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Synthesis and Electrorheological Characterization of Emulsion Polymerized SAN-clay Nanocomposite Suspensions

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SUMMARY: Styrene-acrylonitrile (SAN) copolymer-clay nanocomposite was synthesized by emulsion polymerization, which is the easiest method of intercalation (*e.g.*, melt or solution intercalation). Existence of the intercalated polymer was verified by Fourier transform-infrared spectroscopy and X-ray diffraction (XRD) analysis. From XRD, we confirmed the insertion of styrene-acrylonitrile copolymer between the interlayers of clay, whose separation consequently becomes larger than that of the polymer-free clay. Thermogravimetric analysis showed that the thermal stability of the organic polymers was sustained. Using electrorheological (ER) fluids composed of intercalated particles and silicone oil, we observed typical ER behavior, such as higher shear stress in the presence of an electric field and increasing yield stress with particle concentration. We further observed the critical shear rate at which the ER fluids exhibit pseudo-Newtonian behavior.

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Introduction

The study of molecular nanocomposites in which inorganic solids are associated with organic parts has opened the door for the development of new materials. These nanocomposites offer characteristics and potential properties that are drastically different from their bulk counter-parts[1)]. Various nanocomposites have been synthesized by different preparation methods, one being polymer intercalation into the layers of clay. Clay minerals are introduced into the field of nanocomposites because of their small particle size and layer expanding properties, especially in the development of reinforcement materials[2,3)]. A large number of polymer-clay nanocomposites have become accessible in the form of end-functionalized derivatives[4-7)]. Montmorillonite (MMT) clay has been widely used for this purpose. The structural characteristics of MMT exhibit an octahedral aluminate sheet sandwiched between tetrahedral silicate layers. When the clay is exchanged with Na^+, it possesses a good swelling rate in water, and its interlayer spacing becomes large enough for penetration by monomer. Using this concept, we performed an emulsion intercalation for SAN-Na^+-MMT nanocomposite[8)] and observed the polymer intercalated structure. The emulsion system consisting of an aqueous medium can contribute to maximization of the affinity between the hydrophilic host and hydrophobic guest by the action of the emulsifier. Furthermore, emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

Among various potential applications for polymer-clay nanocomposites, the electrorheological (ER) characteristics of synthesized SAN-clay nanocomposite suspended in silicone oil were recently reported[9,10)]. Research on new materials that respond to electric or magnetic stimuli has greatly increased. Among these materials, ER fluids were found to be very useful. ER fluids are 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 an electric field is observed. This reversible fibrillation of particles due to the electric field produces a significant increase in apparent viscosity[11,12)]. ER fluids have been the subject of intense theoretical and experimental research due to their emerging technological applications[13-15)]. Special attraction has recently been paid to the synthesis and characterization of various anhydrous dry-base ER systems, such as semiconducting polyaniline and copolyaniline[16, 17]. These systems could overcome several shortcomings of hydrous wet-base systems, such as the temperature limitation caused by the presence of water, sedimentation due to the density mismatch between the particle and the oil, and an insufficient amount of yield stress. Choi *et al.*[18] observed the optimum conductivity of polyaniline for ER applications, synthesized by a chemical oxidation of aniline monomer in an acidic medium. Furthermore, using N-substituted copolyaniline, Choi *et al.*[19] also found that the superior ER performance of the copolyaniline system can be explained from electrical relaxation analysis obtained from a dielectric spectrum.

In this study, we synthesized the SAN-Na^+-MMT nanocomposite particles via the emulsion method and characterized it using Fourier transform-infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). We then prepared ER suspensions using these particles and observed their ER characteristics.

Experimental

Using emulsion polymerization, Na^+-MMT clay sample was adopted to synthesize the SAN-clay nanocomposite with SAN in the presence of potassium persulfate and sodium lauryl sulfate. At first, a 2*l* four-neck flask fitted with a mechanical stirrer, thermometer, and condenser was charged with 600 m*l* of aqueous dispersions containing 5 wt% Na^+-MMT. After the clay solution was sonicated for 1 hr at 60 ℃, styrene/acrylonitrile (70/30 wt%), sodium lauryl sulfate, and potassium persulfate ($K_2S_2O_8$) were added while applying a constant and gentle agitation. We then raised the temperature to 82 ℃ and initiated the copolymerization. The polymerization was continued for 8 hrs with a stirring rate of 450 rpm. The reaction was terminated by the addition of 700 m*l* 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 into water. The products were then vacuum dried at 60 ℃ for 2 days.

