Electroresponsive characteristics of highly substituted phosphate starch

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Electrorheological (ER) fluids, suspensions typically formed by dispersing polarizable particles in an insulating oil, respond rapidly and reversibly to external electrical fields, leading to a sharp increase in shear viscosity [1] due to polarized and chain-like structures, which span the electrodes as a result of attractive forces generated between the dipoles.

Because of their physicochemical stabilities, dry-base anhydrous ER systems have attracted much attention as compared to the wet-base hydrous ER systems. Anhydrous ER materials include various semiconducting polymers [2–4], biopolymers [5, 6], and polymer/clay nanocomposites [7, 8], as well as modified cellulose and chitosan [9]. These ER materials possess either branched polar groups, such as amine, hydroxyl, and amino-cyano, or semiconductive repeating groups. The polar groups may affect the ER behavior by playing the role of the electronic donor under the external electric field.

Starch has also been used as a wet-base ER material at an early stage of an ER research, in which the water coats the starch surface to induce polarization [10]. We adopted an esterification process using a mixture of ortho-phosphoric acid and urea to substitute the phosphate groups at ambient temperature [11]. The phosphate group in amylose of the potato starch is substituted in order to produce more polar groups in the potato starch under an applied electric field, and is adopted as a potential candidate for anhydrous ER material.

Starch as one of the polysaccharides is comprised of both amylose and amylopectin. Although the phosphate in potato starch is located in the amylopectin portion, the substituted phosphate groups from the esterification are added to the amylose group. Potato tuber starches have a high content of phosphate relative to cereal starches. The phosphate groups are located as monoesters at the C-6 (∼70%) and at the C-3 (∼30%) positions of the glucose residues. In general, native potato starch has 0.3–0.4% of the glucose residues in the amylopectin [12]. To substitute pristine potato starch with a high degree of potato starch phosphate (HPSP), we used a mixture of disodium hydrogen phosphate and sodium hydrogen phosphate with water. Initially, 2.5 mole fraction of phosphate was dissolved in distilled water at 35 °C and controlled to make pH 6 using hydrochloric acid and sodium hydroxide. The potato starch powder was added in the salt solution and stirred for 20 min. This starch slurry was then filtered with a glass funnel and dried for 12 hr. To enhance phosphorylation, this mixture was heated at 150 °C for 3 hr and cooled in 50% methanol aqueous solution at 25 °C. This product was filtered again and washed with ethanol three times. The final powdered product, potato starch phosphate, was sieved using a 100-μm molecular sieve after drying in a vacuum oven for 3 days. ER fluids were prepared by dispersing the HPSP particles in an insulating silicone oil. ER properties were examined by a rotational rheometer (Physica MC120, Germany) equipped with a high-voltage generator using a Couette geometry.

Fig. 1 shows the scanning electron microscope (SEM) image of HPSP, which is oval-shaped, and the sizes are in the range of 50–70 μm. The HPSP particles were dried to remove any trace of water for an anhydrous ER application. SEM micrographs also indicate that the phosphorylation of high substitution does not change the general granular morphology of potato starch.

The phosphorus content of HPSP was measured with an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer Elan 6100, USA). The degree of substitution (DS) of potato starch phosphate was calculated by the following Paschall's equation [13]:

$$\text{DS of potato starch phosphate} = \frac{162P}{3100 - 102P} \quad (1)$$

where P indicates dry basis percentage of phosphorous in the phosphorylated starch. The phosphorous contents of raw potato starch are 2.04% and those of HPSP are total 4.45% (2.42% + 2.04%) indicating the DS value of 0.137. More phosphate groups than raw potato starch exist near the surface. It is likely that at a higher reagent concentration, more reactant molecules are available in the proximity of starch hydroxyl groups, thus giving rise to higher degrees of phosphorylation [14].

Fig. 2 shows the thermal decomposition of HPSP. The phosphate group in potato starch degrades or evaporates at 250–380 °C. As a second step, the amylase group may be decomposed at 380–650 °C. Temperature range of 650–850 °C indicates the degradation of the crosslinked amylopectin group. The thermal stability of HPSP is slightly higher as compared with that of raw potato starch. Increased phosphorous contents result in a higher degree of crosslink with a good thermal

