Electrorheology of polymers and nanocomposites

Hyoung Jin Choi* and Myung S. Jhon

DOI: 10.1039/b818368f

This highlight aims to report electrorheological (ER) materials in state-of-the art polymeric particles and their various nanocomposites with clay, mesoporous inorganics and carbon nanotubes along with their potential application. ER fluids, suspensions of these particles having higher dielectric constant or electrical conductivity than the low-viscosity fluids in which they are suspended, are currently regarded as a smart/intelligent material, because their structural and rheological properties can be systematically tuned by controlling electric field strengths. In this highlight, various conducting polymers, including polyaniline, polypyrrole, poly(p-phenylene), poly(naphthalene quinone) and copolyaniline, are introduced and different types of polymer nanocomposites are emphasized. Flow curves for shear stress of the ER fluids are also examined.

1. Introduction

Electro-responsive electrorheological (ER) fluids, composed of electrically polarizable particles 1–100 μm in size with volume fractions of 0.05–0.5 dispersed in insulating oils such as mineral or silicone, exhibit fascinating field-induced rheological properties including a rapid and reversible change in suspension microstructures under an applied electric field strength up to several kV mm⁻¹. By controlling the electric field strength to vary the fibrillar structures, a microstructural transition of the ER fluids from fluid-like to solid-like is obtained. Likewise, the analogous magnetorheological (MR) suspensions can be controlled by application of an external magnetic fields. All physical and mechanical property changes induced by the applied electric fields are virtually instantaneous (within a millisecond) and are reversible upon removal of the field, as shown schematically in Fig. 1(a), where particles form chains that span the gap between the field-generating electrodes. The reversible nature of the ER response, the significant change in viscosity and yield stress, and the short response times observed in these systems are desirable characteristics for various engineering applications such as torque transducers, vibration attenuators, control systems, smart materials, and ER polishing. Therefore, the ER phenomenon has been extensively studied since its discovery, not only due to its broad potential engineering applications but also due to its scientific interests as one of the most exciting and complicated of soft matters.

The principle behind the ER phenomenon originates from the electrostatic polarization mainly attributed to the field-induced polarization of the dispersed particles relative to the continuous phase, including electronic, atomic, dipolar, and interfacial polarization. A hydrous ER suspension results in an electric double-layer, which can be polarized and distorted; water can move out of pores and migrate from one particle to another under the applied electric field to make an adhesive water bridge between the particles. This water bridge shows a high surface tension, and...
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Fig. 1 (a) Schematic diagram of the microstructure change of the ER fluid and (b) flow curves for a PANI/BaTiO3 composite-based ER fluid.

a similar surfactant bridge also displays an electrostatic energy distribution in the surrounding particles.\textsuperscript{14,15} This polarization model relates the material parameters, such as dielectric response of both liquid and solid particles and particle volume fraction, to the rheological properties, as well as other microstructural fibrillar chains. Using an idealized ER system—a uniform, hard dielectric sphere dispersed in a Newtonian fluid medium—the derived electrostatic force was found to be dependent on the dielectric constant mismatch between the particle and continuous medium.\textsuperscript{16,17}

On the other hand, as the gap between the conducting particles in the fluid decreases, the electric response of the fluid becomes nonlinear, and often exhibits electrical breakdown or particle discharge at high electric field strength. In this case, the ER effect is caused by the fluid-induced conductivity enhancement between nearly touching particles. The conductivity mismatch between particles and liquid media, rather than the dielectric constant mismatch, is considered to be a dominant factor for the dc and low frequency ac excitation.\textsuperscript{15} This conduction model considers only the particle interaction, regardless of the microstructural changes after an electric field is applied. However, a major shortcoming remains in the polarization and conduction models since both of them are static, and do not take into account the dynamic processes.\textsuperscript{18} Furthermore, it can also be noted that different mechanisms for the polar-molecule-dominated ER effect have been reported during the recent development of giant ER materials. For the case of urea-coated dielectric nanoparticle systems, the yield stress can reach hundreds of kPa, exceeding the predicted upper bound of the conventional systems. This indicates that no universal theory is available to cover these different cases simultaneously.\textsuperscript{19,20}

2. Polymeric ER materials

In this highlight, we mainly focus on anhydrous ER materials with semi-conducting polymers, their modified forms and nanocomposites. Fig. 2 demonstrates the basic concept for the development of our materials from polyaniline (PANI) particles.

