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Synthesis and electrorheology of aniline/pyrrole copolymer

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An electrorheological (ER) fluid is an electroresponsive system whose rheological and viscoelastic characteristics are drastically changed by an applied electric field. The ER fluid in general consists of polarizable particles and insulating media. Dielectric constant mismatch between polarizable particles and insulating media has been considered to enable ER fluids to form a fibrillar structure [1–3]. To obtain the dielectric constant mismatch, the dielectric constant of the polarizable particles should be greater than that of the media [4]. In the absence of an electric field, the ER fluid exhibits Newtonian fluid behavior. However, in the presence of an applied electric field, polarization of the particles causes the particles to form a column-like structure, producing Bingham plastic characteristics [5]. Dry-based ER fluids were selected to complement the shortcomings of previously developed wet-based ER fluids [6]. Many studies on dry-based ER material have been reported, which include discussion of inorganic and semi-conducting polymeric particles such as zeolite [7], carbonaceous particles [8], semiconducting polyaniline (PANI) [9] and its copolymers [10], and polypyrrole [11]. To systematically control the conductivity of polyaniline and polypyrrole, several methods have been introduced including preparing nanocomposites with insulating clay [12, 13] as well as encapsulation by insulating polymeric materials [14].

In this letter, we examine the ER properties of aniline/pyrrole copolymer particles, synthesized via a chemical oxidation polymerization. Equal amounts (0.075 mol) of aniline and pyrrole were mixed under 200×10^{-6} m^3 of 1 M HCl with stirring for 30 min in a reactor. We used ammonium persulfate (APS) as a chemical oxidant initiator, so that 0.15 mol of APS can be mixed with 100×10^{-6} m^3 of 1 M HCl. The APS solution was then dropped (by stirring for 30 min) into a reactor which contained aniline and pyrrole monomers in HCl solution at 0 °C. Further agitation was applied for 24 h after the dropping process was completed. The product was then washed and filtered three times with de-ionized water to eliminate unreacted oxidants and the oligomers. The electrical conductivity of the resulting polymeric samples, without any after treatment, was too high to be directly used as ER fluids. Note that the conductivity of the PANI particles was 10^{-9} S cm^{-1} [9], and it was found that the temperature dependence of dc electrical conductivity of the PAPP (aniline:pyrrole = 8 : 2) follows the quasi 2-dimensional (2D) variable range hopping (VRH) model, while that of the PANI and polypyrrole systems follow the 1D and the 3D VRH models, respectively [15]. Therefore, we performed a de-doping process, which is a treatment of the particles in water by adding 1 M NaOH solution to fix the pH of the particles at approximately 9. The pH-controlled particles were again washed and filtered. The sample was then dried in a convection oven at 60 °C for 24 h and further dried in a vacuum oven at 25 °C for 48 h. The completely dried samples were ground and filtered through a 100 μm pore sized sieve [15]. The chemical structure

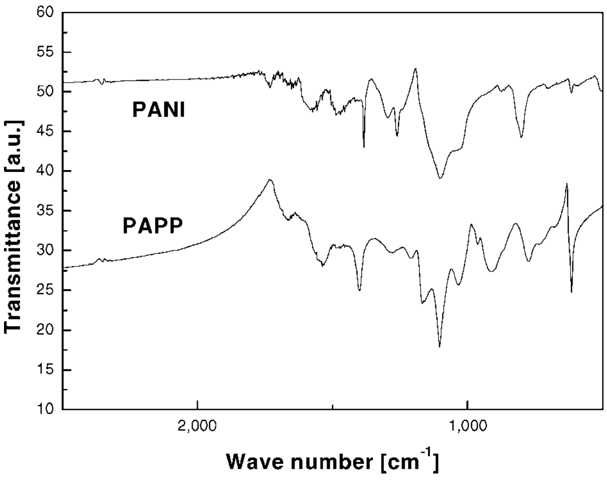

Figure 1 FT-IR spectra of PANI and PAPP.

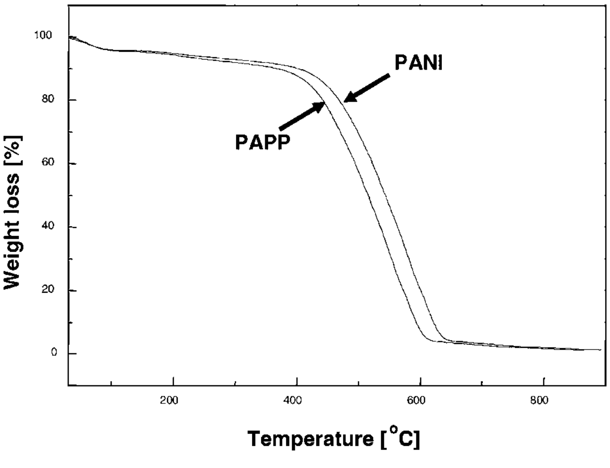

Figure 2 TGA results of PANI and PAPP.

