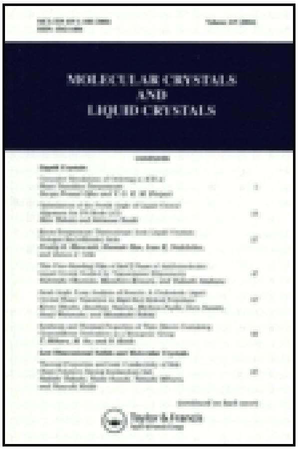

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EFFECT OF POLY (SODIUM 4-STYRENESULFONATE) STABILIZER ON SYNTHESIS AND CHARACTERIZATION OF POLYANILINE NANOPARTICLES

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EFFECT OF POLY (SODIUM 4-STYRENESULFONATE) STABILIZER ON SYNTHESIS AND CHARACTERIZATION OF POLYANILINE NANOPARTICLES

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Monodisperse polyaniline (PANI) nanoparticles were synthesized from an oxidative dispersion polymerization using poly(sodium 4-styrenesulfonate) as both a polymeric stabilizer and a doping agent due to its acidity. Particle size and shape of the PANI were examined via SEM, TEM and dynamic light scattering (DLS). The particles were also characterized spectroscopically by UV-VIS, and its conductivity was determined to be between 10^{-1} *and* 10^{0} $S\,cm^{-1}$. *The electrorheological fluids of the PANI nanoparticles were further prepared and their rheological properties were investigated using a rotational type rheometer equipped with a high voltage generator.*

INTRODUCTION

Polyaniline (PANI) occupies an important position in the inherently conducting polymer family for various electrochemical applications because of its facile synthesis, good environmental stability, doping capacity, low material cost and easy conductivity control [1]. Nevertheless, its successful application depends on how effectively one can overcome the difficult

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*Correspondening author. E-mail: hjchoi@inha.ac.kr processability induced by its insolubility in common solvents. Thus, the improvement of dispersion quality is an attractive approach for improving processability, since colloidal dispersions may be directly applied to their industrial application.

In this study, to enhance dispersion stability of the PANI, we used poly(sodium 4-styrenesulfonate) (PSSS) with pendant benzene sulfonate group as both a polymeric stabilizer and a doping agent due to its acidity. This experimental approach to synthesize nanoparticles was adopted to stabilize the dispersion in nanoscale with the polymeric stabilizer. We then examined both its electrical property and the potential use as an electrorheological (ER) fluid. ER fluids, dispersions of polarizable or semiconducting particles in insulating oils, are a class of materials whose rheological characteristics are controllable through the application of an electric field. The drastic change in rheological and electrical properties under an applied electric field originates from the particle migration and formation of a chainlike or columnar structure oriented along the electric field direction over the gap between the electrodes [2–5], and can be fine-tuned by an applied electric field.

EXPERIMENTAL

The PANI particles were synthesized by an oxidative dispersion method. The PSSS (Aldrich, $M_w = 70,000$) was slowly dissolved in deionized water. Based on the conductivity of the particles, the effectiveness of PSSS as a dopant could be examined. Aqueous HCl and aniline were added to the solution and the reaction mixture was continuously stirred at 0°C [6]. An aqueous solution containing oxidant and ammonium peroxydisulfate was added through dropping, with continuous stirring for 24 h at 0°C. The light yellow solution gradually darkened and acquired an emerald color over a period of 40 min. The color of the solution eventually turned into dark green, indicating a characteristic of the doped PANI with PSSS stabilizer (PAPSSS). The resultant dark green dispersions were purified three times by centrifugation. Then the particles were filtered and washed in order to remove oligomer and excess monomers. A four-probe method and a Janis closed-cycle refrigerator system were used for measuring the temperature-dependent dc conductivity $\sigma_{dc}(T)$ from 300 to 10 K. The conductivity was controlled to an appropriate conductivity range for their ER application by controlling pH of the dispersed solution to be 12. ER fluids were prepared by dispersing the dried PAPSSS particles in silicone oil (viscosity: 30 cS) at 15 wt%. The properties of PANI based ER fluids were measured by a rotational rheometer (MC120, Physica) equipped with a high DC voltage generator.

RESULTS AND DISCUSSION

In general, the size and shape of the PANI particles are determined by a rate balance between the adsorption rate of stabilizer and the rate of polymerization during the synthesis. A spherical shape will be observed when the adsorption rate of the stabilizer exceeds the rate of polymerization. Since the polymeric stabilizer chain is adsorbed onto the semiconducting polymer particles during synthesis, agglomeration of the particles would be prevented by the steric stabilization, which, in turn, results from due to the excluded volume effect of the stabilizer adsorbed on the particle surface. TEM of Figure 1 and DLS data indicate that the PAPSSS particles in the dispersion have a spherical shape with a uniform size. However, the larger aggregates of the primary particles might be formed during filteration and drying process of the particles, as observed via the scanning electron microscopy (SEM).

