

Chemical Structure Designing to Enhance the Yield Stress of Electrorheological Fluids Based on Modified Chitosan Compounds

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ABSTRACT: For studying the influences of alkyl chain length, end groups of the side chains, and mixture on enhancing the shear stress of electrorheological (ER) fluids, chitosan carboxylates were synthesized for ER particles and prepared ER fluids by dispersing the particles in silicone oil. After comparing the shear stress of all prepared ER fluids, the conclusion obtained was that ER particles having two functional groups showed higher shear stress than those

having one functional group. However, after mixing two ER particles having one functional group respectively, the ER fluid having those particles showed a lower shear stress. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1559–1566, 2004

Key words: anhydrous ER fluids; structure effects; chitosan derivatives; shear stress; ER suspension image

INTRODUCTION

The phenomenon of electrorheology (ER) was reported first by W. M. Winslow in 1947 and occasionally bears his name.¹ The electrorheological (ER) fluids are one kind of suspension in which rheological properties can reversibly change several orders of magnitude under a sufficiently strong electric field.² Many researches have been conducted for practical utilizations of such suspensions in active control devices such as dampers, shock absorbers, clutches, and brakes,³ and in new devices including gripping devices,⁴ seismic controlling frame structures,⁵ human muscle stimulators,⁶ and spacecraft deployment dampers.⁷ However, they have remained unsuccessful due to such problems as particle sedimentation, aggregation or solidification, particle or electrode abrasion, and poor durability or temperature dependence.

Positive ER materials have rheological properties that dramatically increase with the applied electric field. Many efforts have been spent on developing high-performance positive ER materials,^{8,9} and many shortcomings are pertinent to these systems, for example, a narrow working temperature, solidification at low temperature, a high current density due to the

high conductivity of water, and device erosion caused by water.¹⁰ Water-free ER fluids were developed¹¹ under the assumption that they do not have the shortcomings of hydrous ER fluids. However, anhydrous ER fluids have a different problem—particle sedimentation, which could make ER fluids malfunction and severely limit practical applications.¹² Also, anhydrous ER fluids show aggregations under a strong electric field.

The modeling for understanding ER phenomena has been well studied.^{13–15} Though the chemical structure designing studies of ER particles are important to apply for the practical utilizations, these studies still leave much to be desired. In this study, modified chitosan compounds were synthesized to solve these problems. Synthesized chitosan compounds showed good yield stress, durability, and particle dispersion. Specifically, modified chitosan having carboxyl groups and hydroxyl groups as the dispersed phase showed good yield stress and particle dispersion. This paper focuses on designing chemical structures to enhance the yield stress of electrorheological fluids. The influences of alkyl chain length, end groups of the side chains, and mixture on enhancing the shear stress of ER fluids were studied.

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EXPERIMENTAL

Synthesis and FT-IR analysis

Chitosan adipate was synthesized by the following method. Chitosan (10 g, Jakwang Co., Ansong City,

Korea), adipic acid (1 mol, Aldrich, Milwaukee, WI), triphenyl phosphine (0.01 mol, TPP, Aldrich), 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 35°C oil bath for 24 h with stirring. After a reaction, modified chitosan was washed with DMF and distilled water and dried at a 40°C 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 becomes longer. Then, no OH should be observed. In this work, OH didn't react with adipic acid. This was confirmed by FT-IR (GX FTIR spectrum, Perkin-Elmer, Boston, MA). Chitosan malonate, chitosan sebacate, and chitosan succinate (I) were synthesized using malonic acid, sebacic acid, and succinic acid, respectively, instead of adipic acid.

IR (KBr): 3452 (OH, carboxylic acid), 3350 (OH, hydroxyl group), 1717 ($C=O$, carboxylic group), 1658 cm^{-1} ($NH-C=O$, 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 Co.) and pyridine (200 mL) solution at a 60°C oil bath for 5 h with stirring. After a reaction, modified chitosan was washed with DMSO and distilled water and dried at a 40°C vacuum oven. The reaction yield was 67.5%.

