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Graphene oxide/poly(2-methylaniline) composite particle suspension and its electro-response

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HIGHLIGHTS

- GO/P2MAN composite was fabricated by Hummers method and oxidation polymerization.
- The composite particles based fluid exhibited typical electrorheological properties.
- The fluid was correlated to conduction model and showed solid-like characters.
- GO was helpful to improve stability of fluid due to large surface area and compatibility.

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ABSTRACT

Graphene oxide (GO)/poly(2-methylaniline) (P2MAN) composite particles were prepared by chemical oxidation polymerization and adopted as an electrorheological (ER) material. Because of its electrical conductivity originating from both semi-conducting P2MAN and GO, it could be tuned finely using P2MAN for ER applications. The morphology and chemical structure of the composite were examined by scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. The ER properties of the GO/P2MAN composite particles dispersed in silicone oil were examined with and without an applied electric field. The fibrillation phenomenon of this GO/P2MAN-based electro-responsive fluid was also observed by optical microscopy under an electric field. The flow curves and dynamic modulus of the GO/P2MAN suspension were measured by rotational rheometry under a range of electric field strengths, exhibiting typical ER characteristics and a slope of the dynamic yield stress of 1.5. GO appeared to improve the compatibility of the composite particles within the medium, which resulted in improved sedimentation stability compared to that of the P2MAN-based ER fluid.

1. Introduction

Controlling the viscoelasticity of stimuli-responsive materials by external electric or magnetic fields has become quite attractive because of their potential use in a wide range of engineering applications, such as biomedical, mechanical, robotic fields as well as other control systems [1–3]. An electrorheological (ER) suspension consisting of electrically conducting particles dispersed in an insulting liquid is considered a noteworthy smart material with electrically tunable viscoelasticity [4–6]. These adjustable rheological characteristics are derived from the particulate phase, which is ordered by self-assembly in an ER suspension under an external electric field. The properties of ER suspensions under an electric field resemble those of magnetorheological (MR) suspension under an applied magnetic field [7]. Nevertheless, ER suspensions still require improvements in their performance and they have problems, such as a large current density, particles sedimentation, low yield stress, and thermal instability. The ER fluid is a type of smart material whose rheological properties are precisely adaptable under an electric field. Under the application of an external electric field, the fluid exhibits dramatic, immediate changes in its rheological properties and forms chain-like structures due to polarization between the ER particles [8,9]. The transition of structures from a liquid-like to solid-like state results in attractive changes in its rheological properties, such as shear stress, shear viscosity, dynamic yield stress, storage modulus and loss modulus [10–12]. The ER fluid characterized by this controllable and reversible transition has promising applications for a wide range of electromechanical engineering devices such as vibration dampers, shock absorbers,

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brakes, clutches, and engine efficiency [13].

Several electro-responsive materials have been applied as ER particles, such as inorganic materials with high dielectric properties, polymeric or organic semiconducting materials and their composites [6]. Polyaniline (PANI), a conducting polymer, has been evaluated as a prospective ER material for a long time [10,14–16]. PANI derivatives and even PANI-based composites have been also chosen because of their excellent environment stability and ease of preparation [5,17,18]. On the other hand, PANI is intrinsically brittle and has poor compatibility because of its insolubility in typical organic solvents [19]. This problem has been overcome by applying substituted derivatives of anilines, such as N═CH_2– or N–CH_2CH_3– functionalized anilines, anisidines, toluidines, etc. [20]. As derivative of PANI, poly(2-methylaniline) (P2MAN), where the ortho position is substituted with a methyl group, has also attracted considerable interest [21–23]. P2MAN in its emeraldine salt form has attracted particular attention because of its high thermal stability, easy synthesis, conductivity, and outstanding environmental stability [24,25]. In addition, its electrical conductivity can be controlled by a doping/dedoping process for practical use. Graphene oxide (GO), acting as a dopant in oxidation polymerization, was also added to reduce the conductivity and dedoping process of P2MAN. GO is an oxidized form of graphene with oxygen functional groups on the base planes and edges, such as epoxide, hydroxyl, carboxyl and carbonyl groups [26,27]. Although GO has an identical lamellar structure to graphene, it has a wide range of properties because of its functional groups and large surface area. In particular, the polarity of GO is compatible with polymer matrices when used as a principle material in composites, and it is quite stable in aqueous and other organic solvents [28]. This hydrophilicity offers a facile route to the synthesis of the GO/polymer composites [29]. Polymers, such as poly(methyl methacrylate), poly(acrylonitrile) and PANI have been studied as promising candidates for the preparation of GO/polymer composites for a range of applications [30,31]. The fabrication of composites with graphite and graphite oxide with PANI has been also reported [32–34].

