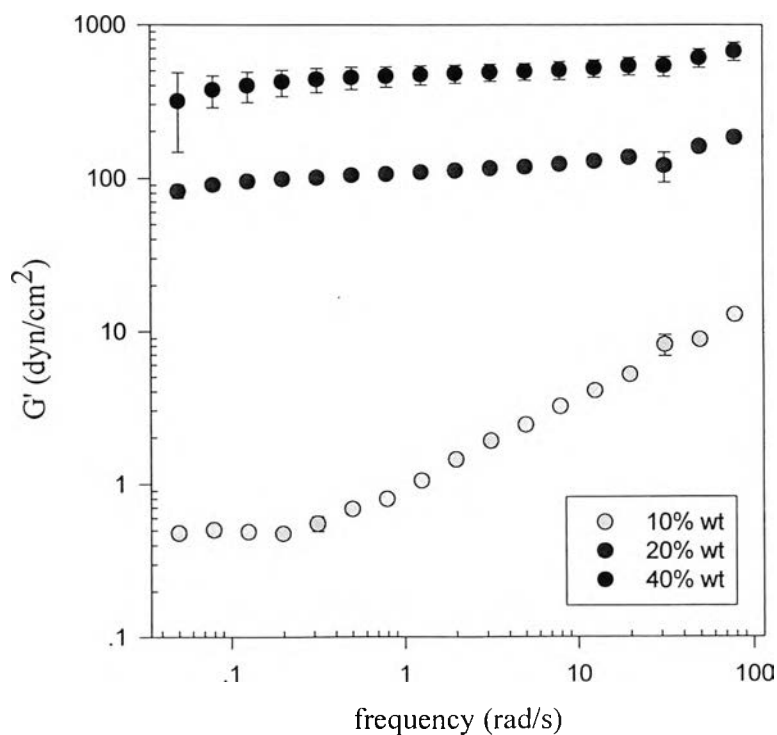


Figure 4.14a G' dependence on % wt silica (S5631) concentrations at the electric field strength of 2 kV/mm.

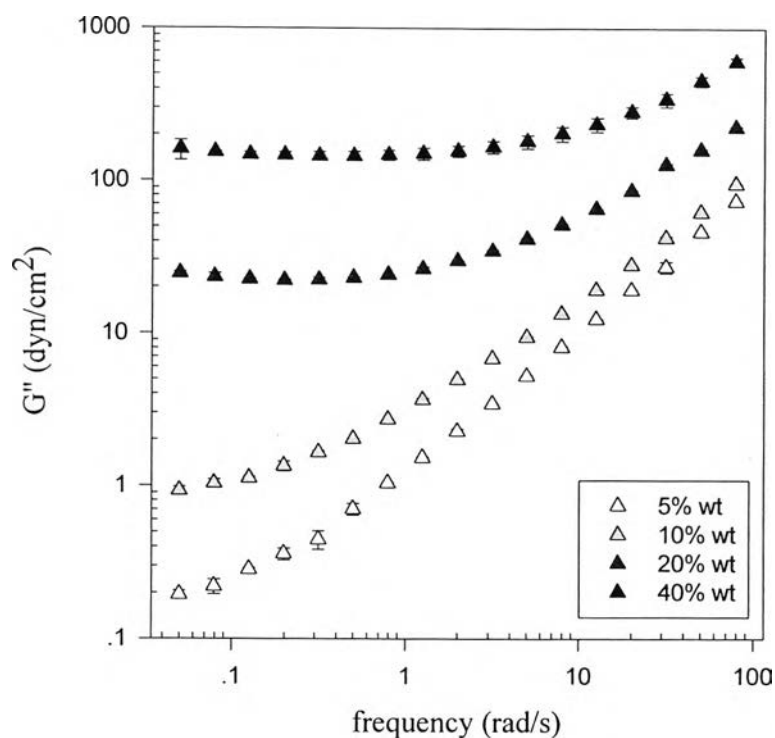


Figure 4.14b G'' dependence on % wt silica (S5631) concentrations at the electric field strength of 2 kV/mm.

The storage and the loss moduli for various % wt concentrations of silica (S5631) particles were investigated by the oscillatory test. G' and G'' increase with particle concentration for all sample ER fluids which we have examined. The dependence of the storage and loss moduli at the electric field of 2 kV/mm on frequency were obtained as shown in Figure 4.14a and Figure 4.14b, respectively. As discussed in last section, the storage modulus of 5%wt silica (S5631) was too small to be measured. Therefore, only G' of 10, 20, and 40% wt suspensions will be compared. The influence of the particle concentration on G' and G'' is weak at low particle concentration but becomes more pronounced at higher concentration. At a higher concentration, the interparticle distance is smaller and the number of particle chains increases, resulting in a larger ER effect (Yatzusuka *et al.*, 1995). Furthermore, at high

particle concentration, the rearrangement of the chains may include crosslinking to construct a network structure, because isolated chain segments can be formed between the fully developed chains (Otsubo *et al.*, 1992b).

4.5.5 Effect of Electric Field Strength: Nonlinear Viscoelastic Region

An electric field was applied for 5 minutes in order to obtain an equilibrium chain-like or columnar structure before each measurement. All measurements were performed at $25 \pm 1^\circ\text{C}$. In order to obtain reproducible data, the ER fluid samples were redispersed before each measurement, and the measurements were carried out at least two or three times. Several experiments were performed with the frequency sweep measurement at a constant % strain (600%) for all suspensions (5, 10, 20, and 40 % wt silica (S5631) particles in silicone oil). The frequency was varied from 0.05-100 rad/s. The rheological properties of each suspension were measured as a function of frequency, electric field strength, and particle concentration.

Many structuring fluids such as suspensions and polymer solutions show nonlinear viscoelasticity under large deformation. The strain sweep results (Figure 4.9) shows that at very low strain, the storage modulus is predominant and shows very little dependence on the strain. When the strain is increased above some critical level, the storage and the loss moduli are drastically decreased. The rapid decrease of the storage and the loss moduli can be related to the breakdown of internal structures (Otsubo *et al.*, 1998). To examine the nonlinear effect, the strain dependence of the storage and the loss moduli was measured. As shown in Figure 4.9, at strain less than 5%, the storage and the loss moduli are independent of strain and the viscoelastic response are linear. With increasing strain amplitude, both moduli decreased. The strain-dependent of storage and the loss moduli indicate that the elastic and viscous contributions become comparable near 20% strain. When the strain

is increased above 20%, the storage modulus shows a rapid drop relative to the loss modulus. Because of a dominant viscous contribution to the total dynamic response, the elastic effect in electrified ER fluids can be neglected at large strains. So, we will not discuss the storage modulus in the nonlinear viscoelastic region.

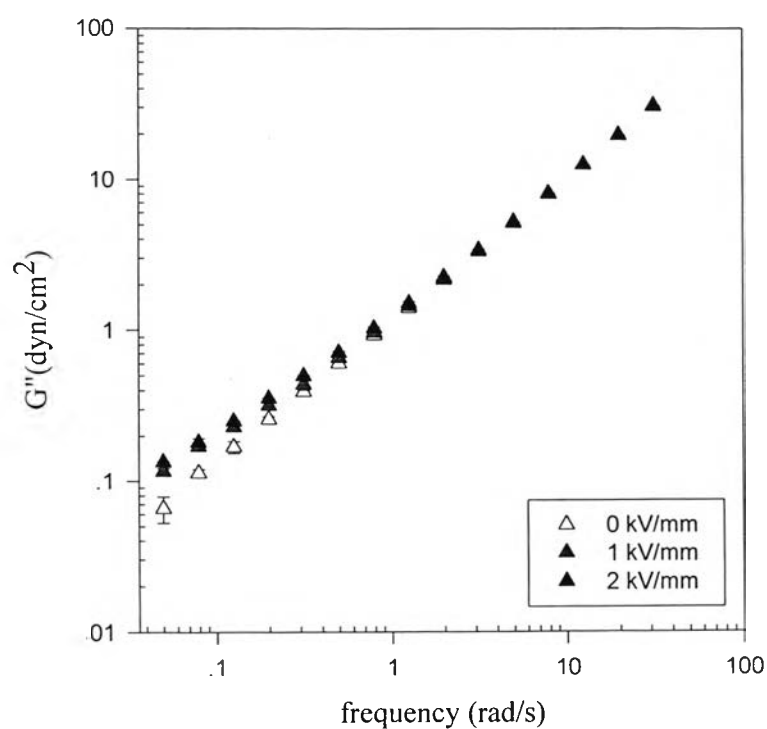


Figure 4.15a G'' dependence of 5% wt silica (S5631) suspension at various electric field strengths at 600% strain.

