Viscoelastic Characterization of Semiconducting Dodecylbenzenesulfonic Acid Doped Polyaniline Electrorheological Suspensions

SEONG G. KIM,[1] JI W. KIM,[1] MIN S. CHO,[1] HYOUNG J. CHOI, MYUNG S. JHON[2]

[1] Department of Polymer Science and Engineering, Inha University, Inchon, 402-751, Korea

[2] Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

ABSTRACT: Dodecylbenzenesulfonic acid (DBSA)-doped polyaniline particles were synthesized via emulsion polymerization, and electrorheological (ER) fluids were prepared by dispersing the synthesized polyaniline particles in silicone oil. The viscoelastic properties of DBSA-doped polyaniline/silicone oil ER systems were examined using a vertical oscillation rheometer (VOR), which is designed for the rheological measurement of ER fluids, with a high voltage generator. Viscoelastic data obtained from the VOR were compared with those obtained from a commercial Physica rotational rheometer. The data from VOR were quite reliable in a broad range of both strain and frequency. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 108–114, 2001

Key words: electrorheological fluid; dodecylbenzensulfonic acid; polyaniline; vertical oscillation rheometer

INTRODUCTION

In general, electrorheological (ER) fluids are suspensions whose rheological properties are strongly influenced by an imposed electric field.[1] The suspensions behave like a typical fluid in the absence of an electric field (although they may be pastes or gels if mixed with a high concentration of the dispersed particles). However, under the influence of an external electric field, the shear viscosity increases drastically, and the suspensions become solidlike. Furthermore, all of the physical and mechanical property of the suspensions changes induced by the applied electric field are reversible (i.e., they disappear as soon as the electric field is removed).[2]

The rheological properties of an ER fluid vary when an electric field is imposed by forming a characteristic fibrillation structure, with the strings of particles oriented along the electric field direction. These particle structure are caused by the dielectric constant mismatch of the particles and the insulating oil. Stress is required to break the chainlike or columnar structures and initiate flow. These structures produce a yield phenomenon, and ER fluids behave as Bingham plastics. Viscoelasticity is another characteristic property of ER fluids, which arises from particle chain structure.

Initial studies on the ER phenomenon covered various wet-base suspensions, including corn starch, silica gel, and cellulose as dispersed phases.[3,4] In wet-base systems with hydrophilic particles, the particle chain structure develops by the migration of ions in the absorbed water. This

system has significant limitations in applications (e.g., thermal instability) due to the evaporation of water and corrosion.

Recently, the use of dry-base systems employing aluminosilicate,[5] carbonaceous material,[6] zeolites,[7] and polymer particles[8–15] yields rheological properties, superior to those of wet-base suspensions, for application in broad temperature ranges by inducing a dipole moment within the particles.[16] Particularly, semiconducting polymers, including sulfonated poly(styrene-co-divinylbenzene),[8] acene quinone radical polymers,[9,10] polyaniline,[11,17–20] copolyaniline,[12,13] and polymer–clay nanocomposites,[14,15] have been widely adopted as materials for dry-base, nearly anhydrous ER fluids.

In this paper, we investigated dodecylbenzenesulfonic acid (DBSA)-doped polyaniline as a potential candidate for anhydrous particles in high performance dry-base systems.

Typically, a polyaniline is chemically synthesized in an acidic, aqueous medium in which an oxidant is added.[21–23] In contrast to this chemical oxidation polymerization, we synthesized DBSA-doped polyaniline using an emulsion polymerization technique. This polymerization is carried out in nonpolar or weakly polar solvents in the presence of a functionalized protonic acid, which acts simultaneously as a surfactant (or an emulsifier) and as a protonating agent (dopant) for the resulting electrically conducting polyaniline.[24] Recently, Kim et al.[14] synthesized polyaniline–Na^+–montmorillonite clay nanocomposite particles via emulsion polymerization and observed their ER characteristics.