Each component of the clay and SAN was identified by FT-IR analysis. To study the thermal stability of the composite particle, TGA (Dupont 9900) was carried out. For 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 $2\theta = 2\sim32°$. We then prepared three different weight fractions (10, 20, and 25 wt%) of ER fluids composed of synthesized SAN-clay nanocomposite particle and silicone oil (viscosity: 0.029 Pa·sec) using a mechanical stirrer (1,500-1,800rpm). Rheological properties were measured with a rotational rheometer (Physica MC-120, Germany) with a Couette-type cylinder and equipped with a high voltage generator, which supplies dc electric fields to the insulated bob. In order to obtain reproducible data, the ER fluid was redispersed at least three times for each sample before every measurement. The static yield stress was measured from the controlled shear stress mode. In addition, to measure the conductivity (2-probe method) of the SAN-clay nanocomposite material, pellets of dried composite particle were prepared, and the electrical resistance of the pellet was measured by a picoammeter (Keithely 487). The molecular mass and polydispersity of SAN were also determined by GPC with a differential refractometer using tetrahydrofuran as the solvent. The weight-average molecular weight of the extracted SAN was 5.3×10^5 g/mol.

Results and Discussion

The structure of the composites was analyzed by using both FT-IR and XRD. Figure 1 shows the FT-IR spectra for the SAN-Na^+-MMT nanocomposites, which reveal the presence of both inorganic clay and organic polymer components.

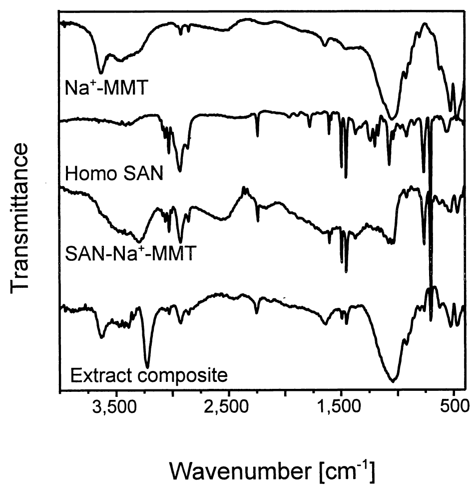

Figure 1. FT-IR spectra of the SAN-Na^+-MMT nanocomposite.

The peak at 1,040 cm^{-1} can be associated with Si–O stretching vibrations, and peaks between 600 and 400 cm^{-1} with the stretching of Al–O and bending of Si–O, respectively. However, the organic polymer component showed characteristic bands at 1,300~1,100 cm^{-1} (C–O stretching) and 1,730 cm^{-1} (C=O stretching).

XRD analysis shows that the interlayer spacing of the clay increases with SAN polymer loading as shown in Fig. 2. The interlayer spacing increases from the base distance of the clay itself (9.8 Å) to that of the SAN-clay composites (17.4 Å) due to the insertion of the SAN polymer.

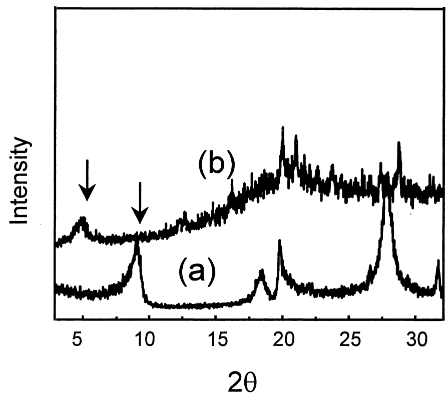

Figure 2. XRD patterns for (a) Na^{+}-MMT only and (b) the polymer-clay composite.

Purification of the products was accomplished by hot THF extraction (for 5 days) in preparation for TGA analysis. Considerable amounts of copolymer remained even after extraction, and these residual polymers can be regarded as copolymer intercalated in the layer of MMT. Whether the copolymer in the nanocomposite was extracted or not can be determined from TGA. In particular, it is noticeable that approximately 33 wt % of the copolymer (on the average) was not extracted, indicating that they are intercalated. Using this analysis, we observed the thermal stability of the SAN-clay nanocomposite up to 400 ℃. From the TGA analysis, we observed that the weight loss of the composite material was less than 5 % below 350 ℃. The conductivity of the SAN-clay composite particle was 1.8×10^{-12} S/cm.