In this study, GO/P2MAN composite particles were synthesized together with P2MAN, which was fabricated by in situ oxidation polymerization, in a GO dispersion [35,36]. The acidic groups and low electrical conductivity of GO are reported disadvantages, but these are a favorable and positive factor in the present ER study [35]. The low conductivity can reduce the possibility of dielectric breakdown as an ER material and the acid groups of GO act as dopant sites of P2MAN. The morphology and chemical structures of the product were characterized by field emission scanning microscopy (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD). The ER responses were examined using a rotational rheometer under a range of electric field strengths by dispersing the GO/P2MAN composite particles in silicone oil. A sedimentation test of the ER fluid was also conducted.

2. Experimental

2.1. Materials

Raw materials of graphite (powder, <20 μm, Sigma–Aldrich) and all the chemical reagents of the oxidant, potassium permanganate ($KMnO_4$, Sigma–Aldrich), sodium nitrate ($NaNO_3$, Junsei Co., Japan), sulfuric acid (H_2SO_4, 98%, DC Chemical, Korea), hydrogen peroxide (H_2O_2, 30%, OCI), 2-methylaniline (98%, Sigma–Aldrich), ammonium persulfate (APS) (Daejung Co., Korea), and hydrochloric acid (HCl) (35%, Duksan, Korea) were used as received. Distilled water was used in all experimental processes.

2.2. Preparation of graphene oxide (GO)

GO was synthesized from graphite powder using a modified Hummers method [37]. In a typical synthesis procedure, 0.1 g of graphite was added to 50 ml H_2SO_4 in an ice bath, followed by the addition of 0.3 g of $KMnO_4$ and 0.05 g of $NaNO_3$. After stirring for 4 h, 50 ml of distilled water was slowly added to the mixture and maintained at 22 °C for 30 min. A H_2O_2 solution was then added slowly to the mixture with stirring until the color changed to brilliant brown, indicating fully oxidized graphite. The acquired graphite oxide slurry was exfoliated to generate GO sheets by sonication using a custom-made powerful ultrasonic generator (600 W, 29 kHz, Kyungil Ultrasonic Co., Korea) for 3 h with stirring. Finally, the mixture was separated by centrifugation and washed 3 times with 5% HCl and distilled water [38].

2.3. Preparation of graphene oxide/poly(2-methylaniline) composite particles

First, 0.15 g of GO was added to 200 ml of distilled water and sonicated for 30 min. Subsequently, 1.5 g of 2-methylaniline was added to the resulting GO suspension. The mixture was transferred to a 500 ml reactor and stirred at 120 rpm. After cooling to 0 °C, 2.22 g of APS and 7.2 g of HCl dissolved in 30 g of distilled water were added dropwise to the reactor. The mixture was stirred for 10 h. The resulting product was washed 3 times with ethanol and distilled water and dried overnight in a vacuum oven at 60 °C.

To be applied as an ER suspension, the electrical conductivity of the obtained GO/P2MAN composite particles was controlled by a dedoping process. In detail, the particles were dispersed in distilled water and their pH was adjusted to 9 using a 1 M NaOH solution. Finally, the product was washed and dried in a vacuum oven.

Pure P2MAN without GO was also synthesized under the same conditions for comparison.

2.4. Preparation of ER fluid

The GO/P2MAN composite particles were shaken through a 100 μm sieve to obtain small particles. A 10 vol% ER fluid was prepared by dispersing the composite particles in silicone oil (dynamic viscosity: 30 cS, density: 0.96 g/cm^3). The densities of P2MAN and GO/P2MAN were 1.27 and 1.43 g/cm^3, respectively.

2.5. Characterization

The morphology of the fabricated GO/P2MAN composite particles was observed by FE-SEM (S-4300, Hitachi). The chemical structure was analyzed by FT-IR spectroscopy (Perkin Elmer System 2000). The crystalline structure of the product was determined by powder XRD (DMAX 2500, Rigaku) using Cu $K\alpha_1$ radiation ($\lambda = 0.154$ nm). The density of the GO/P2MAN composite particles was measured using a gas pycnometer (AccuPyc 1330). A fibrillation phenomenon was captured by optical microscopy (OM) (Olympus BX51). The rheological properties of the ER fluid were examined by rotational rheometry (MCR 300, Anton-Paar) equipped with a high voltage power supplier (Fug, HCN 7E-12 500) using a Couette-type sample loading geometry (CC 17, the gap distance between the bob and cup was 0.71 mm). To confirm the improvement in the sedimentation stability, a Turbiscan lab expert system (Turbiscan Classic MA2000, Formulaction) was used to determine the degree of light transmission as a function of time.

3. Results and discussion

Fig. 1 presents FE-SEM images of the pure GO, P2MAN and GO/