

Biodegradable Modified Corn Starch and Its Electrorheological Properties

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Abstract: In this study an electrorheological (ER) effect of the suspensions containing both native starch (S) and modified starch (MS) particles in corn oil under various externally applied electric field strengths are reported. To prepare an ER active material, biodegradable starch was partially hydrolyzed and converted to its Li⁺ salt. Both biopolymers were characterized by ¹³C-NMR, Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Thermogravimetric Analysis (TGA). Suspensions of Starch and modified Starch particles were prepared in corn oil at concentrations ranging from 5-40% by mass. Rheological measurements were carried out via a rotational rheometer with a high voltage generator to investigate the effects of electric field strength and particle concentration on ER performance. Effects of various parameters such as sedimentation stability, dispersed particle concentration, electric field strength, shear rate, frequency and temperature onto ER activity were investigated. Modified starch suspension was accepted as a biodegradable anhydrous ER fluid.

Introduction

Biodegradation is the process by which organic substances are broken down by the enzymes and microorganisms. The term is often used in relation to ecology. Starch is a linear polymer (polysaccharide) made up of repeating glucose groups linked by glucosidic linkages in the 1-4 carbon positions. Biodegradation of starch based polymers is a result of enzymatic attack (Ogungbenle 2007) at the glucosidic linkages between the sugar groups leading to a reduction in chain length and the splitting of sugar units (monosaccharides, disaccharides and oligosaccharides) (Kato et al. 2003).

ER fluids can potentially be used as a smart material for active devices, which transform electric energy to mechanical energy. They are composed of a suspension of polarization solid particles dispersed in a nonconducting liquid media (Block & Kelly 1988). When an electric field is imposed, the rheological properties of the fluid vary, showing a characteristic fibrillation (Winslow 1949); the strings of the particles are oriented along the direction of the electric field. This structure is known to be induced by a mismatch of the dielectric constants and conductivity of the suspended particles and the insulating oil (Parthasarathy & Klingenberg 1996). ER fluids are divided into two categories (Tao et al. 2001): one is called dry-base ER system (or anhydrous, which shows ER activity without adding any polar promoter) the other one is called wet-base ER systems (or hydrous, which needs a polar promoter to be added to show ER activity).

In this study, we investigate native starch and modified starch as a vigorous nominee for anhydrous particles in high performance dry-base systems by analyzing the effect of particle concentration, electric field strength, shear rate and frequency via shear tests.

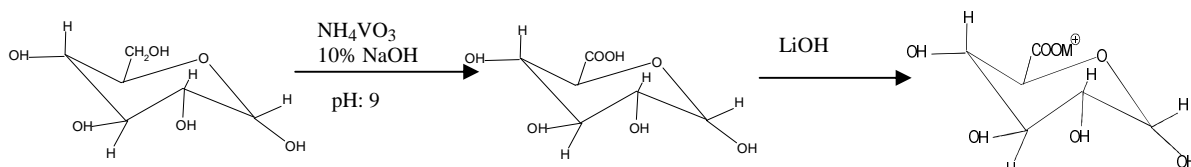
Experimental

1. Material

The chemicals were Aldrich, Acros and Merck products, with analytical grade. The base fluid used was corn oil with a density $\rho = 0.936 \text{ g/cm}^3$, viscosity $\eta = 45 \text{ mPa s}$, dielectric constant $\epsilon = 3.34$, and conductivity ($E = 1 \text{ kV/mm}$) $\sigma = 4 \times 10^{-11} \text{ S/m}$ at 25°C . The starch was (used as dispersed phase) produced by Acros Organics products.

