

# Synthesis and Electrorheology of Potato Starch Phosphate

Dong P. Park,<sup>1</sup> Jun H. Sung,<sup>1</sup> Chul Am Kim,<sup>1</sup> Hyoung J. Choi,<sup>1</sup> Myung S. Jhon<sup>2</sup>

<sup>1</sup>Department of Polymer Science and Engineering, Inha University, Incheon, 402-751, Korea

<sup>2</sup>Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

Received 3 February 2003; accepted 21 June 2003

**ABSTRACT:** Potato starch phosphate (PSP) particles were synthesized via an esterification process of potato starch with a mixture of various concentrations of phosphoric acid and urea. The electrorheological (ER) characteristics of the synthesized PSP particles, suspended in a silicone oil, were examined. The PSP granule-based ER fluid exhibited typical ER behavior, possessing a nonvanishing yield stress under

an applied electric field. Enhanced polarization and higher yield stresses were observed as the content of phosphate groups in the starch increases. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1770–1773, 2004

**Key words:** potato starch phosphate; electrorheological fluid; yield stress

## INTRODUCTION

Electroresponsive electrorheological (ER) fluids belong to a class of colloidal suspensions that exhibit a reversible rheological behavior. With and without an applied electric field,<sup>1–5</sup> they show transition from liquid-like to solid-like behavior. Due to their tunability and reversible nature, these fluids are often termed “smart” or “intelligent” materials.

When an external electric field is applied, a fraction of the particles suspended in an isotropic insulating fluid becomes polarized. The dipole–dipole interactions among the particles lead to fibril structures via chain formation and alignment of particles along the applied electric field direction. These fibrillar particle structures result in the dielectric constant mismatch between the particles and the insulating oil.<sup>6</sup> As a result, these colloidal suspensions with high electric field strength and particle concentration exhibit strong resistance against a shear deformation.

ER fluids are classified into either anhydrous<sup>7–10</sup> or wet-base systems<sup>11</sup> via the specific conducting mechanism. Anhydrous ER systems have attracted more attention due to their physicochemical stabilities as compared to the wet-base systems. Many semiconducting polymers,<sup>12–16</sup> biopolymers,<sup>17</sup> and polymer/clay nanocomposites<sup>18–21</sup> are known as smart ER materials when dispersed in an insulating oil. Due to the importance of biopolymers in ER applications, modified cellulose and chitosan have also been examined as

anhydrous ER materials.<sup>22</sup> Starch, one of the most common biopolymers, has been widely used, is without environmental pollution, is abundant in nature, and is easily modified to phosphate forms. Potato tuber starch is characterized by 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.<sup>23</sup> Starch has also been used as a wet-base ER material at an early stage, in which the water can coat the starch surface, thus inducing polarization.<sup>1</sup> Notice that the dried starch and cellulose particles do not exhibit ER properties.

In order to increase the polarization of the potato starch under an applied electric field, and to be adopted as a potential anhydrous ER material, phosphate group in the amylose of the potato starch is substituted. To substitute the phosphate groups, we adopted an esterification process using a mixture of *ortho*-phosphoric acid and urea at ambient temperature according to the previously suggested method.<sup>24</sup> Note that the modified cellulose by an esterification process has been recently examined as an anhydrous ER fluid.<sup>25</sup>

## EXPERIMENTAL

Starch is one of the biopolymers predominately comprised of two polysaccharides, amylose and amylopectin, and made of glucose monomers. As the smaller portion of two polysaccharides that make up starch, the amylase is a linear molecule comprised of (1–4)-linked  $\alpha$ -D-glucopyranosyl units, with a small degree of branching by (1–6)  $\alpha$  linkages. On the other hand, amylopectin, the larger portion of the two com-

Correspondence to: Hyoung J. Choi (hjchoi@inha.ac.kr).

Contract grant sponsor: Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC) at Korea University, Korea (2003).

ponents, is highly branched with much higher molecular weights.

Although the exact fractions of the contents in the potato starch are uncertain, the potato starch generally contains 78% moisture, 18% starch source, and 4% other substrates, including phosphorus.