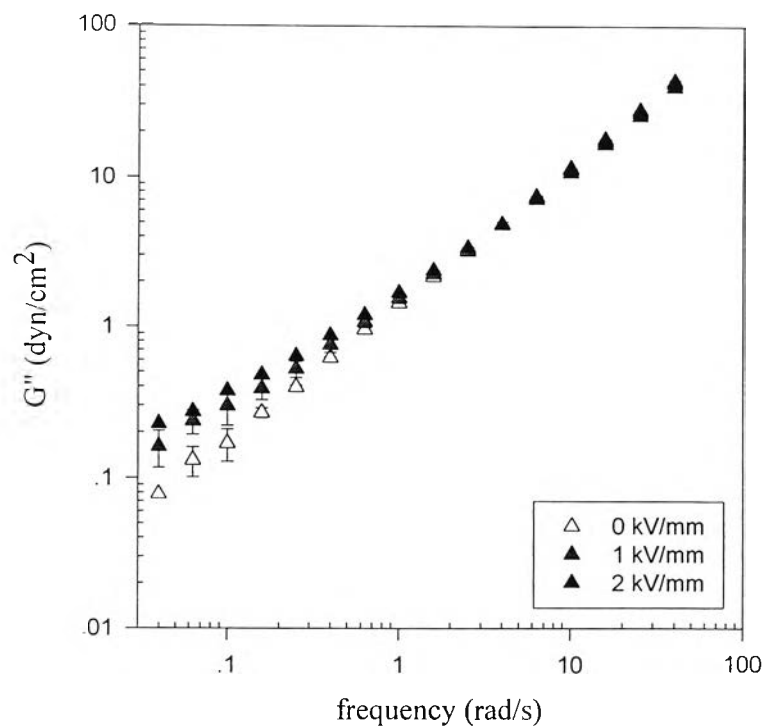


Figure 4.15b G'' dependence of 10% wt silica (S5631) suspension at various electric field strengths at 600% strain.

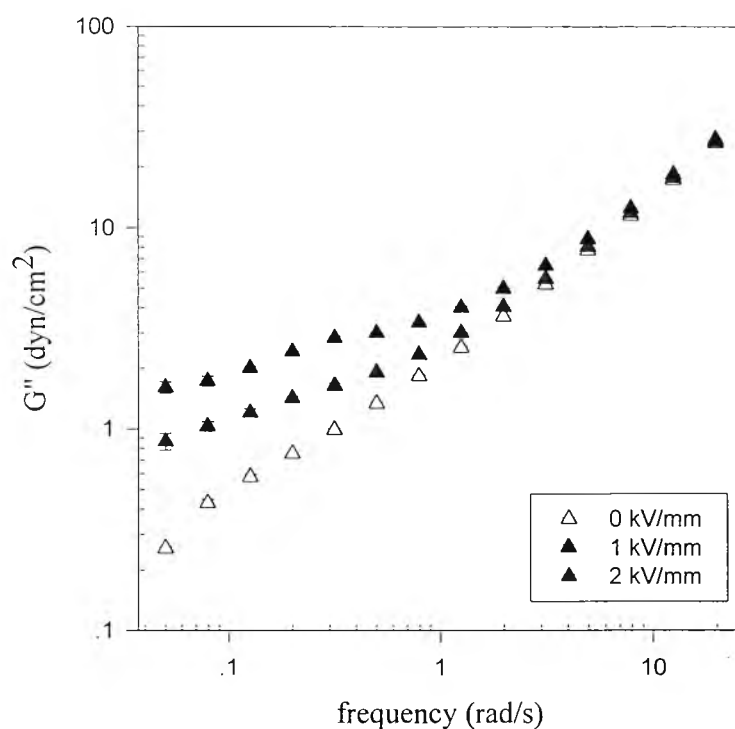


Figure 4.15c G'' dependence of 20% wt silica (S5631) suspension at various electric field strengths at 600% strain.

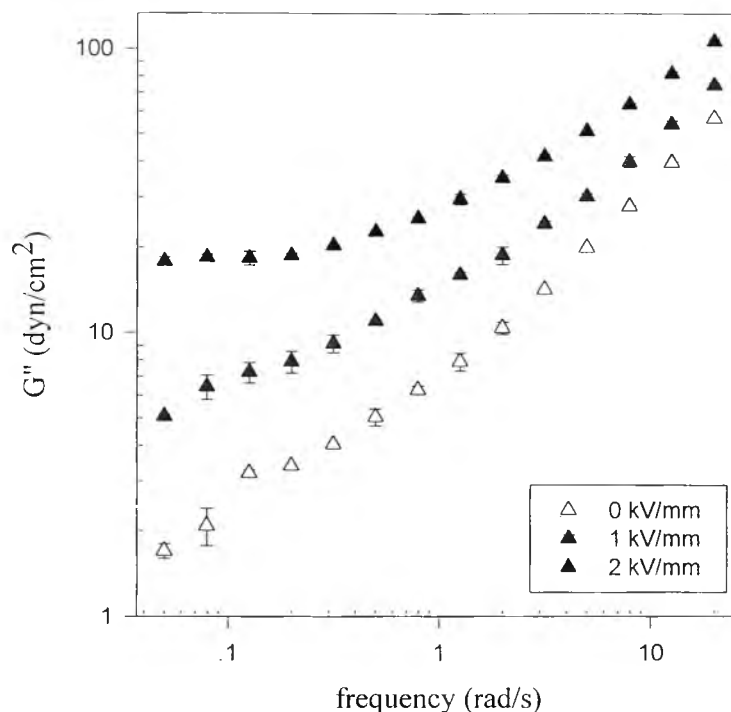


Figure 4.15d G'' dependence of 40% wt silica (S5631) suspension at various electric field strengths at 600% strain.

Comparing Figure 4.15a, b, c, and d, reveals that as the electric field strength increased, the loss modulus increases to different degrees, depending on the particle concentration. The increase in the loss modulus of the 5% and 10%wt silica (S5631) suspension is approximately 0.06 dyn/cm^2 . For the 20 and 40% wt silica (S631) suspensions, G'' at the frequency of 0.001 rad/s increase to 1.19 and 15.94, respectively. However, these G'' values are much smaller than in linear viscoelastic region for the same particle concentration and electric field strength. This can be explained by cluster statistics and micro-structural observations, which show that the response at large strain amplitude and small frequencies was dominated by rupture and reformation of chains. At large frequencies, the suspension behavior is that of a purely viscous fluid. The fibrous structures observed at lower frequency are degraded into much smaller aggregates under large strain amplitude (Parthasarathy and Klingenberg, 1999).

4.5.6 Effect of Particle Concentrations: Nonlinear Viscoelastic

Region

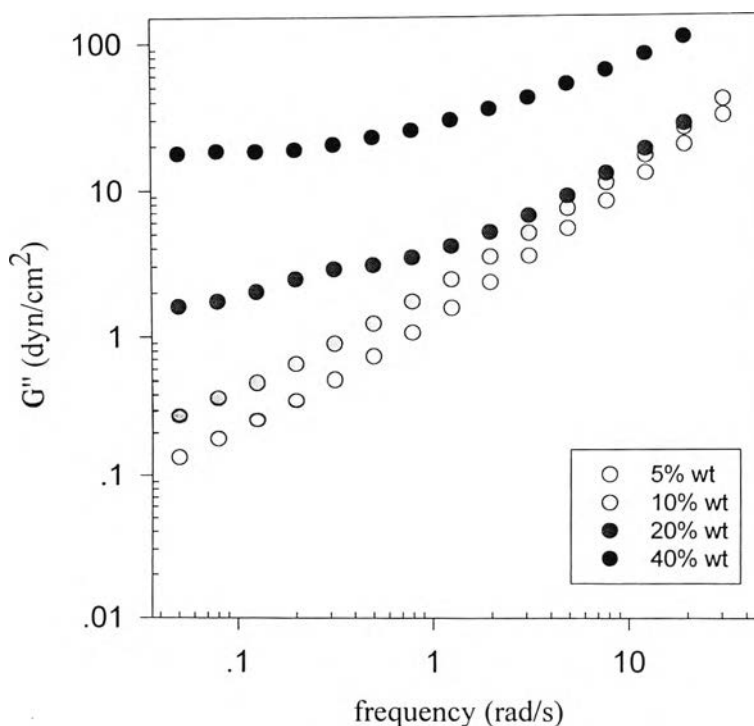


Figure 4.16 G'' dependence of various % wt silica (S5631) concentrations at electric field of 2 kV/mm at 600% strain.

