Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 316 (2008) 125–130
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Electrorheological properties of chitosan nitrate suspension

Li Huo [a,b], Fu-Hui Liao [a], Jun-Ran Li [a,*], Shao-Hua Zhang [c], Olivia Zhang [d], Shu-Zhen Ma [b], Ming-Yuan Xu [b], Yu-Mei Lu [b]

[a] *State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[b] *Department of Chemistry, Baoding University, Baoding 071000, China*
[c] *School of Vehicle and Transmission Engineering, Beijing Institute of Technology, Beijing 100081, China*
[d] *Beijing Eastern-Dataphy Instruments Co. Ltd., Beijing 100089, China*

Received 7 May 2007; received in revised form 16 August 2007; accepted 23 August 2007
Available online 30 August 2007

Abstract

Chitosan nitrate (CTS-HNO_3) as an electrorheological (ER) material was synthesized by a simple method. The nontoxic and facile chitosan (CTS) as a substrate of the materials, as well as nitric acid were chosen as starting materials. The ER properties of the suspensions of the CTS and CTS-HNO_3 materials were researched. The CTS-HNO_3 suspension has much better ER performance than the CTS suspension. The ER effect (relative shear stress, $\tau_r = \tau_E/\tau_0$) of the CTS-HNO_3 suspension (25 wt%) in silicon oil under a dc electric field reached 94 at a shear rate of 14.5 s^{-1}, which is eight times higher than that of the CTS suspension, where τ_E and τ_0 are the shear stresses at the electric field strengths of 4.2 and 0.0 kV/mm, respectively. The formation of chitosan nitrate helped to decrease effectively the shear stress at zero electric field, and to enhance the ER effect of chitosan material markedly. The influence of the surface energy, conductivity, dielectric constant and dielectric loss tangent on the ER property of the particle materials was investigated, and the results indicate that surface energy played a predominant role. Moreover, the magnitude of the ER effect of the CTS-HNO_3 suspension was closely related to the shear rate. In addition, the chitosan nitrate had better thermal stability. The properties of CTS-HNO_3 are advantageous in its application as an ER material.

Keywords: Chitosan nitrate; Electrorheological effect; Shear rate; Surface energy

1. Introduction

The rheological properties (viscosity, yield stress, etc.) of an ER suspension could change reversibly, by several orders of magnitude, under an external electric field with the strength of several kilovolts per millimeter. Since its mechanical properties can be easily controlled within a wide range, the ER fluid could be used as an electric and mechanical medium in various industrial applications; for example, it could be used in the automotive industry for clutch, brake and damping systems [1]. It could also be used in other areas, such as polishing, ink jet printers, human muscle stimulators, mechanical sensors, seismic controlling frame structures, spacecraft deployment dampers and so on [2–5]. However, ER fluids have not been utilized largely because they do not have a high enough ER effect that fits the requirements of most of these applications. In order to obtain highly active ER materials, various types of ER materials have been synthesized and studied, and the mechanism of their ER effect has been intensively discussed in many articles. Many researchers [6,7] considered that ER effect arises from polarization, especially surface polarization of dispersed particles under an electric field. The conductive, dielectric and surface properties of several water-free polymeric or inorganic material-based ER fluids were investigated by Hao et al. [8]. They found that interfacial polarization would contribute to the ER effect, and indicated that a large interfacial polarization can result in the particle turning to form a fibrillation structure along the electric field direction. The conductivity, dielectric property and surface energy would influence the interfacial polarization, and the surface energy of a particle material should be a dominant factor in influencing the interfacial polarization. Therefore, it is neces-

* Corresponding author. Tel.: +86 10 62753517; fax: +86 10 62751708.
E-mail address: lijunran@pku.edu.cn (J.-R. Li).

0927-7757/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2007.08.039

sary to study the relationship between the ER effect and surface energy of a material.

In 2000, Choi and co-workers [9] reported the existence of critical shear rate in the flow curve of styrene-acrylonitrile copolymer/clay nanocomposite based ER fluid. Below the critical shear rate, the shear stress decreased as a function of shear rate; whereas above the critical shear rate, the fluid exhibited pseudo-Newtonian behavior. Choi and co-workers [10] proposed a model constitutive rheological equation of state for the ER fluids under an applied electric field, which was used to analyze the shear stress distributions versus shear rate in 2005. The suggested constitutive equation model describes the shear stress behavior well at a low or high shear rate region, namely it fits the flow curve data very accurately through the whole shear range, especially shown by the data investigated at relative low shear rate region [11–16]. The ER properties of biocompatible chitosan [17,18] and chitosan derivative [5,19–23] as disperse phases have been investigated, and chitosan presented weaker ER effect than that of its derivative. In order to find an ideal ER material that not only has better ER performance, but is also economical, facile and nontoxic, and to gain a better understanding on the mechanism of ER effect, especially the influence of surface energy on ER property, we have synthesized a new ER material, chitosan nitrate. The shear stress behavior with the shear rate in zero electric field and the relationship between the ER effect as a relative shear stress (τ_r) and the shear rate were examined for the suspensions of CTS and CTS-HNO_3, and the effect of the surface energy (SE), conductivity (κ), dielectric constant (ε) and dielectric loss tangent ($\tan\delta$) on the ER property was investigated. Here we report some novel results acquired therein.

