[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 4, No. 2 (1994)

제올라이트 분말을 기본 재료로한 전기유변유체의 전기 및 유변학적 특성

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The electrical and rheological properties of zeolite based electrorheological (ER) Fluids

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초 록 제올라이트 분말을 기본재료로 하는 전기유변유체의 전기및 유변학적 특성이 연구되었다. 전기장 인가시 높은 한계응력을 얻기 위하여 비교적 유전상수가 큰 5종류의 유전유체를 선택하여 제올라이트 분말과 혼합하여 전기유변유체를 준비하였다. Couette형 rheometer를 이용하여 유변유체의 한계응력을 인가된 전기장및 온도의 함수로서 측정하였다. 이중 chlorinated hydrocarbon oil과 제올라이트 분말을 혼합한 전기유변유체의 한계응력은 6KPa(E=4KV/mm, T=25℃)로서 최대치를 기록하였다. 측정된 한계응력은 온도가 상승하면 점차 감소하는 반면 전류밀도는 온도에 따라 증가하였다. 전류밀도에 대한 Arrhenius 그라프에서 전기전도에 대한 활성화 에너지는 약 0.7eV였으며 이는 제올라이트 분말에 포함된 Na^+ 이온의 확산에 기인하는 것으로 분석되었다.

Abstract The electrical and rheological properties of zeolite based electrorheological (ER) fluids were reported. The ER fluids were constructed by mixing zeolite powder with five different dielectric oils. Yield stresses of the fluids were measured on the Couette cell type rheometer as a function of electric fields, particle concetrations, and temperatures. The maximum stress of 6kPa was observed from the zeolite-chlorinated hydrocarbon oil based ER fluid at 25℃ and at 4kV. The yield stress decreased as temperature increased. The current density increased with increasing temperature which was caused by the dissociation of sodium ions from a zeolite molecule. Arrhenius plot on the current density showed that the activation energy for the dissociation of sodium ions was about 0.7eV.

1. Introduction

In 1947, W.M. Winslow first reported the phenomenon of electrorheology (ER) which means the rheology of fluids modified by the imposition of electric fields[1]. A flood of ER fluids constructed with various particle phases whose sizes are within 0.1 and 5㎛, and dielectric oils were discovered thereafter[2-5]. With the discoveries of new ER fluids, many experimental and theoretical work on ER effect give rise to the empirical conclusion in that the higher the dielectric constant of a particle phase, the stronger the ER effect of the fluid[9]. After the report by Flisko et al. in 1988[10], zeolite powders have been a good candidate for a particle phase in constructing an electrorheological (ER) fluid. Since a zeolite exhibits a comparably high dielectric constant, a zeolite based ER fluid has capabilites to show relatively high shear strength. Other advantages such as easy availability, non-toxicity, and stability enable a zeolite to be widely studied for the ER fluid as a particle phase. However, the efficient study of zeolite based ER fluids still faces a number of technical problems, the main one being the absence of a clear understanding of the mechanism of the ER effect in the fluids.

Generally a zeolite has 3-dimensional framework structures consisting of linked SiO_4^{4-} and AlO_4^{5-} tetrahedra, and their surrounding channels which are constructed with alkaline or alkaline earth metals and water molecules. The maximum amount of water a zeolite molecule can contain is 23 Wt%. Upon heating temperatures and time, one can control the amount of water in a zeolite molecule, which is believed to be important for the strength of a zeolite based ER fluid. However, it is quite difficult to handle the dried zeolite during the process to prepare ER fluids since a zeolite is a very strong water absorbant.

In this report, we describe the maximum strengths and weak points of various ER fluids consisting of a zeolite and various dielectric oils including silicone oil, mineral oil, dioctylphthalate(DOP), chlorinated hydrocarbon oil dodecylalclhol and ethyleneglycol. Also expressed are the change of strengths as a function of temperature as well as the concentration of a particle phase and applied electric fields.

2. Experiments

Zeolite 3125 from Sigma chemicals Co., whose average particle sizes are about 2㎛, were employed in the present study. As received zeolite 3125 powder was completely dried at 500℃ for 10 hours. It is assumed that the ER fluid containing dried zeolite be non-aqueous although the zeolite may absorb some amount of water during the process to prepare an ER fluid. Zeolite based ER fluids were prepared by spreading the dried zeolite 3125 particle into a continuous fluid such as mineral oil, chlorinated hydrocarbon oil, silicone oil, dioctylphthalate (DOP), ehtyleneglycol (EG), and dodecylalcohol. These oils were chosen because they have comparably high boiling points and exhibit various dielectric constants from 2.2 (for mineral oil) to 37.0 (for ethyleneglycol). The long range of dielectric constants of oils were expected to show an important clue of the dependence of those on the strength of the ER effect. The sources and properties of these oils are summarized in Table 1. The concenrations of particle phases in various ER fluids were in the range of 30-45Wt%.