Both steady and dynamic shear tests have been applied to examine the rheological properties of ER fluids. Using the steady shear experiment, flow properties with a yield stress are obtained. On the other hand, in the dynamic test, viscoelastic properties [including the storage modulus (G'), loss modulus (G''), and tan δ] due to the chain structure change during deformation are obtained.

It has been reported that the stress response of an ER fluid subjected to a sinusoidal strain of small amplitude and an intermediate electric field exhibits a linear viscoelastic behavior.[25,26] The amplitude and phase angle of the stress response are dependent upon the applied electric field strengths.[26,27] However, this response becomes nonlinear with increasing strain amplitude due to the breaking of chain structures induced by the electric field. In other words, the viscoelastic

parameters of an ER suspension, in an imposed electric field, strongly depend upon the strain amplitude.[25] Jordan et al.[27] observed that G' was much greater than G'', and the suspension behaves like a linear viscoelastic material up to 4% strain for ERX-02 (Lord Corporation).

For a nonaqueous silica suspension, on the other hand, Shulman et al.[28] reported that the dependence of G' and G'' on the strain amplitude obviously shows nonlinear behavior for a wide range of frequency. This contrast seems to be relevant to the material characteristics.

Many researchers have investigated the dynamic, mechanical properties of ER fluids with various types of rheometers. The most frequently used rheometers are either a rotational Couette or parallel-plate type.[16,29–32] The Couette type is better than the parallel plate type, since it produces a uniform shear field.

In general, because sinusoidal oscillations can be used to follow viscoelastic changes with time, the most commonly measured viscoelastic material function is the complex shear modulus ($G*$). A cross-correlation analysis of the signal can provide accurate G' and G'' over a broad range of frequency and signal levels. Therefore, many measurements of the dynamic moduli have been performed.

The simplest experiment is the forced-oscillation method, which is by far the most common and versatile. It is based on driving one surface with a known periodic displacement and measuring the resulting periodic force at the surface on the other side of the gap with a sensing device. The force is proportional to the stress and the displacement is proportional to the strain. Therefore, monitoring these sinusoidal functions is equivalent to tracing the sinusoidal variation of stress and strain with time.[33,34] A general advantage of this test is that a single instrument can cover a broad frequency range, and the flow geometry induces cone-and-plate, parallel-plate, and concentric-cylinder configurations.

The VOR designed by our group can acquire the rheological parameters of ER fluids from dynamic testing by manipulating the output data recorded on an oscilloscope. In this device, the oscilloscope (connected to strain and force sensors simultaneously) represents both an input strain wave and an output force wave. Phase angle (δ), frequency (ω), maximum amplitude of strain (z_0), and force (F_0) are measured from oscilloscope data and viscoelastic parameters are obtained by calculating these parameters. This rheometer can

also control the amplitude of the strain in the range from 0.003 to 1 and the frequency in the range from 0.1 to 100 Hz.

EXPERIMENTAL

Synthesis of Polyaniline and Preparation of the ER Fluids

For the emulsion polymerization of DBSA-doped polyaniline, a solution composed of 19.52 g (0.2 mol) of aniline, 97.92 g (0.3 mol) of DBSA, and 1 L of xylene were placed together in a 2 L reactor.[24] The polymerization was then initiated by the addition of 9.36 g (0.04 mol) of ammonium peroxy-sulfate, $(NH_4)_2S_2O_8$, in 80 mL distilled water, over a period of 30 min to avoid overheating the reaction mixture. The polymerization temperature was kept at 25°C, and the total polymerization time was 24 h. The polymerization was terminated by pouring 3 L of acetone into the emulsion system, precipitating the polyaniline–DBSA complex.

A dark green powder of the synthesized polymer particles was recovered, filtered, and sequentially washed three times with 600 mL acetone, three times with 600 mL distilled water, and three more times with 600 mL acetone. After these filtering and washing procedures, the polyaniline particles were ground using a pearl mill and passed through a 38 μm sieve to control the particle size and distribution.