2. Experimental

2.1. Synthesis of chitosan nitrate particle material

All reagents were provided by Beijing Chemistry Reagent Co. (China) and used without further purification.

Chitosan nitrate was synthesized using a simple method. First, 2 cm^3 of nitric acid (16 mol L^{-1}) was dissolved in 20 cm^3 acetone, and then 2.5 g CTS was sufficiently mixed with the solution under stirring. After drying for 4 h at 50 °C to remove acetone, the CTS nitrate particles were ground, and dried in a vacuum oven at 50 °C for 2 days. The CTS nitrate material was thus obtained.

2.2. Preparation of ER fluids and electrorheological experiment

The electrorheological experiments were carried out using a German Rotary Viscometer (Type HAAKE CV20). The apparatus can function at the desired temperature and electrode clearance to measure the anti-shear stress and apparent viscosity of a fluid at various shear states; and it has various operating modes such as rate control, stress control and oscillation. The measurements were carried through in a ZA15 sensor system, which consists of a pair of coaxial cylinders with a 0.545 mm gap in between. The system is connected to a power supply, the voltage of which can be controlled and adjusted from 0 to 5 kV/mm. The suspensions are placed in the gap, the inner cylinder is kept stationary and the outer cylinder rotating at preconcerted rates, when the apparatus is operating. The measured ranges are 0–3000 Pa for shear stress and 0–300 s^{-1} for shear rate (γ). In this paper, the sample shear stresses and viscosities have been determined under different electric field strengths (E, dc field) at a given temperature (20 °C).

The chitosan or chitosan nitrate particle materials were mixed quickly, after water removal, with dimethyl silicone oil (density $\rho = 0.98$ g mL^{-1} and viscosity $\eta = 98$ mPa s at 25 °C) under stirring and ultrasonically dispersing for 5 min, to yield the ER fluid (25% weight fraction) samples. The suspensions were then put in the gap between the cylinders as soon as possible for electrorheological experiments.

2.3. Characterization of the materials

The N, C, H and O contents in the materials were determined on a German Elementar Vario EL instrument. The FT-IR spectra of the materials were measured using a Nicolet Magna-IR 750 spectrometer at 295 K. To obtain the surface energy, and compare the conductive and dielectric property of the materials, the dried powders (0.3 g) of the samples were dry-pressed at 6 MPa for 5 min to pellets of 8 mm × 2 mm in diameter and thickness. The contact angles between the pellet and water drop were measured on Video-based contact angle measuring device (model: OCA20, manufacturer: Dataphyisics Instruments GmbH). The surface energies of the materials were calculated using the SCA21 software and the EOS method. The capacitance C and dielectric loss tangent ($\tan\delta$) at room temperature and different frequencies (f) were obtained on a HP4274A Multi-frequency LCR Meter. The dielectric constant (ε) and conductivity (κ) were derived from the measured C and $\tan\delta$ according to the conventional relations, $\varepsilon = Cd/(\varepsilon_0 S)$, $\kappa = (2\pi f)\tan\delta\, Cd/S$, where ε_0 is the dielectric constant of vacuum, i.e. 8.85×10^{-12} F m^{-1}, d and S are the thickness and area of the pellet, respectively. The thermal decomposition properties of the materials were obtained on a Simufaneous Thermal Analysis and Mass Spectrometer Coupling System made by German NETZSCH (Type STA449CQ + MS403C), and samples were heated at a rate of 10 °C/min up to 700 °C in argon.

3. Results and discussion

3.1. Composition of materials

The elemental analysis results show that the contents of N, C, H and O are 10.35, 33.40, 5.95 and 41.71% in the chitosan (deacetylation degree ≥ 90%) used in this study, and 11.54, 30.86, 5.56 and 47.73% in CTS-nitrate, respectively, the increases of nitrogen and oxygen and the decrease of carbon indicate the formation of CTS-nitrate via the reaction between CTS and HNO_3.

The IR spectra [24] of the materials provide further evidence for the formation of CTS-nitrate (see Fig. 1). Comparing CTS-