2. Modification Of Native Starch

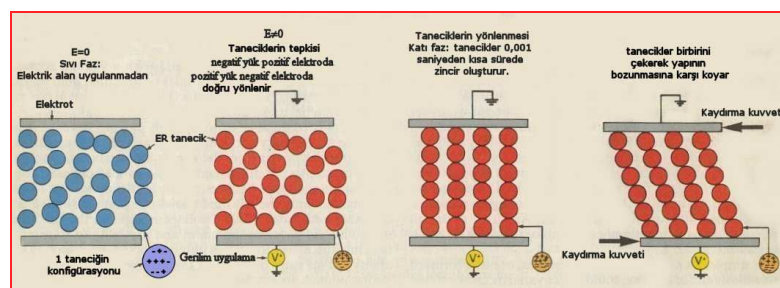
Suspensions of the air-dried corn starch (50 g) in distilled water (500 mL) were supplemented with ammonium vanadate (NH_4VO_3). A marine blue color was appeared. The pH of each suspension was adjusted to 9.0 by adding 10% NaOH(aq) . Each suspension was continuously stirred for 48 h at a constant temperature of $35\text{--}40^\circ \text{C}$, under atmospheric conditions. After the reaction was completed, its color turned to yellowish. The reaction mixture was filtered through a sintered glass and the filtrate washed with cold water to remove any impurities present. The products were dried in desiccators over molecular sieves. The dried products were dispersed in 0.1 M LiOH(aq) and the lithium-salt of partially modified starch was obtained. The final product was also dried under the same conditions. The modification reaction mechanism of the native starch is given in Scheme 1.



Scheme 1. Oxidation reaction mechanism and chemical structure of modified starch.

3. Electrorheological Measurements

Suspensions of starch derivative particles were prepared in corn oil at a series of concentration ($c = 5\text{--}40\%$ m/m). Suspensions were mechanically stirred before each measurement against sedimentation. Rheological properties of the suspensions were determined with a Thermo-Haake RS600 parallel plate Electro-rheometer (Germany). The gap between the parallel plates was 1.0 mm and the diameters of the upper and lower plates were 35 mm. All the experiments were carried out at a controlled rate (CR) mode and at various temperatures ($25\text{--}125^\circ \text{C}$, with 25°C increments.). The voltage used in these experiments was also supplied by a 0–12.5 kV (with 0.5 kV increments) dc electric field generator (Fug Electronics, HCL 14, Germany), which enabled resistivity to be created during the experiments.



Scheme 2. Mechanism of ER behavior.

Results and Discussion

1. Characterizations

Both native starch and modified starch were subjected to the following characterizations before ER measurements to be carried out; The ^{13}C -NMR spectra were obtained in DMSO-d_6 and CDCl_3 at ambient

temperature using a 400 MHz Bruker DPX Avance Nuclear Magnetic Resonance Spectrometer at the Scientific and Technical Research Council of Turkey (TUBITAK), Ankara Test and Analysis Laboratory (ATAL). Modified starch showed similar ¹³C-NMR spectra to that of the native starch, indicating that modification did not have an effect on the molecular packing of the double helices in the crystalline regions but a new additional signal of the carbonyl carbons in ester groups formed by the formulation at 176.15 ppm is clearly visible; some differences exist also in C₆ region.

The samples were scanned by Scanning electron micrographs (SEM) with an extra of EDAX analyzer (Jeol JSM-6360 LV, Japan). The study of EDAX analysis reveal that reactions of modification were completed positively. EDAX analysis evaluated the extent of ionic types (Mi et al. 2003). Spectra (a) is shown energy profiles coming from starch as oxygen and carbon but spectra (b) shows that one more energy profile became the Li⁺.