On the other hand, the synthesized polyaniline particle itself has a high conductivity and electrical short due to high current density occurs during ER measurement, in general if we apply it directly into an ER material. Therefore, we must decrease the conductivity of the polyaniline particles by decreasing their protonation level. Thereby, to lower the conductivity of polyaniline and make semiconducting polyaniline for ER study, we dedoped the polyaniline particles with decreasing the protonation level by increasing the pH of the aqueous medium to pH 10, using an aqueous NaOH solution.[35] The pH of the aqueous polyaniline suspension was kept constant for one day. The pH-controlled particles were again filtered and washed using distilled water, ethanol, and cyclohexane to remove both oligomer and excess monomer and to make the particle surfaces hydrophobic. Finally, the products were dried in a vacuum oven at 25°C. The conductivity of the
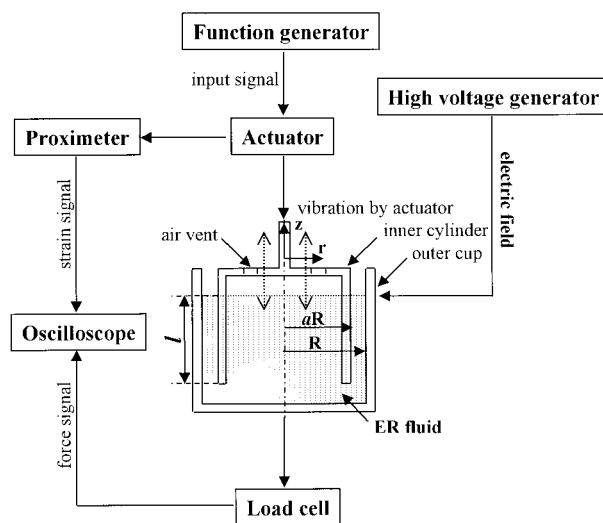

Figure 1 A schematic of the VOR.

polyaniline was measured to be 1.78×10^{-10} S/cm by the two-probe method using compressed disks.

ER fluids were then prepared by dispersing the synthesized DBSA-doped polyaniline particles in silicone oil, which was dried in a vacuum oven and stored with molecular sieves prior to use. The density and kinematic viscosity of the silicone oil at 25°C were 0.956 g/mL and 50 cS, respectively. The prepared ER fluids were stored in a desiccator prior to use and redispersed before every rheological measurement.

Dynamic Mechanical Test Using the VOR

The VOR was designed for the dynamic testing of ER fluids. As shown in Figure 1, the measuring unit of the rheometer is composed of an inner cylinder (vibrator) and an outer cup; the former is able to move up and down, while the latter is stationary. The sample is placed in this measuring unit, which is connected to a high voltage generator. On the upside of the inner cylinder, an air vent has been placed to reduce the experimental error generated by the air between the sample and the inner cylinder. Because the inside of the inner cylinder and the bottom of the cup are insulated, an electric field is applied only in the gap of measuring unit. The cylinder is attached to the actuator (speaker), the cup is placed on the load cell, and the sensors for each are connected to the channels of the oscilloscope.

The strain as a function of frequency is supplied to the speaker amplifier from a function generator. The vibrating inner cylinder deforms

the sample, and a resulting force is transferred to the cup. The input strain and output force appear on the oscilloscope screen in terms of the voltage from the proximeter and load cell, respectively.

From these input and output signals, δ, ω, z_0, and F_0 are obtained. The viscoelastic parameters (G', G'', and tan δ) can be calculated using the following equations[36]:

$$G' = \frac{F_0 \cos \delta \ln a}{2 \pi l z_0},$$

$$G'' = \frac{F_0 \sin \delta \ln a}{2 \pi l z_0}, \text{ and } \tan \delta = \frac{G''}{G'}$$

where a is the ratio of the inner cylinder wall ($r = R$), and the outer cylinder wall ($r = a$R), F_0 is the magnitude of the force that is transferred to the load cell, and l is the height of the inner cylinder.

In addition, a commercial rotational rheometer (Physica MC 120: Germany) with a high voltage generator (HVG 5000) is also used for the calibration of the VOR data with a Couette-type flow geometry. The temperature of the rotational rheometer is controlled by an oil bath (VISCO-THERM VT 100). Electric fields were applied for about 3 min before each test.

