

Electrorheological Properties of Chemically Modified Chitosan Suspension with Various Functional Pendants

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ABSTRACT: In this study, functional pendants of chitosan were focused on enhancing the shear stress of electro-rheological (ER) fluids. Chitosan succinates and chitosan phthalate were synthesized for ER particles and ER fluids were prepared by dispersing the particles in silicone oil. After comparing the shear stress of all prepared ER fluids, obtained conclusions were that ER particle having two functional groups (one is +ve charge and another is -ve charge) showed higher shear stress than that having only one functional group like the comparison between chitosan

succinate(I) and chitosan succinate(II). However, though expect of the intermolecular overlapping between the π electrons clouds supporting the charge carrier generation and transport leading to a significant delocalization of electrons, chitosan phthalate shows lower shear stress than chitosan succinate(I) and chitosan succinate(II). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4937–4942, 2006

Key words: anhydrous ER fluids; chitosan derivatives; pendent effects; shear stress; colloidal suspensions

INTRODUCTION

Many researches about electro-rheological fluids have been studied since the phenomenon of electro-rheology was first reported by W. M. Winslow in 1947 and this phenomenon occasionally bears his name.¹ The electro-rheological (ER) fluids are one kind of suspension whose rheological properties can reversibly change several orders of magnitude under a sufficiently strong electric field.² Positive ER materials have rheological properties that dramatically increase with the applied electric field.³ Many researches have been conducted for practical utilizations of such suspensions in active control devices such as dampers, shock absorbers, clutches, and brakes,⁴ and in new devices such as gripping devices,⁵ seismic controlling frame structures,⁶ human muscle stimulators,⁷ and spacecraft deployment dampers.⁸ However, they remained unsuccessful due to problems like particle sedimentation,⁹ aggregation or solidification, particle or electrode abrasion, poor durability or temperature dependence, and a high current density due to the high conductivity of water, and device erosion caused by water.¹⁰ For solving these problems, water-free ER fluids were developed under the assumption that they do not have the shortcomings of hydrous ER fluids.¹¹

The modeling for understanding ER phenomena has been well studied.^{12–14} The chemical structure designing studies of ER particles for the practical utilizations

still leave much to be desired despite of various studies of chemical structures including polymethyl methacrylate-*block*-polystyrene,¹⁵ acene quinine radical polymers,¹⁶ polyaniline,¹⁷ polyphenylenediamine,¹⁸ poly(2-acrylamido-2-methyl-1-propane sulfonic acid),¹⁹ polystyrene-*block*-polyisoprene,²⁰ and polymer-diatomite composites with polyacrylonitrile²¹ or polyaniline.²²

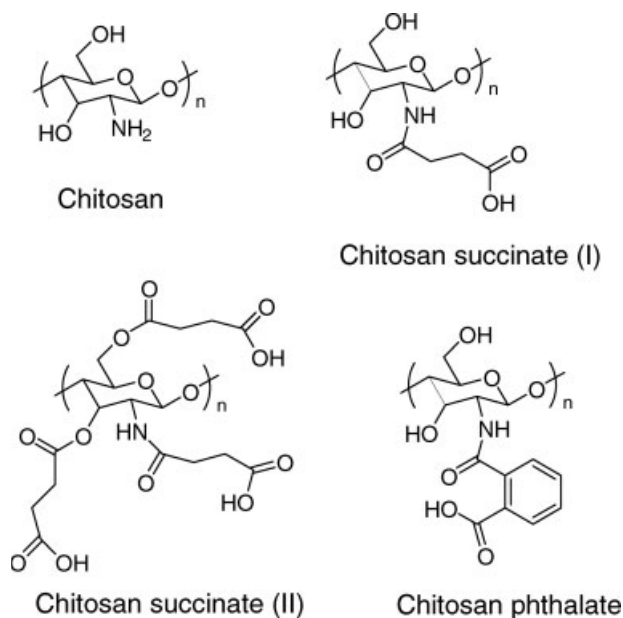
The high-performance ER materials are closely related to their molecular structures. With the development of ER materials, it is clear that those materials possess branched polar groups such as amine ($-\text{NH}_2$), hydroxyl ($-\text{OH}$), and aminocyano ($-\text{NHCN}$), or semi-conducting repeated groups. The polar groups may affect the ER behavior by playing the role of the electronic donor under the imposed electric field.²³ ER material is far from a green process because of its toxicity.²⁴ Therefore, chitosan has been studied for solving environmental problems recently.^{25–29} This material shows the ER effect due to amine and hydroxyl groups, and these groups can be substituted to other functional groups easily. In this study, carboxyl groups are introduced to chitosan with various pendant and linkage groups. Then the ER properties of the suspensions of these modified chitosan particles in silicone oil have been investigated under DC electric fields.