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

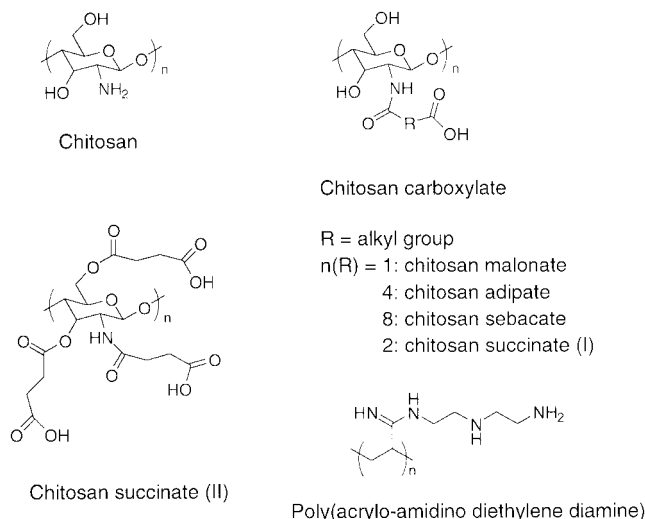
Poly(acrylo-amidino diethylene diamine) (PAADD) was synthesized by the reaction of polyacrylonitrile (6 g, PAN, Hanil Synthetic Fiber Co., Masan, Korea) fiber with diethylene triamine (500g, DETA, Acros Organics, Geel, Belgium) under the catalysis of $AlCl_3 \cdot 6H_2O$ (40 g, Junsei Chemical Co., Tokyo, Japan) with a condenser and reacted at a 120°C oil bath for 3 h with stirring. After a reaction, the modified PAN fiber was washed with distilled water and dried at a 40°C vacuum oven. The reaction yield was 97.2%.

IR (KBr): 3500–2000 (amine groups), 1650 ($N-C=N$), 1600 (NH_2), 1580 (NH), 1481 (CH_2), 1453 cm^{-1} (CH_2).

All synthesized polymers were depicted in Scheme 1.

Suspension preparation and methods of measurement

These polymers were ground to 5–30 μm particles using a ball mill. ER fluids were prepared by dispersing these particles into silicone oil whose viscosity was 30 cS 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



Scheme 1

suspension were investigated in a static DC field using a Physica Couette-type rheometer (Physica US200, USA) 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 to 300 s^{-1} and electric fields of 0–3 kV/mm.

The dc current density J of chitosan compound suspensions was 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 voltage drop across a $1M\Omega$ resistor in series with the 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 3kV/mm using an optical microscope.

RESULTS AND DISCUSSION

To observe the alignment of particles in the ER fluid, the chitosan succinate (II) particles were used in this study. A SEM image of chitosan succinate (II) particles is shown in Figure 1(a). Not all shapes of the particles were uniform. The range of the particles' sizes was 5–20 μm . Figures 1(b) and (c) were observed using an optical microscope. In Figure 1(b), the electric field is zero; therefore, the particles have a random distribution. In Figure 1(c), 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

