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Fabrication of electric-stimuli responsive polyaniline/laponite composite and its viscoelastic and dielectric characteristics

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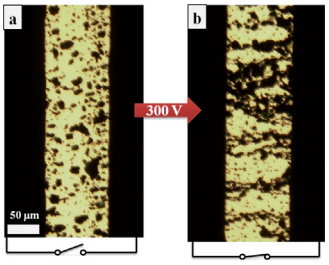
HIGHLIGHTS

- Polyaniline (PANI)/laponite composite was synthesized via an in-situ chemical oxidation polymerization.
- PANI/laponite composites were adopted for electrorheological (ER) application.
- PANI/laponite composite exhibited typical ER characteristics with a polarization model.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline (PANI)/laponite composites were synthesized via an in-situ chemical oxidation polymerization process using ammonium persulfate as the oxidant in an aqueous solution. Scanning electron microscopy confirmed the morphology of the synthesized composite. The chemical structure of the synthesized product was characterized by Fourier transform infrared spectroscopy. The PANI/laponite composites, which were dedoped to a relatively low conductivity for the electrorheological (ER) measurements, possessed ER characteristics when dispersed in silicone oil at a volume fraction of 10%. The particle structures of the ER fluid under an electric field were analyzed by optical microscopy. The rheological properties, such as the shear viscosity, shear stress and yield stress, which were analyzed using a rotational rheometer under an applied electric field, exhibited typical ER characteristics with a polarization model.

1. Introduction

Electric stimuli-responsive electrorheological (ER) fluids are smart materials composed of an insulating oil and polarizable or semiconducting particles with micrometer- or nanometer sizes. When applied to a relatively high electric field, the ER fluid forms chains by joining the dispersed particles along the direction of the external electric field, resulting in a phase transition from a liquid-like to a solid-like state [1–4]. These structural and rheological changes observed upon exposure to an electric field produce a significant reversible increase in shear viscosity and shear stress, which occur within only a few milliseconds. Therefore, breaking the formed fibrillar structures coincides with flow in a shear flow fluid due to the electric field strength under a yield stress.

On the other hand, morphological variation of the dispersed particles in ER fluids is known to be related to their ER performances. The ER fluid with anisotropic rod-like particles is reported to demonstrate superior ER response compared to that with spherical particles [5]. Hierarchical structures made of microscale or nanoscale building blocks including hierarchical TiO_2 also display high surface area, leading to an increased interfacial polarization to connect with strong ER effect [6].

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The immediate response to an electric field and controllable mechanical properties of the ER fluids broaden their engineering applications. For example, the ER fluid can be applied to the automotive industry, such as shock absorbers, engine mounts and clutches [7]. In addition, robotic elements in biomedical applications have been evaluated [8]. Hence, research on the development of novel ER materials has increased tremendously [9–14].

Among the various electro-responsive ER materials available, conducting polymer/inorganic composites have attracted considerable attention because of their heterogeneous physical properties and unique structure that combine the merits of the two phases [15,16]. Conducting polymers have promising applications in electrochemical devices, photodiodes, antistatic and anticorrosion coatings, batteries, sensors, and solar cells [17,18]. Polyaniline (PANI), as an applicable conducting polymer, has been used as an ER material because of its low cost, good environmental and chemical stability, ease of synthesis, high sensitivity to an electric field, controlled conductivity by doping/dedoping process, and various other potential applications [19]. Note that the PANI is generally synthesized by chemical oxidative polymerization which is well known for the most widely adopted synthetic route to make conducting PANI. The reaction occurs in a strongly acidic environment because low pH condition leads the head-to-tail coupling of aniline monomers in the para position. Its green form as a protonated emeraldine salt can be collected and purified. Then, it can be dedoped by the addition of oxidizing agent to produce the blue, emeraldine base form of the semi-conducting polymer [20,21].

Therefore, it has been also used as a dispersed phase in ER fluids [22–26]. A variety of PANI/clay nanocomposites fabricated using many different methods have also been applied as ER materials [27,28].

Concurrently, among the various nanoclay types, laponite is a synthetic clay material [29–31], and has been used to stabilize emulsion systems owing to its uniform and smaller dimensions than other clay species, such as montmorillonite and bentonite, in addition to its surface characteristics [26,32,33]. Laponite also plays an important role as a multifunctional physical cross linker, which has the effect of intercalation [34,35]. Cross-linking between monomers which contain amide groups and laponites can occur. Furthermore, ionic and polar interactions are induced, leading to non-covalent cross-linking at the clay-polymer interfaces. Therefore, laponite facilitates physical cross-linking without the need for a chemical cross-linker [36,37] but more work is still needed. On the other hand, pure laponite is known to have an ER effect itself [35]. In addition, one of the novel syntheses using laponite is Pickering emulsion with polystyrene [38] and poly(methyl methacrylate) [32].