EXPERIMENTAL

Synthesis and FTIR analysis

Chitosan succinate(I) was synthesized by the following method. Chitosan (10 g, Jakwang, Korea), succinic acid (1 mol, Aldrich, Milwaukee, WI), triphenyl phos-

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Scheme 1 Structures of chemically modified chitosan.

pine (0.01 mol, TPP, Aldrich, Milwaukee, WI), diethyl azo dicarboxylate (0.01 mol, DEAD, Aldrich), and dimethylformamide (500 mL, DMF, Aldrich) were put into a round flask under N_2 purging and reacted at a temperature of 35°C in an oil bath for 24 h with stirring. After reaction, modified chitosan was washed with DMF and distilled water, and dried at a temperature of 40°C in vacuum oven. The reaction yield was 64%. Note that all OH (hydroxyl group) react with adipic acid if the reaction temperature increases or the reaction time become longer. Then, any OH should not be observed. In this work, OH did not react with adipic acid. This was confirmed by FTIR (GX FTIR spectrum, Perkin-Elmer, Wellseley, MA).

IR (KBr): 3452 (OH, carboxylic acid), 3350 (OH, hydroxyl group), 1717 ($\text{C}=\text{O}$, carboxylic group), 1658 cm^{-1} ($\text{NH}-\text{C}=\text{O}$, amide group).

Chitosan succinate(II) was obtained by the reaction of chitosan (10 g) with succinic anhydride (80 g) in dimethyl sulfoxide (400 mL, DMSO, Aldrich) and pyridine (200 mL) solution at a 60°C oil bath for 5 h with stirring. After reaction, modified chitosan was washed with DMSO and distilled water, and dried at a temperature of 40°C in vacuum oven. The reaction yield was 67.5%.

IR (KBr): 3452 (OH, carboxylic acid), 1733 ($\text{C}=\text{O}$, ester group), 1717 ($\text{C}=\text{O}$, carboxylic group), 1658 cm^{-1} ($\text{NH}-\text{C}=\text{O}$, amide group).

Chitosan phthalate was synthesized by the following method. Chitosan (10 g, Jakwang, Korea), phthalic acid (1 mol, Aldrich, Milwaukee, WI), triphenyl phosphine (0.01 mol, TPP, Aldrich, Milwaukee, WI), diethyl azo dicarboxylate (0.01 mol, DEAD, Aldrich), and dimethylformamide (500 mL, DMF, Aldrich, Milwaukee, WI) were put into a round flask under N_2 purging

and reacted at a temperature of 35°C in an oil bath for 24 h with stirring. After reaction, modified chitosan was washed with DMF and distilled water, and dried at a temperature of 40°C in vacuum oven. The reaction yield was 58%.

IR (KBr): 3005 (OH, carboxylic acid), 3350 (OH, hydroxyl group), 1692 ($\text{C}=\text{O}$, carboxylic group), 1652 ($\text{NH}-\text{C}=\text{O}$, amide group), 1584, 1495, 1403, 1156, 1073 cm^{-1} (benzene group).

All synthesized polymers are depicted in Scheme 1, and their FTIR spectra are shown in Figure 1.

