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Influence of amine- and sulfonate-functional groups on electrorheological behavior of polyacrylonitrile dispersed suspension

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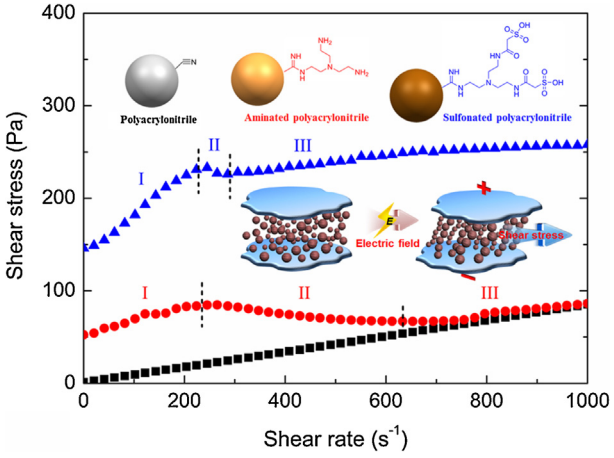
HIGHLIGHTS

- The nitrile group of PAN sphere was substituted with amine and sulfonate groups.
- The modified PAN sphere dispersed suspensions showed trembling behavior at 3 kV/mm.
- The sulfonated PAN dispersed suspension showed better ER performances than others.

GRAPHICAL ABSTRACT



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ABSTRACT

Aminated polyacrylonitrile (PAN-TAEA) and sulfonated PAN (PAN-TAEA-SAA) dispersed suspensions have been prepared with a size- and shape-controlled PAN homopolymer sphere as a raw material, to observe the influence of amine- and sulfonate-functional groups on electrorheological behaviors. The electrorheological properties of prepared suspensions are measured by using a rheometer under various electric fields. The pristine PAN and PAN derivatives dispersed suspensions showed noteworthy shear stress values in the order of PAN-TAEA-SAA, PAN-TAEA, and pristine PAN under an electric field. And the PAN derivatives dispersed suspensions showed trembled shear stress curves which are distinguished

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into three regions, while the pristine PAN showed linear behavior in shear stress-shear rate curve at 3 kV/mm. As a result, an effective strategy to estimate the effects of functional groups on electrorheological properties has been offered by the modification of a PAN homopolymer sphere whose nitrile group can be easily substituted with a target group.

1. Introduction

Electrorheological (ER) fluid, the polarizable particles dispersed suspension, is one of the smart material which can show controllable rheological property under an electric field. The ER phenomena are based on the viscosity change of ER fluid by forming a fibril structure of dispersed particles in the direction of applied electric field [1]. The ER fluids have been received much attention in industrial fields such as damping devices, clutches, shock absorbers, human muscle stimulators, gripping devices, and so on, because the ER fluids have a potential applicability thanks to their rapid response time and controllable viscosity [2–5]. In this effort, new promising devices such as microfluidic chips, microfluidic pumps, haptic devices, and polishing technology using ER fluid were developed recently [6–8]. As the use of ER particles has been increased, required properties of ER particle became more diverse and complex. For example, shear stress, yield stress, current density, conductivity, dispersion stability, and cost of ER particles have to be considered for their application to industrial areas. In order to develop the ER particles which satisfy these conditions, the natural polymers [9,10], graphene oxides [11,12], conductive polymers [13–15], dielectric inorganics [16–18], and inorganic/organic composites [19] have been investigated. However, it is hard to predict the ER effects of developed ER particles before actual use because the ER effects are complexly influenced by chemical interaction and dipole moment by functional group, size, shape, and concentration of ER particle, operating temperature, etc [20–22]. Thus, we had been studied the influence of particle size on the ER effect using aminated PAN particles, previously [23]. However, the influence of the other variables on the ER effects was hard to confirm because the used PAN particles have irregular shape and wide size distribution.

