Electrorheological Properties of Suspension of Diphenyldiacetylene Annealed Under Elevated Pressure

INTRODUCTION

Electrorheological (ER) fluids display dramatic changes in their viscosity when subjected to a large electric field. They were first discovered by Winslow in the 1940s and the phenomenon sometimes bears his name.[1] The fluids generally consist of micronmeter-size particles suspended in a dielectric liquid. The particles strongly polarize in the presence of an electric field. It has been observed that the characteristic chainlike structure results in the ER fluids.[2] The electric field induces a dipole moment on the suspended particles that subsequently form chains and energy is required to break them.

It is well known that the conductivity of wet particles is ionic and ER active.[3,4] However, the use of the moist fluids is limited to a low-temperature range because of their large conductivity arising from mobile ions at high temperature. Recently, dry suspension based on conducting material such as poly-*p*-phenylene-absorbed $CuCl_2$ showed the high-temperature working limit to be at least 100°C.[5]

In a previous article, we synthesized a unique class of conjugated compound composed of the derivative of a condensed polycyclic aromatic compound with a phenyl group and a diphenyldiacetylene oligomer by the annealing of diphenyldiacetylene under elevated pressure.[6] The dc conductivity of the compound increased from below 10^{-15} to 10 S cm^{-1} with increasing annealing pressure.[7] The conduction of this compound was electronic. It is expected that the suspension of the conjugated compound will increase the shear stress under the electric field and decrease the current density under high temperature. In this article, we report the ER properties of our newly created conjugated compound (pressure-annealed diphenyldiacetylene)-based suspension.

EXPERIMENTAL

Materials

The conjugated compound was made by reaction of diphenyldiacetylene under elevated pressure. The reaction was carried out using a piston cylinder apparatus in the annealing pressure of 0.1–1.3 MPa at 210°C.[5] After crushing using a mortar, the compound was made into a particle. It was observed that the particle had a dispersed range of size from 20 to 200 μm by scanning electron micrography. The particles of 40 wt % were then dispersed in silicone oil with a kinetic viscosity of 20 cSt (Shinetsu Chemical Co.) as a suspension of pressure-annealed diphenyldiacetylene.

Electrorheological Properties

The ER properties of the suspension were examined by using a concentric cylinder rheometer (Iwamoto Seisakusho Co.). Figure 1 shows a schematic diagram of the electrified apparatus. To apply the large electric field strength across the concentric cylinders, each cylinder was insulated from the rest of the rheometer. The inner cylinder has an outer diameter of 16 mm and height of 30 mm. The outer cylinder has an inner diameter of 18 mm and height of 45 mm. The annual gap is 1 mm, making the electric-field strength across the gap. The electric-field strength was applied to the gap by grounding the outer cylinder and connecting the inner cylinder to a high-voltage source. A high-voltage power supply (Spellman High Voltage Electronics Corp.) was used to generate the electric-field strength of 3–3.5 kV/mm (dc). An ammeter was placed in series to monitor the current. A suspension was loaded into the rheometer, and the electric field and shear rate were applied. The shear stress was then measured. The current density was obtained at a shear rate of 0.

Electrical Properties

The conductivity of the pressure-annealed diphenyldiacetylene was investigated with a DuPont 2970 dielectric analyzer. The experiments were carried out at room temperature. Specimens in particle form were used for the measurement of conductivity. The powdered specimen was compressed between the single-surface module and sensor at a pressure of 1.72 MPa and a sinusoidal voltage was applied. The conductivity is divided into a frequency-independent contribution and a frequency-dependent con-

Journal of Applied Polymer Science, Vol. 53, 1393–1396 (1994)

CCC 0021-8995/94/101393-04

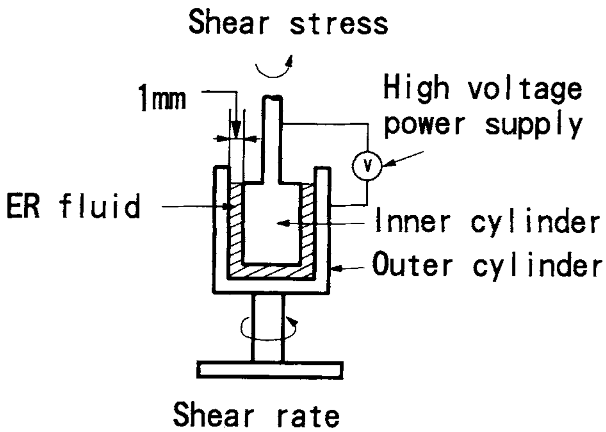

Figure 1 Schematic diagram of the electrified rheometer apparatus.

ductivity. The dc conductivity was obtained from the frequency-independent contribution.[7]

RESULTS AND DISCUSSION

Figure 2 presents photomicrographs of the suspension of the pressure-annealed diphenyldiacetylene subjected to an electric-field strength of 0 and 2.3 kV/mm, respectively. The photomicrographs were taken using the microscope. The top and bottom regions of the photographs are electrodes employed to generate the electric field in the suspension. Figure 2(a) shows the random structure of the suspension when the electric-field strength is not generated between the electrodes. Figure 2(b) shows the dramatic change in the structure of the suspension upon de-