As shown in figure 4.16, the loss modulus at a given strain amplitude (600%) increase with increasing particle concentration under the application of the electric field of 2 kV/mm. In addition, there is a plateau of G'' only for the 40% wt silica (S5631) suspension at the electric field of 2 kV/mm. For the 5 and 10% wt silica (S5631) suspensions, at high frequency (> 2 rad/s), the data superpose, i.e. the loss modulus in the absence and in the presence of the electric field is the same. For the 20% wt suspension, G'' becomes the same as in the absence of the electric field at the frequency of 10, while G'' of the 40% wt suspension still increase in the presence of the electric field. Parthasarathy and Klingenberg (1999) explained that the nonlinear behavior first arises from only slight rearrangements of unstable clusters under shear as opposed to gross

rupture of electrode percolating clusters. Intra-cluster rearrangements are more common at very small concentrations, where clusters are far apart, as well as at large concentrations, where cluster contained many particles. Inter-cluster rearrangements are more prevalent at the higher concentrations.

4.5.7 Effect of Size of the Particles

Silica (H927), which has a size of 17 micron, was used to be the dispersed particles in the same silicone oil suspension, and comparison made with the rheological properties of dispersions of the silica (S5631) type which has a size of 3 micron. We selected the strain of 50% to use for frequency sweep measurements.

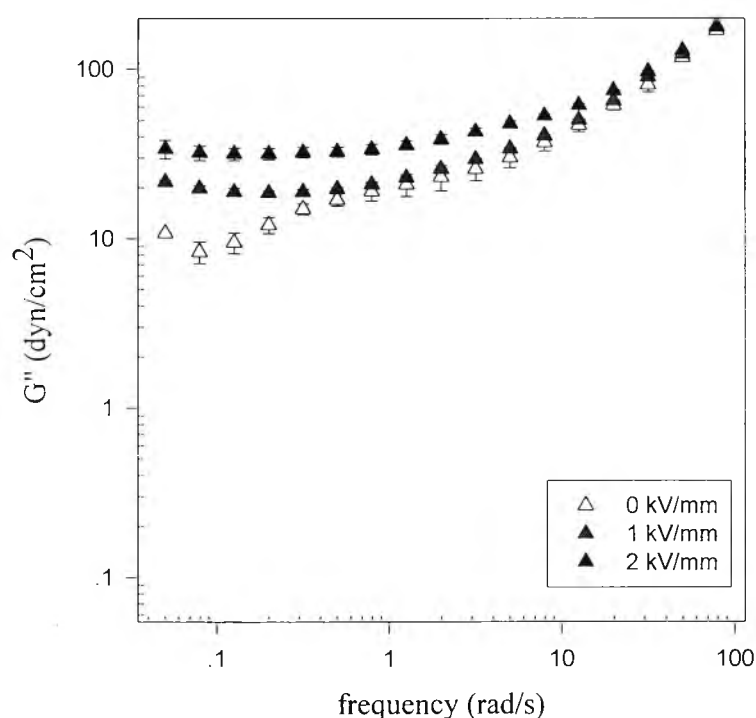


Figure 4.17a G'' dependence of 5% wt silica (H927) suspension at various electric fields at 50% strain.

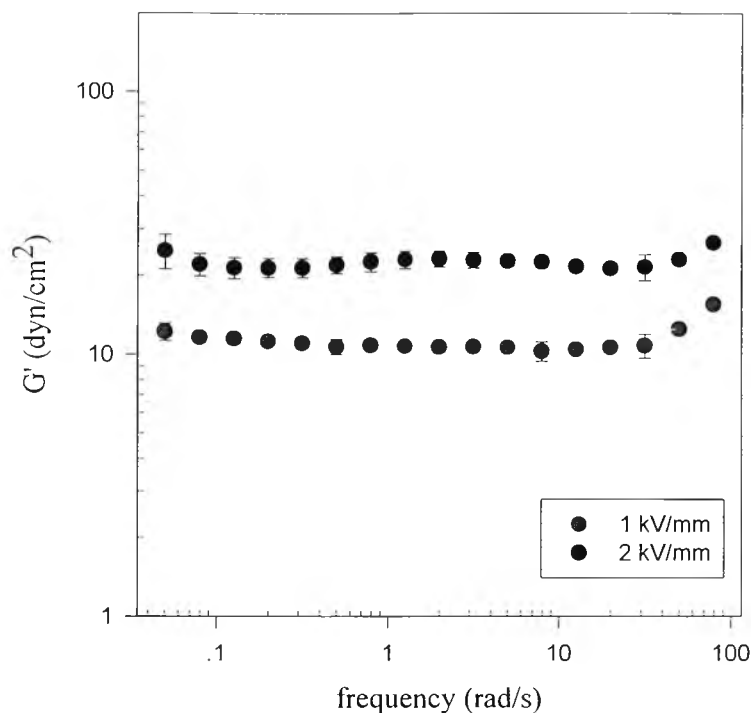


Figure 4.17b G' dependence of 5% wt silica (H927) suspension at various electric field strengths at 50% strain.

Figure 4.17a and b show, respectively, the frequency dependence of the storage and the loss moduli of the 5% wt silica (H927) suspension at 50% strain under the electric field of 1 and 2 kV/mm. Both G' and G'' increase with the strength of the applied electric field. The magnitude of the increase in G'' at the electric field of 0 to 2 kV/mm is approximately 24.99 dyn/cm², which is much higher than that of silica (S5631) suspension, which is only 0.15 dyn/cm². Moreover, the storage and the loss moduli of 5% wt silica (H927) suspension also exhibit a plateau in the presence of the electric field of 1 and 2 kV/mm, unlike that of silica (S5631) (see Figure 4.11a). This is due to the increase in the attractive force between the particles that forms chain-like structures. Since the attractive force between larger particles is greater, larger particles are preferable in designing ER fluids, provided problems of colloidal stability can be overcome (Yatzusuka *et al.*, 1995).

4.6 ER Measurement of Polyaniline Suspensions

In the preparation of ER fluid samples based on polyaniline, at a particle concentration of 40% wt, the suspension became a gel even in the absence of an applied electric field, and so could not be used for ER studies. Thus, measurements were performed for 5, 10, and 20% wt PAN suspensions to study the influence of the strain amplitude, electric field strength, and particle concentration on the ER effect.

4.6.1 Effect of strain amplitude

To determine the linear viscoelastic behavior of the suspensions, strain sweep tests were conducted in the presence of an electric field of 2 kV/mm at a frequency of 1 rad/s.

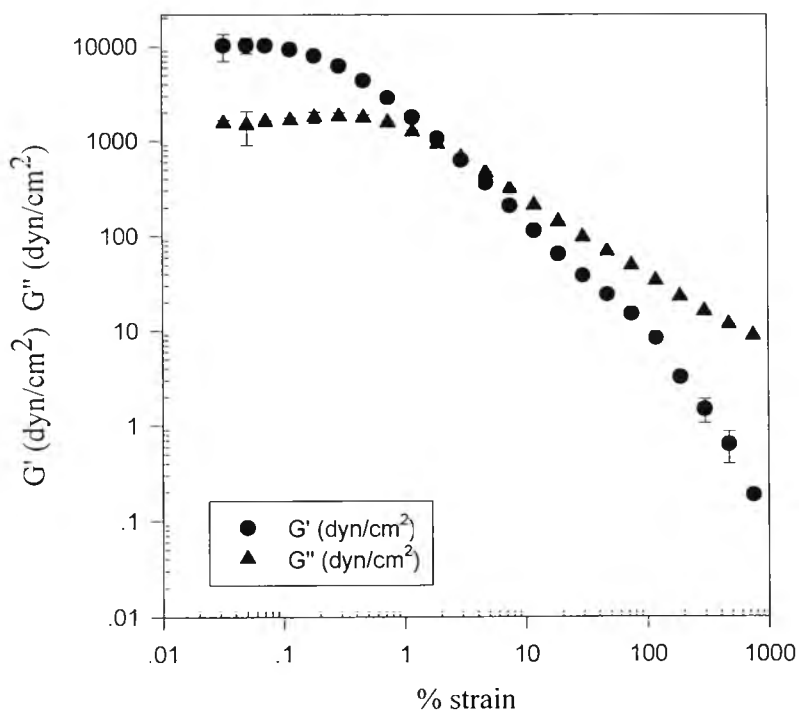


Figure 4.18 G' and G'' dependence on % strain of 20% wt PAN suspension at the electric field of 2 kV/mm.

