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Enhanced effect of dopant on polyaniline nanofiber based electrorheological response

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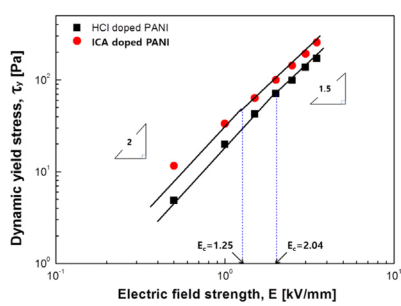
HIGHLIGHTS

- Polyaniline nanofibers were synthesized *via* an interfacial polymerization route.
- Polyaniline nanofibers were doped with indole-2-carboxylic acid.
- Typical electro-responsive characteristics were observed for polyaniline nanofibers.

GRAPHICAL ABSTRACT



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ABSTRACT

As a potential candidate for electrorheological (ER) materials, polyaniline (PANI) nanofibers were synthesized *via* an interfacial polymerization route, because of their easy synthesis, high stability, controllable conductivity and good ER response. In this study, a new dopant, indole-2-carboxylic acid, was used to improve the ER performance. The synthesized PANI nanofibers were dispersed in silicone oil at 10 vol% and their rheological properties as an ER fluid were examined using a rotational rheometer under a variety of electric field strengths. In addition, their dielectric properties were studied using a LCR meter. The results showed that indole-2-carboxylic acid, which has high polarizability, enhanced the ER effect of PANI nanofibers, showing that polarizability is an important parameter affecting the ER behavior.

1. Introduction

Electrorheological (ER) fluids, which consist of polarizable solid particles dispersed in a non-conducting medium, have been studied extensively owing to the excellent tunable characteristics of their states under an applied electric field strength. The rheological and mechanical properties of ER fluids are changed dramatically by an external electric field based on their phase transition from a liquid-like to solid-like state [1-5]. The changes induced by an external electric field are virtually instantaneous and reversible by controlling the electric field strength. As the beneficial effects with a rapid and reversible change, their potential applications have attracted considerable attention in a range of industrial [6] and scientific areas.

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The ER phenomenon results from the fibrillation chains in the presence of electric fields, where fibrillated particulate structures are induced by dielectric constant mismatch of the particles and insulating oil. In various theories to account for the ER mechanisms [7,8], a dielectric polarization theory has been widely adopted. According to the polarization model, the suspending particles are polarized under an applied electric field. The interactions among the polarized particles cause then them to form chains themselves along the electric field direction [9]. Therefore, the strength of the fibrillation chains is determined by the polarization force of the particles, which is affected by their dielectric constant [10–13]. In particular, because the interfacial polarization is one of the important factors in the performance of ER fluids, the polarizability of the particles in dry-base ER fluids is the most important factor, considering their higher ER performance.

Under the present conditions, the ER effect still requires considerable improvement before high performance ER materials can be used in practical applications. Among the many anhydrous ER materials available, polyaniline (PANI) is frequently used as the dispersed solid particle owing to its environmental stability, simplicity, low cost of synthesis, and tunable conductivity with doping and dedoping processes [14–16]. In addition to conventional PANI, many other types of PANIs have been developed in ER research, which not only differed in structure or morphology but also exhibited different ER effects, such as oligomers and derivatives [14,17], modification [18], composites, core–shell structured particles [19–21], nanospherical or fibrous PANI [22] and etc. Recently, Yin et al. [23] reported that PANI nanofiber-based ER fluids show higher yield stress, being more stable than granular PANI-based ER fluids. They also reported the effect of the particle morphology on the ER performance of the PANI suspension to achieve a better understanding of the morphological factors affecting the ER properties. The shape effect on the ER performance with a mainly anisotropically elongated or fibrous configuration has been studied widely for various particles ranging from whisker-like aluminum borate [24], titanate nanofibers [25], goethite nanorods [26] to polypyrrole nanofibers [27], all which show better ER properties. In the case of nanofiber-based ER fluids, improved suspension stability was also observed [9]. On the other hand, Hong et al. [28] examined the influences of the particle shape on the ER activity along with titania-coated silica nanomaterials.