In the early stage of ER fluid research, extrinsically polarizable particles, including silica,\textsuperscript{21} alumina, and cellulose with various types of additives to induce polarizability, attracted enormous attention. However, these particles, used as hydrous ER fluids, have several drawbacks including device corrosion, water evaporation, narrow operational temperature range, and dispersion instability in applications.\textsuperscript{22} To overcome these shortcomings, materials intrinsically possessing polarizable species such as electrons and ions were introduced.\textsuperscript{23}

Most anhydrous ER fluids include inorganic non-metallic, organic, and polymeric semi-conducting materials, where the inorganic materials are typically ionic crystalline materials, while the organic and polymeric semi-conducting materials generally have a π-conjugated structure, and are electronically conductive. Polymers with π-conjugated electron systems display unusual properties, including high electron affinities and low ionization potentials. The local electron distribution of particles induces the ER effect under the applied electric fields.\textsuperscript{24} Among these, various polymeric particles have been especially well-used as dry-base ER materials to avoid the above-mentioned drawbacks. These include PANI,\textsuperscript{25,26} polypyrrole (PPy),\textsuperscript{27} poly(p-phenylene) (PPP),\textsuperscript{28,29} poly(naphthalene quinone radicals) (PNQR),\textsuperscript{30,31} polyphenylenediamine,\textsuperscript{31} and polythiophene.\textsuperscript{22} Among these conducting polymer-based ER materials, the most popular are PANI and its derivatives, e.g., PANI copolymers,\textsuperscript{33} PANI nanoparticles,\textsuperscript{34} microencapsulated PANI,\textsuperscript{35} PANI core-shell structures,\textsuperscript{36} as well as PANI–PPy copolymer.\textsuperscript{37} PANI consists of repeated structural units formed by two aniline molecules in a reduced or oxidized form, and its conductivity can be controlled by protonation and charge transfer doping. Furthermore, the protonation/deprotonation equilibrium occurs for two of the oxidation states, depending on the pH value. PANI particles can be easily synthesized using chemical oxidation polymerization of aniline, and then can be used as ER materials.

However, the, electric conductivity of PANI needs to be controlled due to the semi-conducting range requirement of ER materials. Therefore, the PANI particles must be dedoped by reducing their pH value in aqueous media. Additional doping and dedoping steps are
reported to control the electric conductivity of the particles for improved ER performance, while a simple proton acid treatment can alter the PANI properties from a conductor to an insulator. Alternatively, microcapsules containing PANI with low pH as the core material were synthesized by polymerizing melamine resin (which plays the role of an insulator between the PANI particles), which was then used as an ER material. It is well known that microencapsulation can easily produce diverse microcapsules by controlling reaction parameters, in which melamine–formalin resin as a shell material causes the electric conductivity of the core PANI particles to decrease.

Suspended ER particles are normally assumed to be mono-disperse and spherical in theoretical analyses, and the morphology of the dispersed phase is one of the critical parameters in theoretical modeling. Therefore, spherical mono-disperse polymer microspheres consisting of a poly(methyl methacrylate) (PMMA) core and PANI shell (PAPMMA) have been examined as dispersed materials for ER fluids. In PAPMMA, electric conductivity originates primarily from the conducting PANI layer on the surface, and this allows a change in the particle dielectric constant and conductivity while maintaining all other particle properties and suspension characteristics.

On the other hand, PPy particles have been also widely used as conducting polymers (due to their excellent thermal and environmental stability as well as superior electric conductivity) and as ER materials. However, they are known to be insoluble in common organic solvents due to their strong inter- and intra-molecular interactions and crosslinking, so control of the electric conductivity of synthesized PPy particles by post-treatment is known to be difficult.

