Preparation of polystyrene/polyaniline composite particles and their electrorheology

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Abstract. Monodisperse polystyrene (PS) seed latex was initially prepared by a dispersion polymerization, and then polyaniline (PANI)-coated PS composite particles were synthesized by diffusion and polymerization of aniline at the interface. Characteristics of the obtained PS/PANI composite particles such as morphology and thermal property were examined using SEM and TGA, respectively. In addition, we employed a rotational rheometer to investigate rheological behaviour of the ER fluids based on both PANI particles and PS/PANI composites. Yield stress and flow response were investigated under electric field strengths showing typical ER behaviours. Further, the Cole-Cole plot and the dielectric spectra gave relaxation times of the ER systems, confirming the correlation of dielectric properties with ER performance.

1. Introduction
Electrorheological (ER) fluids, suspensions of polarizable particles in non-conducting liquids, exhibit drastic changes in their rheological properties including a large increase in the apparent viscosity and formation of reversible suspension microstructures with an applied electric field [1-4]. When a certain electric field is imposed to the ER fluids, they can flow by an applied shear stress exceeding a minimum limiting value. Therefore, the ER fluids are often considered as ‘Bingham fluids’, and the minimum limiting stress for flowing is designated by a yield stress. In addition, the apparent viscosity and shear stress of the ER fluids increase under an electric field.

These ER fluids also represent a phase transition from a liquid-like state to a solid-like behavior by forming a chain-like structure within milliseconds when an electric field is applied [5]. This can be understood qualitatively in terms of particles polarization induced by the mismatch between the dielectric constants of the particles and suspending fluid. Due to these unique variations of the rheological properties, the ER fluids have great potential applications in designing torque transducer, damper, actuator and other control systems [6, 7].

As a dispersed phase of the ER fluid, the latex particles are coated with thin overlayers of conducting polymers to form core-shell composite particles [8]. The combination of polymer latex and conducting polymers is expected to produce composite materials with new and unique properties intrinsic to dispersed microspheres and the improvement of polymer processability [9]. These are based not only on the electrical parameter, but also they often employ the chemical, electrochemical, optical and other physical properties of conducting polymers [10-12].
Polyaniline (PANI) is known to be an air-stable organic conducting polymer which is relatively easy to polymerize and to control its electrical conductivity [13]. As a potential material for the ER fluids having an environmental stability [14-16], the PANIs are adopted in this study.

In this work, we prepared surface conductive particles with a polystyrene (PS) microbead as a core and PANI as a shell. First, aniline was added to swell PS microbead under vigorous stirring, then aniline swollen PS was transferred into a water phase consisting of the APS, by which way oil in water system was formed. An overlayer of the conducting polymer is formed by a diffusion-interface-polymerization process of the aniline pre-absorbed on PS seed latex without any surface modification [17]. Core-shell structured 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.

2. Experimental

2.1. Synthesis of PS seed particles
The PS seed latex was prepared by a dispersion polymerization. Initially, the purified styrene was dispersed in methanol containing polyvinylpyrrolidone as a stabilizer at room temperature. The temperature of the mixture was increased up to 60ºC and then a radical initiator 2, 2-azobisisobutyronitrile (AIBN) was added into the reaction system. The polymerization continued for 24h at 60ºC. After the reaction, products were centrifuged with both methanol and distilled-water, and then dried using a freezing-drier. Final product was obtained in a powder form.

2.2. Preparation of PS/PANI composite particles
PS/PANI composite particles were formed by a diffusion-interface polymerization process of the aniline pre-absorbed on PS seed latex without any surface modification. Aniline (DC chemical, Korea) and ammonium persulfate (APS) (Daejung, Korea) were used as monomer and initiator, respectively. The PS seed latex was dispersed in 500ml of distilled water by vigorous stirring (200rpm) at 0ºC, after then aniline was added to the reactor. The PS seed latex/monomer weight ratio was fixed at 3:1. The mixture was stirred for 12h at 0ºC to allow sufficient absorption of aniline into the PS seed particles. The aqueous solution of APS was added to the dispersion in reactor and the initiator/aniline molar ratio was fixed at 1:0.6. This was followed by the addition of hydrochloric acid (1mol/L), also in an equi-molar amount relative to aniline, being dropped via syringe. Thus, aniline existed within polystyrene while the APS was dispersed in water phase, and there was no obvious reaction. In order to initiate polymerization of PANI, hydrochloride acid which diffused to polystyrene to initiate the reaction was dropped. The mixture was kept stirring with 200rpm at 0ºC for the first 6h of the polymerization, after which the polymerization was carried out for 20h at room temperature. The resulting PS/PANI composite was filtered with distilled-water and acetone sequentially to remove the excess initiator, monomer and oligomer. It was finally dried at 60ºC in vacuum oven for 2days. Furthermore, PANI particles were also synthesized using the conventional oxidation polymerization of aniline to produce a fine emeraldine hydrochloride form following our previous method and the details of PANI particles are same as previously reported [17].