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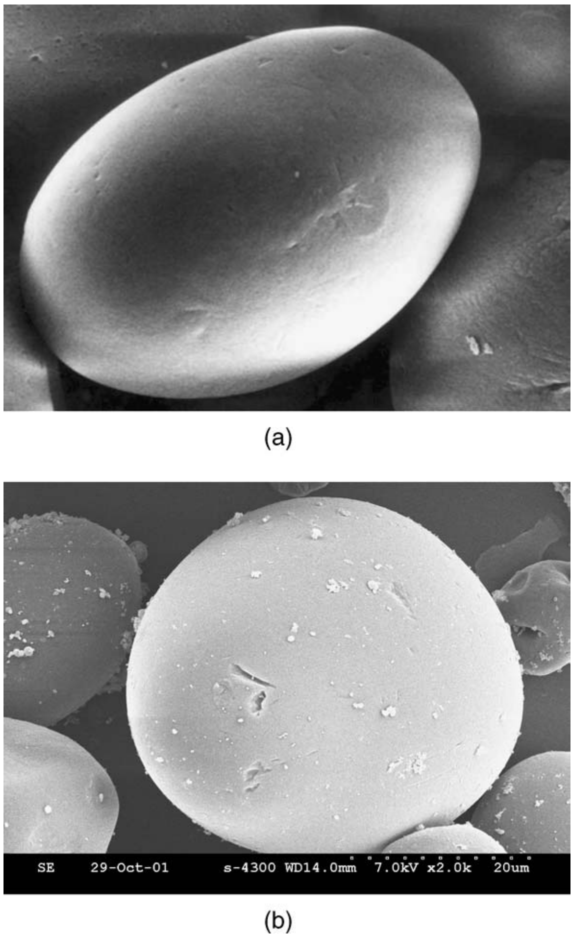

Figure 1 SEM photograph of (a) raw potato starch and (b) HPSP.

stability. Therefore, the residue above 800 °C implies some inorganic components included in the pristine HPSP sample.

ER phenomenon can be explained by the fact that an applied electric field induces electric polarization within each particle relative to the suspending medium. The basic mechanism of the ER is described with the relative polarization and electrostatic interaction among the potato starch phosphate particles, which induce the fibrillar structure in the direction of electric field. Fig. 3 describes shear stress as a function of shear rate for HPSP-based ER fluid (10 vol%) at five different electric field strengths. ER fluid exhibits solid-like behavior in high electric field strength with a residual shear stress because the chain of ER particles resists the shear deformation. As a result of the aggregated structure, ER fluids under an applied electric field exhibit a Bingham fluid behavior possessing a nonvanishing yield stress (τ_y). The relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) for the Bingham model is [9]

$$\begin{aligned} \tau &= \eta\dot{\gamma} + \tau_y \quad (\tau > \tau_y) \\ \dot{\gamma} &= 0 \qquad\qquad (\tau \le \tau_y) \end{aligned} \tag{2}$$

In general, τ_y can also be modeled as a non-analytic power law of the electric field strength (E) as [15]

$$\tau_y = E^{\alpha} \tag{3}$$

The yield stresses of the HPSP increase with E. The original potato starch without esterification did not exhibit any ER behavior. It is observed that η and τ_y depend on E and the phosphate degree of HPSP [16]. Furthermore, the static yield stress shown in Fig. 4, exhibits a critical electric field strength, E_c, exhibiting two different values of the slope in the $\tau_y - E$ plot. E_c was introduced by Choi *et al.* [15] to improve the yield stress expression stemmed from the polarization model. This yield stress expression predicts two limiting behaviors, both at low and high electric field strengths, and describes the yield stress of ER fluids very well for the broad range of the electric field strengths [6, 15]. Although E_c is proportional to the particle conductivity mismatch between the suspended particles and liquid media, α was related to the attractive forces via polarization and conduction mechanisms. For our ER fluids

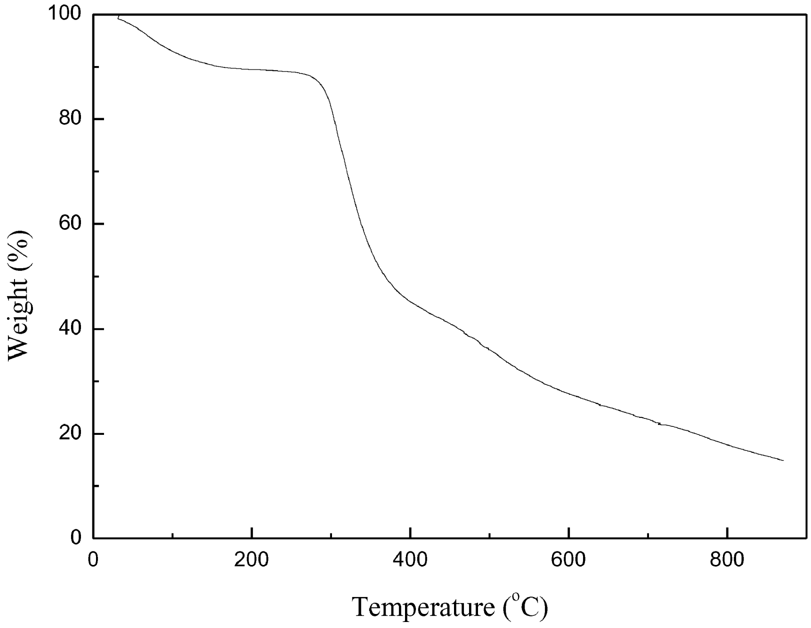

Figure 2 Thermogravimetric analysis diagram for HPSP.

