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Application of Emulsion Intercalated Conducting Polymer-Clay Nanocomposite

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Nanocomposites of conducting polymers (polyaniline (PANI) and polypyrrole (PPy)) with inorganic Na⁺-montmorillonite (MMT) clay were synthesized using dodecylbenzenesulfonic acid (DBSA) as both a dopant and an emulsifier. These nanocomposites were then adapted as both electrical conducting and electrorheological (ER) materials. The yield stress and current density of these ER fluids were found to increase with electrical field strength. The electrical properties and molecular structure of these nanocomposites were also investigated.

Keywords emulsion; electrorheology, nanocomposite; polypyrrole

INTRODUCTION

Among clay minerals which have recently been introduced to the field of nanocomposites because of their intercalation properties, especially in the application of reinforcement materials with polymers, MMT, a hydrous alumina silicate mineral whose lamellae are constructed from an octahedral alumina sheet sandwiched between two tetrahedral silica sheets has been widely used. In this study, we synthesize the polymer-clay nanocomposites, and then investigate both the electrical property of particles and the ER properties of their suspension^[1,2]. An ER fluid exhibits reversible changes in rheological properties when an electric field is applied. ER fluids usually consist of semiconducting particles and insulating oil. Because of the controllable rheological properties, ER fluid can potentially be used as a smart material for active devices. Among various ER materials, semiconducting polymeric systems are frequently selected due to their advantages, such as thermal stability, low density, and easy handling^[2]. In particular, PANI and PPy based on oxidation state modification, dopants and polymerization conditions are of great technological interests^[3].

EXPERIMENTAL

Na⁺-MMT clay in an aqueous medium was prepared. Concurrently, DBSA dissolved in distilled water was mixed with aniline monomer solution in xylene while stirring for 1 hr. When the emulsion was formed, the clay and emulsion solution were mixed in a 4-neck reactor by stirring. The oxidant initiator solution was then dropped into the reactor. Reaction was terminated by introducing excess acetone into the reaction mixture. The pH of the product was then adjusted to 10 by adding either NaOH or HCl solution. On the other hand, for the synthesis of PPy nanocomposite, an inverse emulsion polymerization

was adopted. DBSA was dissolved in isooctane, and then it was mixed with APS solution in distilled water. Once the emulsion formed, it was mixed with clay dispersed in distilled water. Pyrrole with toluene was then dropped into the reactor. The particles were finally obtained from the sequential aftertreatment of washing, filtering, drying, milling and sieving. The ER fluids were prepared by suspending the PANI-(PACL) and PPy-clay nanocomposite (PPCL) particles in silicone oil using a mechanical stirrer. Rheological properties were measured using a rotational rheometer with a Couette type cylinder and a high voltage generator, which can supply dc electric fields to 10kV/mm.

RESULTS AND DISCUSSION

Figure 1a) represents X-ray diffraction patterns (XRD; $\lambda=1.542 \text{ \AA}$) of the clay, PACL and PPCL. The shift of (001) peak due to the intercalation of PANI and PPy material between the clay layers is observed. From the Bragg formula $n\lambda = 2d\sin\theta$, we calculate the d -spacing in the direction of (001) of the pristine clay, PACL and PPCL with 9.7 \AA , 15.2 \AA and 16.0 \AA , respectively. No crystalline peak at 9.7° in both composite samples was detected, demonstrating the intercalation of conducting polymer materials between clay layers. Figure 1b) shows static yield stress (τ_y) as a function of electric field (E), in a functional form of $\tau_y \propto E^{1.7-2.2}$. This result differs from theoretical prediction, in which τ_y is proportional to E^2 . The difference is due to several factors such as particle concentration and shape of the particle. In addition, the $\sigma_{dc}(T)$ measured from four probes method of PACL is $\sim 0.8 \text{ S/cm}$ and that of PPCL is $\sim 6 \text{ S/cm}$ at room temperature. Temperature dependence of σ_{dc} of PACL follows quasi 1D variable range hopping (VRH) model, while that of PPCL follows 3D VRH model^[3].

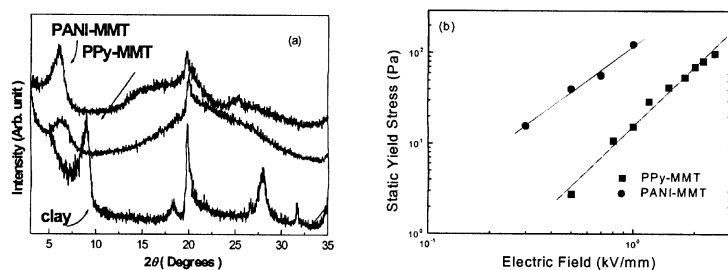


FIGURE 1.a) X-ray diffraction patterns of clay, PACL, and PPCL, b) Yield stress of polymer-clay nanocomposite based ER suspensions.

CONCLUSION

Intercalated PACL and PPCL were synthesized by two different emulsion polymerization methods with DBSA, and the intercalated layer structures were confirmed by XRD. From the conductivity study, $\sigma_{dc}(T)$ s of the PACL and PPCL were found to follow quasi 1D and 3D VRH models, respectively. Their suspensions in silicone oil further showed typical ER behavior with high yield stress under applied electric field.

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