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Chapter 6

Clay/Biopolymer Composite and Electrorheological Properties

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Additional information is available at the end of the chapter

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Abstract

The combination of clays with polymers having different characteristics opens a way to new composite materials showing novel properties. Electrorheological (ER) fluids show phase transition from a liquid to a solid-like state between the electrodes of a rheometer due to the interactions of polarized particles. Composite systems comprising biodegradable chitosan (CS) and natural bentonite (BNT) are important in ER applications. In this study, BNT/CS composites were synthesized by the in situ method. The structure and morphology of the synthesized composites were characterized using X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and scanning electron microscopy (SEM) techniques. Thermal stability was observed to increase with the presence of BNT clay. Conductivity of the composites was found the suitable range for ER measurements. According to ER results, BNT/CS composites were found to be sensitive to external electric field strength, exhibiting a typical shear thinning non-Newtonian viscoelastic behavior.

Keywords: Bentonite, clay/biopolymer composite, electrorheology, viscoelastic material

1. Introduction

The combination of clays with polymers having different characteristics opens a way to new composite materials showing novel properties [1]. The clay component of the composites provides a potential for high carrier mobility; band gap tunability; a range of electric, magnetic, and dielectric properties; and thermal/mechanical stabilities. On the other hand, polymer component of the composites offers structural flexibility, convenient processing, and tunable electrical and electronic properties. A major attraction of such research activities is to combine these desired advanced properties in the organic/inorganic hybrid materials, which can even be improved in comparison with the intrinsic properties of each component. Various polymer/clay composites can be synthesized via different preparation methods, including polymer

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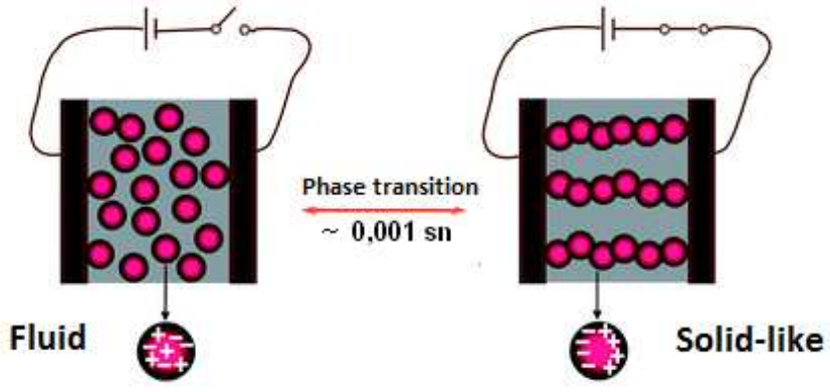
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intercalation into the layers of clays, in which clay minerals are offered various advantages such as high thermal stability, enhanced reinforcement, small particle size, layer expanding capabilities, and insolubility [2].

Bentonite (BNT) clays are largely composed of the mineral montmorillonite. It is constructed from octahedral alumina sheets sandwiched between two tetrahedral silicate sheets, which exhibit a net negative charge on the surface and can adsorb positive charges. BNT dispersions are widely used in industrial processes because of their exceptional rheological behavior. Compatibility with various polymers is accomplished by modifying the layers of BNT with surfactants via an ion-exchange reaction. When the BNT clay is exchanged with Na^+ ion, it possesses an excellent swelling behavior in water, and interlayer spacing becomes large enough for the penetration of polymer chains [3].

2. Electrorheological fluids

Electrorheological (ER) fluids are heterogeneous colloidal suspensions whose properties strongly depend on an externally applied electric field [4]. Commonly, these kinds of fluids are suspensions containing polarizable solid particles (dispersed phase) and non-conducting oils (continuous phase). When an electric field is imposed, suspended particles in the suspension are polarized due to the mismatches of electrical conductivity and dielectric permittivity between the dispersed particles and the continuous phase. The ER fluid shows phase transition from a liquid to a solid-like state between the electrodes of a rheometer due to the interactions of polarized particles (Scheme 1). This solid-like fibrillation of particles is due to the electric field–induced increase in the apparent viscosity of suspensions [5].