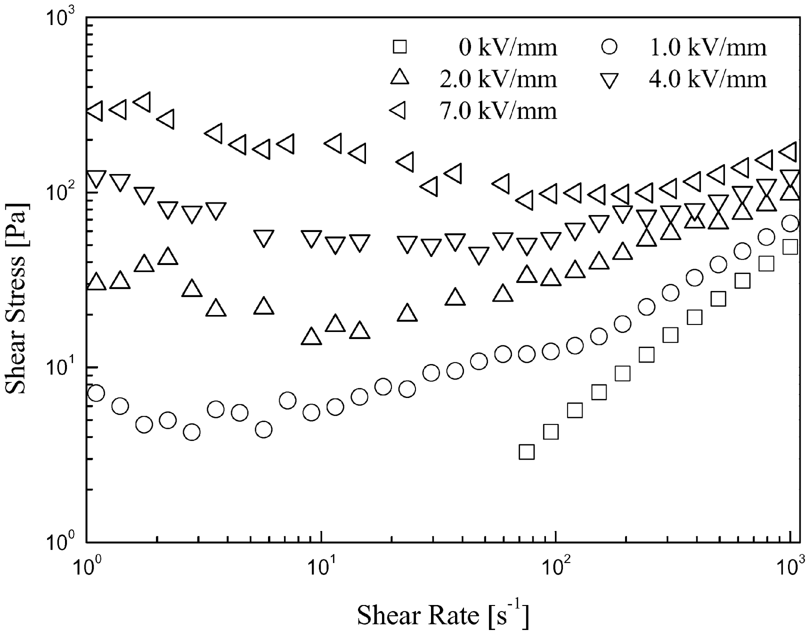

Figure 3 Shear stress vs. shear rate for ER fluid with 10 vol% of HPSP for five different applied electric field strengths.

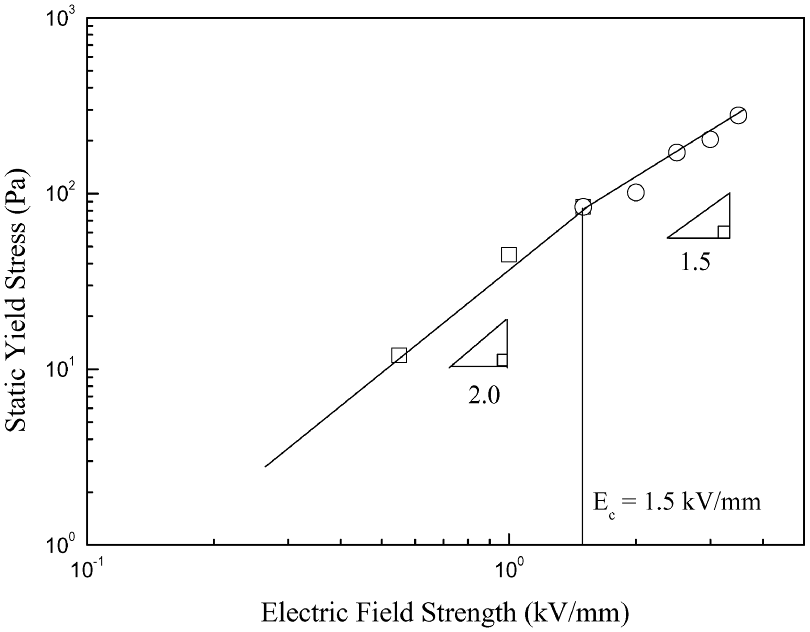

Figure 4 Static yield stress vs. electric field strength for HPSP-based ER fluid.

(HPSP particles suspended in silicone oil), we found that $\alpha \cong 2$ for $E < E_c$, and $\alpha \cong 1.5$ for $E > E_c$ with $E_c \cong 1.5$ kV/mm.

In conclusion, we synthesized the HPSP with different phosphate contents and examined ER characteristics. We found that the content of phosphate groups in starch plays a critical role in ER response. Improved ER properties were obtained with increasing phosphorus contents and electric field strength as it induces polarization more effectively.

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