

Preparation of polyaniline coated poly(methyl methacrylate) microsphere by graft polymerization and its electrorheology

Il Sang Lee, Min Seong Cho, Hyung Jin Choi*

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, South Korea

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Abstract

Monodisperse acrylic microspheres (diameter 9.2 μm) (An-PGMA) with aniline moieties on the surface were initially prepared by a seeded emulsion method, and then composite particles (PA-PGMA) possessing polyaniline (PANI) shell were prepared via an in situ polymerization of aniline using An-PGMA particles as a core material inducing grafting polymerization of aniline. The PANI layer was found to be formed on the An-PGMA surface from the microscopic image, ^{13}C FT-NMR and TGA of the PA-PGMA particles. Suspension of the PA-PGMA particle dispersed in silicone oil showed typical electrorheological (ER) characteristics under external electric fields.

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1. Introduction

Electrorheological fluids in general are suspensions of dielectric (either semiconductive or polarizable) particles in a medium such as nonconducting liquids [1,2]. They exhibit drastic changes in their rheological properties including a large increase in the apparent viscosity and the formation of reversible suspension microstructures with an applied electric field [3] by gelling. According to the phenomenological model, the suspended particles are polarized due to a dielectric mismatch between the particles and the suspending fluid under an applied electric field, and then the interaction among the polarized particles causes them to arrange into strings along the direction of the electric field. Clearly, the ER performance critically depends on the electrical properties of the suspended particles. While the magnitude of the response depends on material properties, the increase in suspension viscosity on application of the electric field is very rapid and reversible. Since their first discovery, this inherent feature has triggered an enormous amount of research activity both in theory [6] and in the

development of various engineering applications, such as shock absorbers [7], engine mounts and smart structures [8].

Among the many promising materials for ER suspensions, conducting polymers in a semiconducting regime including polyaniline (PANI) [9,10], copolyaniline [11], poly(*p*-phenylene) [12], polythiophene [13], polyphenylenediamine [14], poly(acene quinone) radicals [15], and polymer–inorganic nanocomposite [16,17], have been adopted as anhydrous dry-base ER fluids because of their ease in handling and superior physical properties, compared to various hydrous wet-base ER materials [18].

As a dispersed phase of the ER fluid, surface conductive particles with an acrylic polymer as a core and polyaniline (PANI) as a shell were synthesized. The systems using poly(methyl methacrylate) PMMA particles as a core material prepared by dispersion polymerization [5] with uniform size distribution, were studied and characterized as the potential ER material [4,19]. The composite particles were monodisperse and spherical in shape, and partial electrophoresis was observed for these ER fluids during particle chain formation under an applied DC electric field indicated by a reduction in the particle fibrillation density between two electrodes.

To improve the adhesion between PANI shell and acrylic core with uniform PANI layer thickness, we newly

* Corresponding author. Fax: +82 32 865 5178.

E-mail address: hjchoi@inha.ac.kr (H.J. Choi).

introduced a grafting polymerization of aniline on the surface of the core. Aniline was attached to the surface through a reaction of a reagent having two aniline moieties with glycidyl groups on the acrylic core, which provides grafting sites during the PANI polymerization. Core/shell particles prepared by this process were found to have uniform thickness of the conducting PANI shell, and these particles were adopted as an ER material in the present work.

2. Experimental

Overall procedure of our particle synthesis for the ER fluid is given in Fig. 1. The monodispersed spherical acrylic cores with $9.2\ \mu\text{m}$ were prepared by a seeded emulsion process [20]. At first, spherical seeds with a diameter of $6.5\ \mu\text{m}$ were made of PMMA by a dispersion polymerization method, and they were swollen by glycidyl methacrylate with a radical initiator, benzoyl peroxide (BPO) to about $10.95\ \mu\text{m}$. A polymerization was followed by increasing temperature of the reaction system up to $75\ ^\circ\text{C}$, and the reaction system was kept at this elevated temperature for 24 h with vigorous continuous stirring. The yield of PGMA is about 86%, that is, we obtained 82.5 g of PGMA from the reaction of PMMA seed (12 g) and GMA (84 g). The obtained glycidyl functionalized acrylic beads (PGMA) were dispersed in acetone containing oxydianiline, and the reaction between glycidyl group and amine took place at $55\ ^\circ\text{C}$ (An-PGMA).