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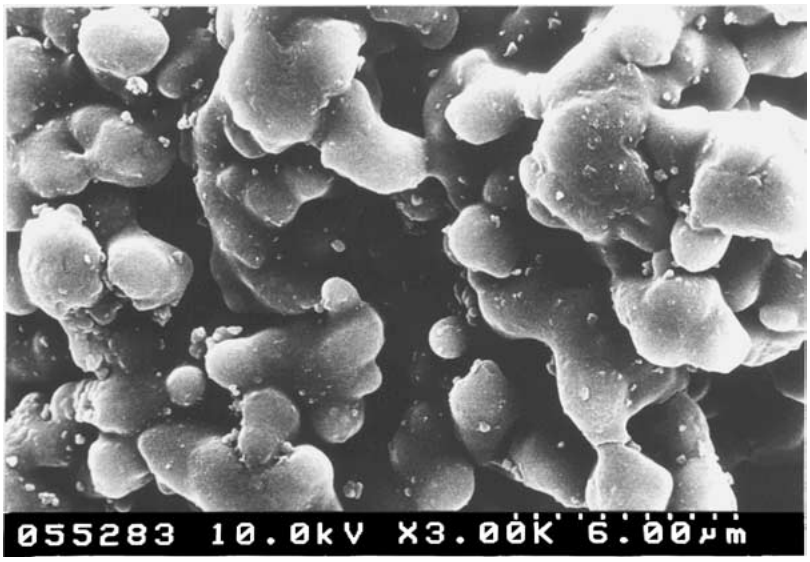

Figure 3 SEM image of PAPP.

of the synthesized particles was analyzed via a Fourier transform infrared spectrometer (FT-IR, Perkin Elmer System 2000, Norwalk, CT) using KBr pellets. The particle size and shape were determined by scanning electron microscopy (SEM, S-430, Hitach, Japan), and thermal stability was investigated by using a thermogravimetric analyzer (TGA, PL-TGA, Polymer Laboratories, Amherst, MA).

An ER fluid was prepared by suspending aniline/pyrrole copolymer (PAPP) (aniline:pyrrole = 5:5) particles in silicone oil (kinematic viscosity of the silicone oil was 30 cS at 25 °C) with a particle weight fraction of 15%. Their rheological properties under an applied electric field were measured by a rotational rheometer (MC120, Physica, Germany) with a Couette type geometry. A high voltage generator was used to generate a DC electric field strength of 1–3 kV/mm. A controlled shear rate (CSR) mode was applied using the rheometer. The DC field was applied for 3 min before our rheological measurements commenced in order to ensure an equilibrium, column-like structure.

Fig. 1 shows the FT-IR spectrum for both PANI homopolymer and PAPP particles. Characteristic peaks of aromatic amine of PANI are shown at 1294 and 1217 cm^{-1}. The peaks of 1539 and 1034 cm^{-1} originated from the characteristic peaks of the polypyrrole, which represents the C—H vibration and C=C stretching, respectively [15]. The TGA data in Fig. 2 indicate that the thermal stability of PAPP is slightly worse than that of PANI. The thermal degradation temperature of the conducting polymer is relatively higher than that for the other nonconducting conventional polymeric systems. Note that despite the attempted complete drying of the sample, weight loss due to water is observed around 100 °C. Fig. 3 is the SEM image of our PAPP particles. In contrast to the rough surface of PANI [16], a smooth and spherical shape was confirmed for PAPP particles. Fig. 4 provides the flow curve for our PAPP based ER fluid measured in CSR mode with an electric field strength of 1–3 kV/mm. In the absence of an electric field, shear stresses of ER fluid increased monotonically with shear rates. The shear stress also increased with an increase in electric field strength, indicating that the ER effect increases due to increased particle interactions [17]. Furthermore, the shear stress decreases in a low shear rate region for electric field strengths range between 1 and 2 kV/mm. In these regions, the electrostatic force among particles (induced by an applied electric field) is dominant as compared to the hydrodynamic force (induced by an applied shear). Also the partially reformed fibrillar structure made the shear stress decrease. At an electric field strength of 3 kV/mm, the shear stress plateau was observed for a low shear rate region since the electrostatic force overwhelmed the hydrodynamic force [18]. The critical shear rate, a transition point between the electrostatic force dominating region and the hydrodynamic force dominating region, was 11 s^{-1} at electric field strengths of 1–2 kV/mm. At the electric field strength of 3 kV/mm, the critical shear rate shifted towards 37 s^{-1}[19]. This phenomenon is due to the increased electrostatic force among the particles resulting from the electric field strength.

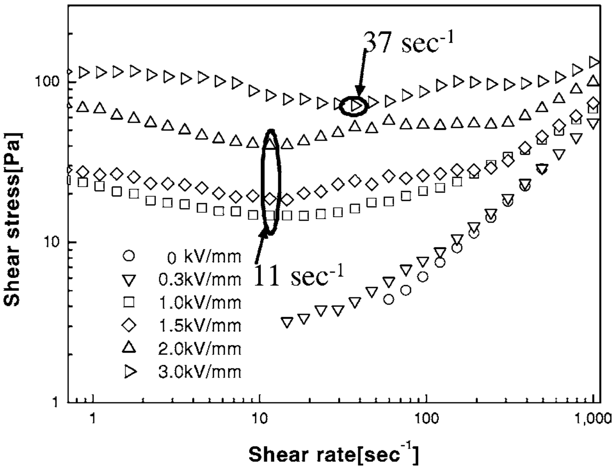

Figure 4 Flow curve for PAPP based ER fluid under five different electric field strengths.

In conclusion, we synthesized the PAPP particles (aniline:pyrrole = 5:5) via a chemical oxidation polymerization technique. A chemical structure was investigated by FT-IR spectroscopes. A round and smooth surface was observed by SEM. In regards to ER characteristics, a critical shear rate exists and is a function of the applied electric field strength; i.e., a critical shear rate at the high electric field strength is larger than that at low electrical field strengths.

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