Suspension preparation and methods of measurement

The size distribution of particles was examined by dynamic light scattering (DLS, BI9000AT, Brook heaven). Synthesized polymers were grinded to 5–30 μm particles using a ball mill and their particle sizes are shown in Figure 2. ER fluids were prepared by dispersing these particles into silicone oil whose viscosity was 30 cSt at 25°C . The silicone oil was dried by molecular sieves before use, and the particle concentration was fixed at 30 vol %. The rheological properties of the suspension were investigated in a static DC field using a Physica Couette-type rheometer (Physica US200, Germany) with a high voltage generator. The measuring unit was of a concentric cylindrical type, with a 1 mm gap between the bob and the cup. The shear stress for the suspensions was measured under shear rate of $1\text{--}300\text{ s}^{-1}$ and electric fields of 0–3 kV/mm.

The dc current density J of chitosan compounds suspension were determined at room temperature by measuring the current passing through the fluid upon application of the electric field E_0 and dividing the current by the area of the electrodes in contact with the fluid. Current was determined from the voltages drop across a 1 M Ω resistor in series with the

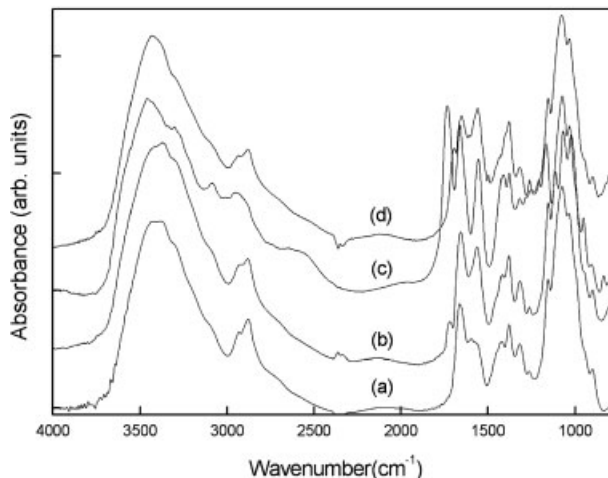


Figure 1 FTIR spectra of (a) chitosan, (b) chitosan succinate(I), (c) chitosan succinate(II), and (d) chitosan phthalate.

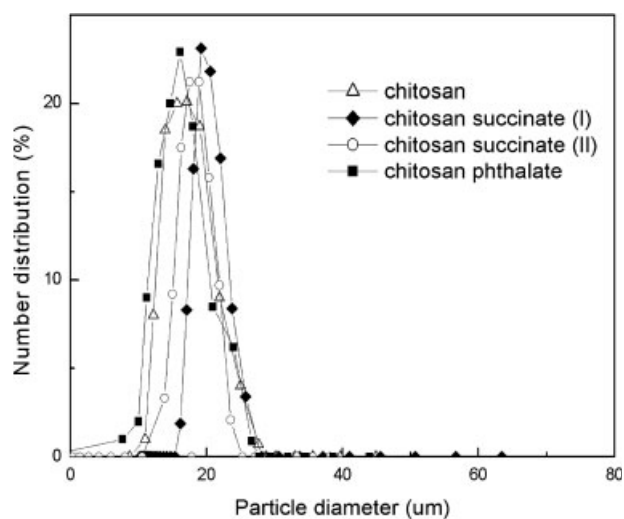


Figure 2 Size distribution of chemically modified chitosan.

metal cell containing the oil, using a voltmeter with a sensitivity of 0.01 mV.

The experimental cell was assembled by mounting two parallel electrodes with 1 mm gap on a Teflon slide in which a drop of well-mixed ER fluid was dispersed. The behavior of ER fluids was observed under 3 kV/mm using an optical microscope.

Thermal analysis data were obtained using a Dupont 910 differential scanning calorimeter (DSC) and 915 thermogravimetric analyzer (TGA), with a heating rate of 10°C/min under nitrogen atmosphere. In the case of DSC, indium metal was used for calibration ($T_m(\text{In}) = 156.7^\circ\text{C}$ and $\Delta H_m(\text{In}) = 28.36 \text{ J/g}$).