The reaction was confirmed from both ^{13}C FT-NMR spectra and SEM images. In addition, surface change from glycidyl to aniline groups was also analyzed by zeta-potential values measured using electrophoretic light scattering spectrophotometer (Otsuka ELS-8000, Japan), which are $-12.48\ \text{mV}$ for PGMA and $0.39\ \text{mV}$ for An-

PGMA. The cationic characteristic of the An-PGMA measured is the evidence of the presence of aniline functionality on the PGMA surface. The aniline was polymerized within an aqueous acidic medium containing poly(vinyl alcohol) (PVA) as a dispersing stabilizer and An-PGMA. Concurrently, ammonium peroxydisulfate was used as an initiator and the polymerization was continued for 24 h at $0\ ^\circ\text{C}$ [9], in which PA-PGMA particles were synthesized using the same amounts of both seed PMMA and PANI.

In order to adopt this synthesized core/shell particle (PA-PGMA) as an ER material, the electrical conductivity of PA-PGMA particle was controlled to be in a semiconductive range via a dedoping process [4]. The conductivity of PA-PGMA, $3.02 \times 10^{-4}\ \text{S/cm}$ was decreased to $7.16 \times 10^{-11}\ \text{S/cm}$ by dedoping. Finally, the particles were dried and dispersed in silicone oil to make an ER fluid with a particle concentration of 10 vol%. The ER fluid was characterized by a rotation-type rheometer (Physica MCR-300, Germany) equipped with a high voltage generator.

3. Results and discussion

Scanning electron microscopic images of both PGMA core particles and surface treated An-PGMA particles are shown in Fig. 2(a) and (b), respectively. Particle size of the PGMA particles is about $9.2\ \mu\text{m}$ with uniform size distribution, however with some roughness of their surfaces. After the reaction of oxydianiline with PGMA, the surface of An-PGMA became much smoother, confirming the successful reaction between PGMA and oxydianiline. The core/shell particles, PA-PGMA, have another surface morphology after the polymerization of aniline. The average size of PA-PGMA particles with $10.95\ \mu\text{m}$ is presented in Fig. 3. The content of the PANI can be estimated based on the weight loss from Fig. 4. Sharp

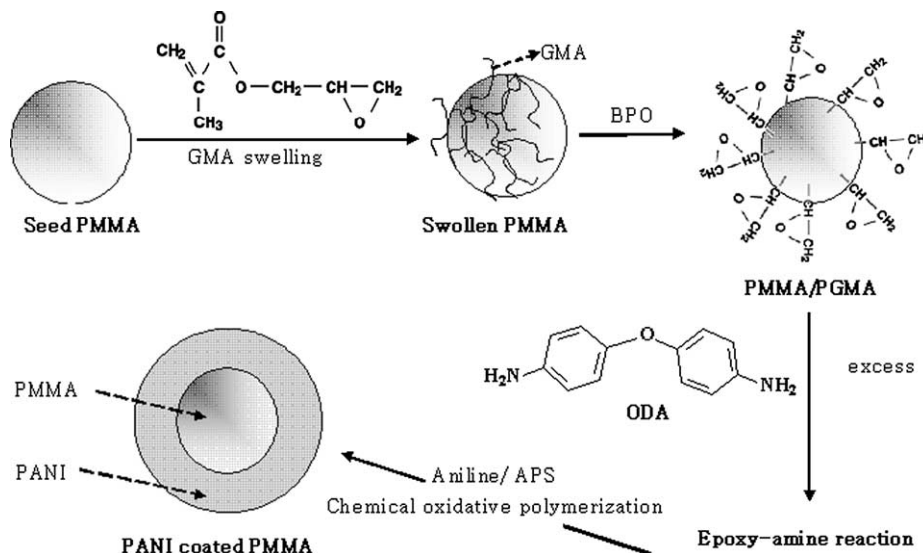


Fig. 1. Schematic diagram on polymerization procedure.

