

Facile and fast synthesis of polyaniline-coated poly(glycidyl methacrylate) core–shell microspheres and their electro-responsive characteristics

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ABSTRACT

Electro-responsive core–shell structured particles were fabricated in two steps. In the first step, a spherical and monodisperse poly(glycidyl methacrylate) (PGMA) core was prepared by dispersion polymerization with an epoxy group, which was then functionalized with an amine functional group (ami-PGMA) via an epoxide–amine reaction with ethylenediamine. In the second step, a conducting polyaniline (PANI) shell was grafted onto the ami-PGMA surface via the in situ polymerization of an aniline monomer with a uniform thickness. The epoxy group on the PGMA microspheres provided a simple and fast way to react with amine functional groups without the need for a further swelling or grafting process. The morphology of the core–shell structure was confirmed by scanning electron microscopy and transmission electron microscopy. The electrorheological properties of the PGMA/PANI particles-based suspension were examined using a Couette-type rotational rheometer under an applied electric field. The shear stress curves were fitted to the Cho–Choi–Jhon (CCJ) model of the rheological equation of state.

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1. Introduction

A range of smart materials with various rheological characteristics, such as viscoelasticity, yield stress and dynamic modulus, that can be controlled by external electric or magnetic stimuli, have promising technological applications in mechanical engineering devices, microfluidics, drug delivery, and robotics [1–3]. Electro-rheological (ER) fluids are typically two-phase colloid suspensions of polarizable particles dispersed in liquid media, and their state can be tuned reversibly from a liquid to solid with using an external electric field [4–7]. The dispersed particles behave as electric dipoles, which become polarized and attract each other to form fibril-chains oriented along the direction of the electric field, producing tunable rheological properties. The short response time, low energy consumption, and simple mechanics also highlight the distinctive superiority of ER fluids. On the other hand, the application of ER fluids still faces several problems, such as low yield stress, colloidal instability, and issues in designing steady-high voltage supply devices. Among the range of promising ER smart materials, conducting polymers in the semiconducting regime, such as polyaniline (PANI) [8] copolyaniline [9], polypyrrole [10], polyphenylenediamine [11], and composites composed of inorganic/conducting particles including TiO₂, BaTiO₃, silica, in addition to graphene or graphene oxide/conducting polymer

systems [12–15], have been reported as the prevailing ER particulates. Polymeric materials with polar groups such as amino, hydroxyl groups also affect the ER performance positively because polar groups can play the role as an electric donor [16]. In addition, the morphology of the suspended particles is one of the most critical parameters for improving the ER effect from a theoretical viewpoint, in which the suspended electro-responsive materials are generally assumed to be monodisperse and spherical. Novel core–shell structured composites with a monodisperse core and uniform shell with the appropriate conductivity and optimal interfacial polarization have been reported as ER materials. In addition, in a core–shell structured system, the particle density and size can be controlled, the dispersibility can be improved, and desired materials can be functionalized using single to multiple coating processes. The core–shell structured systems with a monodisperse and spherical core were reported to show a typical even enhanced ER effect and colloid stability [17–19]. Among the many conducting polymers reported thus far, PANI is used most widely as potential ER particles because of its ease in handling (morphology and electrical conductivity), facile fabrication, superior physical properties, and potential for improving the ER effect [20]. A range of core–shell structured ER systems have been reported may including PANI shell-coated poly(methyl methacrylate) (PMMA) microsphere [21], PANI/polystyrene composite microsphere [22], coaxial cable-like PANI@titania nanofiber [23,24], silica nanoparticle decorated polyaniline nanofiber [25], PANI/bentonite nanohybrid [26], gold nanoparticle decorated silica microsphere [27], and silica–titania composite particle [28]. In addition, the

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core–shell interaction was enhanced using glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) as crosslinking agents and oxydianiline as grafting sites [29,30]. In the later studies, the PMMA core was first swollen by GMA [29] or GMA and EGDMA [30] to possess glycidyl groups, and diamine functional groups were grafted using oxydianiline before being coated by a PANI layer.

In the present study, a facile and direct route was introduced to prepare PANI-coated monodisperse poly(glycidyl methacrylate) (PGMA) core–shell structured particles (marked as PGMA/PANI). The PGMA microspheres possessing a glycidyl group were functionalized with amine groups using ethylenediamine instead of oxydianiline, which is denoted as ami-PGMA without an additional swelling or crosslinking treatment [31], and the conducting PANI shell was then grafted on the ami-PGMA surface using an in situ dispersion polymerization method with ammonium persulfate (APS) as the initiator. The ER properties of the PGMA/PANI particles were examined.