2.3. Measurements
The particle size and surface feature were observed by scanning electron microscopy (SEM, S-4300, Hitachi). In order to study thermal degradation of the sample, thermogravimetric analysis (TGA, TA instrument Q50, USA) was carried out in the temperature range of 100-650ºC at a heating rate of 20ºC/min under an atmospheric condition (air). Electrical conductivity of the composite pellets was measured by a 4-pin probe resistivity meter (LORESTA-GP) and a MCP probe resistivity meter (HIRESTA-UP). To be applied as an ER material, the PS/PANI composites have to possess appropriate value of electrical conductivity. Therefore, we controlled the electrical conductivity of the composite via dedoping process and monitored the pH value to be 10 by adding either 1M NaOH or
1M HCl solution. The product was filtered, dried, and sieved. The conductivity of PANI-coated PS composites, $10^{-8}$ S/cm was decreased to $10^{-10}$ S/cm by dedoping.

We then prepared an ER fluid with 10vol% particle concentration of which the PS/PANI composites were dispersed in silicone oil (kinematic viscosity: 50cS, density: 0.96g/cm$^3$). ER behaviours were investigated by rotational rheometer (Physica MC120, Stuttgart) equipped with a DC high voltage generator. The dielectric spectra of ER fluids were also measured using the HP 4284A Precision LCR meter with HP 16452A Liquid Test Fixture for liquids to investigate their interfacial polarization. Frequency of the AC electric fields varied from 20Hz to 1MHz.

3. Results and discussion
Monodisperse PS latex was prepared initially by a dispersion polymerization, and then polyaniline (PANI)-coated PS composite particles were synthesized by a diffusion-interface polymerization process and used without post-treatment following the similar method we did for PANI-coated PMMA based ER fluid [13]. In order to initiate polymerization of PANI, hydrochloride acid which diffused to polystyrene to initiate the reaction was dropped. At the surface of PS, the hydrochloride acid modified aniline monomer got initiated with the aid of APS. Finally, more and more aniline monomer diffused to the interface and underwent polymerization [18].

Figure 1. SEM images of the PS seed particles (a), PS/PANI composite particles (b).

Figure 2. TGA analysis of PS seed particles and PANI-coated PS composite particles.

SEM images of both PS seed particles and PS/PANI composite particles are shown in Fig. 1 (a) and (b), respectively. We can find that the PS seed particles posses a nearly spherical morphology and uniform size distribution. Figure 1(b) represents that the PS/PANI composite particles are also spherical, indicating that the PANI-coated PS composites possess uniformity and well-defined core-
shell morphology. As for the composite, we observed that the size of the composites gets bigger than that of the PS seed particles. These images demonstrate that the surface of the PS/PANI composite particles is rough because of the deposition of the PANI component.

Figure 2 represents TGA curves of both PS seed particles and PS/PANI composites exhibiting the residual weight percentage versus the temperature. It was shown that the sharp weight loss beginning at nearly 280ºC and continuing till around 450ºC for PS is attributed to the large scale thermal degradation of PS chains. TGA curves of the PS/PANI composites were found to have 79% weight loss in the range between 280–390ºC which are in agreement with the decomposition of PS seed particles. Furthermore, the 21% weight loss of the composites from 390ºC to 610ºC is regarded to the degradation of PANI particles.

