JOURNAL OF MATERIALS SCIENCE **39** (2004) 1377– 1382

Linear viscoelasticity of semiconducting polyaniline based electrorheological suspensions

M. S. CHO, J. H. LEE, H. J. CHOI
Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea
E-mail: hjchoi@inha.ac.kr

K. H. AHN, S. J. LEE
School of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

D. JEON
Department of Mechanical Engineering, Sogang University, Seoul 121-742, Korea

A dry-base electrorheological (ER) fluid was prepared by dispersing synthesized semiconducting polyaniline (PANI) particles into silicone oil, and its viscoelastic properties were investigated under applied electric fields using a rotational rheometer. Within the linear viscoelastic region, the ER fluid was observed to be elastic, due to columnar structure of PANI particles sustaining the deformation. Its rheological functions (G' and G'') were interpreted based on the dimensional analysis, and they showed roughly linear electric-field dependence of the dimensional collapse of the viscoelastic behavior with frequency suggesting that the interactions between highly irregular particles are saturating even at these relatively low values of the dielectric mismatch. Furthermore, the recovery percentage obtained from the creep and recovery experiments increased with applied electric fields.

1. Introduction

It is well known that electrorheolgical (ER) fluid, a suspension of polarizable particles in non-conducting oil, shows dramatic changes in its rheological properties including shear viscosity, yield stress and viscoelasticity when an electric field is imposed to the fluid. This is due to the migration and chainlike structure formation of particles, which is oriented along the electric field direction over the gap between electrodes [1], induced by the mismatch of the dielectric constant between suspended particles and non-conducting oil [2–4]. Thereby, the typical characteristics of ER fluids, including reversible and swift transition between liquid and solid states, potentially provide the most efficient approach to controlling mechanical response by simply adjusting the electric field strength, thereby possessing many industrial application potentials.

Meanwhile, adopting an ER fluid for a particular application requires an accurate knowledge of its dynamic mechanical behavior. In addition to its steady shear characteristics, the viscoelastic properties of an ER fluid are also important especially in vibration damping [5] applications. Most devices using ER fluids operate generally under dynamic conditions, and measurement of small amplitude oscillation is appropriate from a practical point of view [6, 7].

The viscoelastic properties of ER fluids under an electric field are related to the induced particle structures, and these can be obtained through a dynamic test [8–13], in which the viscoelasticity is a material characteristic responding to an applied force by exhibiting both elastic and viscous properties, depending upon the time scale of the measurement. Thereby, viscoelastic materials are capable of balancing strong part of the input energy and dissipating the rest of this energy as heat under a constant deformation. Meanwhile, Gamota and Filisko [9] suggested that not only the nonlinearity and viscoelastic behavior of ER fluid are dependent on the parameters such as strain amplitude and applied electric field strength, but also its rheological properties are different according to the measuring range such as pre-yield, yield and post-yield region. Since the ER fluids dominantly exhibit elasticity in the pre-yield region, a linear viscoelasticity can be adopted. Meanwhile, a nonlinear viscoelasticity and a plasticity were reported to be observed in the yield region and in post yield region, respectively. The plateau region was observed to increase with the number of particles in ER suspension, and be independent of the number of particles near the frequency 10^{-1} Hz [11]. Even though most of viscoelastic measurments on the ER fluids have been performed using a rotational geometries, other types of the measurements such as a thin rectangular tubular channel [12] and a vertical oscillation rheometer [13] were also adopted.

Contrast to hydrous ER systems having either hydrophilic particles in which particle structures under a field are caused by the migration of ion in the adsorbed water [14] or particles [15] with activators such as surfactant [16] and glycerin [17], the anhydrous ER systems with anhydrous particles such as zeolite [8, 18] and semiconducting polymers [19–22] allow to obtain ER properties in a wide temperature range because the polarizing species are not ions in water but electrons in this case. These include PANI [19, 23] and its copolymers [24, 25], poly(p-phenylene) [26, 27], polypyrrole [28, 29], poly(acene quinone) radicals [19, 30], carbonaceous particles [31, 32] and phosphate cellulose [33, 34]. Hybrid particles, i.e. PANI coated silica particle [35], PANI coated poly(methylmetha acrylate) [36], encapsulated PANI [37], SAN/clay nanocomposite [38], PANI/clay nanocomposite [39], and polypyrrole/clay nanocomposite [40] were recently reported to be applied for the ER fluids.