At first, we conducted a strain amplitude sweep at a frequency of 1 Hz under an electric field to determine the linear viscoelastic region. Later, the rheological properties were measured by frequency sweeps from 0.1 to 100 Hz with a strain amplitude in the linear viscoelastic region. In this measurement, both rheometers were tested under the same conditions and the data were compared.

RESULTS AND DISCUSSION

Figures 2(a) represent plots of G' and G'' vs strain amplitude at a frequency of 1 Hz and an electric field strength of 2 kV/mm for the DBSA-doped polyaniline/silicone oil ER fluid system, respectively. These measurements were conducted to determine the linear viscoelastic region of strain from the strain sweep experiment. The open squares and circles represent the data from the Physica rheometer and solid squares and circles are those from the VOR. G' obtained from the VOR give values similar to those obtained from the Physica rheometer over the entire range of strain. In the case of G'', data from the VOR in the
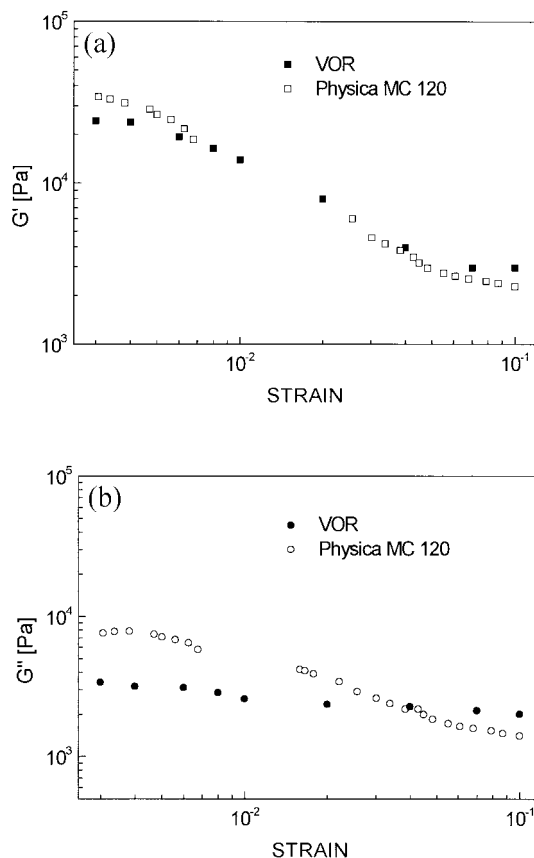

Figure 2   Comparison of (a) G' and (b) G'' as a function of strain amplitude at 1 Hz measured by both the VOR and a Physica rheometer for a 15 wt % DBSA-doped polyaniline in a silicone oil at an electric field strength of 2 kV/mm.

low strain range (e.g., linear viscoelastic region) slightly deviate from those obtained from the Physica rheometer.

