

Polymer Communication

# Synthesis and electrorheological characteristics of SAN–clay composite suspensions

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## Abstract

Particles of non-extractable styrene–acrylonitrile (SAN) copolymer–Na<sup>+</sup>-montmorillonite clay composite were synthesized by emulsion polymerization and then used to create an electrorheological (ER) fluid by dispersing the synthesized SAN–clay composite particles in silicone oil. The structures of the composites determined by FT-IR spectroscopy and X-ray diffraction confirmed the insertion of SAN between the interlayers of clay, whose separation consequently becomes larger than in polymer-free clay. The thermal stability of the organic polymers was found to be sustained. ER properties under the influence of externally applied electric fields were also investigated. ER fluids composed of SAN–clay composite show typical ER behavior and possess “pseudo-Newtonian” behavior at high shear rates. © 1999 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Electrorheological fluids; SAN–clay composite; Emulsion polymerization

## 1. Introduction

Electrorheological (ER) fluids are, in general, heterogeneous colloidal suspensions whose properties strongly depend on the applied electric field, where a characteristic fibrillation with the strings of particles oriented along the direction of electric field is observed. This reversible fibrillation of particles due to the electric field produces a significant increase in apparent viscosity [1,2]. ER fluids have been the subject of intense theoretical and experimental research due to their emerging technological applications. Attention has recently been paid to the synthesis and characterization of various anhydrous dry-base ER systems, because these systems could overcome several shortcomings of hydrous wet-base systems, such as the temperature limitation caused by the presence of water, the density mismatch between the particle and the oil, and an insufficient yield stress. Among various polarizable particles for anhydrous ER materials, semiconducting polymers, including poly(acene quinone) radicals, polyaniline and copolyaniline, have been adopted as anhydrous ER fluids as a result of handling and superior physical properties [3–7]. Choi et al. [7] observed that the optimum conductivity of

polyaniline for ER purposes, synthesized by a chemical oxidation of aniline in an acidic medium, can be achieved by adjusting the pH of an aqueous solution containing polyaniline particles.

Clay minerals have recently been introduced into the field of nanocomposites because of their small particle size and intercalation properties, especially in the application of reinforcement materials with polymers [8,9]. A large number of polymer–clay nanocomposites have become accessible in the form of end-functionalized derivatives [10–13]. The structural characteristics of montmorillonite, a smectic clay, exhibit an octahedral aluminate sheet sandwiched between tetrahedral silicate layers, where the layer charge can easily be controlled by replacement of cations with different charges. When the clay was exchanged with Na<sup>+</sup>, it possessed a good swelling rate for water, and its interlayer spacing became large enough to be penetrated by monomer. Using this concept, we performed an emulsion polymerization instead of dispersing clay into the ready-made polymers [14,15]. Not only were the thermal, mechanical, chemical, electrical and structural properties of the organic polymers substantially enhanced in the adducts, but the cost of resin was also lowered by using inexpensive inorganic material. In this study, using styrene–acrylonitrile (SAN)–clay composite particles with intercalation structure, we present a novel investigation of ER characteristics for this system.

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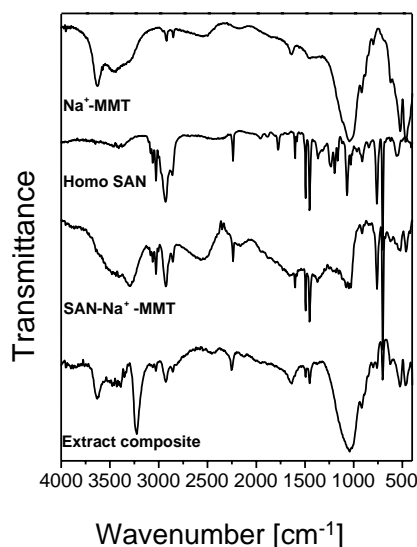


Fig. 1. FT-IR spectra of the SAN–Na<sup>+</sup>-montmorillonite composite.