Among various ER fluids, the PANI, an air-stable organic conducting polymer, has advantages with respect to density, conductivity control, and thermal stability. It is also easy to be polymerized by an oxidation polymerization [41]. Its conjugated structure with alternating single and double bonds has been widely regarded as a prerequisite for polymers to become electronically conducting because it provides a path, through overlapping π-orbitals, necessary for charge carriors to move along the polymer backbone. Since most organic polymers do not possess intrinsic charge carriers, the charge carriers are normally generated by partial charge-transfer with either electron-acceptors or electron donors, a process that has been widely known as doping. The PANI can be changed from an insulator to metal depending upon the degree of doping (10^{-10}–10^5 S/m) by controlling both an oxidation state and pH which are accompanied with the changes of its color (violet-green) [42]. This allows for a change in the particle dielectric constant and conductivity, while all other particle properties and suspension characteristics remain identical for the study [43].

In this study, we examined viscoelastic behavior of the ER suspension with semiconducting PANI particles synthesized from a chemical oxidation polymerization, and then effect of the electric field on its viscoelasticity was carried out via both dynamic and creep tests. The experimental results were then compared with those obtained from a simulation reported by Parthsarathy *et al.* [6].

2. Experiments

The PANI as a dispersed phase in ER fluids, was synthesized following the previously reported modified method [44]. A prechilled ammonium peroxysulfate solution in 1 M HCl was added dropwisely to a reaction system containing aniline in 1 M HCl, with continuously stirring for 1 h. After the dropping, the reaction condition was maintained for 2 h in order to complete the reaction at polymerization temperature of −5°C. After the reaction, the size of PANI particles was controlled using a ball mill and 38 μm sieve. The PANI was dedoped by controlling pH of aqueous suspension containing PANI particles to be 9.0. The particles were then filtered and washed sequentially by using distilled water, ethanol and cyclohexane in order to not only remove oligomer and excess of monomer, but also make the particle surface hydrophobic. Finally, the product was dried in a vacuum oven for 48 h at room temperature.

Chemical structure of the synthesized PANI was identified using an FT-IR (Fig. 1) and its thermal stability was determined by using TGA (Fig. 2). The PANI particles were irregular granules having laminar structures observed from SEM micrograph and the average particle size was 1.8 μm measured by FSSS (Fisher Sub-Sieve Sizer) (Fig. 3). Conductivity was obtained using two probe method to be 5×10^{-11} S/cm and dielectric constant was measured with an impedance

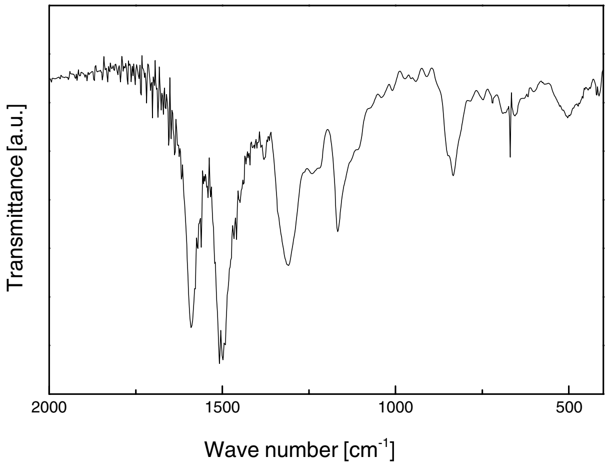


Figure 1 FT-IR spectrum of polyaniline.

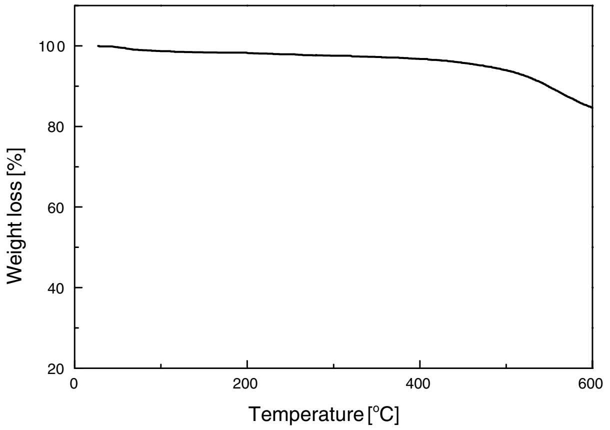


Figure 2 TGA thermodiagram of polyaniline.