The conductivity of the nanoparticles containing PSSS (PAPSSS) was $0.11\,\mathrm{Scm}^{-1}$. The measurement of the DC-electrical conductivity of the dry PAPSSS nanoparticles was carried out at room temperature with a compressed pellet using a four-probe method. Figure 2 shows the temperature dependence of $\sigma_{\mathrm{dc}}(\mathrm{T})$ of the PAPSSS sample. The three-dimensional (3D) variable range hopping (VRH) model [7,8] provides the best fit for $\sigma_{\mathrm{dc}}(\mathrm{T})$ of the chemically synthesized PAPSSS in the present investigation with the

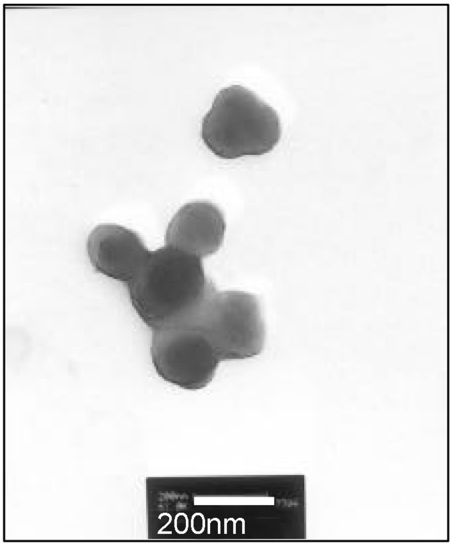

FIGURE 1 TEM micrograph of polyaniline (PANI) particles.

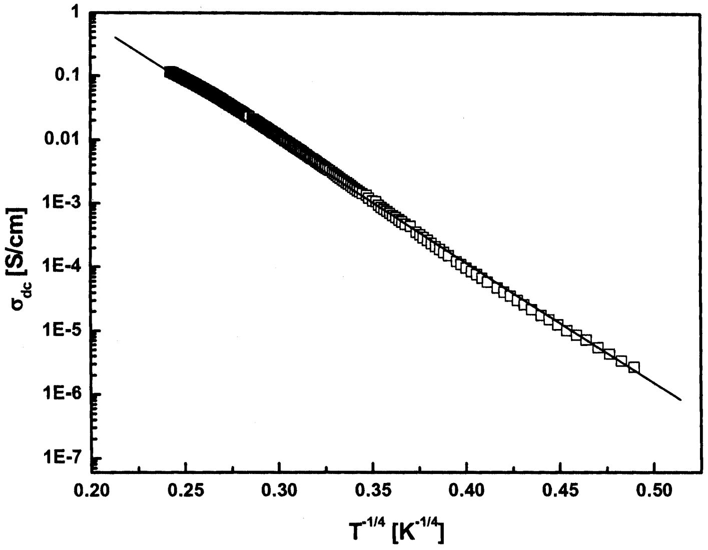

FIGURE 2 Temperature dependence of dc conductivity (σ_{dc}) for PAPSSS.

following equation,

$$\sigma_{\mathrm{dc}}(\mathrm{T}) = \sigma_0 \exp\left[-\left(\frac{\mathrm{T}_0}{\mathrm{T}}\right)^{1/(1+\mathrm{d})}\right], \quad \text{where d} = 3. \tag{1}$$

Here T_0 can be interpreted as an effective energy separation between localized states and can be written as $\mathrm{T}_0 = 16\alpha^3/\mathrm{k_B N(E_F)}$, where $\mathrm{k_B}$ is the Boltzmann constant, $\mathrm{N(E_F)}$ is the density of states at the Fermi level, and α^{-1} is the localization length in the parallel (perpendicular) direction. Usually, $\sigma_{\mathrm{dc}}(\mathrm{T})$ of PANI particles follows a quasi-one-dimensional (1D) variable range hopping (VRH), but the experimental result of $\sigma_{\mathrm{dc}}(\mathrm{T})$ shows that our PAPSSS particles deviate from the 1-dimensional VRH model due to the addition of the polymeric stabilizer. Polypyrrole/clay nanocomposite was recently found to follow 3D VRH model due to its quasi network structure through the interchain links and side chains [9].