Figure 4.18 shows a plot of the storage modulus (G') and the loss modulus (G'') versus % strain at a frequency of 1 rad/s at the electric field of 2 kV/mm for 20% wt PAN in silicone oil system. The response of the 20% wt PAN suspension is similar to that of the silica (S5631) suspension of comparable concentration except that the magnitude of the moduli are much higher. With increasing strain amplitude, the storage modulus decreases rapidly and becomes dependent on frequency. Thus, the suspension behavior varies from predominantly elastic at small strain amplitudes and frequencies to predominantly viscous at large amplitude and frequencies. However, the range of linear viscoelasticity is more limited than for the silica (S5631) dispersion. PAN suspensions show linear viscoelastic behavior only at strains less than 0.05%, while the silica (S5631) suspensions are linear at strains less than 10%. Koyama *et al.* (1994) previously performed strain sweep experiments on polyaniline/ silicone oil suspensions under dc fields. G' was constant at small strain amplitudes, independent of the electric field strength, and decreased in a power-law fashion with increasing strain amplitude. More results from our work on strain sweep for other ER fluids based on PAN are shown in Appendix D.

4.6.2 Transient Response

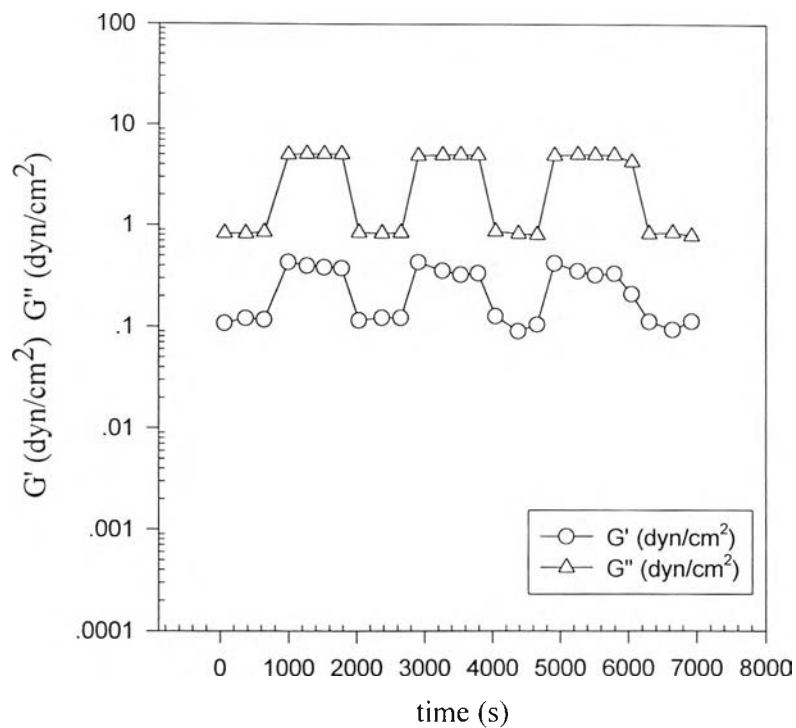


Figure 4.19 G' and G'' dependence of the 20% wt PAN suspension at the electric field of 2 kV/mm and frequency 1 rad/s.

Figure 4.19 shows the change in storage and the loss moduli in response to an electric step field of 2 kV/mm applied to the 20% wt PAN suspension in the time sweep mode at a frequency of 1 rad/s and 600% strain. An electric field of 2 kV/mm was repeatedly applied and released. The suspensions responded and equilibrated with the applied electric field in a time interval around 100 s. When the electric field is released, G' and G'' of the sample completely recovered to the original values.

4.6.3 Effect of Electric Field Strength: Nonlinear Viscoelastic Region

From the results of the strain sweep measurement, the PAN suspensions exhibit the linear viscoelastic behavior, but the torque is too small to measure in oscillatory shear mode at these small strains. Therefore, we studied the effect of the electric field strength and particle concentration in the nonlinear viscoelastic region, which is in fact is pertinent for application in many devices, such as active engine mounts, shock absorber, clutches, brakes and robotic devices. Such devices operate in dynamic or transient modes where the fluid is subjected to finite deformations (Parthasarathy and Klingenberg, 1999).

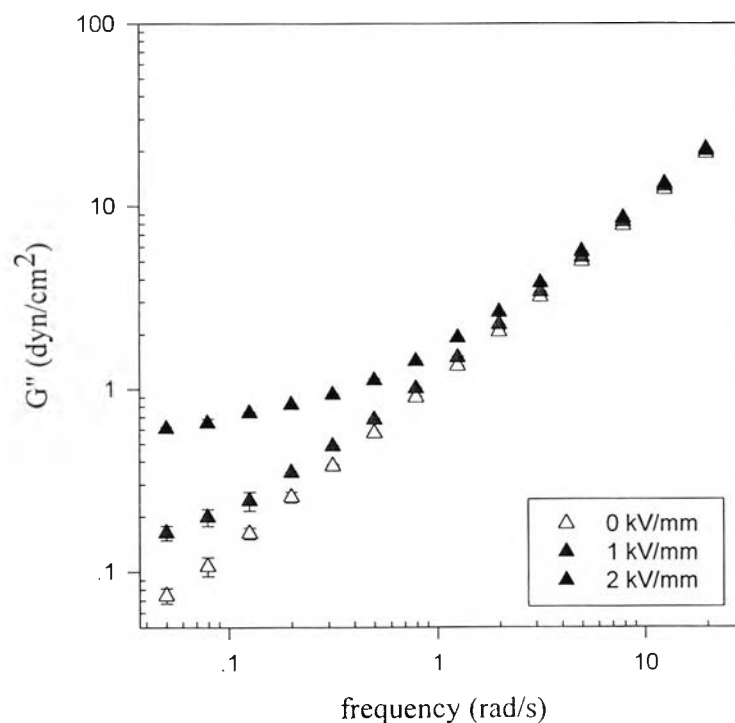


Figure 4.20a G'' dependence of 5% wt PAN suspension on various electric fields at 600% strain.

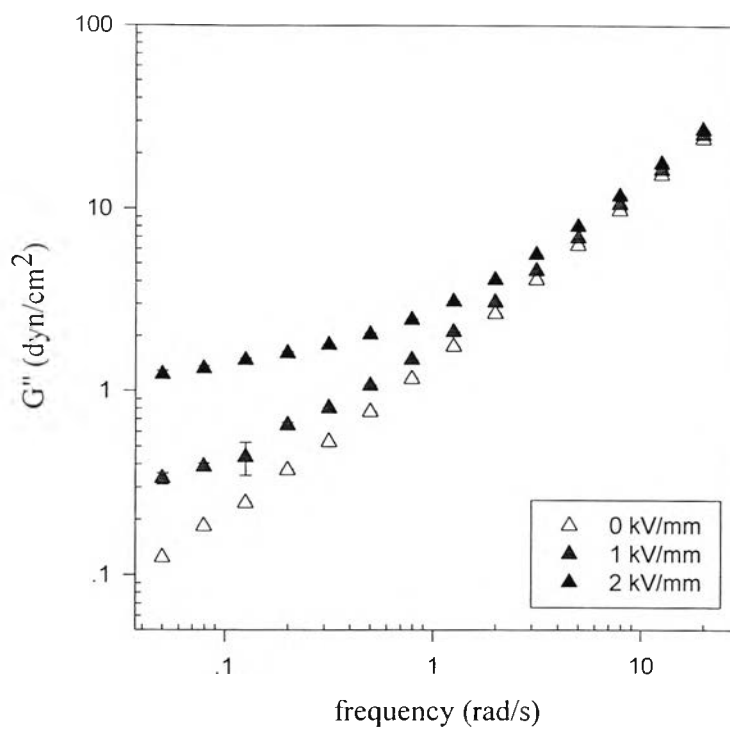


Figure 4.20b G'' dependence of 10% wt PAN suspension on various electric fields at 600% strain.