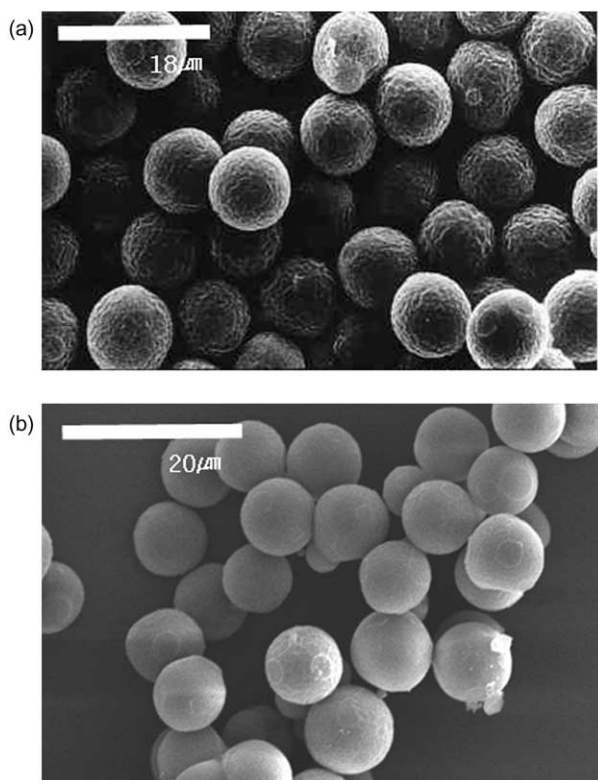


Fig. 2. SEM images of PGMA cores (a), An-PGMA particles (b).

weight loss begins at nearly 350 °C and continues till 550 °C for PANI, and it is considered to be attributed to thermal degradation of the PANI chains.

Comparing with our previous results of core/shell particles made from PMMA core particles [4], the layer of PANI of PA-PGMA particles in this study looks like possessing dense structure, and it seems to be due to the grafting reaction on the surface of An-PGMA during PANI polymerization. A small amount of sub-micron particles shown in Fig. 3 are homo PANI particles, which were formed within the aqueous medium rather than the surface of the core particles with the aid of PVA. These small PANI particles can be separated during a separation process using either a filtering method or a centrifugal method.

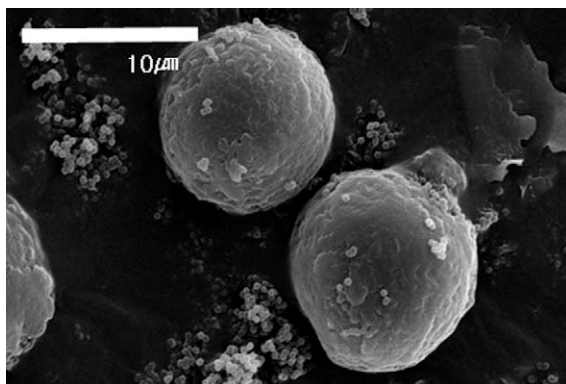


Fig. 3. SEM image of core/shell particles of PA-PGMA.

