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Electrorheological characteristics of semiconducting poly(aniline-*co*-*o*-ethoxyaniline) suspension

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Abstract

Semiconducting poly(aniline-*co*-*o*-ethoxyaniline) was synthesized by chemical oxidation polymerization of aniline and *o*-ethoxyaniline with two different molar ratios in an acidic media. Its chemical structure and other physical properties, such as conductivity, thermal stability and density of the polymer particles, were examined. Electrorheological (ER) fluids were then prepared by dispersing the copolyaniline particles in silicone oil and their rheological properties under electric field were investigated. It was found that the ER fluids using copolyanilines show different ER behaviors than that of the homopolyaniline. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(aniline-*co*-*o*-ethoxyaniline); Polyaniline; Electrorheological (ER) fluids

1. Introduction

Electrorheological (ER) fluids are those fluids whose rheological properties depend strongly and reversibly on an applied electric field. There are homogeneous ER fluids, such as liquid crystalline polymers (LCPs) diluted with dimethylsiloxane (DMS), which have been investigated by Tajiri et al. [1]. However, most ER fluids are heterogeneous colloidal suspensions. It is generally accepted that the ER effect of these suspensions is the result of particle fibrillation with strings of particles oriented along the electric field direction. This can be understood qualitatively in terms of particle polarization induced by the mismatch in the dielectric constant of the particles and the suspending fluid. Nevertheless this may not be the only mechanism, and the ER phenomenon can also be explained by a conductivity model [2]. In general, ER fluids can solidify in the order of ms, and they can fluidize under applied deformation that destroys the chain structure formed by the particles. The enormous change in the rheological properties of these fluids, coupled with the fast response time, offers many advantages in a variety of active devices including actuators, torque transducers and dampers [3]. The ER fluid systems can be classified into wet-base (hydrous) or dry-base (anhydrous) systems, according to the presence or absence of water. The difference between the wet- and dry-base systems is in the type of charge carriers that produce the particle polarization. In a wet-base system, the absorbed water and/or ions move within the particles along the electric field. On the other hand, it is the electrons that move in a dry-base system.

Among various polarizable particles for ER materials, semiconducting polymers including poly(acene quinone) radicals [4], [5] polyaniline (PANI) [6]–[8] and copolyaniline (COPA) [9], [10] have been adopted as anhydrous ER fluids, because of their ease of handling and their superior physical properties. In particular, PANI and its many derivatives based upon modification of oxidation state, dopant and polymerization conditions [11], are of technological interest. This is because they have better thermal stability and smaller density than the other polymers. Furthermore, PANI is easy to polymerize by oxidation polymerization at relatively low temperatures, and it can be doped from a conducting emeraldine hydrochloride form to an insulating state using simple protonic acids. Therefore we can change the dielectric constant and the conductivity of the particle while keeping all other particle properties the same for studying the ER characteristics. In addition, these particles are soft so that they do not abrade the device when used in an ER fluid.

Recently, *N*-substituted COPA containing phenyl sulfonic acid sodium salt pendent has been chemically synthesized, and its ER properties have been compared to the PANI homopolymer ER fluid system [10]. The *N*-substituted COPA ER fluid was found to have a higher ER

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performance than that of the homopolymer. This is probably due to the higher conductivity of the COPA because of the presence of sodium ions in the side chain. This result has been correlated with the dielectric relaxation of the ER fluid in an applied electric field. Furthermore, in order to improve the processability of PANI further, various COPAs have also been synthesized [12] and their properties have been studied accordingly. Among these copolymers, ring-substituted PANIs such as polytoluidines, polyanisidines and polyphenetidines were found to be significantly more soluble than the unsubstituted PANI [13] in *N*-methylpyrrolidone (NMP). They are also soluble in less polar solvents such as chloroform and toluene. Ring-substituted PANIs, however, are less conducting than the unsubstituted PANI [14]. In this paper, we describe the synthesis of poly(aniline-*co*-*o*-ethoxyaniline) (COPA) and we report our study of its ER characteristics for the first time.