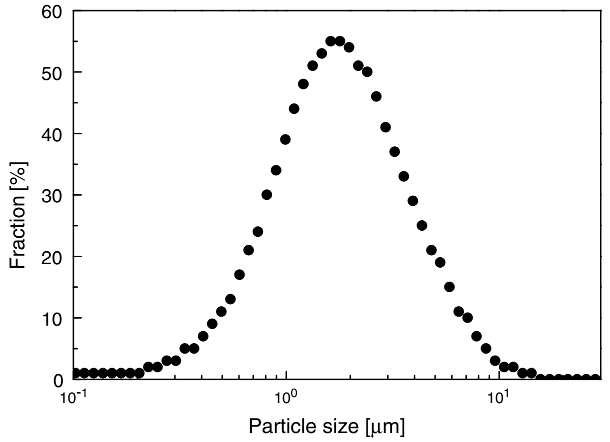


Figure 3 Particle size distribution of polyaniline.

analyzer (HP4284A) to be 5.79 at 1 kHz. Density of PANI was 1.27 g/ml measured by using a pycnometer at 25°C.

The ER fluid was prepared by dispersing the synthesized PANI particles in silicone oil by 20 vol%, in which the silicone oil was dried in a vacuum oven and stored with molecular sieve before using. The prepared ER fluids were kept in a desiccator prior to use.

Rheological properties were obtained by a rotational rheometer (Physica, MC120) with a high voltage generator using cocylindrical geometries (Z3-DIN and Z4-DIN). The ER suspension was placed between a stationary outer measuring cup and a rotating measuring bob. An electric field was then applied for five minutes in order to obtain its equilibrium state of chainlike or columnar structure before the oscillatory test. All measurements were performed at 25°C. A dynamic test was performed in a wide range of both amplitude and frequency. At first, a strain amplitude sweep test with an applied strain from 0.001 to 0.1 at two fixed frequencies (0.16 and 15.9 Hz) was carried out to determine the linear viscoelastic region. Rheological parameters such as storage and loss moduli were then measured by frequency sweep (from 0.01 to 100 Hz) at a fixed strain which was determined to be in the linear viscoelastic condition.

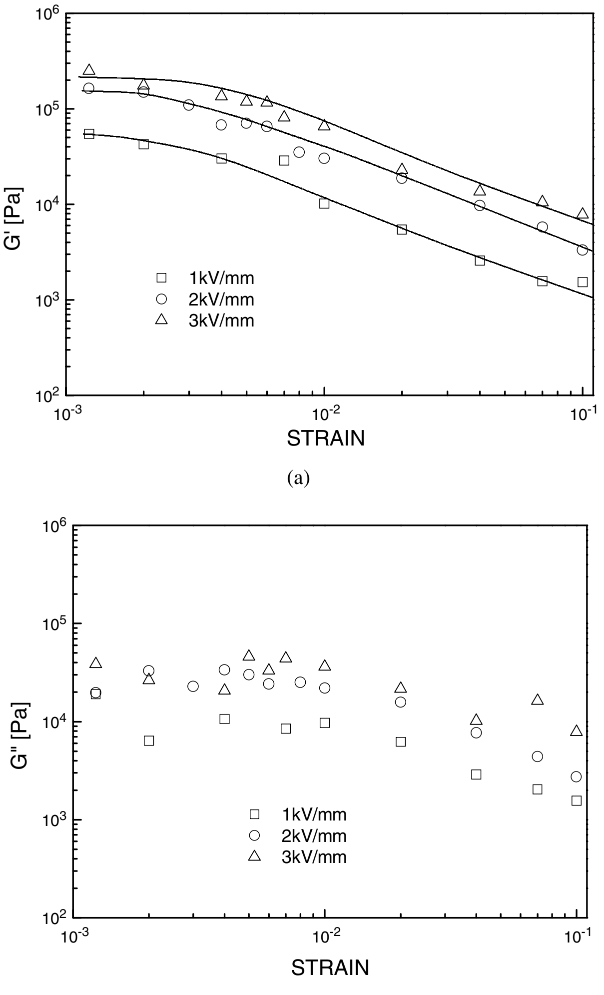
Furthermore, both creep and recovery experiments were also conducted to confirm the viscoelastic properties of the ER fluid. Shear stress was applied on the ER fluid for 700 s, and immediately removed. A strain recovery was then observed for 500 s. The initial strain γ_i was acquired just before removing the applied stress. The recovered strain γ_f was determined from the average value of strains where they were remained constant. Recovery percentage was measured from the following Equation 1.

$$\text{Recovery percentage } (\%) = \frac{\gamma_i - \gamma_f}{\gamma_i} \times 100 \qquad (1)$$

The applied shear stresses were varied from 50 to 400 Pa in the controlled shear stress mode.