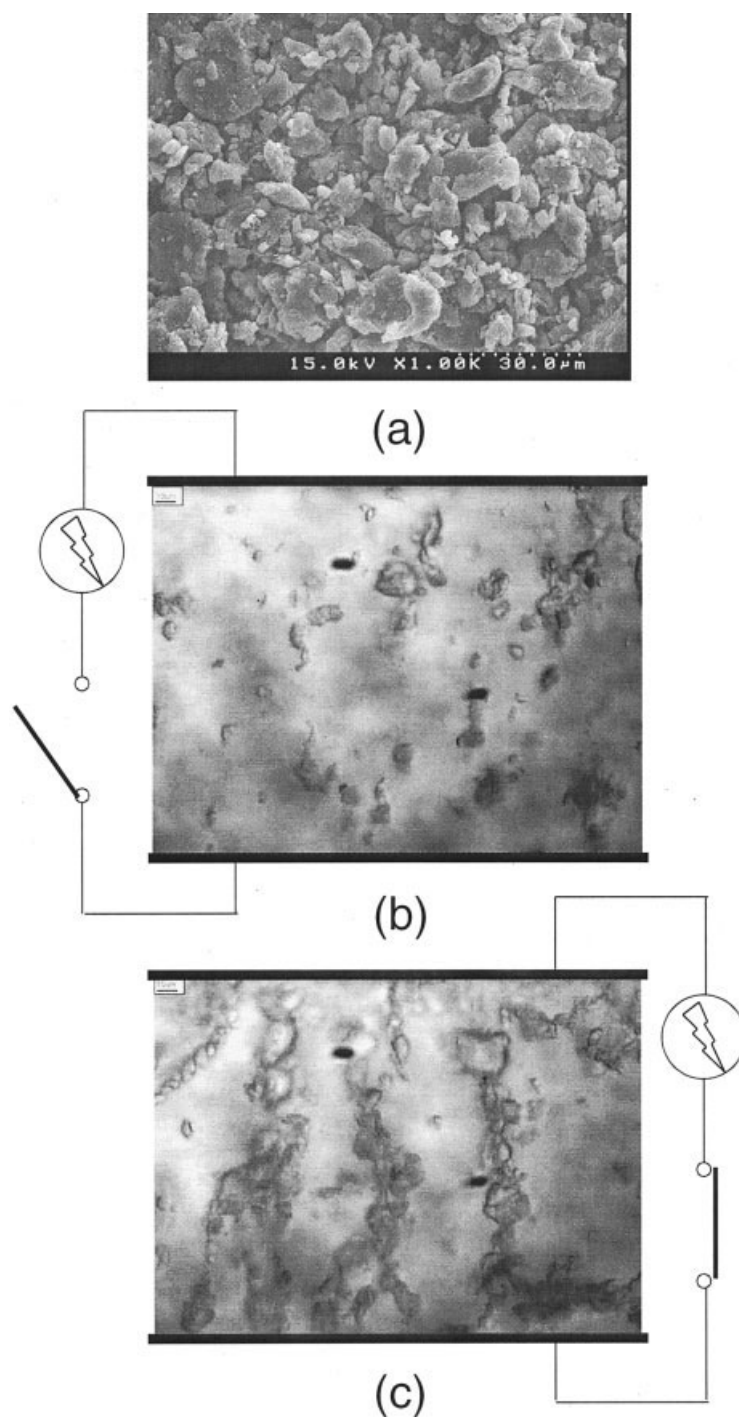


Figure 1 (a) SEM images of chitosan succinate (II) particles, and optical microscopy images of (b) chitosan succinate (II) suspension and (c) same portion of the gel after application of a 3 kV/mm dc electric field.

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 are shown in Figure 2. All chitosan carboxylate series showed the typical Bingham plastic behavior.

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 of 750–1000 Pa. After dispersing chitosan carboxylate particles in silicone oil, the precipitated particle wasn't observed even after one week because of good particle

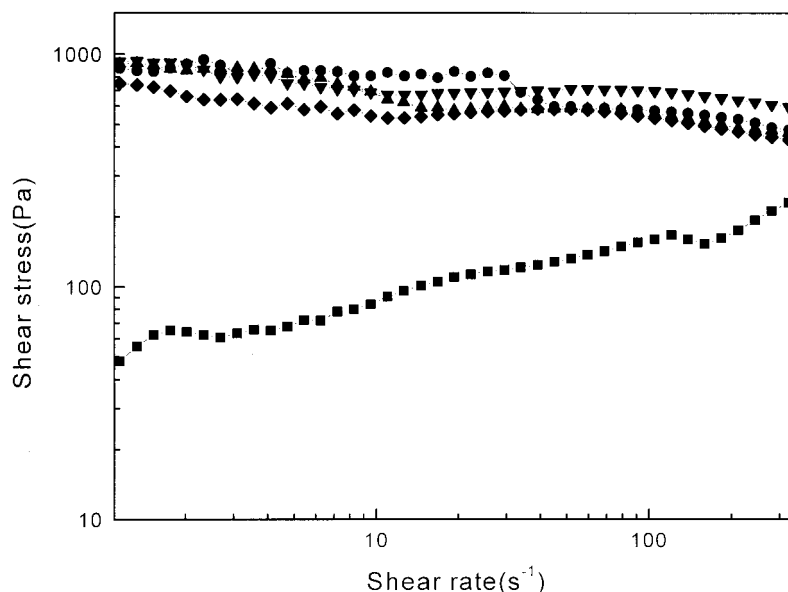


Figure 2 Shear stress vs. shear rate for ■ chitosan raw material, ● chitosan adipate, ▲ chitosan malonate, ▼ chitosan sebacate, and ◆ chitosan succinate (I) particle suspension under 3kV/mm electric field strength.