Figures 3(a) and (b) show results from the frequency sweep experiment. We chose a strain of 0.004 from Figure 2 for the frequency sweep measurement, and then investigated G' and G'' as a function of the frequency, which varied from 0.1 to 100 Hz at 2 kV/mm. Similar to those obtained from the amplitude sweep experiment, the G'' data are quite different from those obtained with the Physica rheometer. Based on the fact that G' shows a plateau over a broad frequency range, we can predict that an ER fluid behaves like a viscoelastic solid in the linear viscoelastic region due to the formation of particle chain structures. However, a slight deviation, observed at high frequency, indicates that the chain structures start to break by showing the transition to nonlinear region. Despite a slight discrepancy, the data
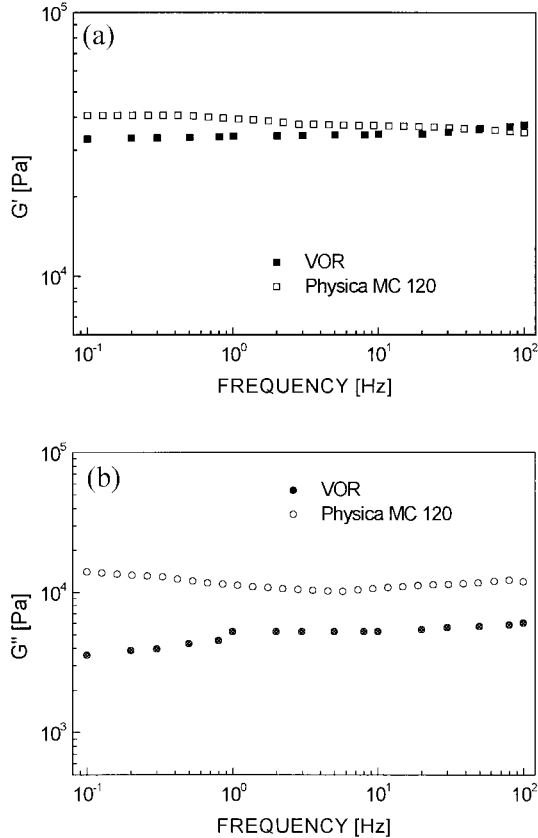
Figure 3 Comparison of (a) G' and (b) G'' as a function of frequency measured by both the VOR and a Physica rheometer for a 15 wt % DBSA-doped polyaniline in a silicone oil at an electric field strength of 2 kV/mm.

from the VOR are found to be reasonable when compared with the data obtained from the Physica rheometer for a DBSA-doped polyaniline/silicone oil ER fluid system.

Figures 4(a) and (b) show G' and G'' as a function of strain amplitude at a frequency of 1 Hz and different electric field strengths obtained using the VOR. Both G' and G'' increase with the electric field strength over the entire range of strain. In the linear viscoelastic region, the G' is larger than the G''. This can be explained by the elasticity of the ER fluid, which arises from the particle chain structures in an imposed electric field. The fibrillar structures of the suspended DBSA-doped polyaniline particles span the electrodes when an electric field is applied. Above a certain degree of stress (yield stress), the structure breaks down, and the elasticity of the ER fluid abruptly disappears.[27,28] This phenomenon can be detected by the stress waves observed from

the oscilloscope. Under an applied sinusoidal strain, the corresponding stress wave is also sinusoidal in the linear viscoelastic region, but it must be represented as the superposition of many sinusoidal waves with different frequencies in the nonlinear viscoelastic region. Panthasarathy and Klingenberg[37] explained this onset of nonlinearity as caused by a "slight rearrangement in the suspension micro-structure."

Figures 5(a) and (b) show the G' and the G'' as a function of ω at a strain of 0.004 and different electric field strengths. Both G' and G'' increase significantly with the electric field strength over a wide range of frequency. However, G' exhibits a plateau over a wide range of frequency at each electric field strength. At a high frequency range, G' increased slightly, showing a transition to a nonlinear region due to the onset of chain breaking.[38] This transition from linear to nonlinear behavior was found to depend on the oscillation frequency.
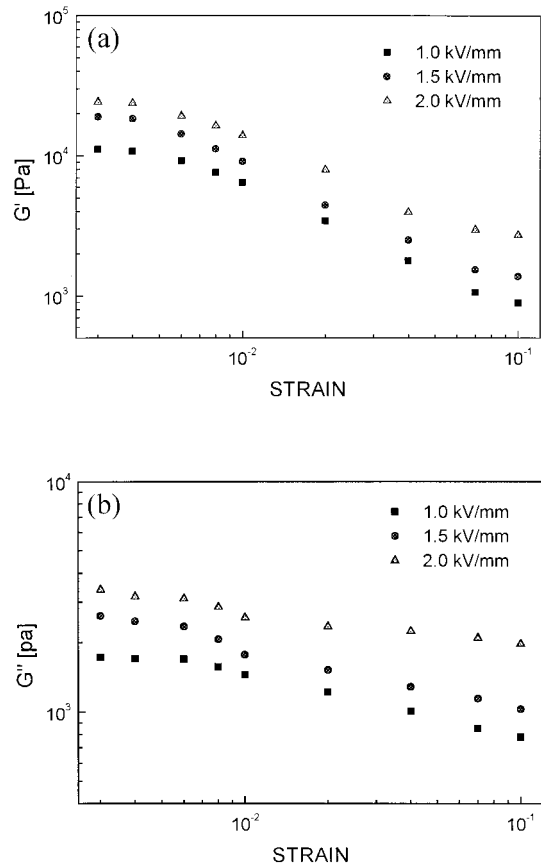