3. Results and discussion

Dynamic tests by an applied oscillatory shear were conducted and adopted to study the viscoelastic properties of the solidified ER fluid under applied electric fields using semiconducting PANI based ER suspensions. Results of the strain amplitude sweep, which is a measurement of moduli as a function of sinusoidal strains at a constant frequency, are shown in Figs 4 and 5. These represent storage (G') and loss (G'') moduli of the ER fluid as a function of strain at fixed frequency of 0.16 and 15.9 Hz with different electric fields. The storage modulus of an ER fluid has previouly been found to increase with an elevation in the applied electric field strength or frequency [6]. G's are independent or slightly dependent on a low strain, and then, decreased rapidly as the strain increases. In general, the stain range in which the G' is independent of the applied strain, is defined by a linear viscoelastic region. Although this is affected by both strain and deformational frequency, the strain is a more critical condition than the frequency.



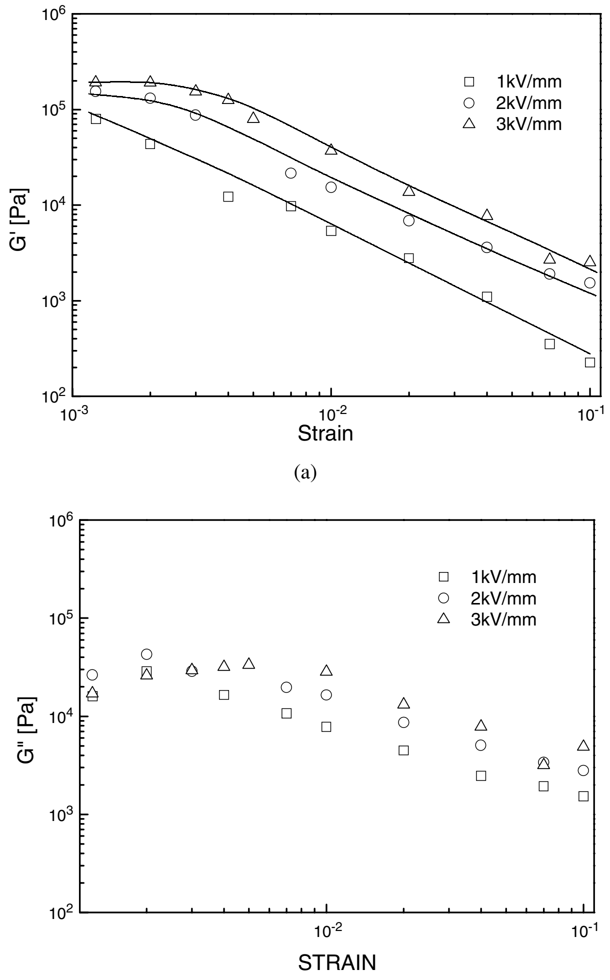
(a)

(b)

Figure 4 G' (a) and G'' (b) as a function of oscillartory strain in three different electric fields with a frequency of 0.16 Hz.

As we apply an electric field, the ER fluid becomes more elastic. Furthermore, with increasing the electric field, a linear viscoelastic region and the magnitude of G' increased, more distinguishably at 15.9 Hz than that at 0.16 Hz. These were also found in ER fluid with another PANI [45]. On the other hand, ER fluids using inorganic particle such as alumina and zeolite, showed the decrease of linear viscoelastic region with applied electric fields [8, 46]. In addition, G' is more sensitive to the electric field than G'' during the strain amplitude sweep test, and the linear viscoelastic range, therefore, was determined based on the G' measured by increasing strain at a fixed constant frequency.

From the Fig. 6 of G' and G'', we found that, as we increase the applied strain, G'' becomes larger than G', and these moduli sharply decrease together. This can be explained in terms of the elasticity of ER fluid, generated by particle chain structures in an imposed electric field. When the fibril structures of the PANI particles sustained the applied strain, the elasticity was dominant and G' being larger than G''. However, as the strain increased, the deformation initiated to distort the structure, and the structure broke down beyond a certain degree of deformation, and finally the elasticity of ER fluid could not be dominant any more.



(a)

(b)

Figure 5 G' (a) and G'' (b) as a function of oscillartory strain in various electric fields with frequency of 15.9 Hz.