dispersion. This experiment was performed to confirm the alkyl chain length effect on shear stress. The CH_2 number of malonic acid, succinic acid, adipic acid, and sebacic acid is 1, 2, 4, 8, respectively. In this work, chain length effect wasn't observed. However, chitosan malonate particles dispersed in ER fluids showed the highest yield stress among them.

Figure 3 shows the current density of chitosan carboxylate suspension. The current density of chitosan raw material was very low. After carboxyl group cou-

pling onto the chitosan, current density values of these modified chitosan were rather high. Only chitosan adipate suspension showed a different value. This showed about $1.0 \mu\text{A}/\text{cm}^2$ of the current density at 3.0 kV/mm.

To verify the effect of the branch groups of particles for ER fluids, chitosan succinate (I) and chitosan succinate (II) were compared with each other. 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

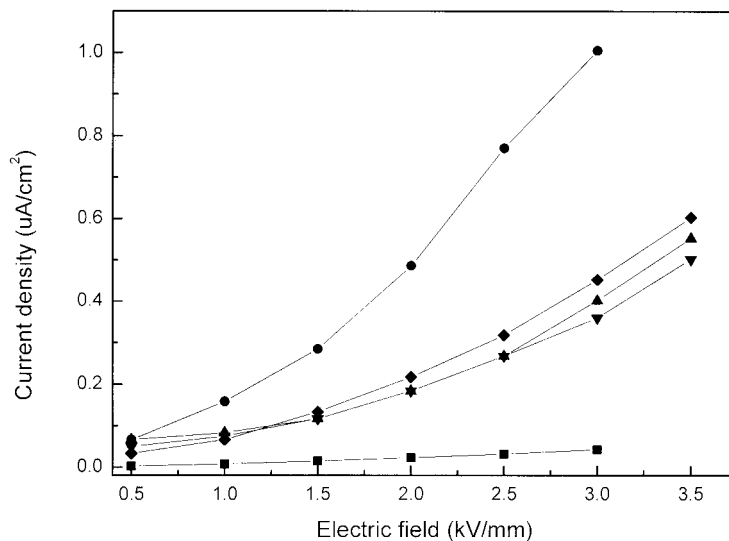


Figure 3 Current density vs. electric field for ■ chitosan raw material, ● chitosan adipate, ▲ chitosan malonate, ▼ chitosan sebacate, and ◆ chitosan succinate (I) particle suspension.