Figure 4 (a) G' and (b) G'' as a function of strain amplitude measured by the VOR for a 15 wt % DBSA-doped polyaniline in a silicone oil at different electric field strengths and a frequency of 1 Hz.
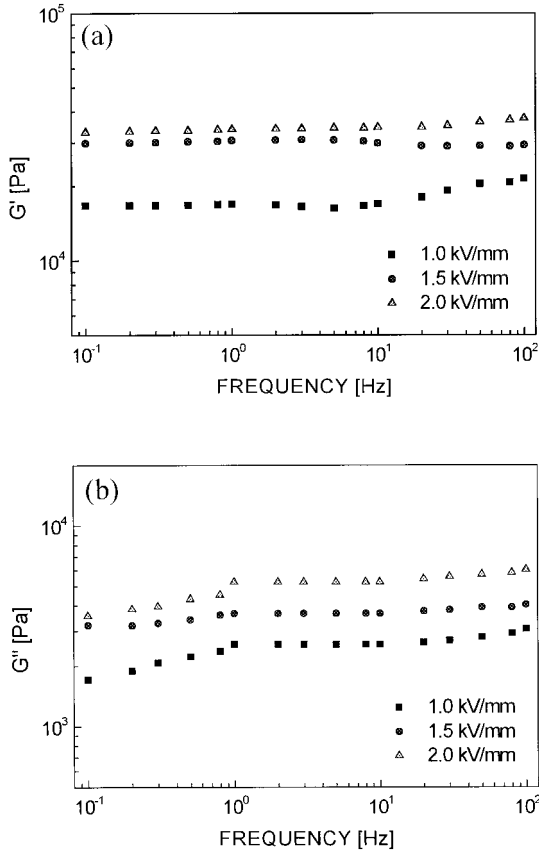
Figure 5 (a) G' and (b) G'' as a function of frequency measured by the VOR for a 15 wt % DBSA-doped polyaniline in a silicone oil at different electric field strengths and a strain of 0.004.

As the electric field strength increases, the frequency at which the chain-breaking begins to increase. The general shape of the G'' curves was similar, but the values fluctuated over a wide range of frequency. It was observed that G'' showed a more sensitive dependence in the frequency sweep than the G'.

Figure 6 represents G' and G'' as a function of strain amplitude at a frequency 1 Hz, an electric field strength of 2 kV/mm, and different particle concentrations. According to Figures 4 and 6, G' was constant and then decreased as the strain amplitude increased. As both the electric field strength and particle concentration increased, the linear viscoelastic region and the magnitude of both the storage modulus and loss modulus increased. The particle–particle interactions due to the polarization contribute to the enhancement of the dynamic moduli and the steady shear viscosity to a great extent. The polarization forces between particles increases with increasing both
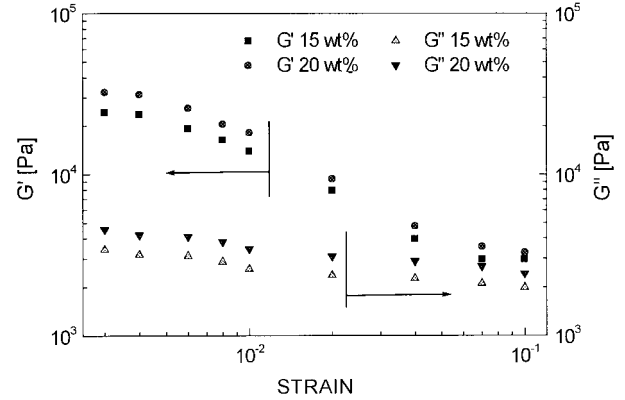

Figure 6 G' and G'' as a function of strain amplitude measured by the VOR for a DBSA-doped polyaniline in a silicone oil at different particle concentrations and an electric field strength of 2 kV/mm.

the electric field strength and particle concentration, which in turn increases both the particle chain length and the magnitude of both G' and G''.