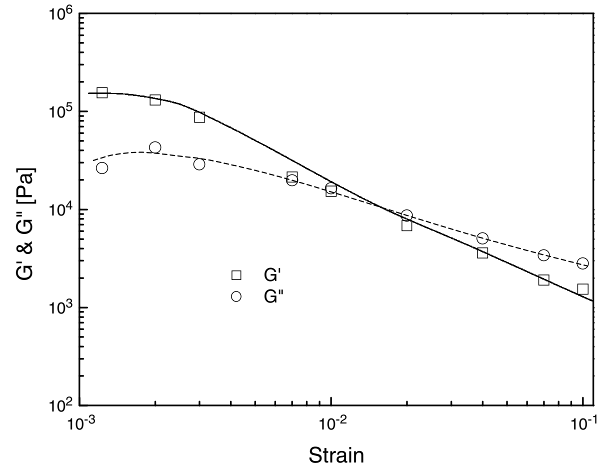
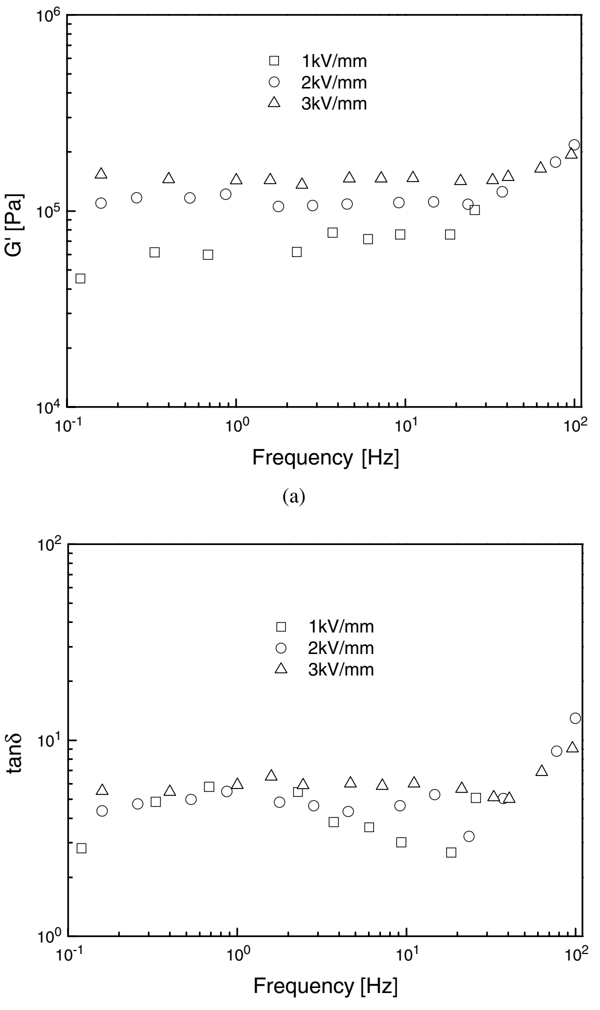


Figure 6 G' and G'' as a function of oscillartory strain in 2 kV/mm with frequency of 15.9 Hz.

Fig. 7a and b show G' and tan δ as a function of frequency for the ER fluid at a fixed strain in the linear viscoelastic region, indicating that G's are either constant or slightly increased as the deformation frequency approaches to 100 Hz. Based on this fact that G' shows a plateau over a broad range of the frequency, we can predict that an ER fluid behaves like a viscoelastic solid



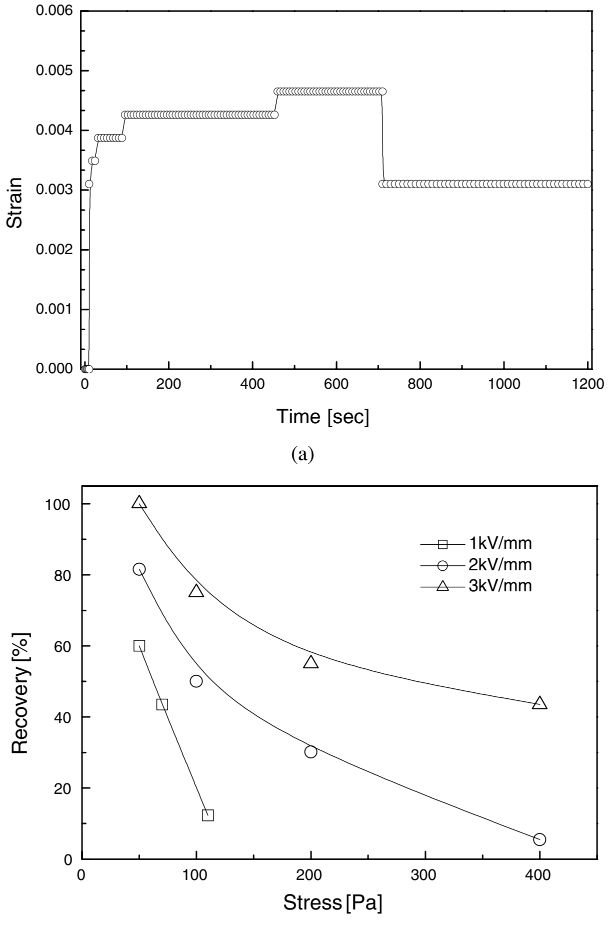
(a)

(b)

Figure 7 G' (a) and tan δ (b) as a function of frequency in three different electric fields with 0.002 of strain.

in the linear viscoelastic region due to the formation of particle chain structures, similar to a typical behavior of crosslinked rubbers, which do not relax at a given range of frequency of the strain. Since the relaxation time for a deformation is quite long, it is expected that the internal chain structures of ER fluids aren't destructible under the given condition of deformation. One can also find that G' increased with applied electric fields, whereas tan δ slightly increased with the electric field, indicating that the energy storage was somewhat dominant rather than the energy dissipation during the sinusoidal deformations. However, since there is not much difference in tan δs for each applied electric field, this explanation seems to be not confident. To confirm this analysis, we conducted creep recovery experiments for the ER fluid in various electric fields.

