



Electrorheological properties of thermo-oxidative polypyrrole nanofibers

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ABSTRACT

Using a chemical oxidative polymerization, polypyrrole (PPy) nanofibers were synthesized. After further thermo-oxidative treatment in air, the conductivity of PPy nanofibers was adjusted to a suitable level for use as a non-conventional nanofiber-based electrorheological (ER) suspension. Under electric fields, rheological properties of thermo-oxidative PPy nanofiber suspension were characterized. It showed that the nanofiber suspension possessed notable ER effect and low current density. Especially, the yield stress and shear modulus of nanofiber suspension were stronger than that of conventional granular suspension at the same volume fraction though the off-field viscosity of former was lower than that of latter. The ER effect and current density of thermo-oxidative PPy nanofiber suspension depended on the thermo-oxidative time and the nanofibers obtained after treatment for 3–5 h at 240 °C exhibited the optimal ER performances. It also showed that the thermo-oxidative PPy nanofiber suspension could maintain good ER properties within a wide operating temperature range of 25–115 °C.

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1. Introduction

As an inherent conducting polymer, polypyrrole (PPy) has attracted much attention due to its excellent characteristics including high electrical conductivity, redox property, facile synthesis, and good environmental stability. PPy has found use in many fields such as biosensors, gas sensors, microactuators, antielectrostatic coatings, solid electrolytic capacitor, displays, polymeric batteries, electronic devices, and so on [1–7]. As an important electrically active polymer, PPy is also frequently employed in electrorheological (ER) fluids [8]. ER fluids are smart suspensions consisting of polarizable particles dispersed in a non-conducting liquid. On the application of an external electric field, ER fluids exhibit drastic and reversible changes in rheological properties (viscosity, shear stress, and shear modulus) due to the formation of particle chains or columns along the electric field [9]. In particular, the rheological properties can be accurately controlled by tuning electric field strengths. This rapid and reversible electrically controlled mechanical response makes ER fluids to have potential applications in mechanical, biomedical, and robotic fields [10–13]. Although the performances of ER fluids are similar to those of magnetorheological (MR) fluids under an applied magnetic field [14], most available ER fluids exhibit a far inferior mechanical property under an applied electric field. To satisfy the practical applications, current researches have focused on the synthesis of anhydrous ER materials with versatile performance including high yield stress,

low current density, low particle settling, wide operating temperature range, etc., [15–18].

As important anhydrous ER systems, conducting polymers such as polyaniline (PANI), PPy, polythiophene (PTh), and their composites have been widely investigated due to their low density, tunable conductivity, high polarizability, environmental stability, and good ER efficiency [19–39]. Among these materials, PPy is one of the most promising candidates for its excellent environmental stability [8]. To satisfy ER fluid applications, however, the conductivity of PPy needs to reduce to a suitable level. The common approach to reduce conductivity is to immerse PPy particles in alkali solution. However, different from other polymer conductors such as PANI, the realization of significant decrease of conductivity of PPy by alkali dedoping is more difficult and consequently the electrical current through PPy-based ER fluids is often large and the power consumption is high. By controlling oxidant amount, Kim et al. have controlled the conductivity of PPy in a certain range and investigated the dependence of ER effect on oxidant amount [30]. Furthermore, Kim et al. also reported a way to restrict high conduction by the formation of double coated PPy particles [31]. Recently, it was reported that another interesting way to decrease conductivity was to intercalate PPy into clays or mesoporous materials [28,32,35–38]. However, the amount of intercalated PPy by this way was too small.

On the other hand, the morphology of ER particles is also important to ER performances [40–44]. In particular, it is interesting that compared with the suspensions of spherical particles the suspensions containing fiber-like particles were found to show enhanced ER and even improved dispersion stability recently [45–53]. And this enhanced effect had also been observed in MR systems [54–57]. In

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the recent report, we confirmed that compared with conventional granular ER fluids, the ER fluids based on elongated nanofibers (such as titanate nanotubes [45], PANI nanofibers [48,49], and carbonaceous nanotubes [52]) exhibited better suspension stability and ER effect because the elongated morphology might have larger induced dipole moments and interparticle interactions. Using titanate nanotubes as hard templates, Li and coworkers further investigated the ER properties of titanate/conducting polymer composites [50,58].

In this study, considering the advantages of PPy as ER materials and to attempt to extend the understanding about particle morphology effect on ER properties, we developed a kind of thermo-oxidative PPy nanofibers by a modified chemical oxidative polymerization and a thermo-oxidative post-treatment in air and investigated their ER properties when dispersed in silicone oil. The merits of thermo-oxidative PPy nanofibers include not only elongated morphology but also tunable conductivity achieved by simple heating treatment in air, which were confirmed to be able to induce notable ER effect and low current density. In particular, when compared to the conventional granular thermo-oxidative PPy suspension, the thermo-oxidative PPy nanofiber suspension showed higher yield stress and shear modulus under electric fields, further indicating the potential of the thermo-oxidative PPy nanofibers as active ER materials. We here present the preparation and structure of the thermo-oxidative PPy nanofibers and the ER properties as a function of the electric field strength, thermo-oxidative time, and operating temperature.