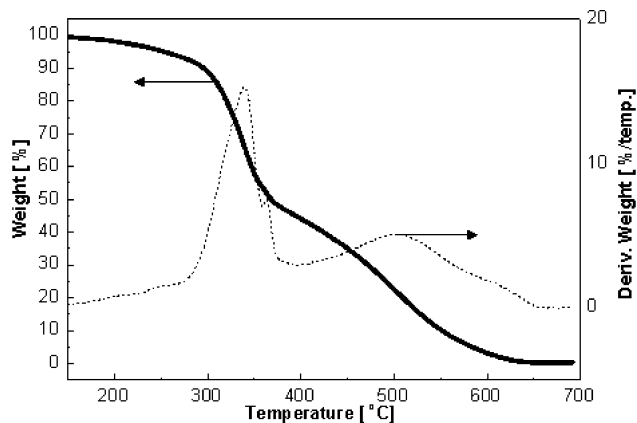


Fig. 4. TGA curves of PA-PGMA.

The ^{13}C FT-NMR spectra which examined the solid-state of PGMA cores and An-PGMA particles are shown in Fig. 5. After the epoxy-amine reaction, a hydroxyl group was appeared in the An-PGMA particles. From these results, the changes of functionality in the particles were confirmed including epoxy groups in PGMA and epoxy-amine group in the An-PGMA particles. In the case of An-PGMA, the presence of aniline moieties on the surface of particles was confirmed through benzene group at 80 ppm by An-PGMA in Fig. 5. We further characterized the surface charge of both PGMA and An-PGMA using a zeta-potential measurement, and the results of zeta-potential measurement of PGMA and An-PGMA were examined to -12.4 and 0.39 mV. Although the PGMA surface was anionic, the An-PGMA was found to have a cationic surface. It is the evidence that An-PGMA possesses aniline groups on the surface via the reaction between glycidyl groups of PGMA and oxydianiline.

The dedoped PA-PGMA suspensions in silicone oil show typical ER behaviors so that the suspensions exhibit Bingham fluid behavior with a yield stress under an externally applied electric field. In general, the structures in a concentrated suspension can be sufficiently rigid

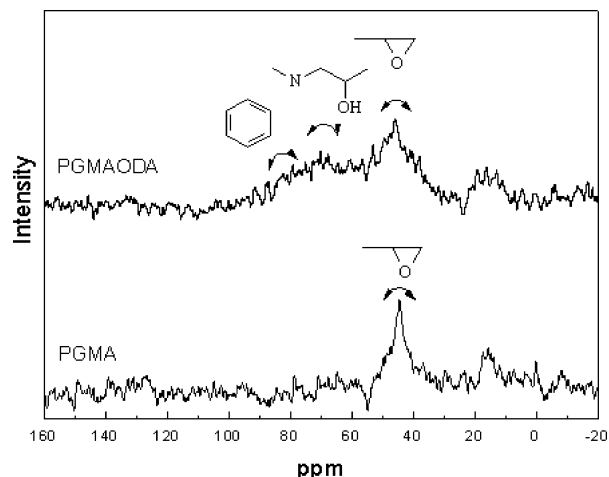


Fig. 5. ^{13}C FT-NMR spectra of PGMA particles and An-PGMA particles.

enough to permit the material withstand a certain level of deforming stress without flowing. The maximum stress that can be sustained without flow is the yield stress. For simple shear flow, this type of behavior is described by a following Bingham model [21,22].

$$\begin{cases} \tau = \mu\dot{\gamma} + \tau_0 & \text{if } \tau > \tau_0 \\ \dot{\gamma} = 0 & \text{if } \tau < \tau_0 \end{cases} \quad (1)$$

Here, τ_0 is the yield stress and μ is the viscosity.

As a representative, flow curves of PA-PGMA ER fluid under various electric fields are shown in Fig. 6 and these are equivalent flow behaviors of the Bingham model as given in Eq. (1). Without an electric field, the PA-PGMA suspension behaves as like a Newtonian fluid, in which the shear stress increases linearly with a shear rate, and it can be figured out with its slope of 1.0. By applying electric fields, the shear stress increases within the whole shear rate range with yielding behaviors such as a plateau shear stress as a function of a shear rate in the flow curves. In addition, the