RESULTS AND DISCUSSION

Thermal and structural characterizations

Figure 3 shows differences in the peak area and position of endotherm, indicating that these macromolecules differ in their water-holding capacity and strength of water-polymer interaction. The peak position of the chitosan raw material is at 143°C and it is higher than that found in other researches.³⁰ In the case of the chitosan succinate(I), the peak position is shifted to higher temperature (166°C), indicating that the water interaction with hydroxyl and carboxylic groups is stronger than with hydroxyl and amine groups of chitosan raw material. Chitosan succinate(II) shows two peak positions. One is at 143°C because of the water interaction with hydroxyl and carboxylic groups, and the other is at 223°C because of the water interaction with carboxylic groups. These temperatures are much higher than the boiling temperature of the water, indicating that water interaction with functional groups is very strong, and these two positions of endotherm indicate that all hydroxyl groups are

not substituted. In brief, hydroxyl- and amine-substituted chitosan coexists with only amine-substituted chitosan. This adsorbed water bond with functional groups of chitosan. Therefore, these synthesized ER materials do not show a high current density and cause device erosion. The glass transition temperature (T_g) can usually be obtained by DSC. The glass transition temperature of chitosan is still a subject of controversy. The main reason may be that some properties like crystallinity, molecular weight and deacetylation degree will influence T_g . Ratto et al.³¹ observed the chitosan glass temperature at 30°C for water contents ranging from 8 to 30%. Lazaridou and Biliaderis³² found T_g ranging from -23 to 67°C , according to the water content, indicating, in both cases, the plasticizing effect of water. On the other hand, Sakurai et al.³³ observed the T_g of chitosan at 203°C , while Kittur et al.³⁴ found no evidence for T_g suggesting that T_g for chitosan could lie at a higher temperature, where degradation prevents its determination. In this study, the DSC curves show no significant stepwise increase in specific heat, showing, therefore, no evidence in favor of the occurrence of a glass transition temperature, and Pereira and coworkers also showed the same result.³⁵

TGA curves of chitosan, chitosan succinate(I), and chitosan succinate(II) are shown in Figure 4. For chitosan, weight loss took place in two stages. The first one starts at 45°C and reaches 215°C. The second stage starts at 275°C and reaches 315°C. The first stage is assigned to the loss of water. The second one, corresponds to the decomposition (thermal and oxidative) of chitosan, vaporization, and elimination of volatile products. Chitosan succinate(I) also degraded in two stages. However, in the case of chitosan succinate(II), first stage is divided into two steps. This well matched

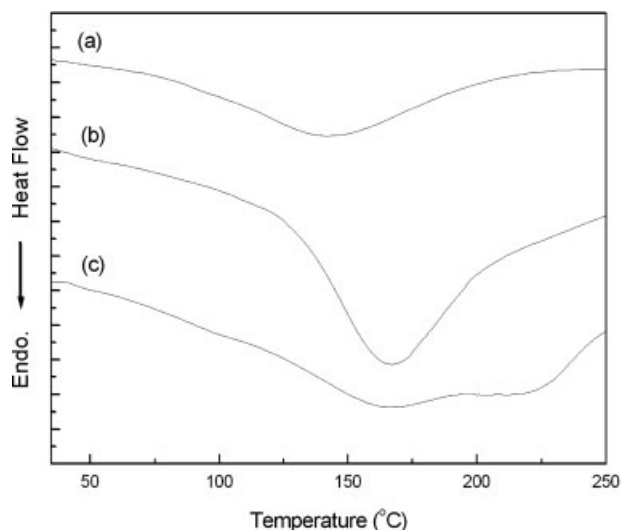


Figure 3 DSC thermograms of (a) chitosan, (b) chitosan succinate(I), and (c) chitosan succinate(II).

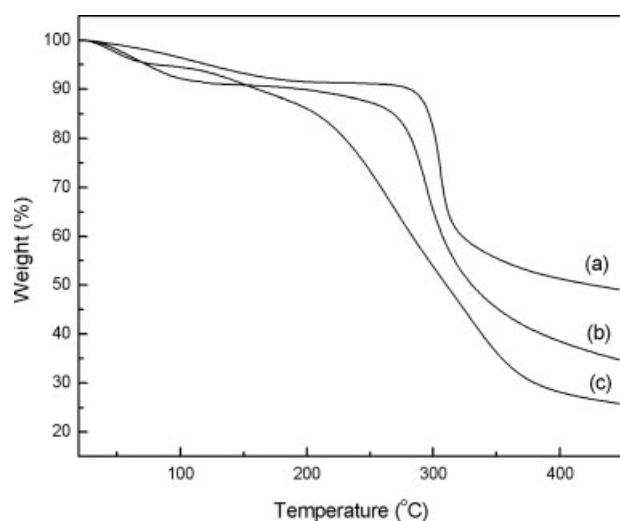


Figure 4 TGA curves of (a) chitosan, (b) chitosan succinate(I), and (c) chitosan succinate(II).