Above all, the polarizability of suspended particles as well as the particle shape affects the efficiency of ER fluids significantly. On the other hand, there still is a room for improvement on the polarizability of suspension particles. For example, less attention has paid to the effects of the dopants used in the PANI synthesis process on the ER performance. Because polarizability of the suspension particles is an important factor for high ER properties, dopants with high polarizability have the potential to enhance the ER effect.

In this study, PANI nanofibers were synthesized using an interfacial polymerization method [29], which can produce uniform and template-free nanofibers. Furthermore, to improve the ER performance of the product, indole-2-carboxylic acid (ICA), which has high polarizability, was used as a dopant instead of common acids, such as hydrochloric, sulfuric, or nitric acid, during the synthesis process. The synthesized PANI nanofibers were characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. The rheological and electrical properties were then examined to understand the role of particle polarizability. Conventional HCl-doped PANI nanofibers were also prepared for comparison.

2. Experimental

2.1. Materials and preparation of ICA-doped PANI fibers

Aniline (DC Chemical, Korea), ammonium persulfate (APS) (98%, Daejung, Korea) and indole-2-carboxylic acid (ICA) (98%, Sigma–Aldrich) were used as received. A 35 wt% HCl solution (DC Chemical, Korea) was diluted to 1 M for use as a dopant.

In a typical synthesis route, the particular shape of PANI can be synthesized by the oxidative polymerization of aniline with APS in an acid aqueous solution. On the other hand, an interfacial polymerization method was adopted to obtain a fiber shape. The synthesis process was as follows. To prepare an organic phase, both the aniline monomer (0.05 mol) and ICA (0.005 mol) were dispersed in dichloromethane with energetic stirring. For the liquid phase, however, APS was dissolved in Di-water with agitation until a transparent solution was obtained. Subsequently, the liquid phase was added to the organic phase slowly and carefully along one side of the inner wall, and the obtained immiscible two phase system was kept in a refrigerator for 24 h. For comparison, HCl-doped PANI nanofibers were also synthesized in the same manner as above using the same reagents, but with HCl (0.005 mol) as a dopant instead of ICA. After polymerization, the product was washed with di-water and methanol from a reaction solution until the washing liquid became neutral to remove the unreacted reagents. These solid products were dried in a vacuum oven at 60 °C.

2.2. Preparation of ER fluid

To use the PANI nanofibers as a solid-phase of the ER fluid, the as-synthesized PANI nanofibers need to be dedoped by controlling the pH of the aqueous suspension of PANI with a 1 M NaOH solution. The electrical conductivity of the dry PANI powders was decreased from 10^{-1} to 10^{-10} S cm^{-1}. Densities of the particles measured by a gas pycnometer (AccuPyc 1340, Micromeritics) were 1.50 and 1.51 g cm^{-3} for ICA and HCl doped PANI, respectively. Subsequently, the ER fluids were prepared by dispersing the PANI nanofibers in silicone oil (ρ = 0.96 g cm^{-3}, kinematic viscosity = 50 cS at 25 °C) under shaking and sonication, respectively. Two types of ER fluids were prepared containing 10 vol% of HCl-doped PANI and ICA-doped PANI, respectively.

2.3. Characterization

The morphology of the PANI nanofibers was examined by field emission-scanning electron microscopy (FE-SEM) (Hitachi S-4300, Japan). Fourier transform infrared spectrometry (FT-IR) (Perkin Elmer System 2000, Norwalk, CT) was used to identify the chemical structure of the PANI nanofibers. The electrical conductivity was measured using a standard probe technique with a resistivity meter (Loresta-GP and Hiresta-UP, Mitsubishi Chemical Analytech CO., LTD, Japan). Optical microscopy (OM) (Olympus BX51, USA) equipped with a DC high voltage generator was used to examine the electro-responsive response of the ER fluid under an electric field. The ER properties of the PANI nanofibers suspension were characterized by steady shear experiments using a rotational rheometer (MCR 300, Physica, Austria) with a cup-bob system (CC17 ERD, the gap between the cup and bob was 0.71 mm) and a DC high voltage generator. In controlled shear rate (CSR) mode, the flow curves of each ER fluid were measured under a shear rate between 0.01 and 1000 s^{-1} with and without an external electric field. In addition, dielectric relaxation spectra of the prepared ER fluids were analyzed using the HP 4284A precision LCR meter with