2. Experimental result and discussion

2.1. Synthesis and preparation of ER material

The COPA was synthesized through chemical oxidation polymerization by feeding different molar ratio of *o*-ethoxyaniline monomer using the modified method that Leclerc et al. [15] suggested. An ammonium peroxysulfate solution in 240 ml 1 M HCl was dropped into a well-stirred reactor containing aniline (Junsei Chemical Co.) and *o*-ethoxyaniline (Aldrich Inc) monomer in 400 ml 1 M HCl. The mole fractions of the comonomer in the reaction system were 0% for the sample PANI and 25% for the sample COPA. Since the monomer reactivity of aniline and *o*-ethoxyaniline is changing, it is difficult to propose the exact structure of the synthesized COPA [11]. Thus, in the chemical structure of the COPA drawn in the inside of the Fig. 1, the mole fraction (y) of the *o*-ethoxyaniline monomer is not directly proportional to the monomer ratio in the polymerization process. During the synthesis, the mixtures are stirred at about 400–500 rpm for 2 h, and the temperature was kept at 0°C. Then the pH of the product was adjusted to 6.5 by adding either NaOH or HCl solution. Afterwards, we obtained the particles for ER fluid by dedoping, milling, washing, filtering and drying. The synthesized copolymer was washed using distilled water to remove the initiator, the unreacted monomer and the oligomer. It was then further washed with ethanol and cyclohexane in order to make the surface of the synthesized particles hydrophobic. Finally, the synthesized COPA particles were put into the vacuum oven for 2 days to get rid of any trace of water. The mean diameter of the particles was found to be 15 μm using a particle size analyser (Malvern), and the density of the COPA particles was measured to be $1.23 \pm 0.03\ \mathrm{g\ cm^{-3}}$ using a pycnometer. To prepare the ER fluid for rheological measurements, we dispersed the COPA particles in silicone oil by agitating the mixture at 1500–1800 rpm using a Pearl Mill (Shinil Co.). In these ER fluids we used silicone oil with a kinematic viscosity of 30 cS (centistokes) and a density of $0.96\ \mathrm{g\ cm^{-3}}$.

2.2. Characterization of particle

Characterization for chemical structure of the synthesized poly(aniline-*co*-*o*-ethoxyaniline) was conducted with Fourier

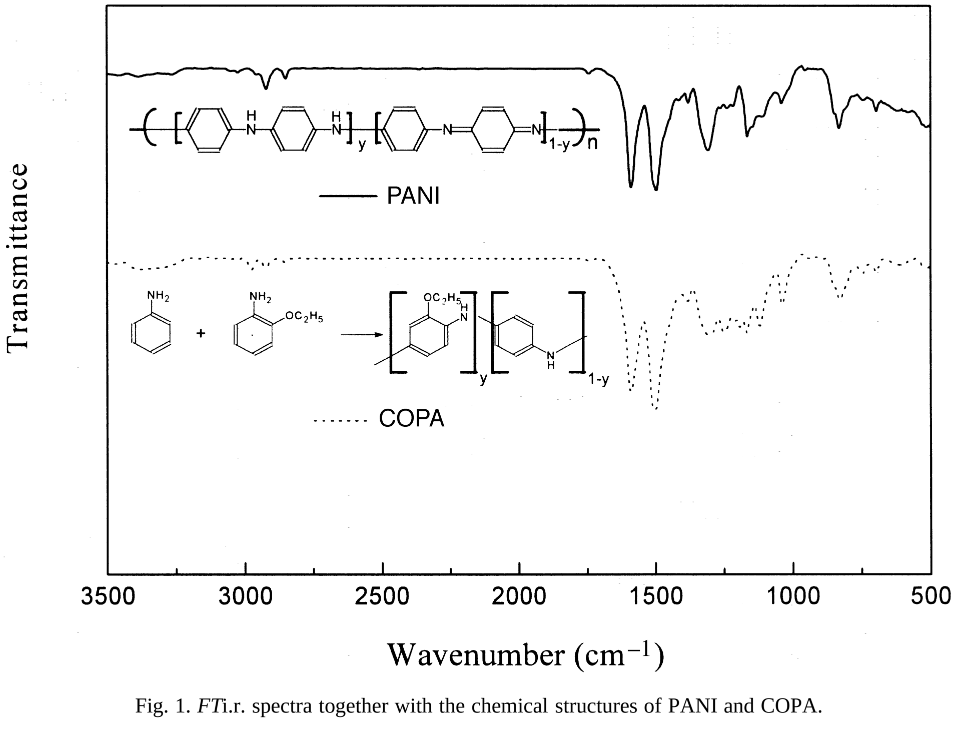

Fig. 1. *FT*i.r. spectra together with the chemical structures of PANI and COPA.