Table 1. Physical properties of oils

Oils	Dielectric constant(ε)	Viscosity (mPa.sec)	Water content	Density (g/cm^3)	Boiling point (C)	Maker
Silicone oil	2.6	52.8	100ppm	0.96	–	Dow corning Corp.
Chlorinated hydrocarbon oil	7.2	55	100-200ppm	0.90	–	Dover chemical Co.
Dioctyl phthalate	5.2	71.2	50~100ppm	1.0	–	High Energy Corp.
Ethylene Glycol	37.0	17.3	0.05Wt%	1.11	198	Fisher Scientific
Dodecyl alcohol	9.0	20	–	0.83	259	Fisher Scientific
Mineral oil	2.2	50	100ppm	0.86	138*	Amoco oil Co.

* Flash point

The strength measurements were conducted on Physica Rheometer made by Physica Inc., in a mode of controlled shear stress at the rate of 2 Pa/sec. The main principle of this rheometer is to adopt the Couette cell which consists of the stationary outer measuring cup and the rotating bob as shown in Figure 1. The gap between the bob and the cup is 1 mm, and the volume of the ER fluid to be tested each time is 5 ml. The point where the inside cylindrical electrode (e.g., the bob) starts to rotate was taken as a yield stress τ_0. Current density was measured uner applied electric field by using a digital volt meter (DVM) at a given temperature and a given electric field.

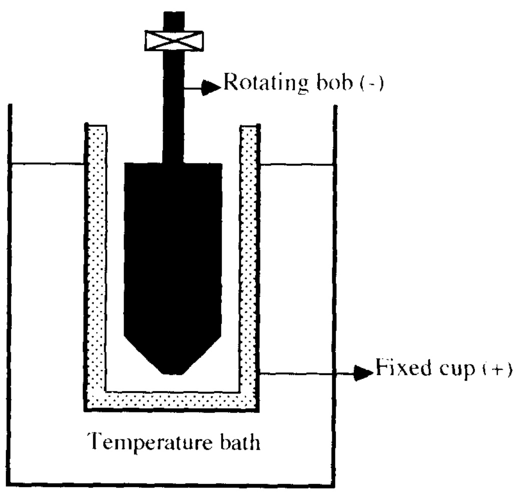

Fig. 1. Schematic diagram of the Couette cell type rotating rheometer.

3. Results and Discussions

The yield stresses of various zeolite based ER fluids at 25℃ and at given particle concentrations are summarized in Table 2. The yield stresses of most ER fluids in Table 2 are low for practical applications such as automatic clutches, engine mounts and vibration damping materials. The maximum yield stress is about 6 kPa which was obtained from the 45Wt% ER fluid constructed with the zeolite and appropriate amount of chlorinated hydrocarbon oil at 25℃. This results is quite encouraging for practical application, however, as temperature is increased the strength decreases at the same applied electric field as shown in Figure 2. Although their intrinsic yield stresses are different as shown in Table 1, same trend was obtained from zeolite based ER fluids constructed with different oils we have studied. Conductivity and current density of ER fluids are expected to be important factors to affect the strength of an ER fluid. As shown in Figure 3, current density of the zeolite-silicon oil

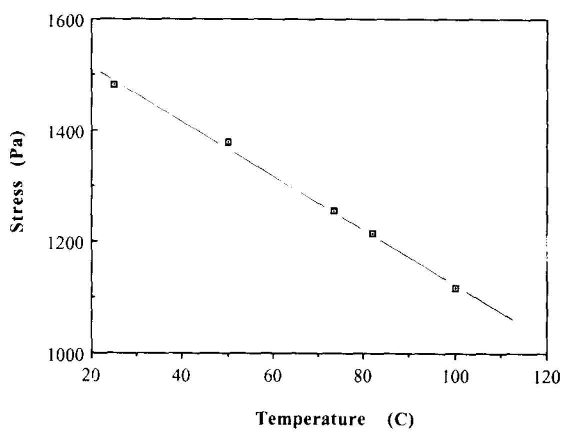

Fig. 2. The dependence of yield stresses on temperature for the ER fluid constructed with zeolite and chlorinated hydrocarbon oil(at 2kV/mm and 45Wt %).

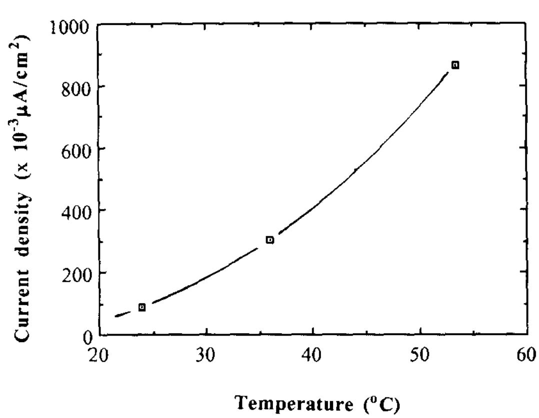

Fig. 3. The dependence of current density on temperature for the ER fluid constructed with zeolite and silicone oil (at 1 kV/mm and 40 Wt%).