The phosphate in potato starch is in the amylopectin group. However, substituted phosphate groups from the esterification is added to the amylose group.<sup>26</sup> To esterificate the potato starch, we prepared 4M urea solutions with different molar ratios of phosphoric acid (85% assay) and added potato starch particles for phosphorylation. After reacting for two days at 25°C, these synthesized potato starch phosphates (PSPs) were washed and filtered five times with distilled water to remove unreacted urea and phosphoric acid on the particle surface. These particles were dried for five days in the vacuum oven. Each PSP was sieved with 38 and 100  $\mu\text{m}$  to control particle size and its distribution. These powders were dried again at 120°C to remove any trace of water in the particles.

On the other hand, in the case of PSPs with a higher phosphate content such as PSP(2.0) and PSP(3.0), the high degree of substituted PSP was further modified from disodium hydrogen phosphate and sodium hydrogen phosphate mixture with distilled water. These mixture solutions with different molar fraction were dissolved in distilled water at 35°C and controlled to make pH 6 with hydrochloride acid and sodium hydroxide. The potato starch powder was added in a salt solution and stirred for 20 min. This starch slurry was then filtered with glass funnel and dried for 12 h. To enhance phosphorylation, this mixture was heated at 150°C for 3 h with a convectional oven and cooled in 50% methanol aqueous solution at room temperature. This product was filtered again and washed with ethanol 3 times. The final powder, potato starch phosphate was sieved under 100  $\mu\text{m}$  after drying in vacuum oven for 3 days. ER fluids were prepared, by dispersing the PSP particles in insulating silicone oil. ER properties were measured by a rotational rheometer (Physica MC120, Germany) equipped with a high voltage generator using a Couette geometry.<sup>27, 28</sup>

## RESULTS AND DISCUSSION

Figure 1 shows the scanning electron microscope (SEM) image of PSP. Both potato starch and PSP are ovoid-shaped and their sizes are in the range of 5–60  $\mu\text{m}$ . As previously studied,<sup>29</sup> the presence of phosphate groups enlarges the size of granules, because this creates a repulsive force that increases the inter-intramolecular space, allowing more water molecules to be included. However, in this study to remove any trace of water, we completely dried the samples to obtain an anhydrous ER suspension. This dehydration process made it possible to get the uncharged particle

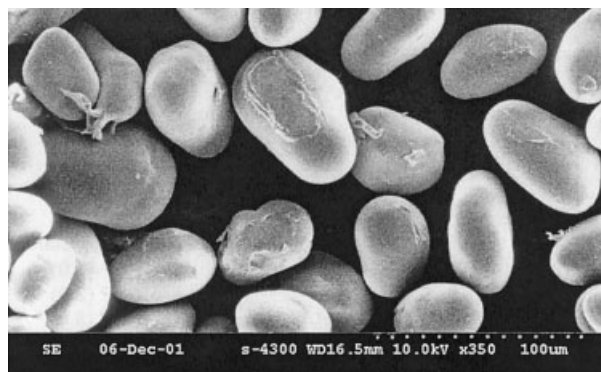


Figure 1 SEM micrograph of PSP(1.0).

shape and size. SEM micrographs also indicate that the phosphorylation of low substitution does not change the general granular morphology of potato starch.

The amount of phosphorylation increased with increasing molar ratio of phosphate to anhydrous glucose, due to the well-known fact that the position of hydroxyl groups in the starch is fixed and their reactivity depends on the availability of reactants into the position of hydroxyl groups. Thus, 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.<sup>30</sup> Generally, phosphorylation processes are evidently due to the inclusion of phosphate groups inside the starch granules, creating certain repulsive forces that enhance the inter- and intramolecular spaces, allowing more hydroxyl groups to be included.

After the removal of water, PSPs possessing the phosphate group were suspended in the insulating oil, and they exhibited ER properties under an applied electric field. From thermogravimetric analysis (Polymer Lab. USA), it was observed that degradation of PSP(2.0) occurred above 260°C with approximately 60% weight loss. This indicates that PSP can be used safely up to 260°C as thermally stable anhydrous ER fluid particles.

The characterization of the phosphorus content of PSP was conducted with an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer Elan 6100, USA). Table I shows that the total amount of reacted phosphorus in modified potato starch increases gradually with increased reagent molar ratio, indicating that PSP(2.0) may include more phosphate groups near surface.