Sheme 1. ER response of clay/biopolymer composite particles dispersed in silicone oil.

According to chemical contents of ER suspensions, dispersed phase can be composed of organic (i.e. polymer) or inorganic (i.e. clay) particles [6]. Composite systems comprising natural materials such as chitosan (CS) and BNT are important in ER applications. In addition, the synthesis and ER properties of composites containing different clay groups (montmorillonite, silica, etc.) were reported in the literature [7, 8].

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2.1. Synthesis of bentonite/chitosan composites

This study was aimed at synthesizing BNT/CS composites by the intercalation method [9]. A definite amount of BNT [SiO_2 (54.82%), Al_2O_3 (20.27%), Fe_2O_3 (9.08%), MgO (3.02%), CaO (2.10%), Na_2O (1.31%), TiO_2 (0.78%), and K_2O (0.06%)] was dispersed in 1 wt.% acetic acid and stirred for 2 h with the presence of 0.1 g cetyltrimethylammonium bromide (CTAB) cationic surfactant. Then, a definite amount of CS [medium molecular weight (i.e. $\overline{Mw}$ = 190,000–300,000 g mol^{-1}) with 75–85% deacetylation degree) that was dissolved in 1 wt.% acetic acid was added into the aqueous dispersions. The mixture was stirred for 12 h for the intercalation of CS chains between BNT layers. Then, the dispersion was transferred into a flask containing 0.5 M $NaOH_{(aq)}$ and stirred for 2 h for neutralization. It is known that CS is soluble in weak acids and insoluble in alkaline medium. The crude BNT/CS composite particles were recovered from $NaOH_{(aq)}$ solution and washed with distilled water until the particles were neutral. Finally, the BNT/CS composites obtained were dried in a vacuum oven at 60°C for 2 days. By this method, three different biodegradable BNT/CS composites were synthesized and coded as BNT/CS(1%), BNT/CS(5%), and BNT/CS(25%).

2.2. Electrorheological measurements

Silicone oil (SO) was used in a continuous phase (ρ = 0.965 g/cm^3, η = 1 Pa s, ε = 2.61 at 25°C). The sample suspensions were prepared in SO at a series of concentrations (c = 5–25 wt.%), dispersing definite amount of dispersed phase in calculated amount of continuous phase (SO) according to formula (1):

$$c = \left(\frac{m_{\text{dispersed phase}}}{m_{\text{dispersed phase}} + m_{\text{continuous phase}}} \right) \times 100 \quad (1)$$

ER properties of the suspensions were determined with a Termo-Haake RS600 parallel plate torque electrorheometer (Germany). The gap between the parallel plates was 1.0 mm, and the diameters of the upper and lower plates were 35 mm. The voltage used in these experiments was supplied by a 0–12.5 kV (with 0.5 kV increments) direct current electric field generator (Fug Electronics, HCL 14, Germany), which enabled the creation of resistivity during the experiments.

3. Results and discussion

3.1. Characterization results

Average particle sizes, densities, and conductivities of the samples were given in Table 1. The diffraction pattern of BNT indicated the crystalline nature, whereas CS showed the amorphous nature. The XRD pattern of pure BNT has sharp peaks around 2θ = 8°, 18°, 21°, 26°, and 28° that are typical of BNT [10]. The XRD pattern of BNT/CS composites has peaks with relatively

lower intensities than that of BNT. This indicates that the amorphous structure of CS covers the crystalline structure of BNT, which confirms the more amorphous nature of the composites. According to the TGA curves of the samples in contrast to pure CS, the residual amounts of the composites increased with increasing BNT content as follows: $(89\%)_{BNT} > (86\%)_{BNT/CS(1\%)} > (81\%)_{BNT/CS(5\%)} > (57\%)_{BNT/CS(25\%)} > (30\%)_{CS}$. This tendency can be attributed to high thermal stability of the BNT component. These thermal stability results of BNT/CS composites are very suitable for potential and industrial applications as new ER materials [11]. According to the SEM results, CS chains not only intercalated inside the interlayer spaces of BNT but also settled on the surface of BNT layers (flocculated) [12]. The flocculated formation of the composites could be due to the hydroxylated edge–edge interaction of the silicate layers between the silicate hydroxylated edge groups and the CS chains.