Table. 2. Maximum stresses of zeolite based ER fluids

System	Concentration (Wt%)	Temperature (℃)	Electric field (kV/mm)	Maximum Stress (Pa)
Zeolite+Chlorinated hydrocarbon oil	37	25	4	2924
Zeolite+Chlorinated hydrocarbon oil	42	25	4	4000
Zeolite+Chlorinated hydrocarbon oil	45	25	4	>6000
Zeolite+Ethyleneglycol	45	25	–	–
Zeolite+Dodecylacolhol	45	25	–	–
Zeolite+Dioctyl-phthalate	45	25	6	2662
Zeolite+Mineral oil	40	25	3	568
Zeolite+Silicone oil	45	25	4.5	3100
Zeolite+Silicone oil	54	25	4.5	4000

ER fluid increases as temperature is increased, and this result was investigated for another zeolite based ER fluids consisting of differen oils. Concerning above results, the strength decrease in the zeolite based ER fluids at higher temperature can be explained as follows: The dielectric constant of a zeolite powder increases with increasing temperature according to the following expression

$$k_p = k_{p_0} \exp(-Q_p/RT) \qquad (1)$$

where k_{p_0} is the dielectric constant of zeolite at 0 K and Q_p is the activation energy. The strength of an ER fluid is expressed as

$$\tau = A k_f \beta^2 E^2 \qquad (2)$$

where A, k_f and E represent a geometry related constant, the dielectric constant of continuous fluid and external electric field, respectively. β is given as

$$\beta = (k_p - k_f)/(k_p + 2k_f) \qquad (3)$$

Therefore the maximum value of β is 1 when k_p is very large compared with k_f. From equations (1)-(3), one can find that the strength of an ER fluid increases with increasing temperature when the fluid is completely insulating. However, the situation becomes complicated if the fluid is not insulating. As shown in Figure 4a where no current flows, two adjacent particles attract each other by attraction force originated from the positive and negative charges distributed on the surfaces of the particles. Once current flows the number of bound charge on each surface is reduced since some part of charge becomes free to carry the current (see Figure 4b). Therefore, net attraction

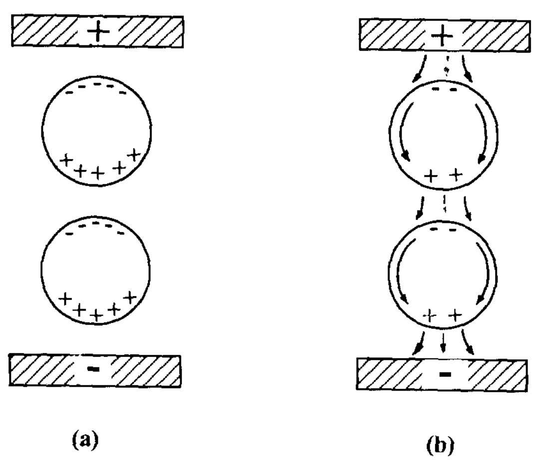

Fig. 4. Charge distribution on the surface of zeolite particles in the case of (a) insulating and (b) conducting.

force between two particles decreases with increasing current density, which leads to the strength decrease in the ER fluid.

The current density of the zeolite-silicone oil based ER fluid increases exponentially with increasing the applied electric field, as shwon in Figure 5. Dissociation reaction of sodium ions in a zeolite molecule is assumed to be the reason. According to the assumption, it is expected that the current density increases faster at higher temperature since the dissociation reaction of sodium ions from a zeolite molecule becomes easier. Consequently, at higher temperature the maximum of applied electric field on a zeolite based ER fluid is lowered, so is the strength.

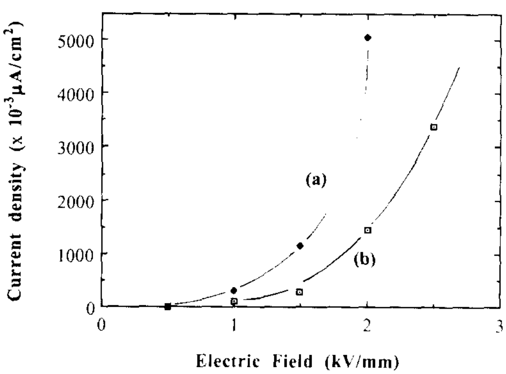

Fig. 5. The dependence of current density on electric field for the ER fluid constructed with 40 Wt% zeolite and silicone oil at(a) 36℃ and (b) 24℃.