with the result of DSC curve. According to the literature,³⁶ pyrolysis of polysaccharides starts by a random split of the glycosidic bonds, followed by a further decomposition forming acetic and butyric acids and a series of lower fatty acids, where C2, C3, and C6 predominate, and the difference of the weight loss

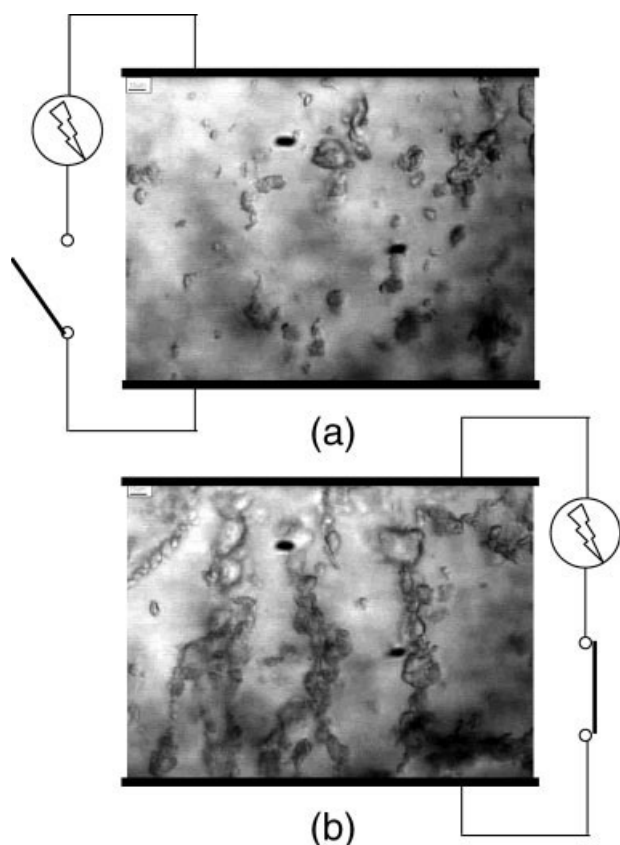


Figure 5 Optical microscopy images of (a) chitosan succinate(II) suspension and (b) same portion of the gel after application of 3 kV/mm dc electric field.

between chitosan and modified chitosans after start of pyrolysis is caused by the weight of functional groups coupled chitosans.

Rheological and electric properties

To observe the alignment of particles in the ER fluid, the chitosan succinate(II) particles were used in this study. Figures 5(a) and 5(b) were observed using an optical microscope. In Figure 5(a), the electric field is zero; therefore, the particles have a random distribution. In Figure 5(b), an electric field of 3 kV/mm has been applied. The presence of fibrils is obvious, although they are not always linear and even have double loops in some cases. These partial fibrils are thought to contribute to the viscosity increase, since an attempt to move one electrode relative to the other would be hindered by the drag of the dangling fibrils.

Shear stress curves as a function of shear rate for chitosan carboxylate series under 3 kV/mm electric field were shown in Figure 6. All chitosan carboxylate series showed the typical Bingham plastic behavior although they showed some deviations.³⁷ This means that flow is observed only after exceeding a minimum yield stress (τ_y). All ER fluids showed good particle dispersion, durability, and yield stress. After dispersing chitosan carboxylate particles in silicone oil, the precipitated particle was not observed even after 1 week because of good particle dispersion. Chitosan succinate(I) was synthesized by the reaction of chitosan with succinic acid. This polymer has two branch groups consisting of a hydroxyl group and a carboxyl group in the side chains. This was detailed in the experimental part. The other side, chitosan succinate(II) was synthesized by the reaction of chitosan with succinic anhydride. This polymer has only one kind of