Samples	Conductivity ($S\ cm^{-1}$) × 10^5	Density ($g\ cm^{-3}$)	Average particle size ((m)
CS	5.88	1.035	65
BNT	1.51	1.245	11
BNT/CS(1%)	1.01	1.158	14
BNT/CS(5%)	1.71	1.122	23
BNT/CS(25%)	3.45	1.116	51

Table 1. Some physical properties of the samples.

3.2. Electrorheological properties

The electric field viscosities of BNT/CS/SO suspensions increased with increasing electric field strength and reached to 470, 980, 550, and 515 Pa s under E = 1 kV/mm, respectively (Fig. 1). BNT/SO ER fluid exhibited to enhance ER effect with applied electric field to improve the particles' polarization ability and a typical shear thinning non-Newtonian viscoelastic behavior [13]. When E was applied to the ER suspension, the magnitude of the polarization forces between particles increased and the particles rapidly formed fibrillar structure perpendicular to the electrodes, which resulted in enhanced electric field–induced viscosity.

For the composites, the highest electric field viscosity (980 Pa s) was obtained for BNT/CS(1%)/SO suspension under E = 1 kV/mm, whereas the lowest electric field viscosity (515 Pa s) was obtained for BNT/CS(25%)/SO suspension under the same field strength. This result may be attributed to a decrease in the mutual action between the particles due to increasing particle size or BNT content, which reduces the possibility of the formation of strong chains between the upper and lower electrodes. Shear stress is one of the critical design parameters in ER phenomenon. The change of electric field–induced shear stress (τ_E) of the suspensions increased with the increasing electric field strength as follows: $(190\ Pa)_{BNT/CS(1\%)} > (118\ Pa)_{BNT/CS(5\%)} > (95\ Pa)_{BNT/CS(25\%)} > (88\ Pa)_{BNT}$ under E = 1 kV/mm.

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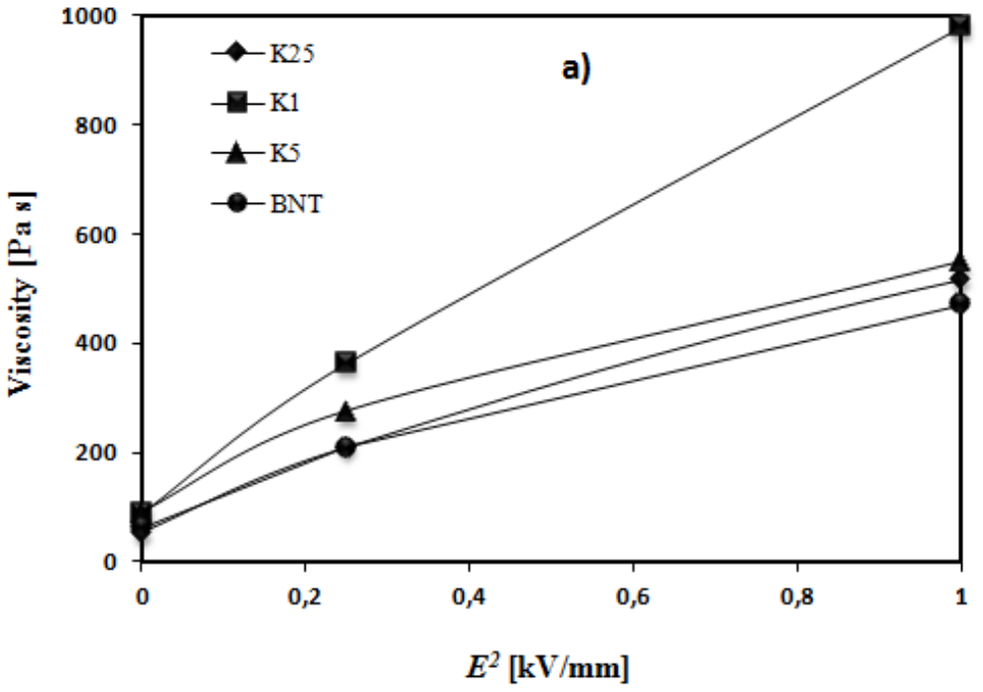