In this study, PANI/laponite composites were synthesized by oxidative polymerization, which is a simpler and more cost effective method than Pickering emulsion. The morphology of the synthesized PANI/laponite particles was analyzed by scanning electron microscopy (SEM). The main purpose of this study was to analyze the ER behavior using a rotational rheometer equipped with a high voltage generator under different electric field strengths. The ER effect of PANI/laponite and pure PANI were then compared by measuring the yield stress.

2. Experimental

2.1. Materials

Laponite clay (grade: RDS, BYK), aniline (DC Chemical, Korea), ammonium persulfate (Daejung, Korea), and hydrochloric acid (Junsei Chem.) was used as received. Distilled water was used in all experimental processes.

2.2. Synthesis of PANI/laponite composite

The PANI/laponite composites were synthesized by the in-situ polymerization of aniline in an acidic medium (HCl). First, 5 g of laponite was added to 200 ml of distilled water and ultra-sonicated until a clear aqueous solution was obtained. Subsequently, 5 g of aniline was added to the laponite dispersion during stirring. The mixture was transferred to a 500 ml reactor at 0 °C. A 1.0 M HCl solution containing 13.7 g of an oxidizing agent ($(NH_4)_2S_2O_8$) was added drop-wise to a solution containing the monomer and clay with constant stirring. Stirring was maintained for 12 h at 120 rpm. The final product was centrifuged with both ethanol and distilled water to eliminate the excessive initiator, monomer and free laponite, and then dried in a vacuum oven at 65 °C.

To fabricate the ER fluid, the dried PANI/laponite composite particles (10 vol%) were dispersed in an insulating silicone oil with a kinematic viscosity of 50 cS. The densities of laponite, PANI and synthesized PANI/laponite composites measured using a pycnometer were 2.24 g/cm^3, 1.36 g/cm^3 and 1.56 g/cm^3, respectively.

2.3. Characterization

The morphology of the synthesized PANI/laponite particle was examined by high resolution SEM (HR-SEM, SU-8010 Hitachi), and the chemical molecular structure of the product particles was examined by Fourier transform infrared spectroscopy (FT-IR, PerkinElmer System 2000). An optical microscope (Olympus BX-51, USA) equipped with a DC voltage generator was used to identify the chain-like structure of the ER fluid formed under an applied electric field. The ER behavior was examined using a rotational rheometer (Physica MCR 300, Stuttgart) equipped with a high voltage generator. The density was measured using a gas pyconometer. The dielectric properties of the ER fluids were examined using an LCR meter (Agilent HP 4284A) over a broad frequency range from 20 to 10^6 Hz.

3. Results and discussion

3.1. Material characteristics

The surface of pure laponite was smooth, as shown in the SEM images in Fig. 1(a). On the other hand, the PANI/laponite composites shown in Fig. 1(b) had a rough surface with the presence of laponite. Ionic and polar interactions at the laponite-PANI surface would induce physical cross-linking [39]. This nanocomposite in a powder form is well consisted of laponite particles and PANI. The corresponding EDAX spectrum is also displayed in Fig. 1(c), in which the EDAX of PANI/laponite composites showed the presence of carbon, nitrogen, oxygen, natrium, magnesium and silicon elements, confirming the presence of PANI at the surface of laponite in the composite.

The chemical structure of the synthesized PANI/laponite was examined by FTIR spectroscopy. Fig. 2 presents the FT-IR spectra of the synthesized PANI, laponite and PANI/laponite composites. The pure PANI sample showed the typical spectrum of PANI with the characteristic peaks at 1586 cm^{-1} and 1498 cm^{-1}, which were assigned to the C=C stretching vibration bands of the quinonoid and benzenoid units, respectively [40]. The same peaks were observed in the PANI/laponite composites [40]. The peak at 1304 cm^{-1} was assigned to the C—N stretching vibration of the second aromatic amine. The bands corresponding to a vibration mode of N=Q=N ring appeared at 1143 cm^{-1}. The peaks at 1142 cm^{-1} and 823 cm^{-1} were assigned to the out-of-plane vibration in the 1–4 substituted aromatic rings [41,42]. The characteristic peaks of laponite at 1015 cm^{-1} and 470 cm^{-1} were assigned to the Si—O bending vibra-