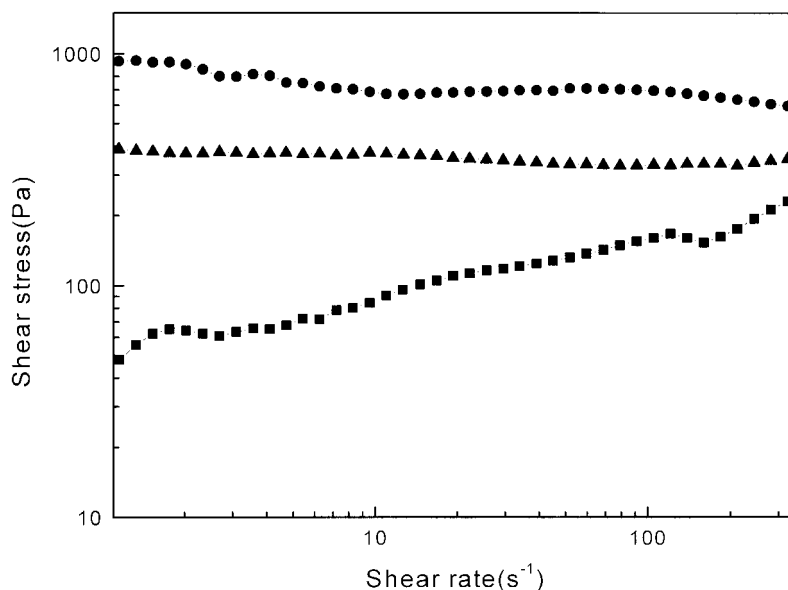
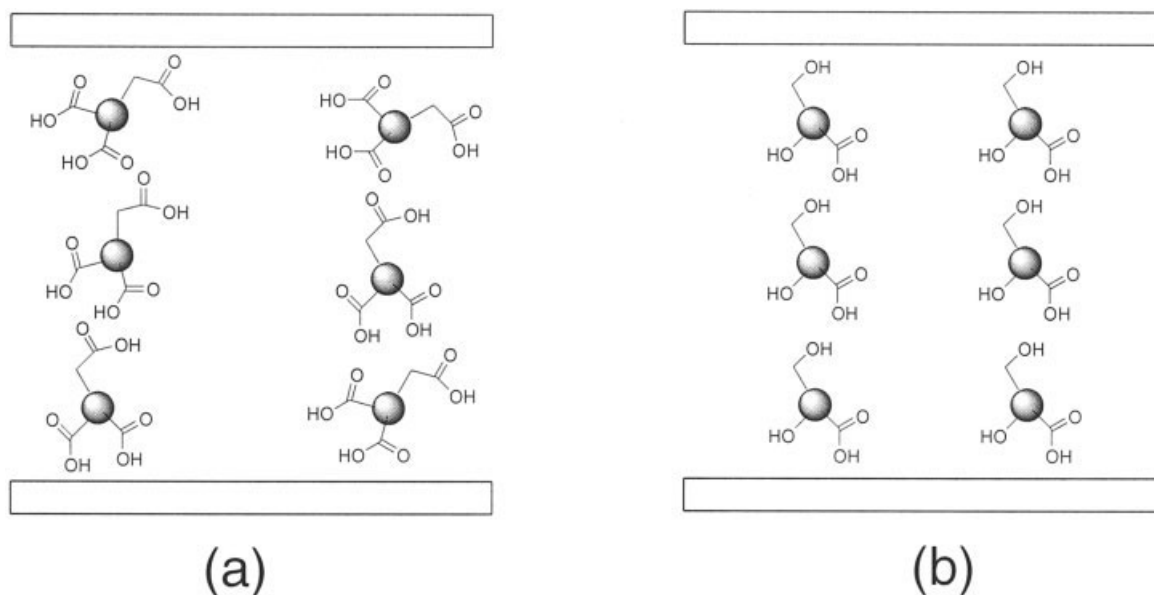


Figure 4 Shear stress vs. shear rate for ■ chitosan raw material, ● chitosan succinate (I), and ▲ chitosan succinate (II) particle suspension under 3 kV/mm electric field strength.

group in the side chains. This was detailed at 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 the branch group of the carboxyl group in the side chains. Figure 4 shows shear stress curves as a function of shear rate for an ER system containing chitosan raw material suspension, chitosan succinate (I) suspension, or chitosan succinate (II) under a 3 kV/mm electric field. Chitosan succinate (I) suspension showed higher shear stress than chi-

tosan succinate (II) suspension. In chitosan succinate (II) suspension, proton exchange doesn't 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. Estimated alignment structures under the electric field were shown in Scheme 2.