PPP, polarizable under an external electric field via electron movement through the polymer backbone, has been investigated as a doped or undoped particle. In oxidative coupling process, PPP is also available by electrochemical coupling, which produces phenolic units, and this is more feasible for electron-rich monomers such as thiophene and pyrrole. PPP particles synthesized by bulk polymerization of benzene were doped with 5 wt% ferroc chloride in aqueous solution to increase electric conductivity, and these particles were used to prepare ER suspensions with various weight fractions, in which the shear stress and viscosity were found to be increasing with increasing electric field strength and doping degree.

It can be also noted that various polysaccharide-based ER materials including cellulose phosphate, potato starch phosphate, as well as chitosan and its derivatives, have also been adopted as anhydrous systems.

3. Nanocomposite-based ER materials

Various (mainly conducting) polymers have been hybridized with inorganic materials such as montmorillonite, mesoporous materials and carbon nanotubes to improve the ER performance, based on synergistic characteristics from both polymers and inorganics. Since the first report on PANI–clay nanocomposite-based ER fluids from an emulsion polymerization method as shown in Fig. 3, polymers (e.g., PANI, PPy, and styrene-acrylonitrile copolymer) and clay nanocomposites have been extensively used as suspended particles, taking advantage of either hydrophobic or hydrophilic surface characteristics of clay. In hybrid nanocomposites, polymer chains are inserted between the layers with an extended single chain conformation owing to the confinement in nanometer-size ‘gallery’. PANI nanocomposites with clay are thermally stable and relatively easy to...
synthesize. PPy has also been intercalated both in hydrophilic clay by emulsion polymerization, and in an organo-clay nanocomposite using synthesized soluble PPy. In the case of the PPy–clay nanocomposite-based ER fluids, significant difference was found in the ER behavior. Unlike the PANI–clay nanocomposite system, as the shear rate increased, the behavior of shear stress decreased initially and then increased above a critical shear rate. Extraordinary flow curves with the appearance of a minimum might be the result of microstructural change of the ER fluid under shear.

A composite material of silica-based mesoporous molecular sieves, MCM-41 or SBA-15, with conducting PANI inside the channels was prepared, and nanocomposite formation was confirmed by several methods such as the N2 adsorption isotherm and conductivity measurements. Since mesoporous materials possess high surface areas, and the size of pores can be tuned within 20–100 Å in a very narrow distribution by varying the preparation conditions, a large number of potential applications of these materials are expected to emerge in the areas of catalysis, separation, adsorption, and advanced ER fluid materials. Calcined mesoporous silica, MCM-41, dispersed in silicone oil demonstrated ER properties. Originally, nanocomposites adopting nano-scale alignments of the encapsulated molecules inside the host channels were investigated using various mesoporous hosts with guest materials such as carbon, polymers, or metals. In addition, in a composite of PANI in MCM-41 (PANI–MCM-41) the dielectric PANI is conducting only within the insulating uniform channels of MCM-41. A suspension of PANI–MCM-41 showed enhanced ER properties compared to those of MCM-41 or PANI alone, due to the anisotropic polarization of PANI–MCM-41, as sketched in Fig. 4.

Recently, nanocomposites of multiwalled carbon nanotube (MWNTs) incorporated into polymeric systems have been specially designed for ER materials, following a report on nanoparticles with MWNT and PANI synthesized by oxidative dispersion polymerization using poly(vinyl alcohol) as a polymeric stabilizer and HCl as a dopant.

MWNT–PMMA nanocomposite systems have been also found to display ER phenomena in the form of either MWNT-adsorbed polymeric microspheres (Fig. 5(a)) or MWNT nanocomposites with PMMA prepared by suspension or dispersion polymerization (Fig. 5(b)).

Fig. 3 Schematic diagram of synthesis route for PANI–clay nanocomposites by emulsion polymerization.

Fig. 4 Proposed diagram illustrating how PANI fills the uniform 1-D channels of MCM-41 (Inset: TEM image of PANI–MCM-41 nanocomposites. Scale bar: 50 nm).