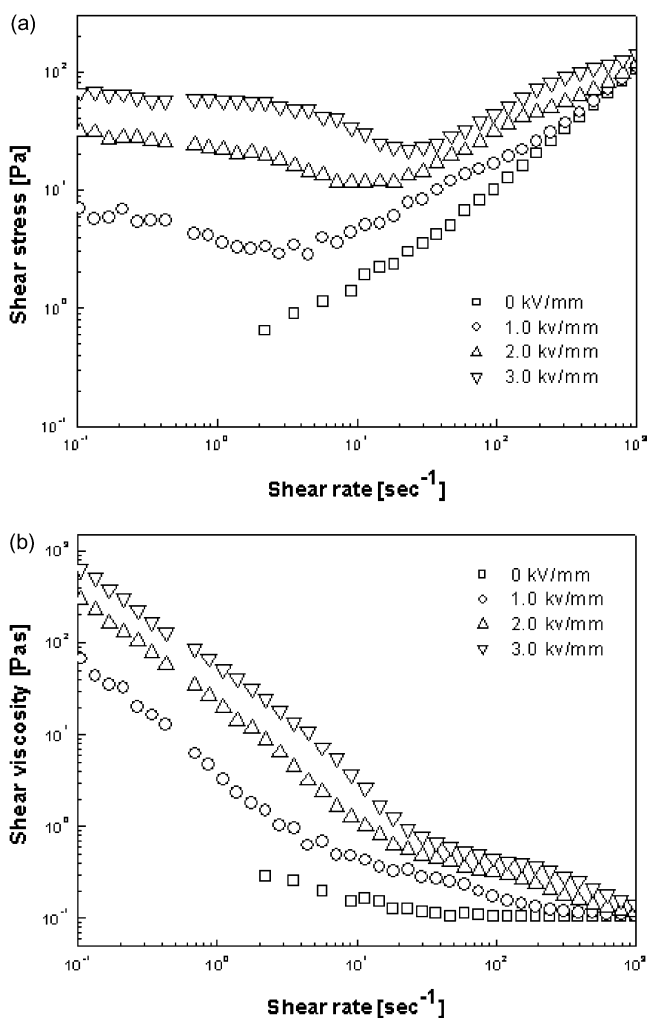


Fig. 6. (a) Shear stress versus shear rate of PA-PGMA based ER fluid under various electric fields. (b) Shear viscosity versus shear rate of PA-PGMA based ER fluid under various electric fields.

region of plateau becomes wider with the strength of electric field, indicating that the ER effects can be maintained up to higher shear rate with applied electric fields [23,24].

Fig. 6(b) shows the apparent shear viscosity of the same ER fluid measured at different electric fields. The viscosity not only increases by 2 or 3 orders of magnitude at a low shear rate region, but a shear thinning behavior of this ER fluid is also clearly observed. Furthermore, at high shear rates, the shear viscosity is observed to be the value obtained in the absence of an induced electric field. These behaviors are due to the microstructural change in the suspension; the destruction rate of the fibrils becomes faster than the reformation rate at the high shear rate.

4. Conclusions

Core/shell structure of PA-PGMA particles containing 50% wt PANI were synthesized with the same ratio of PMMA and PANI by oxidative in situ polymerization, using monodisperse acrylic microspheres (An-PGMA) with aniline moieties on the surface. Synthesized particles were examined using various analysis methods such as SEM, TGA, ^{13}C FT-NMR and zeta-potential meter. Since the pristine PA-PGMA particles right after synthesis were unsuitable for the ER test due to its high conductivity, we controlled their conductivity to be semiconductive via dedoping process of the particles.

The PA-PGMA based suspensions showed typical ER properties under an applied electric field with a yielding behavior, suggesting that the shear stress increases with the electric field strength for broad ranges of shear rate. The ER fluid dispersed in silicone oil showed an ER effect, with a yield stress up to 70 Pa under 3.0 kV/mm dc electric field. The region of plateau becomes wider with the strength of electric field, indicating that the ER effects can be maintained up to higher shear rates with applied electric fields.

Acknowledgements

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