Figure 5 shows shear stress curves as a function of shear rate for Poly(acrylo-amidino diethylene dia-



Scheme 2

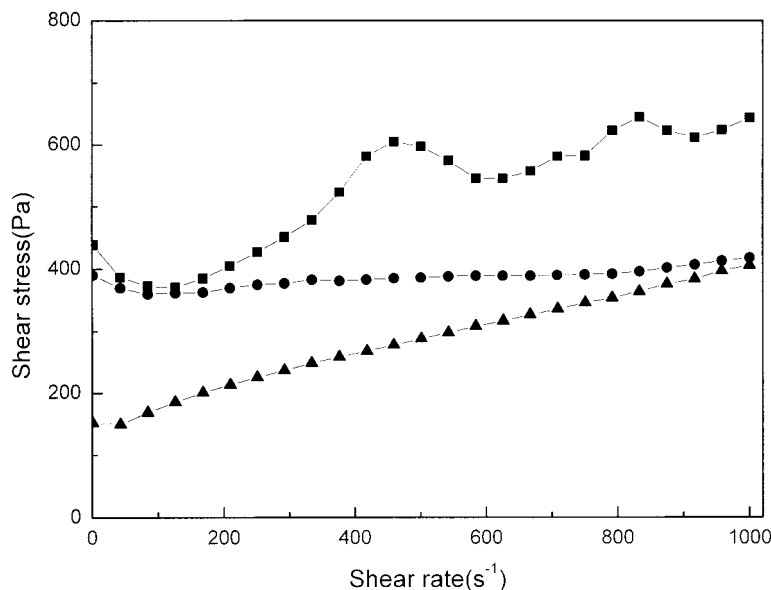


Figure 5 Shear stress vs. shear rate for ■ poly(acrylo-amidino diethylene diamine), ● chitosan succinate (II), and ▲ mixture of poly(acrylo-amidino diethylene diamine) and chitosan succinate (II) particle suspension under 3 kV/mm electric field strength.

mine) (PAADD) suspension, chitosan succinate (II) suspension, and the mixture of these two polymer suspensions under 3 kV/mm. The mixture ratio was 1 (chitosan succinate (II)) : 2 (PAADD). The shear stress curve of PAADD suspension showed as nonlinear. After mixing with chitosan succinate (II) particles, the shear stress curve of this suspension showed as linear. However, the shear stress decreased to 1/3 of the shear stress of PAADD suspension. The synergy effects of the mixture of amine groups and carboxyl groups were expected. However, the result wasn't good. It was confirmed that the different sizes and the chemical structures of particles dispersed ER fluids showed a low shear stress under an electric field. Wu et al. suggested a similar conclusion in their article.¹⁶ It was the suspension for optimum ER response that should contain as many particles of uniform size as possible. This structure is depicted in Scheme 3.