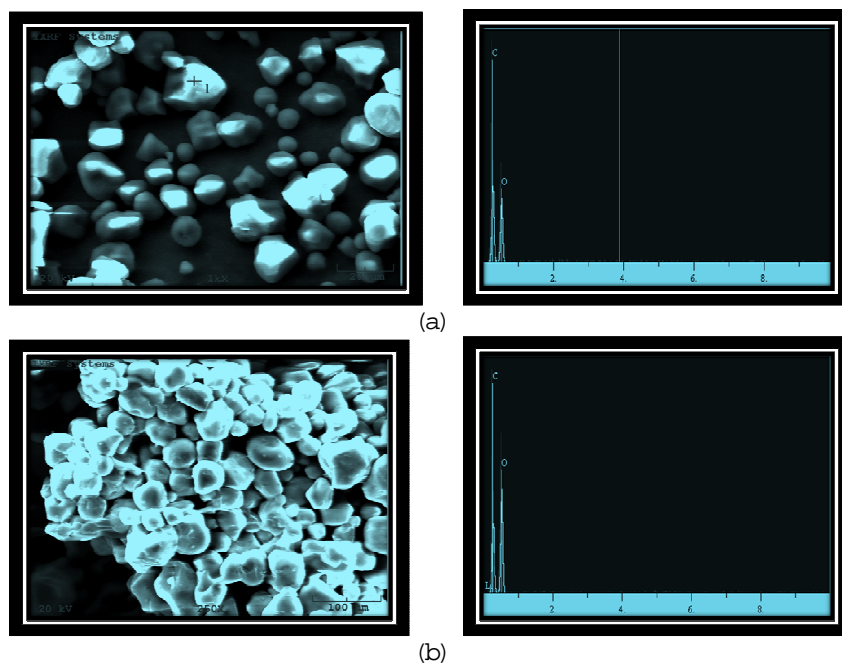


Figure 1. EDAX analysis of energy positions (a) starch (b) modified starch.

Thermal analysis data of particles were obtained using a Setaram 8ET8 V8 Evolution 1760 model thermogravimetric analyzer (TGA) in the presence of nitrogen atmosphere up to 600 °C, at a heating rate of 10 °C / min. The results from TGA are compared for starch and modified starch as a thermogram. Starch has two decomposition stages with one beginning at 250 °C and another beginning at 450 °C. Thermal result of starch and modified starch is similar. There are two weight losses for samples consist at 245 °C and 440 °C. The weight loss is approximately 100 % for starch and 85 % for modified starch at 600 °C. as a result, modified starch was appeared about 15 % end of the analysis (Vijaya et al. 2008).

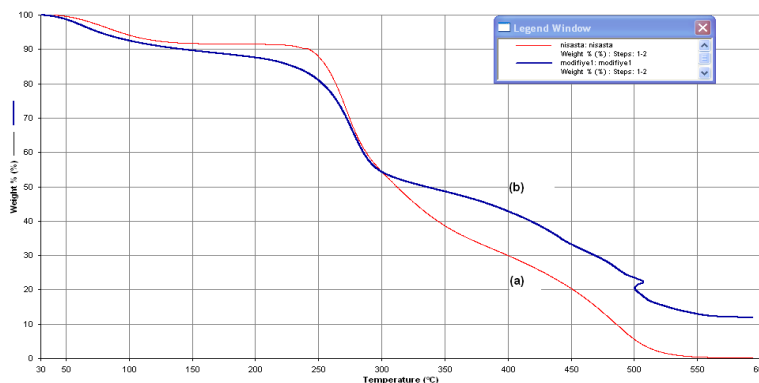


Figure 2. Thermogravimetric curve of (a) starch and (b) modified starch.

2. Electrorheology

2.1. Effect Of Dispersed Particle Concentration

Effect of dispersed particle concentration on viscosity of S and MS suspensions was investigated using five different concentrations (5%–40% m/m) and results obtained are shown in Figure 3. Suspension concentration exerts principle effect on the ER activity (Wu & Shen 1996). The viscosities of both S and MS suspensions were shown increase with rising particle concentration up to $c = 30$ (% , m/m) and then leveled off. The maximum electric field induced viscosities (ηE) of Starch and Modified Starch were observed to be 1976 Pas and 3170 Pas, respectively under $E = 2$ kV/mm and shown a typical strong ER effect.

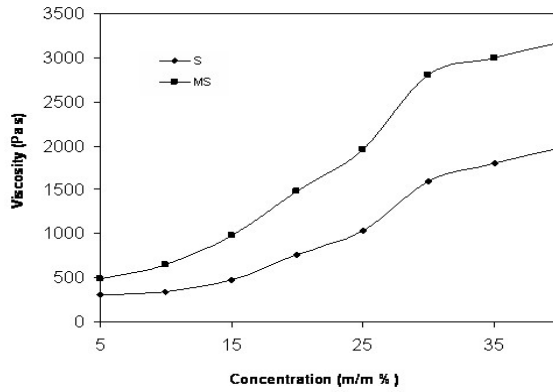


Figure 3. The change in viscosity with concentration, $T = 20^{\circ}C$ and $E = 2$ kV/mm.