2. Experimental

2.1. Synthesis of PPy nanofibers and thermo-oxidative treatment

All chemicals were of analytical grade and other reagents (ammonium persulfate (APS) and β -naphthalene sulfuric acid (β -NSA)) were used as received except for pyrrole monomer which was distilled under reduced pressure before using. The PPy nanofibers were synthesized according to the procedure described in Ref. [59] with modification by our laboratory. Firstly, 6 g of NSA and 0.5 ml of pyrrole monomer were dissolved in 20 ml of deionized water with stirring in ice bath. Secondly, 2.85 g of APS was dissolved in 5 ml of deionized water, and then was added drop wise into the above solution containing pyrrole and NSA under stirring. After reaction for 12 h, a black PPy nanofiber suspension was formed. Finally, the PPy nanofibers were collected by filter with water- and ethanol-washing and then were dried at 80 °C in vacuum. To make a comparison, the granular PPy was also synthesized with the same reagents according to the conventional method [59].

The conductivity of as-synthesized PPy nanofibers and granular PPy was too high to use in ER fluids. Commonly, a dedoping process in aqueous solution of ammonia was used to decrease the conductivity. However, the decreasing level of conductivity of PPy by this way was limited and thus often resulted in high current density and low dielectric breakdown strength. Different from the conventional way, we here employed a thermo-oxidative treatment at 240 °C in air to reduce the conductivity of PPy. Here, the set thermo-oxidative temperature of 240 °C was deduced according to the TGA result and relative Ref. [60]. It is noted that the PPy nanofibers degraded rapidly when the temperature was higher than 250 °C and as a result it was difficult to control the conductivity of PPy to a suitable level for ER fluid application. When the PPy was treated at temperature lower than 220 °C, however, it was very time-consuming to reduce the conductivity of PPy to a suitable level. Therefore, the moderate temperature of 240 °C was chosen for the thermo-oxidative treatment of PPy nanofibers in the present experiment. By adjusting the heating time, we could well control the conductivity of PPy to a suitable level for ER fluid application. At the same time, this method could also ensure the anhydrous characteristic of nanofibers. In

addition, it should point out that the conductivity of as-synthesized PPy nanofibers was much higher than that of as-synthesized granular PPy. This is resulted from higher NSA dosage for the synthesis of PPy nanofibers. For a rational ER comparison, we here controlled the conductivity of both PPy nanofibers and granular PPy to the same level by adjusting the heating time (5 h for PPy nanofibers and 3 h for granular PPy).

2.2. Preparation of ER suspensions

The ER suspensions were prepared by rapidly infusing silicone oil (dielectric constant of 2.7–2.9, viscosity of 50 mPa·s, density of 0.96 g/cm³ at 25 °C) into the bottle of thermo-oxidative PPy at 240 °C. After stirring and ultrasonic treatment, we obtained uniform suspensions, in which most of nanofibers were independently dispersed in medium oil according to optical microscopes. The volume fraction of particles in suspensions was defined by the ratio of particle volume to total suspension volume. The density of thermo-oxidative PPy was measured by a pycnometer [52]. To decrease the effect of porosity on density, the pycnometer was placed in an ultrasonic cleaning bath and connected to a vacuum pump. After sonication under reduced pressure for 10 min, the density was measured.

2.3. Characterization

The particle morphology was observed by scanning electron microscopy (SEM, JSM-6700). The chemical groups were determined by Fourier Infrared spectra (FT-IR, JASCO FT/IR-470 Plus Fourier Infrared spectrometer) in the range 400–4000 cm⁻¹ at 4 cm⁻¹ resolution. The dc conductivities (σ_{dc}) of PPy nanofibers were measured by a two-point method using a digital conductance meter (DDC-11) on pressed pellets. The ER properties were characterized by a stress-controlled electrorheometer (Thermo Haake RS600) with parallel plate system (PP ER35, the gap between plates was 1.0 mm), WYZ-010 DC high-voltage generator (0–10 kV, 0–2 mA), oil bath system (–25 to 125 °C, Phoenix), and PC computer. The steady flow curves of shear stress–shear rate were measured by the controlled shear rate (CSR) mode within the shear rate range of 0.1–1000 s⁻¹. The yield stress was approximately obtained at the low shear rate regions. In dynamic test, the amplitude sweep test of modulus as a function of stress at a constant frequency (0.5 Hz) was initially attempted to find a linear viscoelastic region, and then the dynamic viscoelastic properties were measured as function of frequency at the stress in the linear regions. The same stress was chosen for all ER fluids in order to make a reasonable comparison. To ensure data consistency, all the measurements were repeated three times and electric field was applied for 1 min prior to applying shearing or sweeping. The current through ER suspensions were recorded by an amperometer connected with electrorheometer.

3. Results and discussion

Fig. 1 shows SEM images of the as-synthesized PPy and thermo-oxidative PPy. The as-synthesized PPy by the conventional methods is typically granular sample with spherical morphology (see Fig. 1(a)). The diameter of granular PPy is about 100–200 nm. However, when the NSA concentration is increased and the reaction is taken place in ice bath, most of PPy show nanofiber morphology with diameter of 100–200 nm and length of 1–2 μ m (see Fig. 1(c)). The formation of PPy nanofibers may be induced by the template effect of self-assemble NSA micelles [59]. After further thermo-oxidative treatment at 240 °C in air, the morphology of PPy nanofibers and granular PPy is well preserved as shown in Fig. 1(b) and (d).

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