Damping Characteristics of Polyaniline-Based Electrorheological Fluid

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Abstract: Polyaniline (PANI) particles were synthesized by the chemical oxidation of aniline in acidic media, then the optimum conductivities in a semiconductive range for electrorheological (ER) application were achieved by adjusting the pH of an aqueous solution containing PANI particles. A semi-active ER damper filled with the PANI-based ER fluid was then investigated under different electric field strengths. The damping forces measured could be controlled by tuning the applied electric field for different piston velocities.

Keywords: electrorheological, polyaniline, ER fluid, damper, electrorheology

Introduction

Electroresponsive electrorheological (ER) fluids belong to a class of colloidal suspensions, which exhibit large reversible changes in their rheological behavior when subjected to external electric fields. In general, ER fluids can solidify in the order of milliseconds, and then be fluidified under applied deformation, which destroys the chain structure formed by the particles [1,2]. Furthermore, ER fluids have a very fast response characteristic to an electric field and hence a wide control band width [3]. Since their first discovery, this inherent feature has triggered tremendous research activities both in theory [4,5] and in the development of various engineering applications, such as shock absorbers [6], engine mounts [7], squeeze film dampers [8], clutch/brakes [9], and smart structures [10]. Nonetheless, these attractive and powerful materials have not yet been extensively used for commercial products because of several unsolved problems including colloidal instability, a low yield stress, a high current density and lack of application devices, etc.

Among the various promising materials for ER fluids, semiconducting polymers, including poly(acene quinone) radicals [11,12], polyaniline [13,14], copolyaniline [15, 16,17], poly(p-phenylene) [18,19], and polymer-clay nanocomposite [20-24], have been adopted as anhydrous ER fluids because of their ease in handling and superior physical properties, compared to various wet-base ER materials, including corn starch [25], silica gel [26], and a mesoporous molecular sieve [27]. In particular, polyaniline and its many derivatives based upon modifying the oxidation state, dopant, and polymerization conditions [28] are of technological interest. This is because they have a better thermal stability and smaller density than the other polymers. Furthermore, polyaniline can be easily polymerized by an oxidation polymerization at a relatively low temperature and doped from a conducting emeraldine hydrochloride form to an insulating state using simple protonic acids. Therefore, the ER characteristics can be studied by changing the dielectric constant and conductivity of the particle while keeping all the other particle properties the same.

In this study, polyaniline-based ER fluids are adapted as a smart material for a semi-active ER damper. Among the three types of ER damper, based on the working mode of the ER fluid: flow-mode type, shear-mode type, and squeeze-mode type [29], a cylindrical flow-mode type ER damper was selected because it has a similar geometrical configuration to the conventional damper normally used in passenger vehicles.
Experimental

Materials
The polyaniline was synthesized through an oxidation polymerization. At first, 0.6 mol of aniline was added to 400 mL of 1M HCl, chilled, and stirred. A pre-chilled solution of ammonium peroxydisulfate (0.36 mol in 200 mL of 1 M HCl) was then added dropwise to the reaction system, with continuous stirring for 1 h. The reaction proceeded very quickly. As a result, the solution color became dark-green within a few min of the addition. After adding drops for 2 h, the reaction conditions were then maintained for 2 h for the completion of the polymerization. The polymerization temperature was fixed at 0 °C using a constant temperature bath [30]. After the reaction, the polyaniline particles were ground using a ball mill and passed through a 38 μm sieve. Recently, dodecylbenzenesulphonic acid-doped PANI particles were synthesized via emulsion polymerization, and their ER characteristics were investigated [31]. To obtain semiconducting polyaniline, the polyaniline particles were dedoped by reducing the pH of the aqueous medium containing the particles to pH 9.0 using an aqueous NaOH solution and HCl solution. The pH of the aqueous polyaniline suspension remained constant for one day. The pH-controlled particles were then filtered and washed using distilled water, ethanol, and cyclohexane in order to remove any oligomer and excess monomer and make the particle surface hydrophobic. Finally, the products were dried in a vacuum oven at room temperature.

Rheological Measurement
The ER fluid was prepared by dispersing the synthesized polyaniline particles in silicone oil. The density and kinematic viscosity of the silicone oil were 0.95 g/cm³ and 30 cs at 25 °C, respectively. All ER fluids were prepared by dispersing the particles using an ultrasonicator for 30 min at room temperature. The prepared ER fluids were then stored in a desiccator prior to use. The rheological properties were determined using a rotational rheometer (Physica MC120) with Couette-type geometry, high-voltage generator, and oil bath for temperature control. An electric field was applied for 5 min to obtain an equilibrium chain-like or columnar structure before applying the shear. All measurements were performed at 25 ± 0.1 °C. The current density was also an important property considered in this study. Its limitation for engineering applications is known to be 300 μA/cm² with a 5 kV/mm electric field strength at 25 °C.