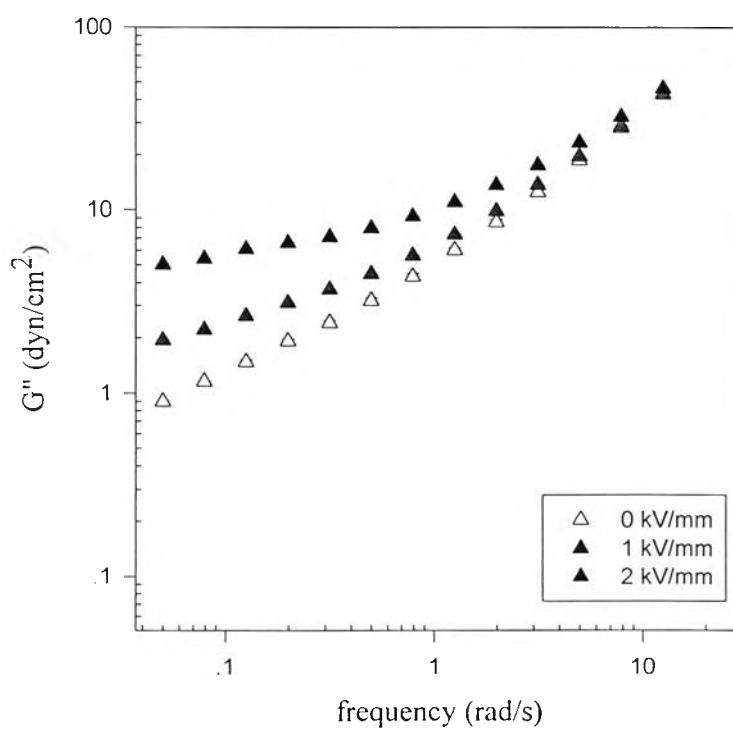


Figure 4.20c G'' dependence of 20% wt PAN suspension on various electric fields at 600% strain.

Figure 4.20a, b, and c show the result of frequency sweep measurements on the 5, 10, and 20% wt PAN suspensions at various electric field strengths. G'' was measured as a function of frequency. Under zero electric field, G'' increases with frequency with the scaling exponent equal to 1. In the presence of the electric field, G'' increases by increments of 0.5, 1.0 and 5.0 dyn/cm² for 5, 10, 20 %wt PAN suspensions, respectively. It was also observed that G'' for all PAN suspensions (5, 10, and 20%wt) exhibits a plateau at the electric field of 2 kV/mm, presumably because electrode-spanning fibrillar structures are formed in the suspension in the presence of the electric field. At low frequency, the increase in G'' with the applied electric field is more pronounced than at high frequency. This is due to the fact that at higher frequency the viscoelastic response is determined by the Brownian motion of subfibrillar elements (individual particles). Thus, at high frequency, the value of G'' becomes similar to that on the absence of the electric field.

4.6.4 Effect of Particle Concentrations: Nonlinear Viscoelastic Region

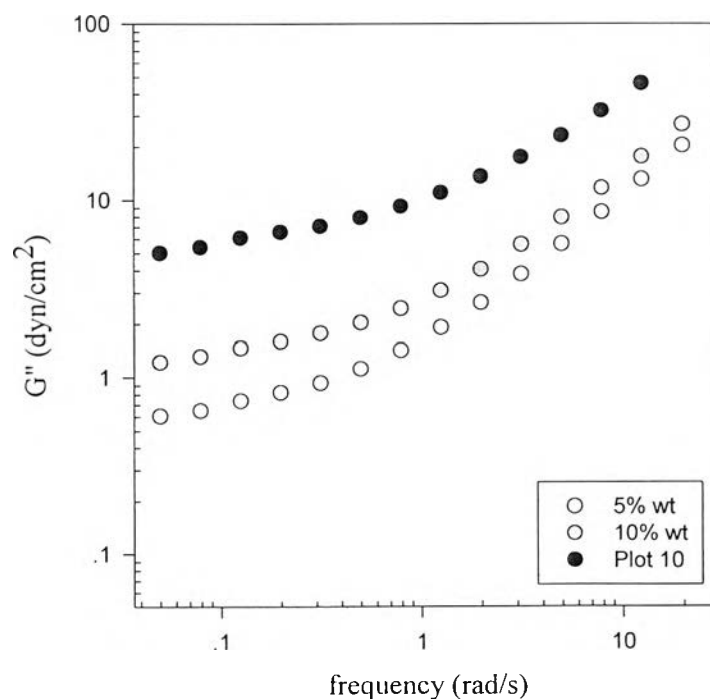


Figure 4.21 Dependence of G'' for various %wt PAN concentrations on various electric field of 2 kV/mm at 600% strain.

The loss modulus of various %wt of PAN particles in silicone oil was investigated by oscillatory test at 600% strain under the application of an electric field strength of 2 kV/mm. As shown in Figure 4.21, the loss modulus (G''), which characterizes the viscous dissipation of the suspension, increases with increase of PAN particle concentration. At low particle concentration, the influence of concentration is weak, but becomes more pronounced at higher concentration. As discussed in the previous section, an increase in particle concentration increases G'' because a larger number of chains are formed and the interparticle distance in the suspension decreases. In addition, it is possible that, at higher particle concentration, thicker clusters are formed; whereas at low concentration, only chains of single particle width are formed (Yatsuzaka *et al.*, 1995).

4.7 ER measurement of Polyaniline-Coated Silica Suspension

4.7.1 Effect of Strain Amplitude

Strain sweep experiments in the presence of the electric field of 2 kV/mm at the frequency of 1 rad/s were conducted to determine the linear viscoelastic behavior of the 20% wt polyaniline-coated silica suspension.

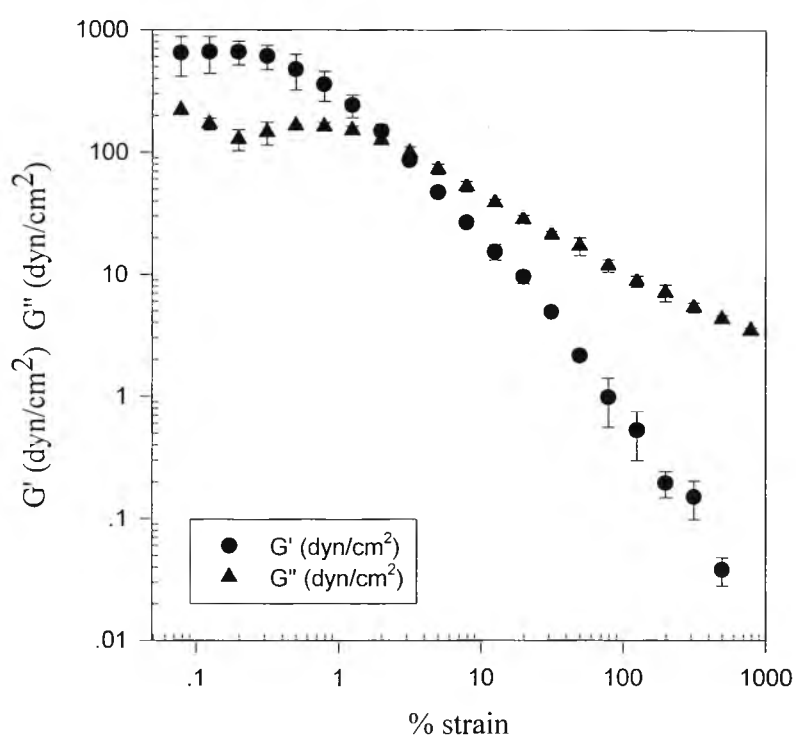


Figure 4.22 G' and G'' dependence on % strain of 20% wt PAN-coated silica (S5631) suspension at the electric field of 2 kV/mm.

Figure 4.22 represents a plot of the storage modulus (G') and the loss modulus (G'') versus % strain at the frequency of 1 rad/s at the electric field of 2 kV/mm for a suspension of 20% wt PAN-coated silica (S5631) in silicone oil. The response of the suspension of 20% wt PAN-coated silica (S5631) is similar to that of silica (S5631) suspensions and PAN suspensions. The magnitude of the moduli and the range of the linear viscoelastic region for the

20% wt PAN-coated silica (S5631) suspension are intermediate between those of the silica and PAN suspensions. The response of the PAN-coated silica is linear up to 3% strain, and then, with increasing strain amplitude, the storage and the loss moduli decrease and become dependent of frequency. In the linear viscoelastic region, the storage modulus is larger than the loss modulus due to the elasticity of the ER fluid, presumably determined by the formation of fibrillar structures in the presence of the electric field. Above a certain degree of deformation or strain imposed, the fibrous structure is broken down, and the suspension behavior became predominantly viscous (Cho *et al.*, 1998).