Herein, in order to estimate ER effects of new ER materials effectively at a development stage of ER particles, we have demonstrated the correlation between functional groups and ER effects by the modification of polyacrylonitrile (PAN) homopolymer. The PAN is a competitive candidate material for studying an influence of the functional groups of ER particles on ER effects because it has only nitrile groups, which can be substituted to various functional groups by chemical reactions, in the alkyl backbone of the polymer [24]. We synthesized the aminated PAN (PAN-TAEA) and sulfonated PAN (PAN-TAEA-SAA) to investigate the effect of amine and sulfonate groups on ER effect by using PAN homopolymer as a raw material. In order to maximize the influence by functional group on ER effect, other parameters, which may influence on the ER effects, were controlled. All of the used ER particles were a globular shape of uniform size. The particle concentration and operating temperature of ER fluid were fixed. Functional groups of PAN, PAN-TAEA, and PAN-TAEA-SAA particles were analyzed by a fourier transform infrared spectroscope (FT-IR), and their shape and size were characterized by a field emission gun scanning electron microscope (FEG-SEM). The formation of fibril structures of PAN-TAEA-SAA particles in direction of applied electric fields was observed with an optical microscope. The ER fluids, containing 30 vol% of ER particles, were used to measure the ER behaviors at 25 °C using a rheometer equipped with a high voltage generator.

2. Experimental

2.1. Materials

Polyacrylonitrile powder (PAN, homopolymer, MW = 200,000, specific gravity = 1.18, Polysciences, USA), tris(2-aminoethyl)amine (TAEA, 96%, Acros Organics, USA), and sulfoacetic acid (SAA, technical grade, Sigma-Aldrich, USA) were used as reagents for the preparation of modified PAN particles. Aluminium chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, 99%, Sigma-Aldrich, USA) was used as catalyst for preparation of aminated PAN (PAN-TAEA) particles. *N*-hydroxysuccinimide (NHS, 98%, Sigma-Aldrich, USA) and *N,N'*-Dicyclohexylcarbodiimide (DCC, 99%, Sigma-Aldrich, USA) were used as activating and coupling reagents for preparation of sulfonated PAN particles. Tetrahydrofuran (THF, anhydrous, >99.9%, Sigma-Aldrich, USA) was used as a solvent. All reagents were used without further purification. Silicon oil (KF-96-30CS, kinetic viscosity = 30 cSt at 25 °C, Shin-Etsu Chemical, Japan) was dried at 30 °C vacuum oven for three days before used as an insulating fluids.

2.2. Preparation of amine-functionalized polyacrylonitrile (PAN-TAEA) particles

Raw PAN particles were sieved using a sieve with the pore sizes of 74 μm. 10 g of sieved PAN particles and 200 mL of TAEA were added into a 300 mL three-neck round bottom flask, and then stirred at 25 °C for 30 min. The solution was reacted at 135 °C for 24 h with stirring and N_2 purging after addition of 1 g of $AlCl_3{\cdot}6H_2O$. After the amination, the obtained PAN-TAEA particles were washed with distilled deionized water (DI water, Millipore Milli-Q water system, 18.2 M Ω cm^{-1}) for 5 times, and then freeze-dried under vacuum for 5 days.

2.3. Preparation of sulfonate-functionalized polyacrylonitrile (PAN-TAEA-SAA) particles

10 g of PAN-TAEA particles, 0.3 g of DCC, and 100 mL of THF were added into the 250 mL three-neck round bottom flask, and then stirred at 25 °C for 30 min. After 30 min, 0.2 g of NHS and 7 g of sulfoacetic acid were added into the mixture solution, and then stirred at room temperature for 24 h. After the sulfonation, the PAN-TAEA-SAA particles were washed with DI-water for three times, and then freeze-dried under vacuum for 5 days.

2.4. Particle characterization

Fourier transform infrared spectroscopy (FT-IR, Frontier, PerkinElmer, Walthan, USA) was carried out to confirm the preparation of modified PAN. The pristine PAN, PAN-TAEA, and PAN-TAEA-SAA particles were blended with potassium bromide (KBr), and then pressed at 10 tons for two minutes for FT-IR analysis. Particle morphology and diameter of the synthesized PAN particles were observed by using a field emission gun scanning electron microscope (FEG-SEM) (Inspect F50, FEI, Hillsboro, US) at 5 kV. The samples for FEG-SEM were prepared by sprinkling of particles onto a double-sided adhesive carbon disk, and sputter-coated