transform infra-red (*FT*i.r.) spectroscopy (Bruker IFS48). Fig. 1 shows the *FT*i.r. spectra together with the chemical structures of the COPA particles and the PANI particles. The peak at wave number 825 cm^{-1} is from aromatic C–H stretching vibration, the peaks at 1145 and 1310 cm^{-1} are from aromatic amine stretching, and the peaks at 1000 and 1300 cm^{-1} are from aromatic ether. In addition, the characteristic peaks at 1490 and 1590 cm^{-1} indicate C–C stretching and vibration [16]–[18], respectively. We thereby confirmed the existence of ethoxy group in this COPA. Thermal stability of the COPA and homopolyaniline were also studied using thermogravimetric analysis (t.g.a.) in the temperature range from 20 to 500°C at a heating rate of 20°C min^{-1}. The resultant thermograms show that a very gradual decomposition of the COPA particles occurs around 180°C. Then a more rapid decomposition starts at 300°C. Nevertheless, even at 400°C, the fractional weight loss of the samples were less than 10%. Thus the samples have very good thermal stability.

2.3. Rheological and electrical properties

We studied the rheological properties of our samples using a Physica rheometer (MC-120) with a Couette type cylinder (Z3-DIN and Z4-DIN) and a high voltage generator (Meyport series 230) which supplied DC electric fields (1–4 kV mm^{-1}) to the insulated bob. Fig. 2 shows the flow curves obtained in controlled shear rate mode for the ER fluids made of 20% volume fraction of COPA at different electric field strengths. One can see that the shear stress increases monotonically but nonlinearly with shear rate at zero applied electric field. It is not surprising to find such non-Newtonian behavior even at zero electric field because of high particle volume fraction in the suspension. Similar to most ER fluids, at finite electric field, the COPA sample possesses a finite dynamic yield stress that increases with increasing electric field. However, the shear stress, as a function of shear rate, decreases initially and then increases again around 5 s^{-1}. In other words, the flow curves exhibit a minimum. Extraordinary flow curves with the appearance of a minimum shown in Fig. 2 may be the result of structural change of the ER fluid due to the shear flow. The particle chains, which are formed by the electric field, are disrupted by the shear flow. When the shear rate is high enough, the particle chains may be broken by the shear and the particles may not have enough time to realign themselves along the electric field. Indeed, such a phenomenon has been observed by Sprecher et al. [19] in suspensions of ultrafine silica particles in silicone oil. They explained that at higher shear rates, the fluid motion was more turbulent. The turbulence field destroyed the fibrillation of the particles and the ER fluid became a homogeneous suspension. As a result, at high enough shear rates the flow curve of the ER fluid should approach that of a Newtonian fluid whose shear stress increases linearly with shear rate.

In contrast, when the electric field is applied to the PANI suspension, the shear stress can sustain at increasing shear rate. Since the PANI and COPA particles have the same size and density, they should have the same hydrodynamic characteristics in the silicone oil. Thus, the difference in the flow curves of these two samples should arise from the difference in their electrical properties (e.g. conductivity and dielectric constant) originating from the difference in their chemical structures.