Figure 6 shows the increasing trend in current density with increasing time under the electric field at 25℃. At 0.5kV, the current density increased about 70 times within 30 minutes after applying electric field. Generally the same trend was observed at 1.0kV, but the current density increased faster than what it did at 0.5kV. These results strongly suggest that the dissociation of sodium ions from a zeolite molecule occurs even at room temperature under the electric field, and the stronger the electric field the faster the dissociation reaction. The activation energy for the dissociation reaction of a sodium cation from a zeolite molecule is obtained from the slope in Figure 7. The activation energy of about 0.7 eV is rather small, therefore, it is possible for sodium ion to be dissociated from a zeolite molecule even at room temperature.

The concentration of a particle phase is another imporant factor to affect the strength of a zeolite based ER fluid. Figure 8 clearly shows that the strength of zeolite based ER fluids increases with increasing the concentration of the particle phase. Uejima et. al.[11] reported that the strength of an ER fluid increases with increasing the concentration of a

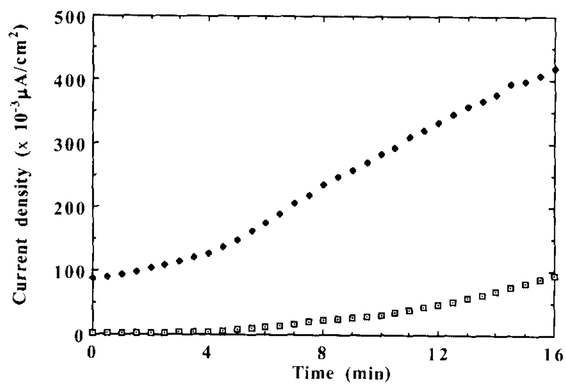

Fig. 6. The dependence of current density on time for the ER fluid constructed with zeolite and silicone oil(at 25℃ and 40Wt%).

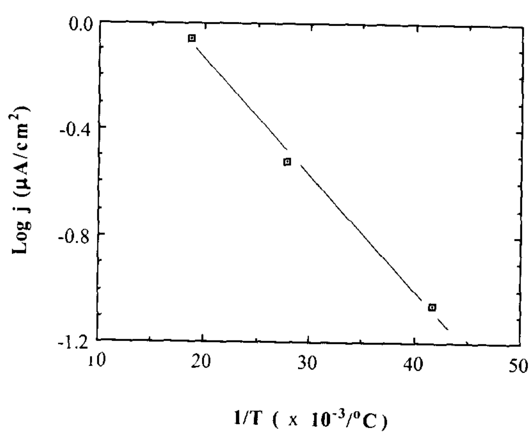

Fig. 7. Arrhenius plot of current density (j) for the ER fluid constructed with 40Wt% zeolite and silicone oil(at 1 kV/mm and 40Wt%).

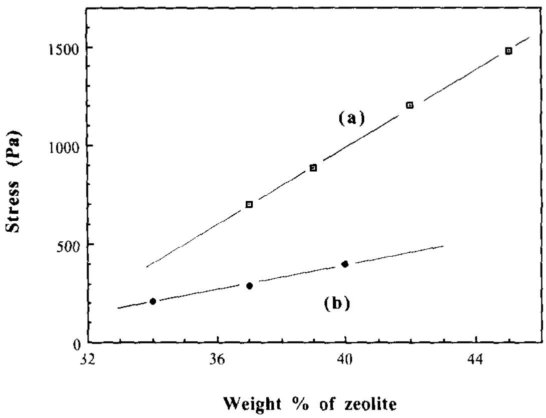

Fig. 8. The dependence of yield stresses on the weight % of zeolite for (a) zeolite+chlorinated hydrocarbon oil and (b) zeolite+mineral oil(at 1 kV/mm and 25℃).

particle phase before it reaches to maximum, and it shows a plateau afterwards. The plateau is not shown in Figure 8 since the most concentrated ER fluid was prepared to be still pourable in our experiments.

4. Summary and Conclusions

The strength of the zeolite based ER fluid increased with increasing the concentration of the zeolite which is consistent with the results reported by the other groups 6(a), 8(b), 9(a). Among many candidates studied in the present study, the ER fluid constructed with a zeolite and chlorinated hydrocarbon oil as particle phase and continuous phase respectively, showed the maximum strength as high as 6 kPa at 25℃ when the particle phase becomes 45 Wt% in the fluid. However, the strength of the ER fluid decreased with increasing temperature. This is partly because the current density of a zeolite-silicon oil based ER fluid increases as a function of time and temperature. The activation energy of 0.7 eV for the dissociation of a sodium ion were obtained from Arrhenius plot(e.g., log[j] vs 1/T). Ionization potential of different cations in a zeolite molecule will be a good topic to be studied later.

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