![Figure 2. TGA curves of PS seed particles and PS/PANI composites.](image)

Figure 3. Shear stress vs. shear rate for the PANI particles and PS/PANI composites based ER fluids (10 vol%) under various electric fields. (□: 0kV/mm, △: 0.7kV/mm, ○: 1.5kV/mm. Open symbol for PANI particles, closed symbol for PS/PANI composites)

![Figure 3. Shear stress vs. shear rate.](image)

Figure 4. (a) Dielectric spectra of PANI particles and PS/PANI composites based ER fluids, (b) Cole-Cole fitting curves for PANI particles and PS/PANI composites based ER fluids. (closed symbol and solid line for PANI particles, open symbol and dash line for PS/PANI composites)

![Figure 4. Dielectric spectra and Cole-Cole fitting curves.](image)
The ER behaviors of shear stress ($\tau$) as a function of the shear rate under various electric field strengths for the PANI particles and PS/PANI composites based ER fluids are shown in Fig. 3. The dedoped PS/PANI suspensions in silicone oil show typical ER behaviors such that the suspensions exhibit Bingham fluid behavior with a yield stress under an externally applied electric field. By applying electric fields, the shear stress increases within the whole shear rate with yielding behaviors such as a plateau with shear rate in flow curves. This could be explained by the reformation of the broken chain-like structure. In addition, the region of plateau becomes wider with the strength of electric field, indicating that the ER effects can be maintained up to a higher shear rate with applied electric fields.

Figure 4 (a) and (b) shows the dielectric spectra ($\varepsilon'$ and $\varepsilon''$) as a function of the frequency and Cole-Cole plots for 10 vol% PANI particles and PS/PANI composites based ER fluids, respectively [19, 20]. These are typical results for the interfacial polarization of suspensions including the ER fluids consisting of polarizable dispersed phases in an insulating media. Even though $\varepsilon_0$s of ER fluids are not shown in experimental results, they can be determined by fitting data with the Cole-Cole plots.

Lines in Figure 4 are fitted from the famous Cole-Cole formula (Eq. 1) [21] with parameters given in Table 1.

$$\varepsilon'' = \varepsilon' + i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_\omega}{1 + (i\omega\lambda)^{-\alpha}} \quad (1)$$

$\Delta \varepsilon \equiv \varepsilon_0 - \varepsilon_\infty$ is an achievable polarizability in ER fluids. The $\Delta \varepsilon$ dependence on ER properties also has some positive effect on good ER performance. Hence, in Table 1, we can see that the $\Delta \varepsilon$ of PS/PANI composite based ER fluids is lower than that of the PANI particles based ER fluids suggesting a weak ER behaviour.

| Table 1. Parameters in Equation 1 for PANI particles and PS/PANI composites (10 vol%) based ER fluids. |
|-----------------|-----------------|-----------------|
| Parameter       | PANI            | PS/PANI         |
| $\varepsilon_0$ | 6.87            | 4.55            |
| $\varepsilon_\infty$ | 2.79          | 2.70            |
| $\Delta \varepsilon$ | 4.08          | 1.85            |
| $\alpha$        | 0.365           | 0.260           |
| $\lambda$       | 0.0012          | 0.0022          |

In addition, the relation time ($\lambda$) for interfacial polarization of ER fluids is known to be related with yield stress and stress enhancement under the applied electric field. When analyzing the dielectric spectra, we can see that the relaxation times are 1.2ms and 2.2ms for the two ER fluids separately. In general, short relaxation time is known to be related with higher shear stress. Obviously, the above analysis on the dielectric spectra coincide with the results obtained from comparing the shear stress.

4. Conclusion

Core-shell structure of PS/PANI composites was synthesized via a diffusion-interface-polymerization process of the aniline to precipitate onto the PS surface without any surface modification. The core-shell structure with rough surface was confirmed by SEM images. TGA data showed that the weight percent of conductive PANI was about 21%, indicating the deposition of the PANI component in the polystyrene core. We also analyzed the flow response as a function of various electric fields to study the different behaviors for the two kinds of ER fluids. PS/PANI composites based on ER fluid
indicated typical ER behaviors, showing lower shear stress than that of pure PANI which was attributed to the influence of PS particles on conducting PANI due to its low dielectric performance. At last, investigated dielectric spectra well interpreted the difference in ER performances.

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