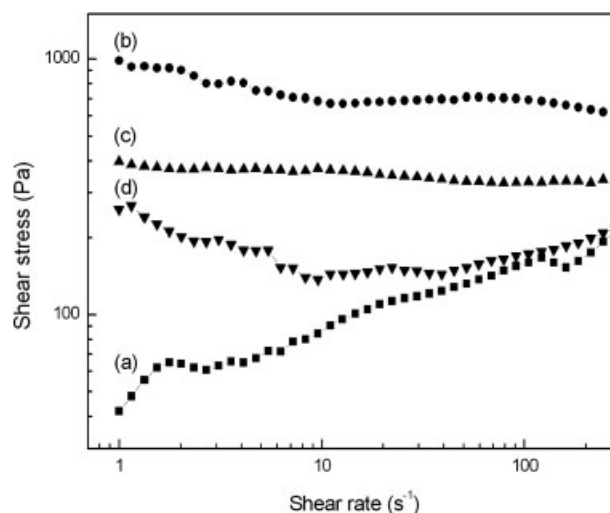
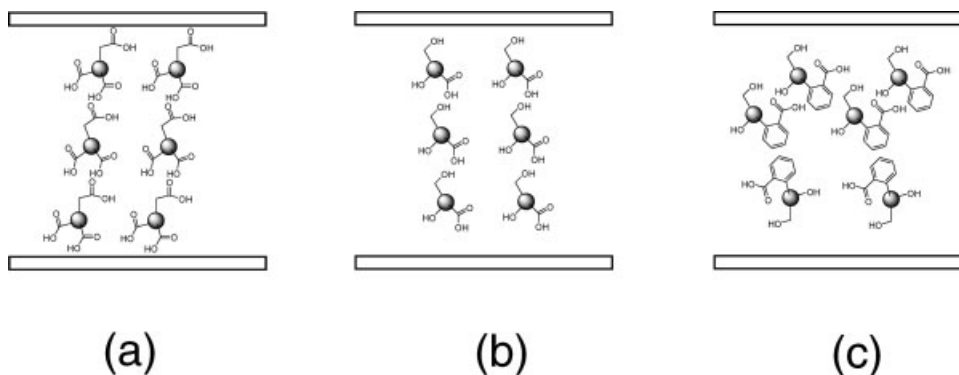


Figure 6 Shear stress versus shear rate for (a) chitosan, (b) chitosan succinate(I), (c) chitosan succinate(II), and (d) chitosan phthalate.



Scheme 2 Estimated alignment structures under the electric field of (a) chitosan succinate(I), (b) chitosan succinate(II), and (c) chitosan phthalate.

the branch group of the carboxyl group in the side chains. However, some amount of chitosan succinate(I) coexists as previous comments on Figure 3 due to nonreacted hydroxyl group with succinic anhydride. End groups of chitosan phthalate are same with chitosan succinate(I). However, benzene ring is used for linking carboxyl group to chitosan unlike the alkyl group of chitosan succinate(I) as depicted in Scheme 1. Chitosan succinate(I) suspension showed higher shear stress than chitosan succinate(II) suspension. In the case of chitosan succinate(II) suspension, proton exchange does not occur, because this suspension has only carboxyl groups for end groups in the side chains. However, a proton can be exchanged between the hydroxyl group and the carboxyl group. Therefore, the attractive force between ER particles increases. Although expect of the intermolecular overlapping between the π electrons, chitosan phthalate showed low shear stress. Estimated alignment structures under the electric field are shown in Scheme 2.

Figure 7 shows the current density of chitosan carboxylate suspension. The current density of chitosan raw material was very low. After carboxyl group coupling onto the chitosan, current density values of these modified chitosan were rather high. Only chitosan phthalate suspension showed very high value. This showed $\sim 2.6 \mu\text{A}/\text{cm}^2$ of the current density at $3.0 \text{ kV}/\text{mm}$. The electronic properties of most organics are dominated by the weak coupling of the van der Waals bound molecules. In benzene ring molecules, the intermolecular coupling is supposed to be stronger because of the significant overlapping between the π electron clouds supporting the charge carrier generation and transport leading to a significant delocalization of electrons and, as a consequence, relatively significant intrinsic conductivity.^{38,39}

The yield stresses obtained from various logarithmic shear stress versus shear rate curves also plotted as a function of electric field strength (E) for eight kinds of ER fluids are shown in Figure 8. Chitosan succinate(I)-suspended ER fluid showed the highest yield stress.