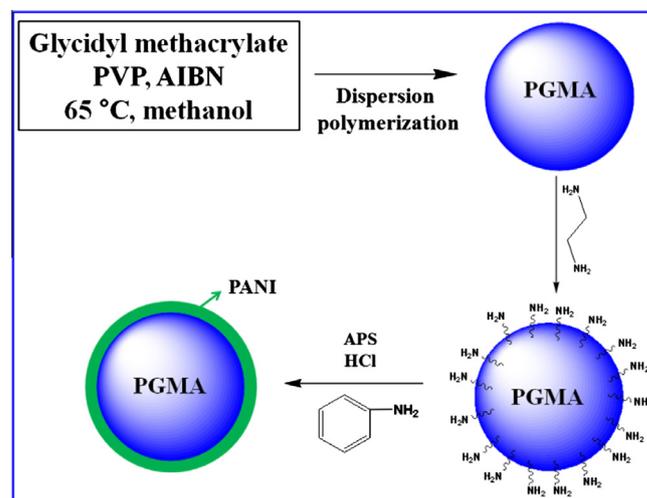
2. Experiment

2.1. Materials

The initiator, 2,2'-azobisisobutyronitrile (AIBN) (98% purity, Junsei Chemical Co., Japan) was purified prior to use. Glycidyl methacrylate (GMA) (97% purity, Aldrich), polyvinylpyrrolidone (PVP) ($M_w = 55,000$ g/mol, Aldrich), ammonium persulfate (APS) (Daejung Co., Korea), methanol (99.9% purity, Seoduck Chemical Co., Korea), ethylenediamine (EDA) (Sigma), and HCl (35%, OCI Co., Korea) were used as received. Deionized (Di) water was used in all experiments.

2.2. Preparation of poly(glycidyl methacrylate) and amine-modified PGMA microsphere

Monodispersed PGMA microspheres were synthesized using a typical dispersion polymerization method [31,32]. Both the GMA monomer (40 g) and PVP (8 g) as a stabilizer were dissolved in methanol (180 g) with mechanical stirring under a nitrogen atmosphere and heated to 65 °C. The polymerization was started by adding an AIBN initiator solution (0.4 g AIBN was dissolved in 25 g methanol), and the reaction was maintained for additional 24 h at 65 °C. The ami-PGMA microspheres were prepared using the following procedure. The resulting PGMA microspheres (10 g) were dispersed in di-water (80 g) by mild sonication and heated to 70 °C. EDA (20 g) was then added to the dispersion, and the reaction was allowed to proceed for 12 h. The amine groups were grafted onto the PGMA surface via an amine–glycidyl reaction between the amine and epoxy functional groups. Compared to the anionic characteristics of pure PGMA particles reported in Ref. [29], the positive zeta-potential value (60.29 mV) of the amine-PGMA microspheres confirmed the successful grafting of amino functional group on the PGMA surface. For the zeta-potential measurement based on electrokinetic phenomena, the ami-PGMA microspheres were re-dispersed in di-water with the aid of sonication for 30 min to generate homogeneous solution. An applied electric field directed along the phase boundary causes a relative motion of one phase with respect to the other, and motion along the charged phase boundary creates an electric potential. Small charged particles suspended in a medium move when a potential gradient is applied, a value of the zeta-potential is obtained from the electrophoretic mobility in the electrophoresis [33].



Scheme 1. Schematic diagram of the experimental route to synthesize PGMA/PANI particles.

2.3. Preparation of core–shell structured PANI-coated PGMA particles

The PANI shell was coated on the PGMA surface using the following procedure. The ami-PGMA particles (1.5 g) were first dispersed in di-water (50 g) with mild stirring. Aniline monomer (0.375 g) dispersed in di-water (120 g) and 35% HCl (15.19 g) were then added to this suspension. The reaction was conducted at 0 °C for 24 h using an aqueous APS (1.16 g) solution as an initiator. Scheme 1 shows the entire experimental process. To be applied as an ER material, the electrical conductivity of the obtained PGMA/PANI particles was controlled using a dedoping process in a semiconducting regime. In detail, the obtained PGMA/PANI particles were dispersed in di-water first, and then, their pH value in the dispersion was adjusted to 9 using 1 M NaOH solution. The final solid product (dedoped PGMA/PANI particles) was centrifuged, washed with di-water and ethanol several times, and then finally dried in a vacuum oven.

2.4. Characterization

The morphology of the fabricated particles was observed by field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi, Japan) with an applied voltage of 15 kV at a working distance of 15 mm and transmission electron microscopy (TEM, Philips CM200). The zeta-potential was determined using an electrophoretic light scattering spectrophotometer (ELS-8000, Photal, Otsuka Electronics Co. Ltd., Japan). The chemical structure was analyzed by Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer System 2000). The thermal properties were examined by thermogravimetric analysis (TGA, TA Instruments, Q50, USA) under a nitrogen flow. The rheological properties of the ER fluid were examined by rotational rheometry (Physica MCR 300, Stuttgart, Germany) equipped with a high voltage generator using a Couette-type sample loading geometry with a bob and cup (CC 17, gap distance is 0.71 mm). The density of the PGMA/PANI was measured using a gas pycnometer (AccuPyc 1330).

3. Results and discussion

SEM images are used to observe the particle size and surface morphology. Fig. 1 shows the surface morphology of the pure PGMA microspheres and PGMA/PANI particles. The PGMA microspheres had a smooth surface with a uniform diameter of

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