Fig. 8a shows the creep and recovery behavior of the PANI based ER fluid as a function of time at a stress of 200 Pa and 2 kV/mm. A recoverable strain, which is a reduced strain just after an applied stress is removed, is a measure of the elasticity of viscoelastic materials. We compared the elasticity of ER fluid at different electric fields based on the recovery percentage calculated by Equation 1 containing the recoverable strain (Fig. 8b). As the electric field increases, the strain recovery percentage increases at a fixed applied stress. Thereby, it



(a)

(b)

Figure 8 (a) Strain measured during a creep and recovery experiment as a function of time at a stress of 200 Pa and 2 kV/mm. The applied stress was removed at 700 s. (b) The strain recovery percent calculated by Equation 1 as a function of applied stresses with various electric fields.

can be confirmed that the elasticity of a solidified ER fluid with PANI, becomes superior to their viscosity as the electric field increases.

Furthermore, we applied a dimensional analysis designated for ER fluids by Parthasarathy *et al.* [6] to our dynamic moduli results of polyaniline based ER fluid. The dimensional analysis makes dimensionless rheological responses be a function of only a dimensionless frequency and, therefore, a universal relationship can be obtained by superposing each data at different electric fields. The linear viscoelastic functions such as G' and G'', and frequency become dimensionless through following equations;

$$\frac{16G'}{3\pi\varepsilon_o\varepsilon_c\beta^2E^2} = f_1\left(\frac{16\eta_c\omega}{\varepsilon_o\varepsilon_c\beta^2E^2}\right) \qquad (2)$$

$$\frac{16G''}{3\pi\varepsilon_o\varepsilon_c\beta^2E^2} = f_2\left(\frac{16\eta_c\omega}{\varepsilon_o\varepsilon_c\beta^2E^2}\right), \qquad (3)$$

where $\varepsilon_o = 8.8542 \times 10^{-12}$ F/m, $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$, ε_c is the dielectric constant of dispersing phase (silicone oil), ε_p is the dielectric constant of dispersed phase (PANI), and E is the applied electric field. These equations imply that both G' and G'' must show linear relationship with E^2 to form the universal curve [47]. For the PANI based ER fluid in this study, however, it was observed that $G' \sim E^{1.0}$ and $G'' \sim E^{0.7}$ as given in Fig. 9, and therefore, the dimensional analysis shows some deviations to the viscoelastic functions of this ER fluid. This is mainly due to the theoretical assumption of the dimensional analysis which regards dispersed particles as point-dipole spheres. Furthermore, above mentioned, the PANI particles in this study are irregular granules and have relatively low dielectric constant of 5.79, comparing with 9 of alumina, where G' and G'' of the alumina ER fluid were imposed to a universal curve through the dimensional analysis. In other words, the roughly linear electric-field dependence of the dimensional collapse of the viscoelastic behavior with frequency determined from Fig. 10 is worthy of

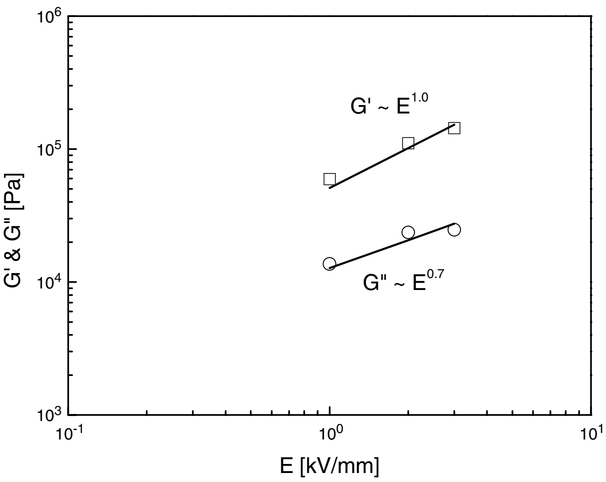


Figure 9 Plateau G' and G'' obtained from frequency sweep experiment (Fig. 6), as a function of applied electric fields.