4.7.2 Transient Response

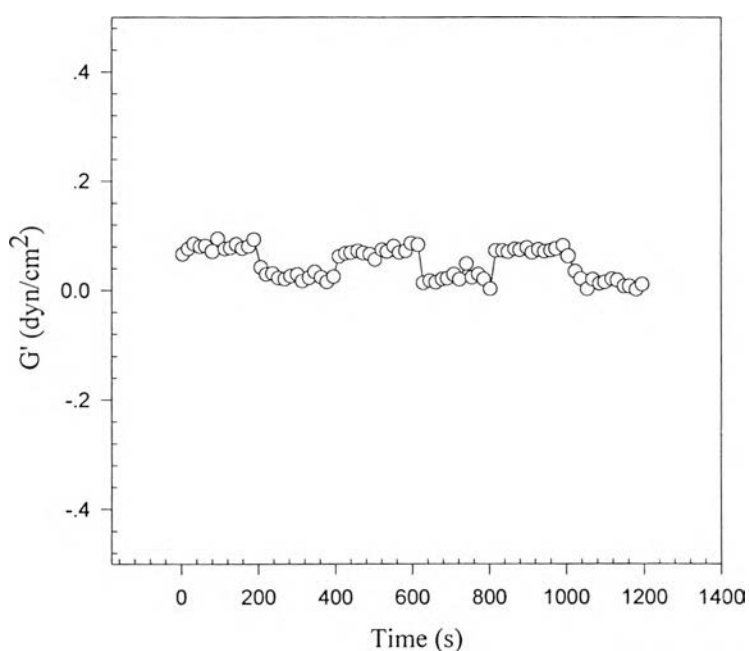


Figure 4.23a G' dependence of the 20% wt PAN-coated silica (S5631) suspension at the electric field of 2 kV/mm and frequency 1 rad/s at 600% strain.

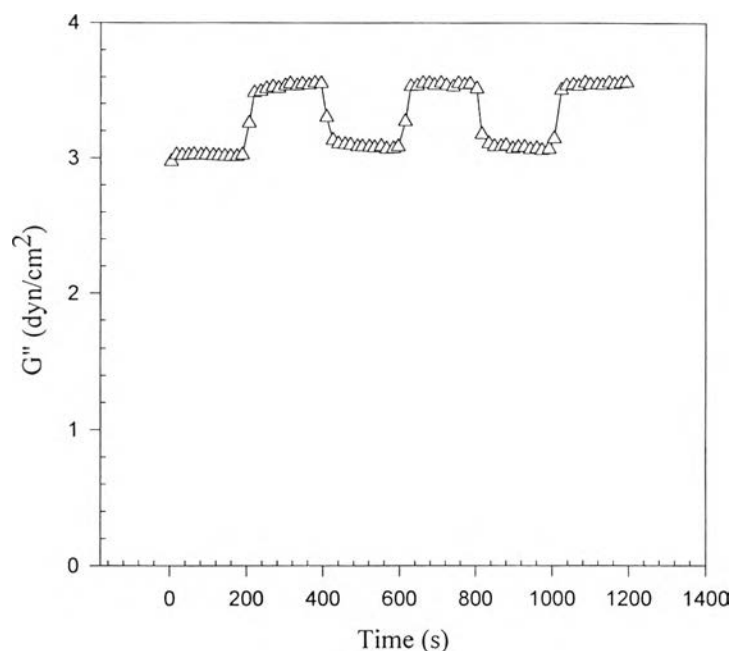


Figure 4.23b G'' dependence of the 20% wt PAN-coated silica (S5631) suspension at the electric field of 2 kV/mm and frequency 1 rad/s at 600% strain.

The response of the storage and the loss moduli of the 20% wt PAN-coated silica (S5631) suspension to an electric step field of 2 kV/mm at the frequency of 1 rad/s and 600% strain by the time sweep mode is shown in Figure 4.23a and b. An electric field of 2 kV/mm was repeatedly applied and released. The suspensions responds and equilibrates with the applied electric field within a time scale of about 70 s. In the presence of the electric field, the storage modulus (G') decreases, while G'' increases, unlike the behavior of other ER fluid samples based on silica and PAN, which both G' and G'' increased with the applied electric field. When the electric field was released, the storage and the loss moduli completely recovered to the original values.

4.7.3 Effect of Electric Field Strength: Nonlinear Viscoelastic

Region

An electric field was applied for 5 minutes in order to obtain an equilibrium chain-like structure before each experiment. All measurements were performed at $25\pm 1^\circ\text{C}$. In order to obtain reproducible data, the ER fluid sample was redispersed before each experiment, and the measurements were carried out at least two or three times. Several experiments were performed on the 20% wt PAN-coated silica (S5631) suspension were performed in the frequency sweep mode at a constant % strain (5 and 600%).

From the strain sweep measurement of the 20% wt PAN-coated silica (S5631) suspension, even though there is a linear viscoelastic region, the torque is too small to be measured in the oscillatory mode. Therefore, we studied the effect of electric field strength and the strain amplitude in oscillatory measurements in a nonlinear viscoelastic region, but at small and large strains.

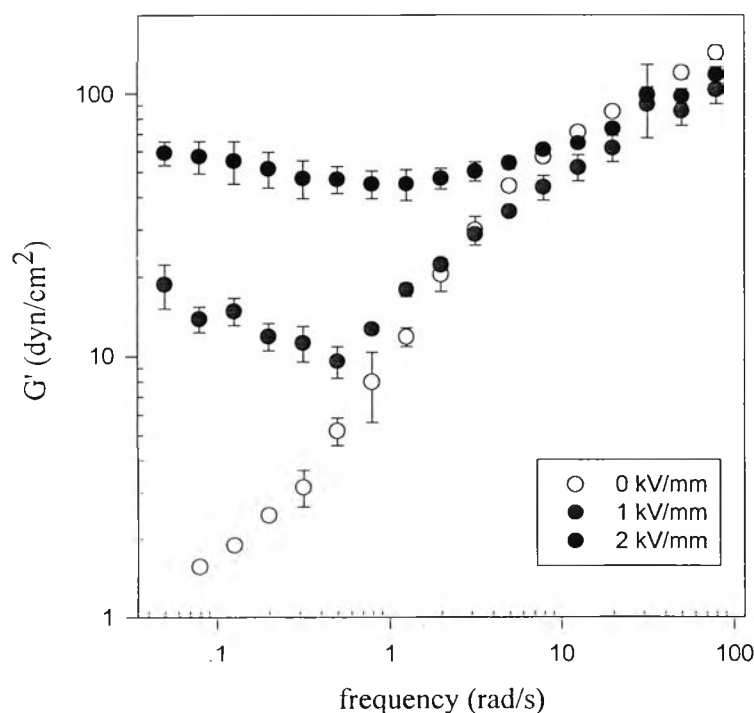


Figure 4.24a G' dependence of 20% wt PAN-coated silica (S5631) suspension at various electric fields at 5% strain.

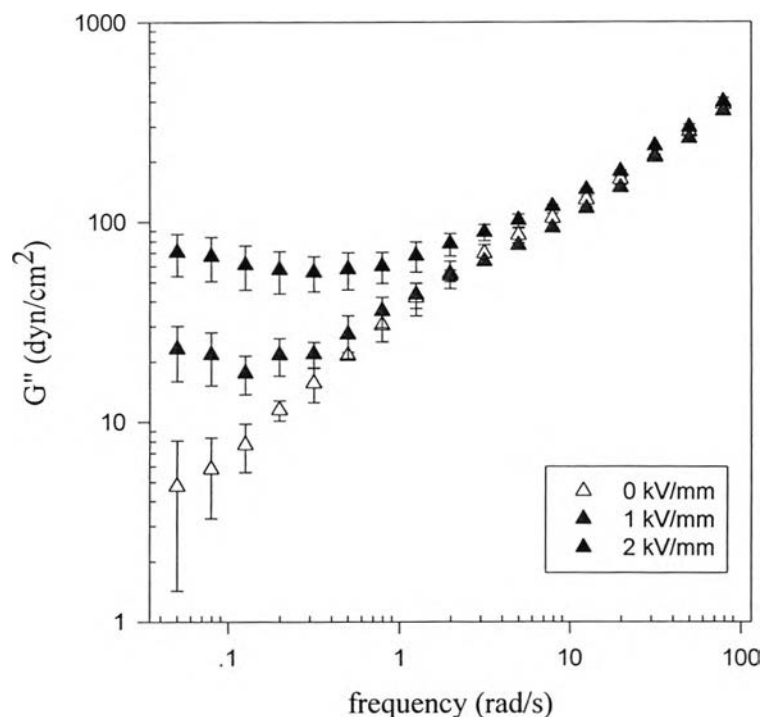


Figure 4.24b G'' dependence of 20% wt PAN-coated silica (S5631) suspension at various electric field strengths at 5% strain.