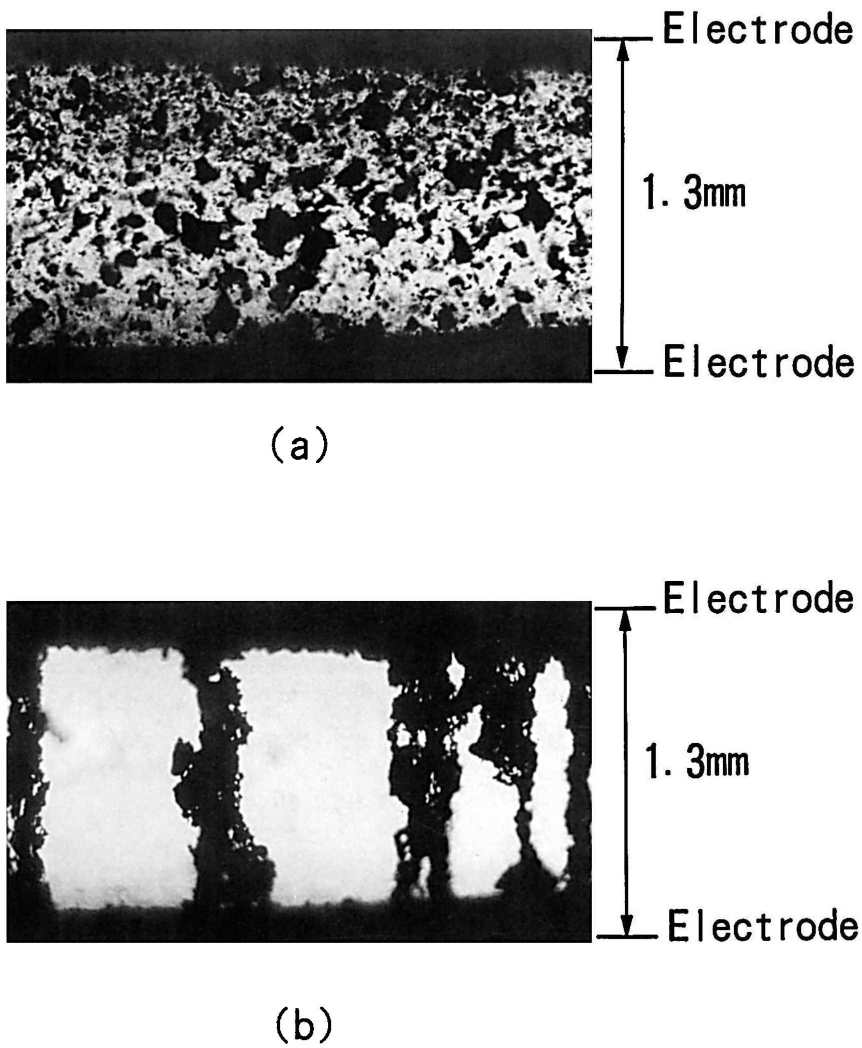

Figure 2 Effect of electric field on particle arrangement in an ER fluid: (a) no field; (b) electric-field strength (dc): 2.3 kV/mm.

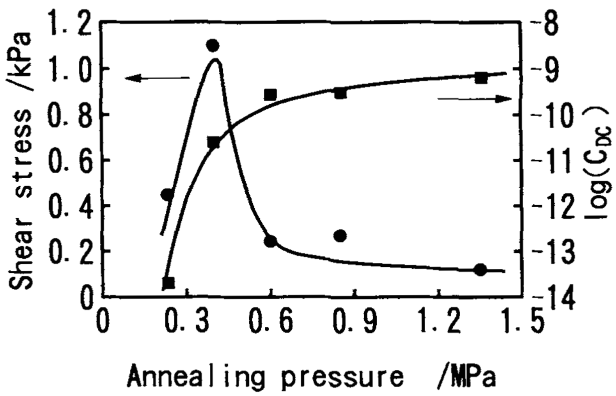

Figure 3 Annealing pressure dependence of shear stress and dc conductivity C_{DC} (shear rate: 13–15 s^{-1}; electric field: 3–3.5 kV/mm).

veloping the electric-field strength between the electrodes of 2.3 kV/mm. In the suspension, the particles orient and a chainlike structure is formed. We found that the suspension has an ER effect.