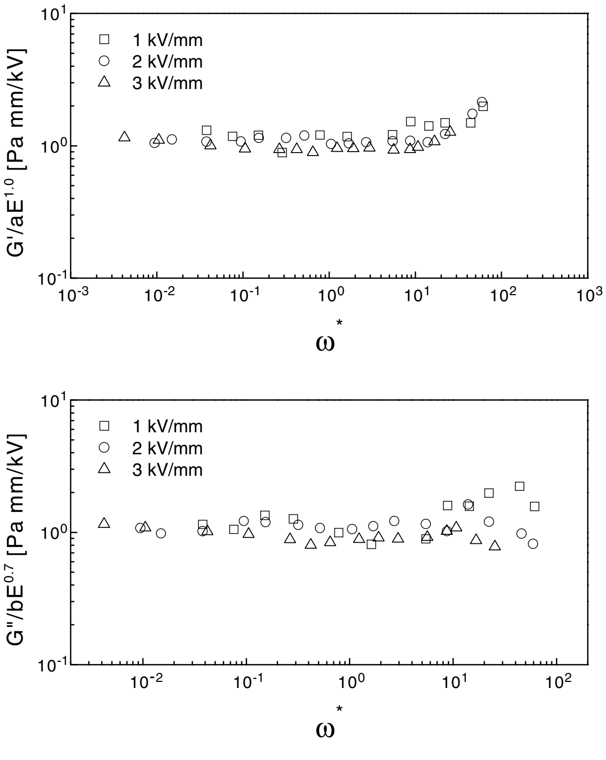


Figure 10 Universal curves of G' and G'' as a function of dimensionless frequency induced from the relationships between moduli and electric fields.

note. This suggests that the interactions between highly irregular particles are saturating even at these relatively low values of the dielectric mismatch.

4. Conclusions

The ER fluid consisted of chemically synthesized semiconductive PANI and silicone oil was investigated in this study. Semiconductive PANI suspension (20 vol%) behaved like viscoelastic solid such as a crosslinked rubber under the electric field. The higher electric field, the broader linear viscoelastic range is observed during strain amplitude sweep only at high frequency. The G' was the positive function of the electric field, and in addition, the recovery percentage obtained from the creep and recovery experiments, also increased with an applied electric field. Furthermore, the roughly linear electric-field dependence of the dimensional collapse of the viscoelastic behavior with frequency was also observed.

Acknowledgment

This study was supported by research grants from the KOSEF through the Applied Rheology Center at the Korea University, Korea.