Damper Test
A cylindrical flow-mode type ER damper was selected for the current study. The ER damper was divided into an upper and lower chamber by the piston, and fully filled with ER fluid flows through a duct between the inner and outer cylinders from one chamber to the other. The positive voltage was produced by a high voltage generator connected to the inner cylinder, and the negative voltage was connected to the outer cylinder. Meanwhile, the gas chamber positioned in the lower part acted as an accumulator of the ER fluid induced by the motion of the piston. The gas in the chamber was nitrogen and the gas pressure was 10 bar. The electrode gap (h) of the damper was 0.75 mm.

The electric field was applied to the ER damper using a high voltage generator which had a gain of 1000 and output voltage range of ±10 kV. Unlike a rheometer test, the ER properties, such as the damping force, were measured without applying an electric field prior to the test. The temperature of the ER damper was controlled by an electric heater surrounding the damper. The excitation magnitude and frequency on the ER damper were ±20 mm and 1.89 Hz, respectively.

Results and Discussion
Polyaniline is regarded as being composed of structural repeating units formed by two aniline molecules. These repeating units can be formed in a reduce state or oxidized form. The molecular structure of polyaniline (emeraldine base) is

\[
\begin{align*}
\text{H} & \text{N} \quad \text{H} \\
\text{H} & \text{N} \quad \text{H} \\
\text{H} & \text{N} \quad \text{H} \\
\text{H} & \text{N} \quad \text{H}
\end{align*}
\]

where \( x+y=1 \), and \( x \) is known to be ~0.5 under general polymerization conditions. The synthesized polyaniline was identified from characteristic IR peaks obtained by an Fourier Transform Infrared (FT-IR) spectrometer. For a rigid main chain and the existence of dopants (e.g. Cl), metallic polyaniline (salt type) is infusible and insoluble in almost all organic solvents, except concentrated acids and N-methylpyrrolidone. These properties are a serious disadvantage in processability, yet good for ER fluids in which they produce thermal stability. The density of polyaniline was measured using a pycnometer at 25 °C and determined as 1.30 g/cm³. The average particle size of the polyaniline particles, as obtained using a Fisher Sub-Sieve Sizer, was 1.8 μm. The conductivity of the
polyanilines measured by the 2-probe method using compressed disks was found to be $9.0 \times 10^{-12} \text{ S/cm}$. Note that different types of conductivity and dielectric [32] measurements have been reported for liquid mixtures [33] and polymer films [34,35]. The PANI-based ER fluid showed a general ER behavior under various conditions. Among these properties, the yield stress measured by a rotational rheometer [36,37] is a representative property for explaining the ER effect.

Figure 1 represents a flow curve showing the shear rate vs. the shear stress at different electric field strengths. From this plot, the dynamic yield stress was obtained, as determined by an extrapolation from the constant stress region (plateau region). In the low shear rate region, the shear stress was sustained because the electrostatic force from polarization is considered to be larger than the hydrodynamic interaction [38]. However, in the high shear rate region, the behavior of the flow curve became a Newtonian flow motion. This process has been previously explained based on a relaxation process from the dielectric spectrum [13]. As given in Figure 1, since the dynamic yield stress obtained at 3 kV/mm was about 0.3 kPa, the PANI-based ER fluid was used in a semi-active ER damper and the effect observed. Recently, using the generalized scaling function, which incorporates both the polarization and conductivity models, the yield stress data for various ER fluids are observed to collapse into a single, universal curve for a broad range of electric field strengths [19,39].

Furthermore, the PANI based ER fluid synthesized in this study exhibited a typical shear thinning behavior [40-42] under an applied electric field. The shear thinning behavior increased with a higher voltage because the higher electric field made the ER fluid more solidified, as shown in Figure 2 [13,18,27].

Figure 3 presents the damping forces as a function of time at an operating temperature of 25 °C. As the electric field increased, the damping forces of the ER damper filled with the PANI-based ER fluid also increased, thereby requiring more force to move the piston. This was mainly attributed to the increment of the yield stress of the ER fluid. From this result, the damping force was determined as 210 N with a 0 kV/mm electric field. In contrast, the damping force at 5 kV/mm was 970 N and thus the increment of the damping force was 760 N. This result implies that a large range of the damping force of the ER damper could be continuously controlled by tuning the electric field. However, the curve shape of the PANI-based ER fluid for the damper was not well developed. It is assumed that the cause of this behavior was from a mismatch of the response time between the PANI-based ER fluid and the applied electric field.

Figure 4 shows the electric field dependent damping force relative to the piston velocity, where the piston velocity was changed by increasing the excitation frequency from 0.4 to 3.0 Hz, while a fixed excitation amplitude value was maintained. The damping force increased with an increase in both the electric field and the piston velocity, except at 5 kV/mm. At a higher
frequency region, a decrease in the damping force occurred. This behavior was related to the chain structure of the ER fluid at a higher electric field, as the higher shear thinning occurs with a higher electric field.

Conclusions

A PANI-based ER fluid was synthesized and then adapted to a semi-active damper system. From both the ER properties and the damping force investigated, the synthesized PANI-based ER fluid exhibited a typical shear thinning behavior under an applied electric field. It was also found that the damping force of the ER damper could be controlled by tuning the applied electric field, and the damping force increased relative to the electric field and piston velocity, except at 5 kV/mm.

Acknowledgements

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References