To check the above speculation, we measured the conductivity of the PANI and COPA particles by the two-probe

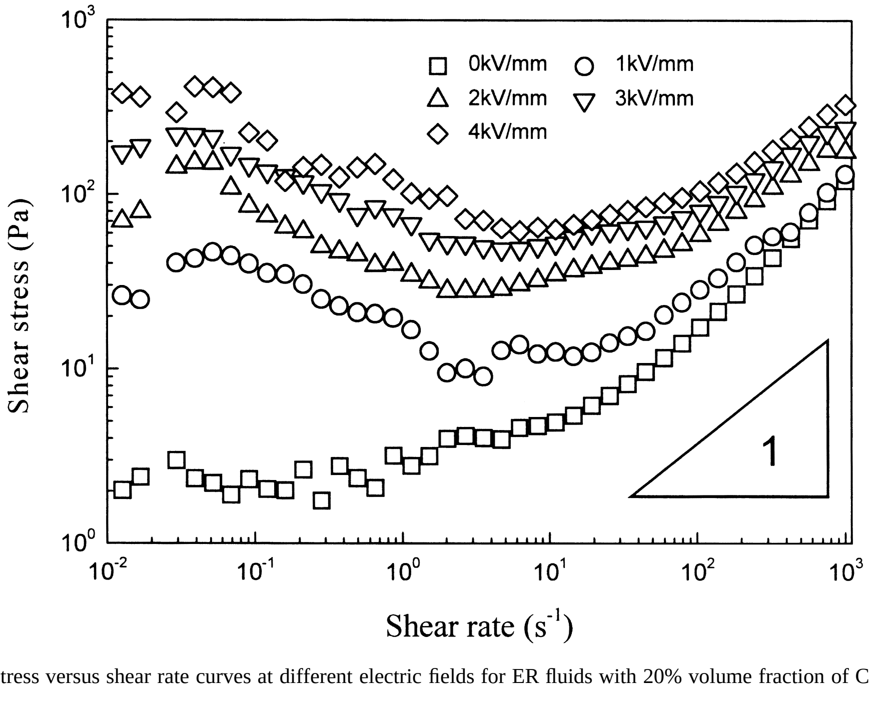

Fig. 2. Shear stress versus shear rate curves at different electric fields for ER fluids with 20% volume fraction of COPA particles.

method. Pellets of dried sample particles were prepared using a 13 mm KBr pellet die and the resistance of the pellet was measured by picoammeter (Keithley model 487) with a conductivity cell. The conductivity (σ) was then obtained from the relationship $\sigma = d/(R \cdot A)$, where A is the surface area, d is the thickness, and R is the resistance of the pellet. The conductivities of the PANI and COPA were found to be 1.0×10^{-11} S cm^{-1} and 1.8×10^{-12} S cm^{-1}, respectively. Therefore, the PANI sample should have better ER performance than the COPA sample. Such prediction is indeed consistent with the flow curves of both the PANI and COPA samples.

Note that the conductivity of the COPA particle is lower than that of the PANI particle, because of the presence of the side group (the ethoxy group) along the main chain of COPA. It has been known that in substituted COPA the conductivity decreases with increasing steric bulk of the substituent [11]. This is because bulk substituent disrupts the coplanarity of the polymer chain and reduces the mobility of the charge carriers along the main chain. In addition, a bulky side group will increase the interchain distance so that the transport of charge carriers between two chains will be reduced. As a result a lower conductivity is observed in COPA. However, it is worth mentioning that Cho et al. [10] found that the *N*-substituted COPA ER fluid has a higher ER performance than the homopolyaniline. In that case, the *N*-substituted COPA contains phenol sulfonic acid sodium salt pendent. It is the presence of the sodium ions in the side chain that increases the conductivity of the COPA [20].

In conclusion, PANI and poly(aniline-*co*-*o*-ethoxyaniline) were synthesized by the chemical oxidative polymerization and their properties are studied. We found that both the PANI and the COPA have good thermal stability. Compare to PANI, the COPA has lower ER performance due to the existence of the ethoxy side group in the main chain of the COPA. In addition, while the ER fluid using homopolyaniline shows a typical ER flow curve (i.e. the shear stress remains almost constant with respect to the shear rate), the COPA has a flow curve which exhibits a minimum around 5 s^{-1}. Such a difference in the ER characteristics may be the result of the difference in conductivity of these samples. In situ electric measurement of the PANI and the COPA samples will be carried out to clarify this speculation.

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