Figure 4.24a and b show, respectively, the storage and the loss moduli of the 20% wt PAN-coated silica (S5631) suspension under various electric field strengths. The storage and the loss moduli increase with increasing electric field strength to 60 and 65 dyn/cm^2 , respectively. From Figure 4.24a, in the presence of the electric field strength of 1 kV/mm, G' slightly decreases with frequency and increases at the frequency above 0.5 rad/s. At the electric field strength of 2 kV/mm, the G' shows a plateau. However, at high frequency (>10 rad/s), G' of the 20% wt PAN-coated silica (S5631) suspension in the presence of the electric field of 1 and 2 kV/mm is slightly lower than that at zero applied electric field. From Figure 4.24b, G'' of the suspension also shows a plateau at low frequency. However, the ER effect tends to diminish at high frequency; G'' becomes similar to its value without electric field. When comparing the storage and the loss moduli at the same

electric field (0,1,2 kV/mm), G' is lower than G'' all over the entire range of frequency due to the disruption of the field-induced chain-like structure in nonlinear viscoelastic region.

Due to the dominating viscous contribution to the total dynamic response of the ER fluid at large strain, the elastic property that is represented by G' in the presence of the electric field can be negligible. Figure 4.25 shows the G'' dependence of the 20% wt PAN-coated silica (S5631) suspension on various electric field strengths at 600% strain. At the frequency below 0.3 rad/s, the loss modulus of the suspension in the absence of the electric field is higher than that in the presence of the electric field (1 and 2 kV/mm). An electric field of 1 kV/mm does not affect G'' at the frequency higher than 0.8 rad/s, i.e. the G'' value in the absence of the electric field is similar to G'' value in the presence of electric field. But with an increase of the electric field strength to 2 kV/mm, G'' increases, slightly, presumably because the stronger electrostatic force between the particles causes particle agglomeration.

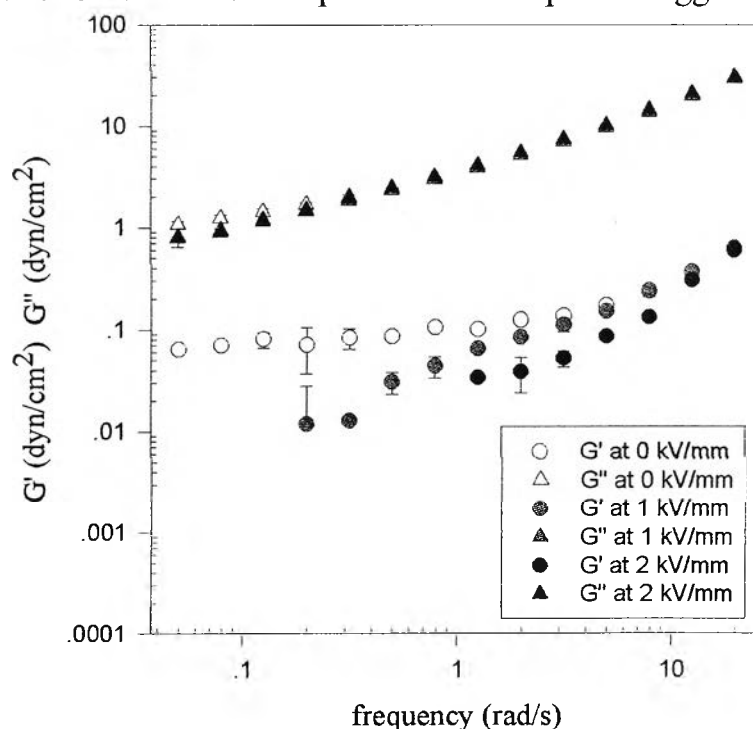


Figure 4.25 G' and G'' dependence of 20% wt PAN-coated silica (S5631) suspension at various electric field strengths at 600% strain.

Comparing Figure 4.24a and 4.25 reveals that as the strain amplitude increased the ER effect tends to diminish due to the higher disruption of the field-induced chain-like structures; G' and G'' of the 20% wt PAN-coated silica (S5631) suspension at 5% strain is higher than that of at 600% strain. The frequency is another factor, which affects to the ER effect. As the frequency increases, the suspension behavior changed from predominantly elastic to predominantly viscous.

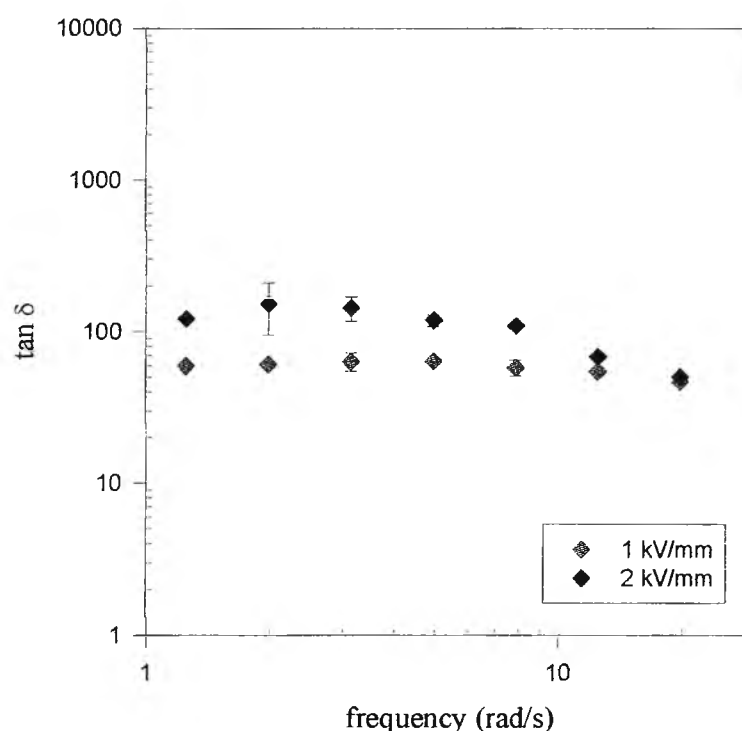


Figure 4.26 $\tan \delta$ of 20% wt PAN-coated silica (S5631) suspension as a function of frequency at 600% strain on various electric field strengths.

In Figure 4.26, $\tan \delta$ is plotted as a function of frequency at 600% strain in the presence of 1 and 2 kV/mm electric field strength for 20% wt PAN-coated silica (S5631). As the electric field strength increases, $\tan \delta$ increased. However, at high frequency, G'' at 1 and 2 kV/mm electric field strength becomes similar. Thus, the electric field strength does not affect to the rheological property of the sample in the high frequency regime.

4.8 Comparison of The Silica (H927) and Polyaniline Systems

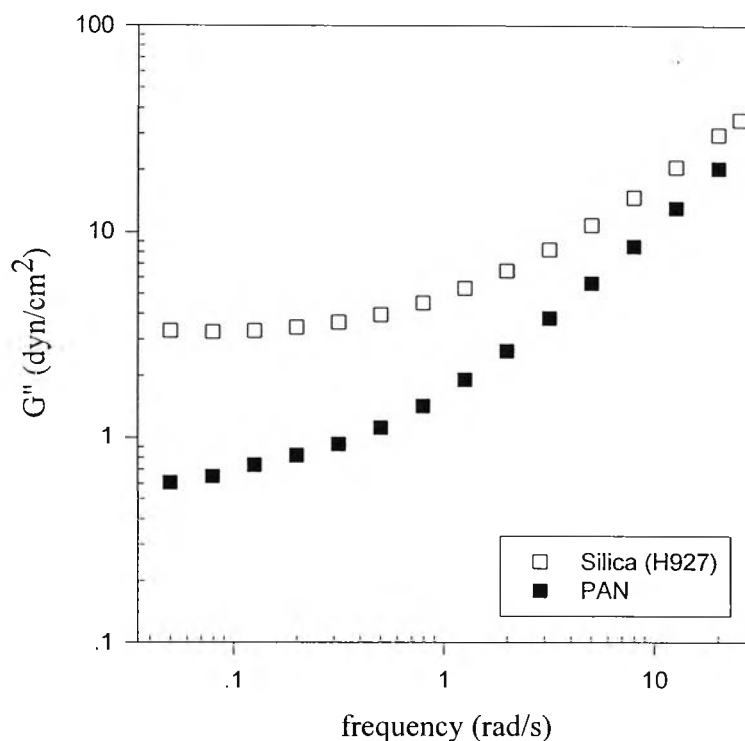


Figure 4.26 G'' dependence of 5% wt silica (H927) and PAN suspensions at the electric field of 2 kV/mm at 600% strain.