The basic mechanism of the ER phenomenon can be explained with the relative polarization concept. Namely, an applied electric field induces electric polarization within each particle relative to the suspending medium. The electrostatic interaction among the

**TABLE I**  
Phosphorus Contents of PSP as Derived by ICP-MS

Material	Phosphorus contents (%)	Degree of substitution of PSP
Raw material (potato starch)	2.04	—
PSP(1.0)	2.55	0.027
PSP(2.0)	2.85	0.044
PSP(3.0)	3.07	0.056

PSP particles induces the aggregating structure in the direction of electric field. As a result of this aggregated structure, ER fluids under an applied electric field exhibit Bingham fluid behavior possessing a yield stress ( $\tau_y$ ). The relationship between shear stress ( $\tau$ ) and shear rate ( $\dot{\gamma}$ ) for the Bingham model is as follows<sup>31</sup>:

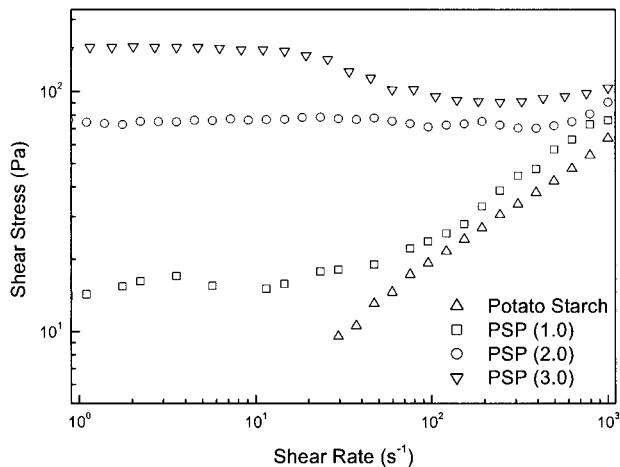
$$\begin{aligned} \tau &= \eta \dot{\gamma} + \tau_y \quad (\tau > \tau_y) \\ \dot{\gamma} &= 0 \quad (\tau < \tau_y) \end{aligned} \quad (1)$$

In general,  $\tau_y$  can also be modeled as a nonanalytic power law form as<sup>32-34</sup>

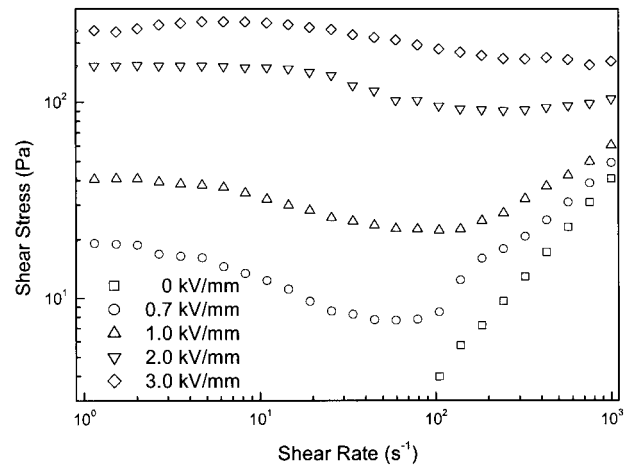
$$\tau_y = E^\alpha \quad (2)$$

The yield stresses of the modified PSP increase with electric field strength ( $E$ ). The values of  $\alpha$  in eq. (2) are found to be 1.6–2.0. These values are different from 2.0, which results from the polarization model, because the morphology of PSP is nonspherical, and has a broad particle size distribution as confirmed by the SEM image<sup>35</sup> (Fig. 1).

Figure 2 describes shear stress as a function of shear rate for each ER fluid (particle concentration of 10 vol



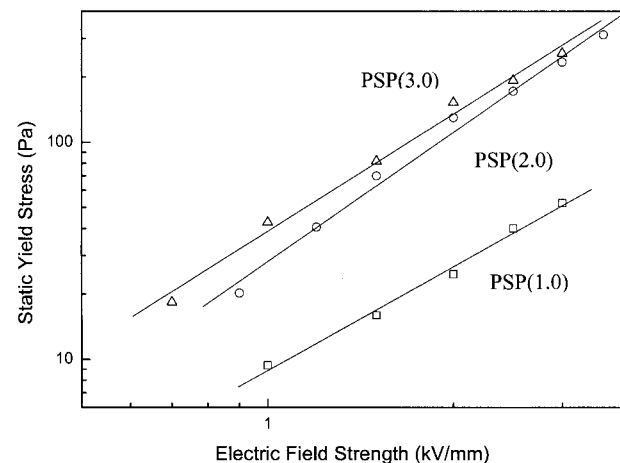
**Figure 2** Shear stress vs shear rate of potato starch, PSP(1.0), PSP(2.0), and PSP(3.0) in an applied electric field strength of 2 kV/mm.