Figure 3 shows the flow curves obtained from the controlled shear rate mode for (a) 10 wt% and (b) 20 wt% suspensions of 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 without an applied electric field, because of the high particle volume fraction[20]. 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 sec^{-1}), the fibrillated structure deformed, however, the structure re-formed immediately after cessation of shear. At intermediate shear rates ($1\sim20$ sec^{-1}), the chain structures slowly break down. For higher shear rates (>20 sec^{-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, and we observed the critical shear rate ($\dot{\gamma}_{crit}$) for pseudo-Newtonian behavior. The SAN-clay suspensions exhibit pseudo-Newtonian behavior in the high shear rate region (>40 sec^{-1}), which is characteristic of other ER fluids[21].

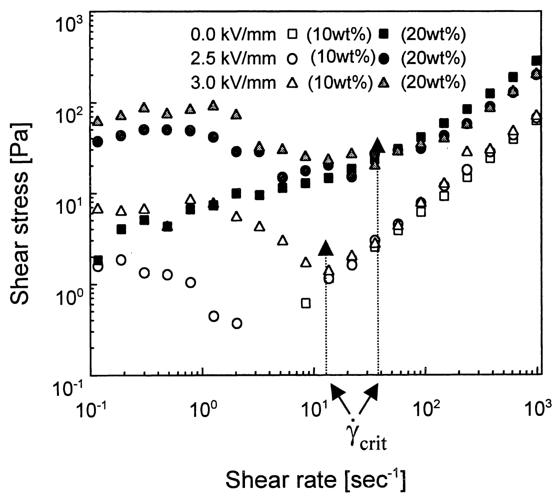

Figure 3. Flow curves for SAN-clay based ER suspensions with different particle concentrations; (a) 20 wt% (■,●,▲) and (b) 10 wt% (□,○,△).

Figure 4 illustrates the particle volume fraction dependence on yield stress under different electric field strength. The static yield stress for higher particle volume fraction SAN-clay based ER fluids was larger than that of lower particle volume fraction fluids. Similar to other ER fluid systems, the SAN-clay composite based ER fluids also show a yield stress increase with electric field strength.

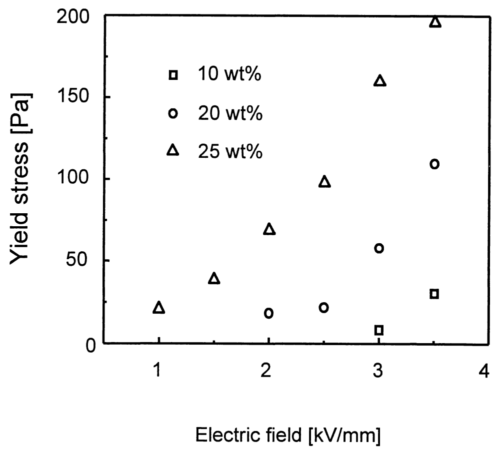

Figure 4. Yield stress as a function of applied electric field for three different particle concentrations

The current density as a function of temperature is presented in Fig. 5. The current density of an ER fluid affects the limitation of its usage as described below.

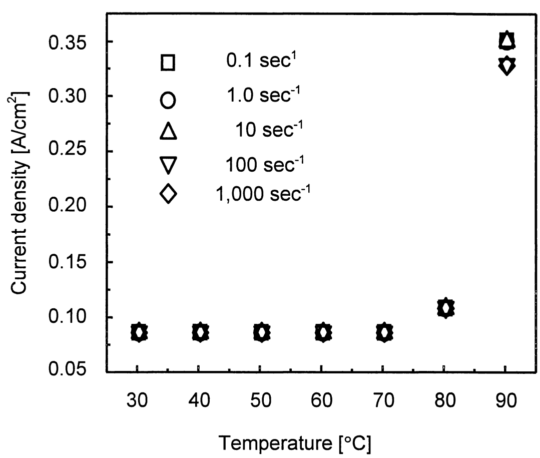

Figure 5. The current density changes with temperature for different shear rates (3 kV/mm, 20 wt%)

Generally, anhydrous ER materials have no limitations, but hydrous ER materials have temperature limitations. SAN-clay nanocomposite based ER fluids show a dramatic change in current density at 90°C, which suggests that the SAN-clay nanocomposite might be a wet-based hydrous ER material. Note also that the current density as a function of temperature is independent of shear rate.

Conclusion

SAN-Na^+-MMT nanocomposite was synthesized by emulsion polymerization, and the existence of its intercalation was verified by FT-IR spectroscopy and XRD analysis. We then used the intercalated particles in an ER fluid and observed the ER behavior of the SAN-clay nanocomposite based suspension. The yield stress and current density of the ER suspension were observed. The yield stress of the ER fluid increases with electric field strength, and the current density increased only slightly below 90°C. Above 90°C, a dramatic change in current density was observed, suggesting that the SAN clay composite might by a wet-based hydrous ER material.

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