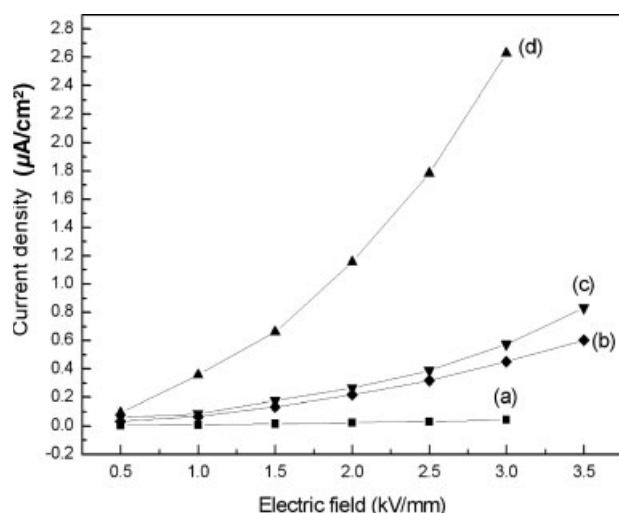


Figure 7 Current density versus electric field for (a) chitosan, (b) chitosan succinate(I), (c) chitosan succinate(II), and (d) chitosan phthalate.

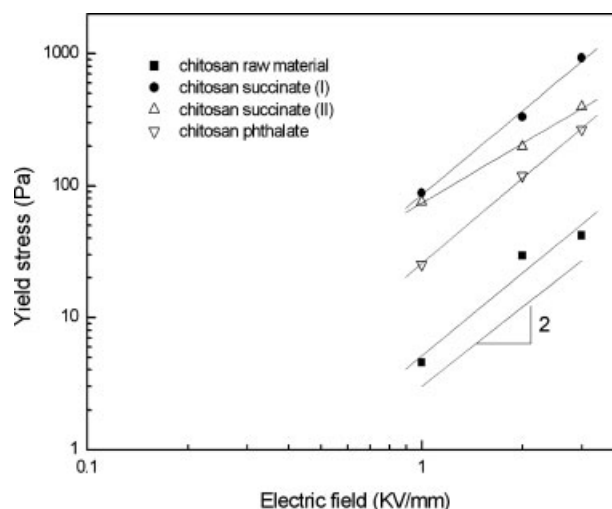


Figure 8 The yield stress under various electric field strengths.

The change of yield stress with different electric field can be represented by the following equation $\tau_y \propto E^a$. The a values of chitosan raw material, chitosan succinate(I), chitosan succinate(II), and chitosan phthalate are 2.10, 2.12, 1.50, and 2.16, respectively. This result differs from the theoretical prediction that τ_y is proportional to the electric field strength E^2 . The difference is due to several factors, such as particle concentration, shape of the particle, etc. Specifically, ER fluids prepared with chitosan succinate(II) particles showed a low a value. We think that the electron transfer between alkyl carboxylic groups in the high electric field is not good in comparison with the electric field power. Choi et al. explained this using a polarization model and a conductivity model.⁴⁰

CONCLUSIONS

In brief, the various ER fluids based on chitosan were prepared for comparing the shear stress under an electric field. The alignment of ER particles like fibrils on an electric field was observed using an optical microscope in this experiment. After comparing the shear stress of all prepared ER fluids, obtained conclusions were that ER particle having two functional groups (one is +ve charge and another is -ve charge) showed higher shear stress than that having only one functional group like the comparison between chitosan succinate(I) and chitosan succinate(II). Though expect of the intermolecular overlapping between the π electrons clouds supporting the charge carrier generation and transport leading to a significant delocalization of electrons, chitosan phthalate showed lower shear stress than chitosan succinate (I) and (II).

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