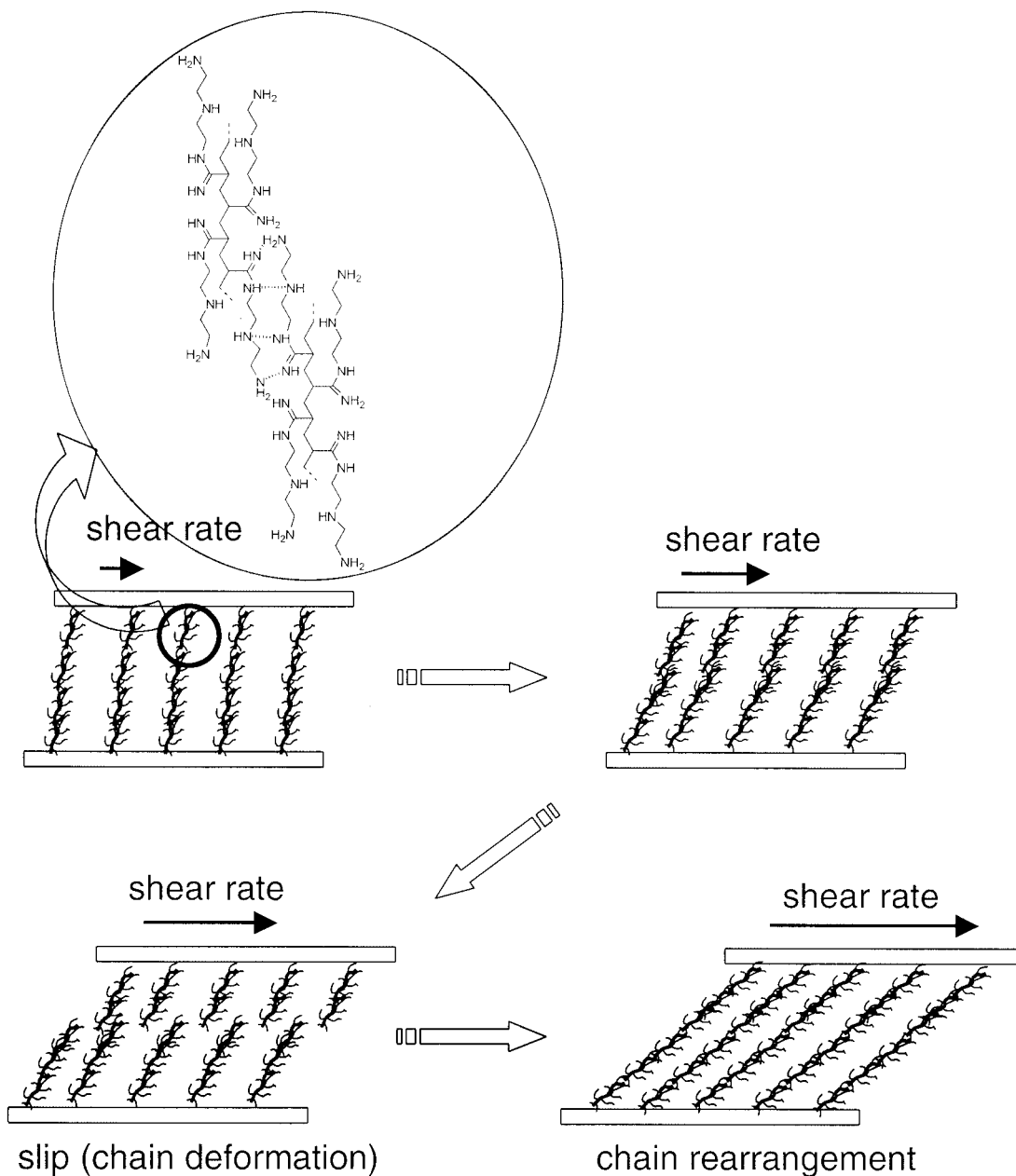
Figure 6 shows the shear stress of PAADD suspension under various electric field strengths (0, 1, 2, and 3 kV/mm). We could see the unique result. Under electric field, flow curves showed vibrations. These vibrations came from the slip of chain alignments.

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 as shown in Figure 7. Chitosan malonate suspended ER fluid showed the highest yield stress. However, that fluid didn't show a significantly different value of yield stress in comparison

with other fluid types of chitosan carboxylate. 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, malonate, succinate (I), adipate, sebacate, succinate (II), PAADD, and mixture are 2.10, 2.03, 2.12, 2.46, 1.90, 1.50, 2.07, and 1.10, 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 a mixture of chitosan succinate (II) and PAADD particles showed a low a value.

CONCLUSION

In conclusion, the various ER fluids based on chitosan and PAN 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 particles having two functional groups (one is + charge and another is - charge) showed higher shear stress than those having only one functional group, and the ER suspension mixed two ER particles having one functional group showed a lower shear stress. The shear stress curves of PAADD suspension showed vibrations under various electric field strengths (0, 1, 2, and 3 kV/mm) due to the slip of chain alignments.



 poly(acrylo-amidino diethylene diamine)