## 2. Experimental

### 2.1. Materials

The cation-exchanged montmorillonite (MMT) sample was emulsion polymerized with SAN in the presence of potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and sodium lauryl sulfate (CH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OSO<sub>3</sub>Na). At first, a 2 l four-neck flask fitted with a mechanical stirrer, thermometer and condenser was charged with 600 ml of aqueous dispersions containing 5 wt% Na<sup>+</sup>-MMT. After being sonicated for 1 h at 60°C, styrene/acrylonitrile (70/30 wt%), sodium lauryl sulfate, and potassium persulfate were added while applying a constant, gentle agitation. The temperature was raised to 82°C, and the copolymerization was initiated. The polymerization was continued for 8 h to complete the reaction with a stirring rate of 450 rpm. The reaction was terminated by the addition of 700 ml of aluminum sulfate solution (10 wt%). Prior to the addition of aluminum sulfate, the coagulated products were subjected to a series of intensive washings by performing four cycles of centrifugation and redispersion

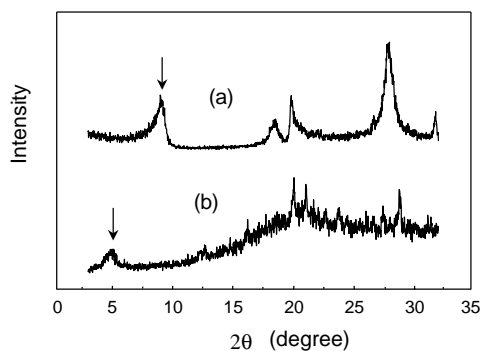


Fig. 2. XRD patterns of: (a) Na<sup>+</sup>-MMT only; and (b) polymer–clay composite samples. Intensity in the ordinate is an arbitrary unit.

into water. The products were then vacuum dried at 60°C for 2 days. The major part of the product was then subjected to hot tetrahydrofuran (THF) extraction for 5 days.

Each component of clay and SAN was identified by FT-IR spectroscopy using a potassium bromide pressed disc. To study the thermal stability of the composite particle, thermogravimetric analysis (TGA) was carried out using a DuPont 9900. The change of weight was measured with a heating rate 20 K min<sup>-1</sup> (from 303 to 773 K). For X-ray diffraction (XRD) analysis, a Guinier focusing camera using a quartz crystal monochromator in a Philips PW-1847 X-ray crystallographic unit, fitted with a copper target, was used (40 kV, 20 mA) for recording data in the range of  $2\theta = 2\text{--}32^\circ$ . The molecular mass and polydispersity of SAN were determined by gel-permeation chromatography with a differential refractometer using THF as the solvent.

### 2.2. Preparation and rheological measurement of ER fluids

Two different weight fractions (10 and 20 wt%) of ER fluids were prepared by suspending the SAN–clay composite particles in silicone oil (kinematic viscosity: 30 cSt) using a mechanical stirrer (1500–1800 rpm). The rheological properties were measured by a Physica rheometer (MC-120) with a Couette type cylinder (Z3-DIN) and a high voltage generator (HVG 5000), which supplies dc electric fields (1–3 kV mm<sup>-1</sup>) to the insulated bob. In order to obtain reproducible data, the ER fluid was redispersed at least two or three times for each sample before every measurement. The shear rate ranged from  $7.2 \times 10^{-3}$  to  $10^3$  s<sup>-1</sup>. The yield stress was measured in the controlled shear rate mode. For the conductivity measurement (two-probe method) of the SAN–clay composite material, pellets of dried composite particle were prepared using a 13 mm KBr pellet die. The resistance of the pellet was measured by a picoammeter (KEITHLEY model 487).

## 3. Results and discussion

The structures of the composites were analyzed by FT-IR and XRD. The FT-IR spectra of composites revealed the presence of characteristic absorption of both inorganic clay and organic polymer components, as shown in Fig. 1.

The peak at 1040 cm<sup>-1</sup> can be associated with the Si–O stretching vibrations, and peaks between 600 and 400 cm<sup>-1</sup> with the stretching of Al–O and bending of Si–O. However, the organic polymer component showed characteristic bands at 1300–1100 cm<sup>-1</sup> (C–O stretching) and 1730 cm<sup>-1</sup> (C=O stretching). In addition, Fig. 2 shows the XRD patterns of the clay and SAN–clay composite studied here. We estimated the variation of *d*-spacing, which is induced from the angular position  $2\theta$  of the observed peaks according to the Bragg formula  $\lambda = 2d\sin\theta$  [16]. The *d*-spacing in the direction of (001) of Na<sup>+</sup>-MMT is  $\sim 9.8$  Å, and that of the SAN–clay sample is  $\sim 17.4$  Å. This result confirms the insertion of SAN polymer between