Figure 7 represents G' and G'' as a function of frequency at a given strain of 0.004, electric field strength of 2 kV/mm, and different particle concentrations. Figures 5 and 7 indicated that the mechanical structure of the suspension was affected by both the electric field strength and particle concentration. It also showed that the structure was less affected by the shear (such as an oscillation frequency) or shear rate as both the electric field strength and particle concentration increased.

Namely, as both the applied electric field and particle concentration increased, both the elastic energy and viscous energy of the ER fluid increased
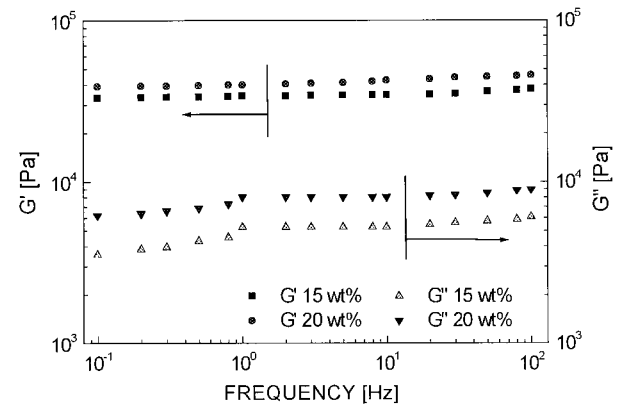

Figure 7 G' and G'' as a function of frequency measured by the VOR for a DBSA-doped polyaniline in a silicone oil at different particle concentrations and an electric field strength of 2 kV/mm.

simultaneously. However, the magnitude of G' is somewhat larger than that of G'', and G' was more affected by the electric field and particle concentration than G''. This result indicates that the elasticity of the prepared ER fluid dominates the viscosity of this fluid, and it increases with the increase of electric field strength and particle concentration.

When subjected to oscillatory frequencies, the ER fluid shows viscoelastic response under electric fields. However, it must be stressed that the driving force for chain formation is induced by electric polarization. During a cycle of chain rupture and reformation, the energy is electrically and continuously fed to the system to compensate for the viscous dissipation by the mechanical rupture of chains. In combined shear and electric fields, the part of stress in phase with the applied strain is coupled not only with energy storage due to elasticity, but also with electrical energy supply to reform the chain structure.

The designed VOR yields reliable data over a wide range of either strain or frequency, and it is found to be very useful for the dynamic mechanical analysis of ER fluid systems. In addition, DBSA-doped polyaniline/silicone oil ER fluids exhibit typical viscoelastic properties under an electric field due to chain formation induced by electric polarization between particles. Further investigation on the detailed relationship between viscoelastic behaviors of semiconductive polymer-based ER fluids and its material parameters is needed for the actual design of application-oriented ER systems.