2.2. Effect Of Electric Field Strength

Shear stress is one of the critical design parameter in ER phenomenon and has attracted considerable attention both theoretically and experimentally. Figure 4 also shows the changes in the shear stress (τ) and viscosity (η) of S and MS in Corn Oil suspensions under various electric field values. Increase in electric field causes increase in τ and η . This is due to the formation of chain-like structure caused by the polarized particles in suspensions under E electric field strength (Choi et al. 1997) .

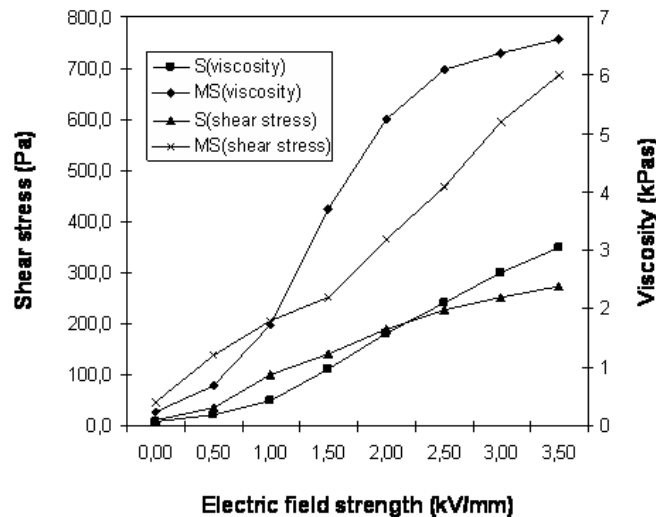


Figure 4. The change of viscosity and shear stress with electric field strength, $T = 20^{\circ}C$, $c = 30\%$ m/m, $\dot{\gamma} = 0.2 s^{-1}$

2.3. Effect Of Temperature

The temperature dependence of the shear stress is shown in Figure5. The results were investigated at

temperatures between 25–80°C. It was observed that, for S/Corn Oil system, τ decreased with increasing T and a shear stress loss of $\Delta\tau = 118$ Pa was measured. An interesting curve was obtained for MS/Corn Oil suspension, showing a decrease in τ up to T = 50 °C, then gave an increase with rising T. This may be attributed to the loss of moisture in the MS/Corn Oil suspension and the increased kinetic energy of Li^+ ions inserted into the structure of starch with the modification process, which gave rise to increased mobility and polarizability of the suspended modified starch. Although shear stress changes with increasing temperature reported in the literature (Unal et al. 2006; Liu & Shaw 2001)

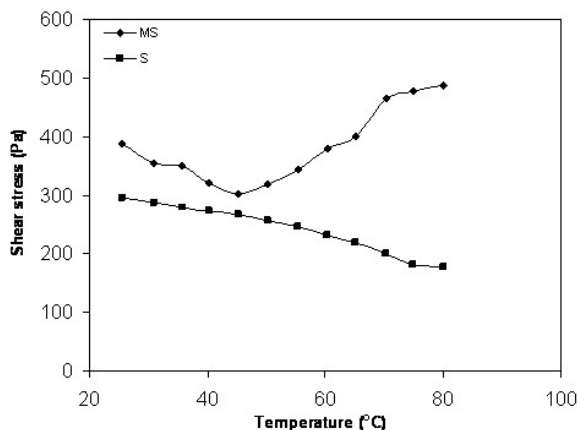


Figure 5. Effect of temperature on the shear stress for starch and modified starch suspension, $c = 30\%$ m/m, $\dot{\gamma} = 0.2$ s⁻¹, $E = 2.0$ kV/mm.