Figure 3 shows a typical evolution of the shear stress of the suspension of pressure-annealed diphenyldiacetylene vs. annealing pressure at an electric-field strength of 3–3.5 kV/mm and a shear rate of 13–15 s^{-1}. The shear stress of the ER fluid at an electric field of 0 was 10–20 Pa. The shear stress shows a maximum value at the annealing pressure of 0.41 MPa. In the same figure, it is indicated that the dc conductivity of the pressure-annealed diphenyldiacetylene increases from 10^{-13} to 10^{-9} S cm^{-1} with an increase of annealing pressure. The strength of the ER fluid should be equal to the polarization force (dipole–dipole interaction). In the presence of the electric field, the conductivity of the semiconductive particles of the pressure-annealed diphenyldiacetylene provides a polarization force to form a fibrous structure along the field

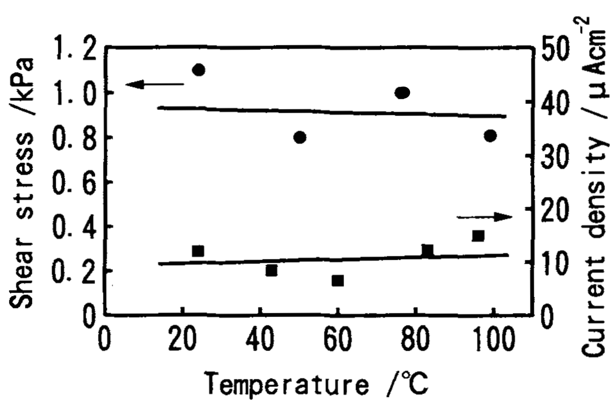

Figure 4 Shear stress and current density as a function of temperature (shear stress: 15 s^{-1}; electric-field strength: 3.5 kV/mm).

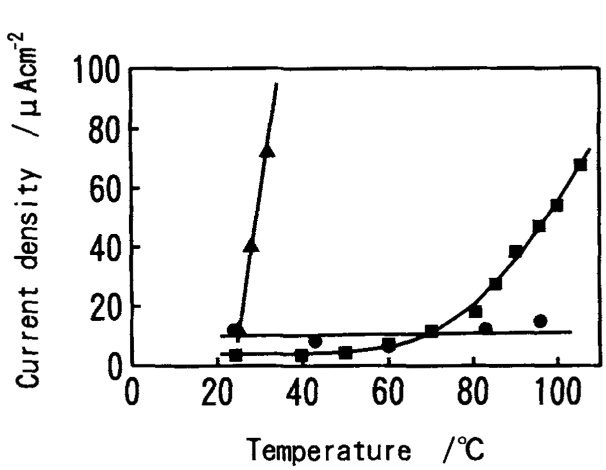

Figure 5 Current density of various ER fluids as a function of temperature (electric-field strength: 3–3.5 kV/mm): (●) suspension of pressure-annealed diphenyldiacetylene (0.41 MPa); (■) suspension of poly-*p*-phenylene-absorbed $CuCl_2$ of 0.21 wt %; (▲) suspension of poly(methacrylic acid) sodium salt containing 11.2 wt % water.

direction. It is considered that there is a conductivity in which the polarization force of the semiconductive particles is maximized.

The temperature dependence of the shear stress and current density for 3.5 kV/mm are shown in Figure 4. The shear stress is 0.8–1.1 kPa and the variation of the shear stress with temperature is small. The current density is 8–15 A cm^{-2} in the temperature range of 23–100°C and is approximately independent of temperature. Figure 5 shows the temperature dependence of the current density of various ER fluids.[4,5,8] We found that the current density of the ER fluid of the pressure-annealed diphenyldiacetylene at temperatures above 70°C was low compared with those of poly-*p*-phenylene-absorbed $CuCl_2$ of 0.21 wt % and that poly(methacrylic acid) sodium salt contained water of 11.2 wt %. It seems that the low current density of the ER fluid composed of the pressure-annealed diphenyldiacetylene at high temperature is attributed to the dry suspension based on semiconducting materials that are made of condensed polycyclic aromatic structure of the conjugated double bond with π-electrons.

CONCLUSION

The electrorheological (ER) effect of the suspension of the pressure-annealed diphenyldiacetylene showed a maximum at the annealing pressure of 0.41 MPa. The current density of the suspension above 70°C was low compared with those of poly-*p*-phenylene-absorbed $CuCl_2$ and poly(methacrylic acid) sodium salt containing water.

REFERENCES

1. W. M. Winslow, *J. Appl. Phys.*, **20,** 1137 (1949).
2. J. C. Hill and H. V. Steenkiste, *J. Appl. Phys.*, **70,** 1207 (1991).
3. Y. Asako, I. Okada, M. Aoki, S. Ono, and M. Kobayashi, *J. Soc. Rheol. Jpn.*, **20,** 61 (1992).
4. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *Jpn. J. Polym. Sci. Technol.*, **49,** 393 (1992).
5. T. Shiga, M. Fujimoto, Y. Hirose, A. Okada, and T. Kurauchi, *J. Soc. Rheol. Jpn.*, **20,** 85 (1992).
6. Y. Kojima, M. Tsuji, T. Matsuoka, and H. Takahashi, *J. Polym. Sci. Polym. Chem.*, to appear.
7. Y. Kojima, T. Matsuoka, and H. Takahashi, to appear.
8. M. Fujimoto, T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, in *21th Annual Meeting of Union of Chemistry-related Science in Chubu Area, Japan,* Preprint, 1993, p. 347.

YOSHITSUGU KOJIMA
TAKAAKI MATSUOKA
HIDEROH TAKAHASHI

Toyota Central Research and
Development Labs, Inc.
Nagakute-cho, Aichi-gun,
Aichi 480-11, Japan