Scheme 3

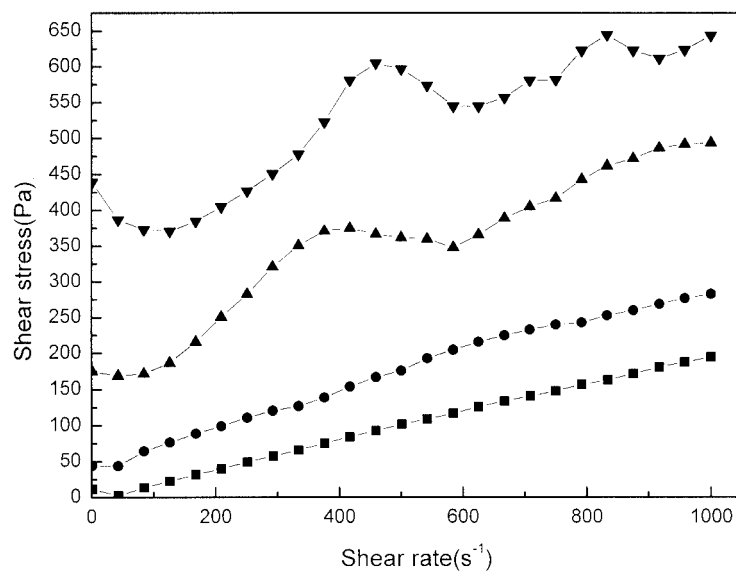


Figure 6 Shear stress vs. shear rate for poly(acrylo-amidino diethylene diamine) under ■ 0 kV/mm, ● 1 kV/mm, ▲ 2 kV/mm, and ▼ 3 kV/mm electric field strength.

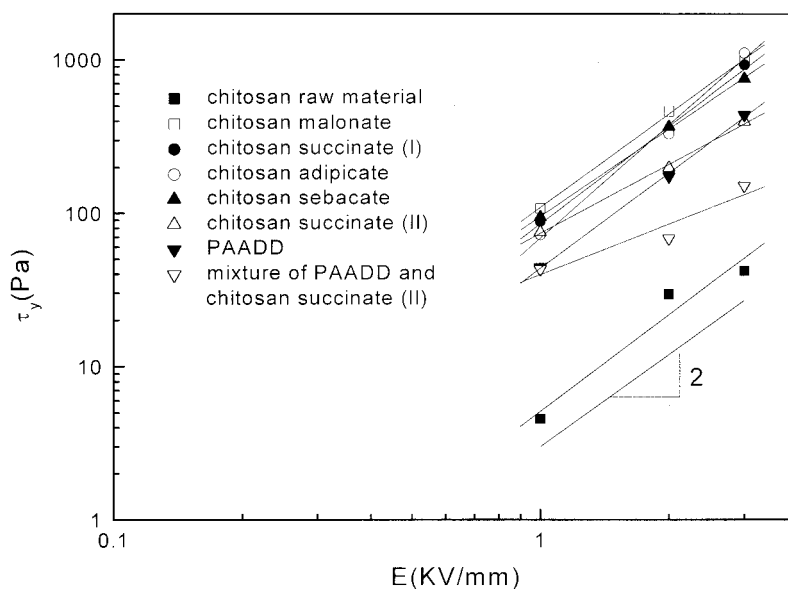


Figure 7 The yield stress under various electric field strengths.

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References

- Winslow, W. M. *J Appl Phys* 1949, 20, 1137.
- Hao, T. *Adv Mater* 2001, 13, 1847.
- Block, H.; Kelly, J. P. *J Phys D Appl Phys* 1998, 21, 1661.
- Chadwick, B.; Nowak, M. U.S. Patent 5 970 581, 1999.
- Xu, Y. L.; Qu, W. L.; Ko, J. M. *Earthquake Eng Struct Dyn* 2000, 29, 557.
- Bohon, K.; Krause, S. *J Polym Sci Part B: Polym Phys* 1998, 36, 1091.
- Starkovich, J.; Shtarkman, E.; Rosales, L. European Patent 0 872 665, 1998.
- Parlínek, V.; Sába, P. *Langmuir* 2000, 16, 1447.
- Choi, U. S.; Ko, Y. G.; Kim, J. Y. *Polym J* 2000, 32, 501.
- Inoue, A.; Ide, Y.; Oda, H. *J Appl Polym Sci* 1997, 64, 1319.
- Hao, T.; Kawai, A.; Ikazaki, F. *Langmuir* 1998, 14, 1256.
- Tse, K.-L.; Shine, A. D. *Macromolecules* 2000, 33, 3134.
- Tang, X.; Conrad, H. *J Appl Phys* 1996, 80, 5240.
- Gonon, P.; Foullic, J.-N.; Atten, P.; Boissy, C. *J Appl Phys* 1999, 86, 7160.
- Davis, L. C. *J Appl Phys* 1992, 72, 1334.
- Wu, C. W.; Conrad, H. *J Appl Phys* 1998, 83, 3880.