REFERENCES

1. Klass, D. L.; Martinek, T. W. J Appl Phys 1967, 38, 67.
2. Wu, S.; Lu, S.; Shen, J. Polymer International 1996, 41, 363.
3. See, H. Korea-Australia Rheol J 1999, 11, 169.
4. Otsubo, Y.; Sekine, M.; Katayama, S. J Colloid Interface Sci 1992, 150, 324.
5. Filisko, F. E.; Radzilowski, L. H. J Rheol 1990, 34, 539.
6. Sakurai, R.; See, H.; Saito, T. J Rheol 1996, 40, 395.
7. Cho, M. S.; Choi, H. J.; Chin, I. J.; Ahn, W. S. Microporous Mesoporous Mat 1999, 32, 233.
8. Ikazaki, F.; Kawai, A.; Uchida, K.; Kawakami, T.; Sakurai, H.; Anzai, H.; Asako, Y. J Phys D Appl Phys 1998, 31, 336.
9. Block, H.; Kelly, J. P.; Qin, A.; Watson, T. Langmuir 1990, 6, 6.
10. Choi, H. J.; Cho, M. S.; Jhon, M. S. Int J Modern Phys B 1999, 13, 1901.
11. Choi, H. J.; Kim, T. W.; Cho, M. S.; Kim, S. G.; Jhon, M. S. Eur Polym J 1997, 33, 699.
12. Cho, M. S.; Kim, T. W.; Choi, H. J.; Jhon, M. S. J Mater Sci Lett 1997, 16, 672.
13. Cho, M. S.; Kim, T. W.; Choi, H. J.; Jhon, M. S. J Macromol Sci Pure Appl Chem 1997, A34, 901.
14. Kim, J. W.; Kim, S. G.; Choi, H. J.; Jhon, M. S. Macromol Rapid Commun 1999, 20, 450.
15. Choi, H. J.; Kim, J. W.; Noh, M. H.; Lee, D. C.; Suh, M. S.; Shin, M. J.; Jhon, M. S. J Mater Sci Lett 1999, 18, 1505.
16. Xu, Y.; Liang, R. J Rheol 1991, 35, 1355.
17. Block, H.; Kelly, J. P. J Phys D Appl Phys 1988, 21, 1661.
18. Block, H.; Chapples, J.; Watson, T. UK Patent Application 1990, 8908825.6.
19. Gow, J. C.; Zukoski, C. F. J Colloid Interface Sci 1990, 136, 175.
20. Block, H.; Kelly, J. P.; Watson, T. High Value Polymers Ed: Fawcett, A. H. RSC Special Pub No, 1991, 87, 151.
21. Angelopoulos, M.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. Synth Met 1987, 21, 21.
22. Chinag, J. C.; Richter, A. F.; Epstein, A. J. Synth Met 1987, 18, 285.
23. Wei, Y.; Tang, X.; Sun, Y. J Polym Sci A Polym Chem 1987, 27, 2385.
24. Österholm, J.; Cao, Y.; Klavetter, F.; Smith, P. Polymer 1992, 35, 2902.
25. Lee, Y. S.; Park, O. O. Nihon Reoroji Gakkaishi 1996, 24(2), 57.
26. Gamota, D. R.; Filisko, F. E. J Rheol 1991, 35(7), 1411.
27. Jordan, T. C.; Shaw, M. T.; Mcleish, T. C. B. J Rheol 1992, 36(3), 441.
28. Shulman, Z. P.; Korobko, E. V.; Yanovskii, Y. G. J Non-Newtonian Fluid Mech 1989, 33, 181.
29. Gamota, D. R.; Filisko, F. E. J Rheol 1991, 35, 399.
30. Yen, W. S.; Achorn, P. J. J Rheol 1991, 35, 1375.
31. Otsubo, Y.; Sekine, M.; Katayama, S. J Rheol 1992, 36, 479.
32. Otsubo, Y.; Edamura, K. J Colloid Interface Sci 1995, 172, 530.
33. Aklonis, J. J.; Macknight, W. J. Introduction to Polymer Viscoelasticity; John Wiley & Sons: New York, 1983; p. 13.
34. Ramos, A. R.; Cohen, R. E. Polym Eng Sci 1977, 18, 639.
35. Lee, J. H.; Cho, M. S.; Choi, H. J.; Jhon, M. S. Colloid Polym Sci 1999, 277, 73.
36. Cho, M. S.; Choi, Y. J.; Choi, H. J.; Kim, S. G.; Jhon, M. S. J Mol Liq 1998, 75, 13.
37. Parthasarathy, M.; Klingenberg, D. J. Rheol Acta 1995, 34, 417.
38. Chin, B. D.; Lee, Y. S.; Park, O. O. J Colloid Interface Sci 1998, 201, 172.