The absorption spectra were obtained for the PAPSSS nanoparticles, and the PANI in a mixed solvent of DMF and deionized water (50:50). In Figure 3, the absorption peak at 320 nm of the PANI is attributed to $\pi - \pi^*$ transition of benzenoid rings and the peak at 602 nm is due to $\pi - \pi^*$ transition of quinoid ring of the polyemeraldine chain. Absorption spectra for redispersed samples of nanoparticles with HCl dopant showed different features from those of the PANI salt dispersion. Two main peaks were slightly shifted to a longer wavelength with a greatly diminished localized polaron band or with a free carrier tail. It could be because of the removal

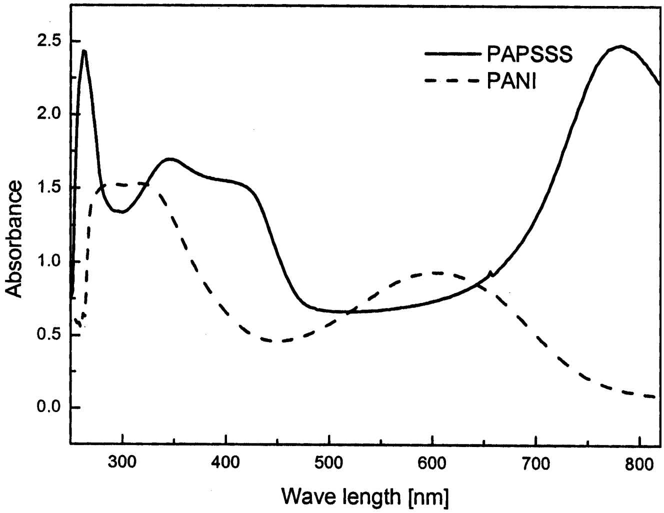

FIGURE 3 Electric absorption spectra of both PANI and PAPSSS.

of undesired components such as excess HCl, unreacted aniline monomers and oligomers. However, in the case of the PAPSSS, the spectra showed a characteristic of emeraldine salt, exhibiting a strong localized polaron band at 780 nm, as well as a second polaron band and a $\pi - \pi^*$ transition band at 440 and 346 nm, respectively. This may be because we could not perfectly remove the PSSS stabilizer adsorbed onto the conducting polymer nuclei [10]. The anionic dopant of PSSS, incorporated as part of the molecular complex, is strongly attached to the PANI chain to form a double stranded structure. The complex does not decompose or unwind in acid, base, solvent, mild oxidant/reductant, or by heat. In contrast, under the same conditions the single-strand PANI loses its dopant and becomes non-conductive. Sun *et al.* [11] reported that the polyelectrolyte strongly influences the pH for deprotonation of the PANI chain. With a small anionic dopant, the single-strand PANI deprotonates at pH 4. The same transition occurs at pH 9 for the molecular complex of PANI and PSSS complex in water. The origin of this effect comes from the electrostatic field near the polyanion chain.

Figure 4 shows flow curves of shear stress vs. shear rate for PAPSSS particle based ER fluid with various electric field strengths. In the absence of an electric field, the fluid is similar to that of a typical concentrated shear-thinning suspension. The slope of the shear stress – shear rate plot (log scale) is less than 1 (which is the Newtonian fluid limit). Shear stresses of the ER fluid increased over the entire shear rate range with an increase in the electric field strength [12,13]. The flow behavior of an ER

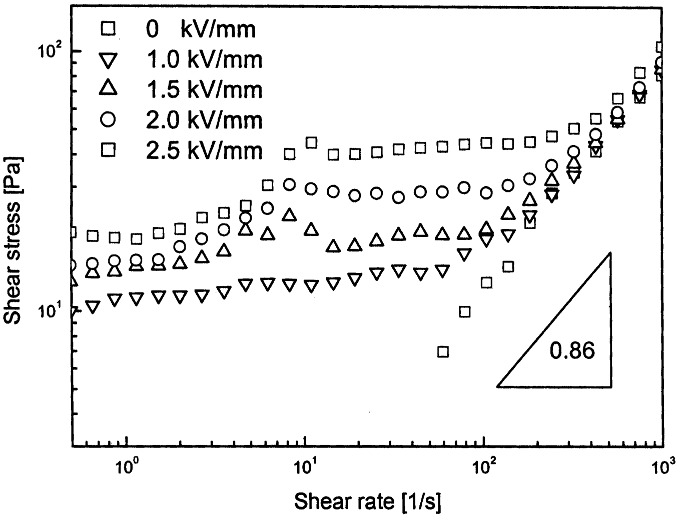

FIGURE 4 Shear stress vs. shear rate for PAPSSS based ER fluid.

fluid under shearing deformation can be represented by the Bingham fluid model where the shear stress τ is given by Eq. (2).

$$\tau = \tau_y + \eta\dot{\gamma} \tag{2}$$

Here $\dot{\gamma}$ is the shear rate, η is the plastic viscosity and τ_y is the yield stress induced by the electric field. After the plateau region, shear stress increases with shear rate in a similar manner to Newtonian fluids [14], implying that the hydrodynamic force begins to dominate over the electrostatic force. The behavior which depends strongly on the electric field strength at low shear rates is due to the deformation, reformation and destruction of chainlike or columnar structures as the shear rate increases below the critical shear rate.

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