References

1. X. P. ZHAO and J. B. YIN, *Chem. Mater.* **14** (2002) 2258.
2. J. H. PARK and O. O. PARK, *Korea-Australia Rheol. J.* **13** (2001) 13.
3. Y. AN, B. LIU and M. T. SHAW, *Int. J. Mod. Phys.* B **16** (2002) 2440.
4. T. C. HALSEY and W. TOOR, *Phys. Rev. Lett.* **65** (1990) 2820.
5. J. W. KIM, H. J. CHOI, H. G. LEE and S. B. CHOI, *J. Ind. Eng. Chem.* **7** (2001) 218.
6. M. PARTHSARATHY, K. H. AHN, B. BELONGIA and D. J. KLINGENBERG, *Int. J. Mod. Phys.* B **8** (1994) 2789.
7. D. JEON, C. PARK and K. PARK, *ibid.* B **13** (1999) 2221.
8. M. S. CHO, H. J. CHOI, I. J. CHIN and W. S. AHN, *Micropor. Mesopor. Mater.* **32** (1999) 233.
9. J. E. MARTIN, D. ADOF and T. C. HALSEY, *J. Colloid Interf. Sci.* **167** (1994) 437.
10. D. R. GAMOTA and F. E. FILISKO, *J. Rheol.* **35** (1991) 1411.
11. T. C. B. MCLEISH, T. JORDAN and M. T. SHAW, *ibid.* **35** (1991) 427.
12. G. B. THURSTON and E. B. GAERTNER, *ibid.* **35** (1991) 1327.
13. M. S. CHO, Y. J. CHOI, H. J. CHOI, S. G. KIM and M. S. JHON, *J. Molecular Liq.* **75** (1998) 13.
14. S. H. CHU, S. J. LEE and K. H. AHN, *J. Rheol.* **44** (2000) 105.
15. H. J. CHOI, M. S. CHO, K. K. KANG and W. S. AHN, *Micropor. Mesopor. Mater.* **39** (2000) 19.
16. Y. D. KIM and D. J. KLINGEBERG, *J. Colloid Interf. Sci.* **183** (1996) 568.
17. S. WU, F. ZENG and J. SHEN, *J. Appl. Polym. Sci.* **67** (1998) 2077.
18. H. BÖSE, *Int. J. Mod. Phys.* B **13** (1999) 1878.
19. H. BLOCK and J. P. KELLY, *J. Phys. D: Appl. Phys.* **21** (1988) 1661.
20. H. J. CHOI, T. W. KIM, M. S. CHO, S. G. KIM and M. S. JHON, *Eur. Polym. J.* **33** (1997) 699.
21. X. P ZHAO and X. DUAN, *Int. J. Modern Phys.* B **16** (2002) 2454.
22. A. LENGALOVA, V. PAVLINEK , P. SAHA, J. STEJSKAL, T. KITANO and O. QUADRAT, *Physica* A **321** (2003) 411.
23. H. J. CHOI, M. S. CHO and K. TO, *ibid.* A **254** (1998) 272.
24. H. J. CHOI, J. W. KIM and K. TO, *Synth. Met.* **101** (1999) 697.
25. J. TRLICA, P. SÁHA, O. QUADRAT and J. STEJSKAL, *Eur. Polym. J.* **36** (2000) 2313.
26. B. D. CHIN, Y. S. LEE and O. O. PARK, *Int. J. Mod. Phys.* B **13** (1999) 1852.
27. I. S. SIM, J. W. KIM, H. J. CHOI, C. A. KIM and M. S. JHON, *Chem. Mater.* **13** (2001) 1243.
28. J. W. GOODWIN, G. M. MARKHAM and B. VINENT, *J. Phys. Chem.* B **101** (1997) 1961.
29. J. W. KIM, F. LIU, H. J. CHOI, S. H. HONG and J. JOO, *Polymer* **44** (2003) 289.
30. J. I. SOHN, M. S. CHO, H. J. CHOI, C. A. KIM and M. S. JHON, *Macromol. Chem. Phys.* **203** (2002) 1135.
31. R. SAKURAI, H. SEE, T. SAITO, S. ASAI and M. SUMITA, *Rheol. Acta* **38** (1999) 478.
32. H. J. CHOI, J. W. KIM, S. H.YOON, R. FUJIURA, M. KOMATSU and M. S. JHON, *J. Mater. Sci. Lett.* **18** (1999) 1445.
33. S. G. KIM, H. J. CHOI and M. S. JHON, *Macromol. Chem. Phys.* **202** (2001) 521.
34. S. G. KIM, J. W. KIM, W. H. JANG, H. J. CHOI and M. S. JHON, *Polymer* **42** (2001) 5005.
35. J. TRLICA, P. SÁHA, O. QUADRAT and J. STEJSKAL, *J. Phys. D: Appl. Phys.* **33** (1999) 1773.
36. Y. H. CHO, M. S. CHO, H. J. CHOI and M. S. JHON, *Colloid Polym. Sci.* **280** (2002) 1062.
37. Y. H. LEE, C. A. KIM, W. H. JANG, H. J. CHOI and M. S. JHON, *Polymer* **42** (2001) 8277.
38. J. W. KIM, M. H. NOH, H. J. CHOI, D. C. LEE and M. S. JHON, *ibid.* **41** (2000) 1229.
39. J. W. KIM, S. G. KIM, H. J. CHOI and M. S. JHON, *Macromol. Rapid Commun.* **20** (1999) 450.
40. J. W. KIM, F. LIU and H. J. CHOI, *J. Ind. Eng. Chem.* **8** (2002) 399.
41. J. JOO, S. M. LONG, J. P. POUGET, E. J. OH, A. G. MACDIAMID and A. J. EPSTEIN, *Phys. Rev.* B **57** (1998) 9567.
42. J. STESKAL, T. SULIMENKO, J. PROKEŠ and I. SAPURINA, *Colloid Polym. Sci.* **278** (2000) 654.
43. O. QUADRAT, J. STEJSKAL, P. KRATOCHVÍL, C. KLASON, D. MCQUEEN, J. KUBÁT and P. SÁHA, *Synth. Met.* **97** (1998) 37.
44. M. LECLERC, J. GUAY and L. H. DAO, *Macromolecules* **22** (1989) 649.
45. K. KOYAMA, K. MINAGAWA, T. YOSHIDA and N. KURAMOTO, *Mod. Phys. Lett.* **8** (1994) 1563.
46. M. PARTHASARATHY and D. KLINGENBERG, *Rheol. Acta.* **34** (1995) 430.
47. H. J. CHOI, M. S. CHO, J. W. KIM, C. A. KIM and M. S. JHON, *Appl. Phys. Lett.* **78** (2001) 3806.

Received 26 August 2002
and accepted 26 September 2003