2.4. Effect of frequency

The effect of frequency (f) on the shear modulus (G') for S and MS suspension is shown Fig.6. Up to $f = 50$ Hz, viscoelastic properties of both Starch and Modified Starch were not much changed. After $f = 50$ Hz, a sharp increase was observed for each sample as a typical characteristic of a viscoelastic material, which indicates a vibration damping property. The increase in G' with increasing external f was also reported in the literature (Zhao et al. 2008).

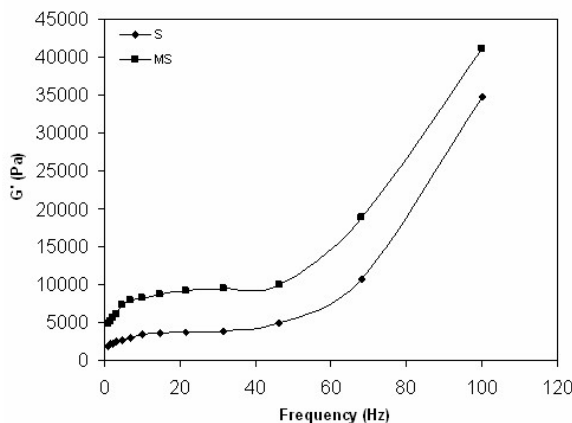


Figure 6. The change of G' with frequency, $c = 30\%$ m/m, $T = 20^\circ$ C, $\gamma = 10$ Pa, $E = 2$ kV/mm .

2.5. Sedimentation stability

Sedimentation ratio curves as a function of time for S and MS suspension at 20% concentration at room temperature are shown in figure 7 that, prepared polymer suspensions exhibited colloidal stability against sedimentation, which the sedimentation ratio is 58% end of 30 days. The sedimentation stability of modified starch suspension is better than that of starch. This is possibly because starch is easily congregation for its flake-like structure, greatly modifies its dispersal ability so as to increase its anti-sedimentation ability (Xiang & Zhao 2006).

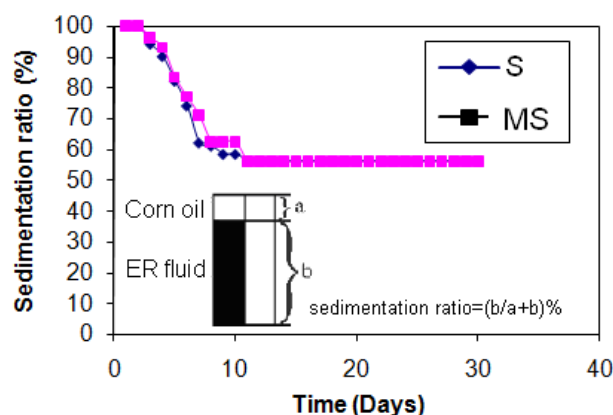


Figure 7. Sedimentation stability of starch and modified starch depend on time, $c = 20\%$ m/m, $T = 20^\circ\text{C}$

Conclusions

In present study we have shown that the native starch can successfully be partially modified and converted to ER active Li salt.

The results showed that, S and MS suspension exhibited ER behavior under electric field strength. The conductivities of S (10^9 S/m) and MS (10^5 S/m) were in the range of ER active materials. Sedimentation stabilities of S and MS suspension were found to be 58% and suitable for potential industrial applications. Optimum particle concentration of the both suspensions was determined to be 30% by mass. The shear stresses of the both materials were shown a linear increase with increasing E. S and MS suspension showed Newtonian behavior when $E = 0$ kV and Bingham behavior when $E \neq 0$ kV. The viscosities of S and MS suspension decreased with increasing shear rate and given a typical of viscoelastic behavior by means of shear thinning. Electric field induced viscosities of the both materials were observed to increase linearly. Temperature was observed to be effective on the both materials and caused shear stress losses on S and shear stress increase on MS, especially at elevated temperatures. Our results revealed that, wet-base ER active S/corn oil suspension system become dry-base ER active after the modification, and shown 3 times stronger ER strength; which is extremely important from industrial point of view.

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