The loss moduli of 5% wt silica (H927) and 5% wt PAN suspensions are shown in Figure 4.26. G'' of silica (H927) system is higher than G'' of PAN system over the entire range of frequency. Hence, we can conclude that, in the non-linear viscoelastic region, the silica (H927) suspension exhibits a greater ER effect than the PAN suspension. However, in classical ER fluids such as silica suspensions, the presence of water on the particle surface, is an essential factor for charge separation on the surface of the ionic double layer (Kuramoto *et al.*, 1996). Otsubo *et al.* (1992), reported that the silica particles do not show any electrorheological effect above 100°C, due to desorption of the water molecules. There are some disadvantages of water-activated ER systems, such as narrow use temperature range and corrosion of the

equipment, compared to nonaqueous ER fluids such as polyaniline in silicone oil.

4.9 Comparison of The Silica (S5631) and Polyaniline-Coated Silica (S5631) Systems

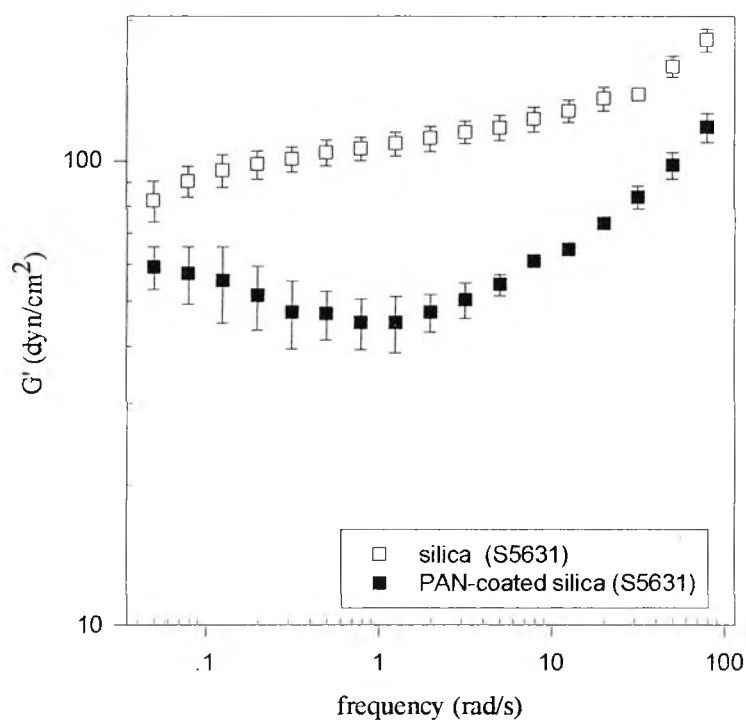


Figure 4.27a G' dependence of 20% wt silica (S5631) and PAN-coated silica (S5631) suspensions at the electric field of 2 kV/mm and at 5% strain.

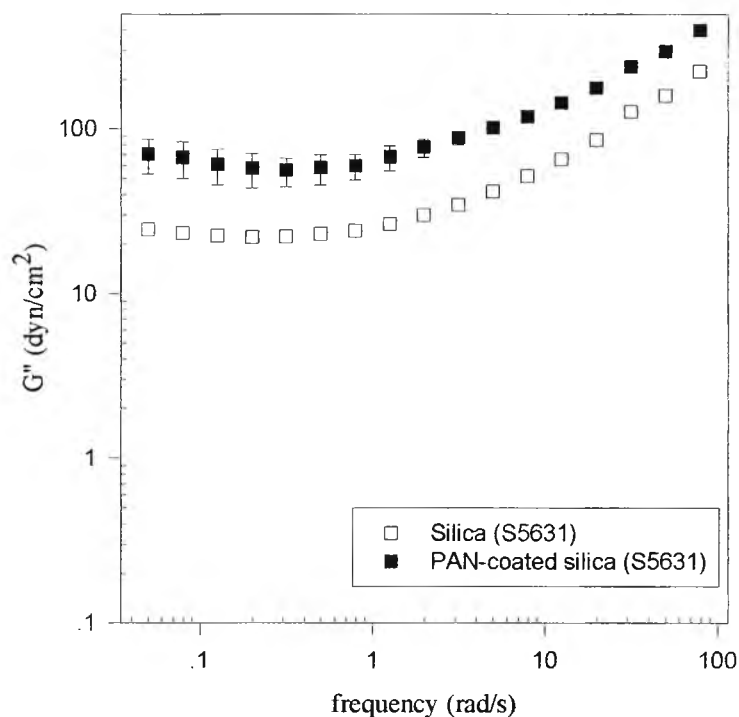


Figure 4.27b G'' dependence of 20% wt silica (S5631) and PAN-coated silica (S5631) suspensions at the electric field of 2 kV/mm and at 5% strain.

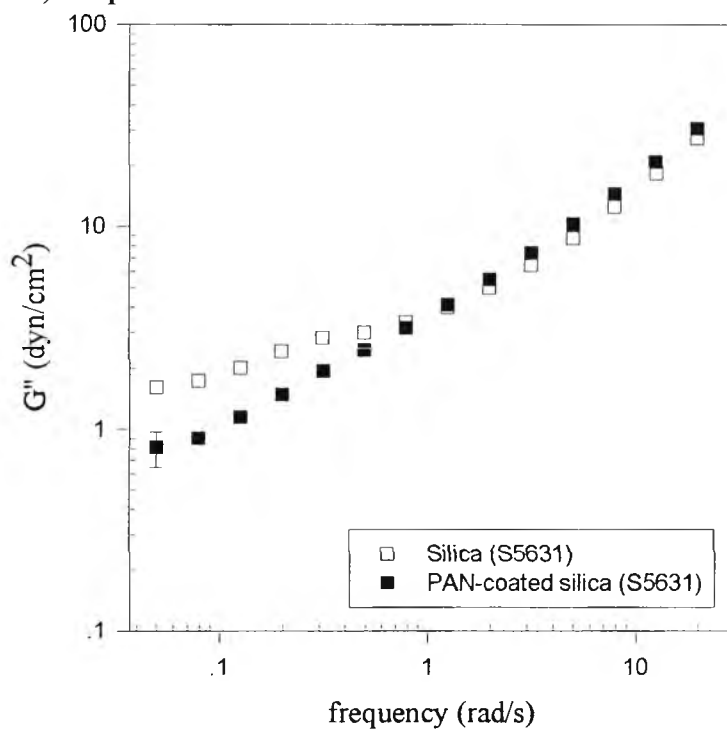


Figure 4.28 G'' dependence of 20% wt silica (S5631) and PAN-coated silica (S5631) suspensions at the electric field of 2 kV/mm and at 600% strain.

Figure 4.27a and 4.27b reveals that G' of 20% wt PAN-coated silica (S5631) suspension in the presence of 2 kV/mm electric field strength is lower than in silica (S5631) system and has a minimum value at $\omega = 1$ rad/s, and the G'' of PAN-coated silica (S5631) is higher than that of silica (S5631) system at 5% strain for the entire range of frequency, while at 600% strain, the loss moduli PAN-coated silica (S5631) suspension is lower than that of silica (S5631) suspension at the frequency below 1.26 rad/s. At the frequency 1.26 rad/s, G'' of both silica and PAN-coated silica suspension are the same. Above the frequency of 1.26 rad/s, G'' of PAN-coated silica suspension is slightly greater than that of silica suspension. As discussed in previous section, the ER fluid based on silica particles was a water-activated system, which presented some problems in the operation standpoints. The PAN-coated silica ER fluid is another kind of nonaqueous ER fluid, silica particles were coated with a polyaniline by chemical means. Kuramoto *et al.* (1996) have reported the preparation and electrorheological properties of polyaniline-coated silica and copolystyrene particles. The particles having anionic species presented on the surface could be encapsulated by a thin film polyaniline. Polyaniline was grown as a thin conducting layer on the surface of anionically doped inorganic and organic particles. The modification of silica with polyaniline was found to lead to an improvement in the yield stress of the silica particles under nonaqueous conditions.