Figure 1. Effect of electric field strength on viscosity, K1: BNT/CS(1%), K5 : BNT/CS(5%), and K25 : BNT/CS(25%), (T = 25°C, c = 25 wt.%, and $\dot{\gamma}$ = 0.2 s^{-1}).

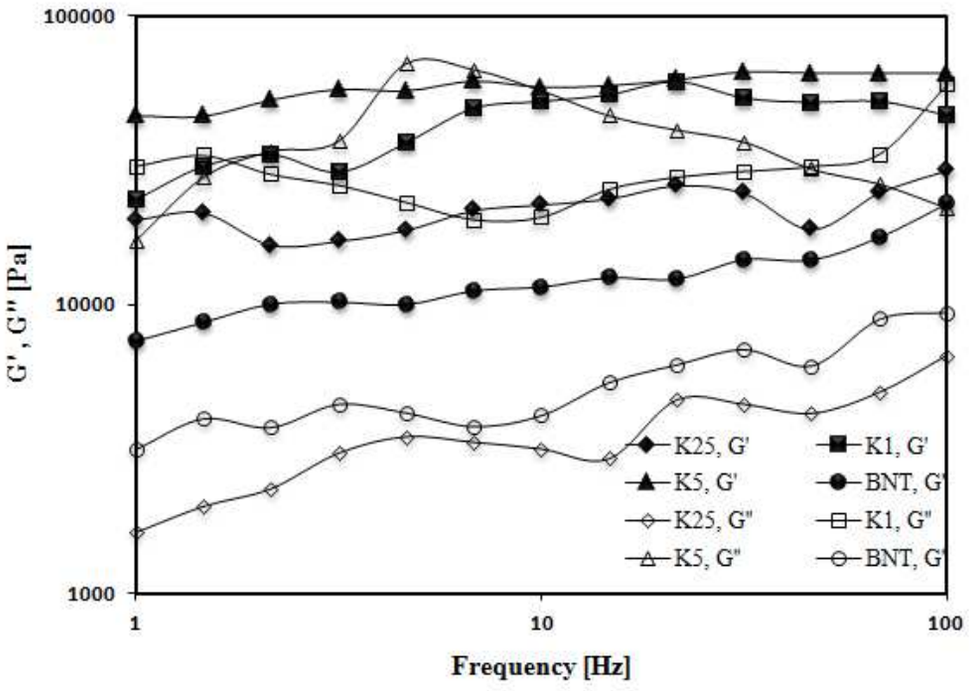


Figure 2. Change in G′ and G″ with frequency, K1: BNT/CS(1%), K5 : BNT/CS(5%), and K25 : BNT/CS(25%), (c = 25 wt. %, T = 25°C, τ = 10 Pa, and E = 1 kV/mm).

The external frequency is an essential factor for characterizing the dynamic viscoelastic properties of ER fluids. Storage modulus (G′) and loss modulus (G″) values of CS/SO, BNT/SO and BNT/CS/SO suspensions slightly increased with increasing frequency (Fig. 2). These variations in G′ and G″ correspond to energy change occurring during dynamic shear process and are strongly dependent on the interactions between CS chains and BNT layer interphases in the suspension [14].

The G′ values of the prepared suspensions are higher than G″ values. According to this result, strong interactions were developed between CS and BNT interphases, which enhance the elastic properties of these composites.

In conclusion, characterization results confirmed the introduction of the CS side chains into the BNT layers. ER activities of the suspensions increased with increasing electric field strength, dispersing particle concentration, and decreasing shear rate. Viscoelastic properties of the suspensions enhanced due to the interactions between BNT and CS. BNT-based ER fluids with improved ER and viscoelastic behaviors could be a good candidate as a smart material for ER applications.

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