Fig. 5 SEM images and corresponding schematic diagrams of MWNT–PMMA microsphere composites from (a) adsorption and (b) in situ dispersion polymerization.
Furthermore, various polymeric/inorganic particle nanocomposites exhibiting ER characteristics were also reported. Fig. 1(b) shows the flow curve obtained from the controlled shear rate test for 10 vol% suspensions of a PANI-BaTiO$_3$ nanocomposite with four different electric field strengths. The shear stress increases monotonically with shear rate in the absence of an applied electric field, exhibiting Newtonian fluid behavior. However, when the electric field strength increases, the shear stress increases with the electric field strength (for all shear rates). Flow curves of the PANI-BaTiO$_3$ nanocomposite-based ER fluid given in Fig. 1(b) as a function of shear rate for various applied electric field strengths were fitted using both the conventional Bingham model, eqn (1) (dashed lines), and a recently proposed constitutive equation, eqn (2) (solid lines).

Note that the Bingham fluid equation given below has been widely used to describe the steady shear response for ER fluids with a non-vanishing yield stress ($\tau_y$), which is defined as a stress where the suspension changes from solid-like to fluid-like at the zero shear rate limit:

$$\tau = \tau_y + \eta \dot{\gamma}$$  

(1)

Here, $\eta$ is shear viscosity and $\tau_y$ is a function of electric field strength and shear rate ($\dot{\gamma}$). However, it is known that the obtained shear stress often gives complex behaviors. In addition, many reported constitutive equations are too complicated to be used. Therefore, a six-parameter model constitutive rheological equation of state, which is known as the Cho-Choi-Jhan rheological equation, suggested by Cho et al. to analyze the ER fluids under an applied electric field, was adopted:

$$\tau = \tau_y + \eta \dot{\gamma} \left(1 + \frac{1}{(t_1 \dot{\gamma})^\alpha} \right) \dot{\gamma}$$  

(2)

Here, $\alpha$ is related to the decrease in the stress, $t_1$ and $t_2$ are time constants, and $\eta$ is the limiting viscosity at an infinite shear rate and is interpreted as the viscosity in the absence of an external electric field. The exponent $\beta$ has the range of $0 < \beta \leq 1$, since $d\tau/d\dot{\gamma} \geq 0$.

The results of fitting shown in Fig. 1(b) demonstrate that this suggested model fits the shear stress curves very well, especially covering the stress decrease phenomena at low shear rate region and provides an accurate value of the actual yield stress for PANI-BaTiO$_3$-based ER fluids. The first term in eqn (2) implies the shear stress behavior at a low shear rate region and the second term describes the shear stress behavior well at a high shear rate region. The particle chains, which are formed by the external electric fields, are disrupted by the shear flow. When the shear rate becomes high enough, the particle chains may be broken by the shear and the particles may not have enough time to realign themselves along the external electric field direction. Furthermore, the decrease in shear stress with increasing shear rate was reported to occur only under dc electric fields. On the other hand, the shear stress enhancement is due to the fibrillar structure of particle formed by an applied electric field. When the shear deformation is applied, the fibrils begin to break and reform repeatedly, depending on the magnitude of the applied shear and the particle–particle interaction in the fibrils. Recently, ‘trembling’ shear behavior has been also reported for a modified chitosan-based ER fluid along with a new rheological equation of state.

Therefore, the field of electrorheology is still wide open for extensive studies regarding the theoretical and experimental understanding of both the basic mechanisms on its origin, regarding the electric and dielectric characteristics of electrorheosensitive materials, and complex rheological flow behaviors. In addition, it can be noted that interesting potential applications of ER fluids have recently been reported in several new areas, such as the permeabilization of skin using a bio-electrorheological concept, the design of a biomicro-fluidic chip, and reducing the viscosity of crude oil.

4. Conclusion

In this highlight, we have reviewed various anhydrous ER materials based on semiconducting polymers and their nanocomposites with inorganic materials such as clay, mesoporous materials, MWNTs, and inorganic particles. Developing conducting polymer nanocomposites for ER materials is a novel way to construct organic–inorganic hybrid systems and provide new synergistic properties that can not be attained from individual materials, including easier control of the conductivity and improvement of the mechanical or thermal stability. In addition, conducting polymer nanocomposite-based ER fluids have been found not only to show excellent ER behavior, but also to follow our previously proposed Cho–Choi–Jhan rheological equation.

Acknowledgements

This work was partially supported by the STAR Collaboration Program, Korea (2008).

References