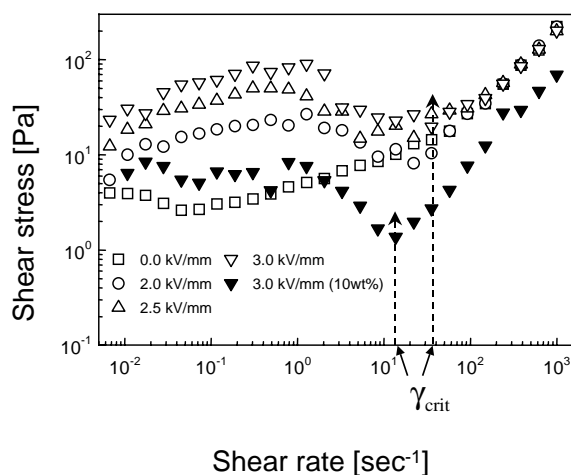


Fig. 3. Electric field dependency of the 20 wt% SAN-clay composite based ER fluids. The flow curve of 10 wt% particle concentration ( $\blacktriangledown$ ) under  $3 \text{ kV mm}^{-1}$  is inserted for comparison with different concentrations. Note that the fluid exhibits pseudo-Newtonian behavior above the critical shear rate ( $\dot{\gamma}_{\text{crit}}$ ).

the clay layers of  $\text{Na}^+$ -MMT, since the interlayer spacing increases from the basal distance of the clay itself (9.8 Å) to that of the SAN-clay composite (17.4 Å) due to the insertion of the SAN polymer.

The weight-average molecular weight of extracted SAN was measured to be  $5.3 \times 10^5 \text{ g mol}^{-1}$ . We also observed thermal stability of the SAN-clay composite from TGA analysis; the weight loss of the composite material was less than 5% below  $350^\circ\text{C}$ . The conductivity of the SAN-clay composite particle was  $1.8 \times 10^{-12} \text{ S cm}^{-1}$ .

Fig. 3 shows the flow curve obtained from the controlled shear rate test for 20 wt% suspensions of the SAN-clay composite with four different electric field strengths.

The shear stress increases monotonically (but non-linearly) with shear rate in the absence of an applied electric field. It is not surprising to find such non-Newtonian behavior, even with no applied electric field, because of the high particle volume fraction [17]. Similar to most ER fluids, at finite electric field, the SAN-clay based ER fluids showed higher shear stresses in the presence of an electric field. Observation of Fig. 3 shows that the shear stress slightly increases, decreases, then increases again as the shear rate increases. Thus, the shear stress as a function of shear rate possesses only one single maximum and minimum. At lower shear rates ( $< 1 \text{ s}^{-1}$ ), the fibrated structure initially deformed. However, the structure re-formed immediately after cessation of shear. At intermediate shear rates

( $1\text{--}20 \text{ s}^{-1}$ ), the chain structures slowly break down. For regions of higher shear rates ( $> 20 \text{ s}^{-1}$ ), the fluid motion becomes more erratic and destroys the chain structure throughout the gap. As a result, the ER fluid exhibits a linear relationship between shear stress and shear rate.

We also observed that the “critical shear rate” for pseudo-Newtonian behavior increases with increasing particle volume fraction. Note that the fluid exhibits pseudo-Newtonian behavior above the critical shear rate ( $\dot{\gamma}_{\text{crit}}$ ). Fig. 3 also shows the particle volume fraction dependency on shear stress under a  $3 \text{ kV mm}^{-1}$  electric field for both 10 and 20 wt% nanocomposite concentrations. The dynamic yield stress of a 20 wt% SAN-clay based ER fluid was an order of magnitude larger than that of a 10 wt% SAN-clay based ER fluid. In addition, although the shear stress increases with increasing particle volume fraction, the SAN-clay suspensions exhibit pseudo-Newtonian behavior in the high shear rate region ( $> 40 \text{ s}^{-1}$ ), which is characteristic of other ER fluids [18].

In conclusion, the SAN-clay composite was synthesized by emulsion polymerization, and the existence of its intercalation was verified by FT-IR spectroscopy and XRD for the first time. We used the intercalated particle as an ER fluid, and observed the ER behavior of the SAN-clay composite suspension.

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