**Figure 3** Shear stress vs shear rate of PSP(3.0) at five different electric field strengths.

%) at an electric field strength of 2 kV/mm. In contrast with the untreated potato starch, each PSP-based ER fluid exhibits ER phenomenon. It is worthwhile to note that PSP(3.0) shows a higher shear stress than those of PSP(1.0) and PSP(2.0). Evident from Table I, both the degree of substitution and the phosphorus content of PSP(3.0) are higher than those of PSP(1.0), PSP(2.0), and the raw material. This indicates that the phosphate groups have an effect on the shear stress and yield stress in the presence of electric field.

The original potato starch without esterification did not exhibit any ER behavior. Each of the ER fluids also showed the same behavior as potato starch at zero electric field strength: non-Newtonian characteristics with a shear thinning behavior. This behavior was also reported for other suspension systems including magnetic particles<sup>36, 37</sup> and silica.<sup>38</sup> It is well-known that  $\eta$  and  $\tau_y$  depend on  $E$  and degree of phosphation of PSP as shown in Figures 3 and 4. The shear stress of ER



**Figure 4** Static yield stress vs electric field strength for PSP(1.0), PSP(2.0), and PSP(3.0).

fluids increased drastically in the presence of a strong electric field strength. The shear stress depends on the applied electric field strength (Fig. 3) and the content of phosphate groups (Fig. 4).

### CONCLUSIONS

We synthesized the PSP and observed that it has different characteristics from potato starch raw material. The content of phosphate groups in starch is a critical parameter in determining ER behavior. Increasing phosphorus contents, electric field strength induced more polarization, and resulted in higher values for yield and shear stresses.

### References

- Hao, T.; Kawai, A.; Ikazaki, F. *Langmuir* 2000, 16, 3058.
- Yethiral, A.; Blaaderen, A. V. *Int J Mod Phys B* 2002, 16, 2328.
- Men, S.; Meunier, A.; Métayer, C.; Bossis, G.; *Int J Mod Phys B* 2002, 16, 2357.
- Zhao, X. P.; Yin, J. B.; Xiang, L. Q.; Zhao, Q. *Int J Mod Phys B* 2002, 16, 2371.
- Osuchowski, M.; Plochanski, J. *Int J Mod Phys B* 2002, 16, 2378.
- Zhao, X. P.; Yin, J. B. *Chem Mater* 2002, 14, 2258.
- An, Y.; Liu, B.; Shaw, M. T. *Int J Mod Phys B* 2002, 16, 2440.
- Zhao, X. P.; Duan, X. *Int J Mod Phys B* 2002, 16, 2454.
- Kim, J. W.; Liu, F.; Choi, H. J. *J Ind Eng Chem* 2002, 8, 399.
- Bocińska, M.; Wyciślik, H.; Osuchowski, M.; Plochanski, J. *Int J Mod Phys B* 2002, 16, 2461.
- Okamura, H.; Suzuki, K.; Mori, T.; Minagawa, K.; Masuda, S.; Tanaka, M. *Int J Mod Phys B* 2002, 16, 2385.
- Hao, T.; Xu, Z.; Xu, Y. *J Colloid Inter Sci* 1997, 190, 334.
- Jang, W. H.; Kim, J. W.; Choi, H. J.; Jhon, M. S. *Colloid Polym Sci* 2001, 279, 823.
- Trlica, J.; Saha, P.; Quadrat, O.; Stejskal, J. *Phys A* 2000, 283, 337.
- Lee, Y. H.; Kim, C. A.; Jang, W. H.; Jhon, M. S. *Polymer* 2001, 42, 8277.
- Choi, H. J.; Kim, J. W.; To, K. *Synth Met* 1999, 101, 697.
- Jang, W. H.; Cho, Y. H.; Kim, J. W.; Choi, H. J.; Sohn, J. I.; Jhon, M. S. *J Mater Sci Lett* 2001, 20, 1029.
- Kim, J. W.; Noh, M. H.; Choi, H. J.; Lee, D. C.; Jhon, M. S. *Polymer* 2000, 41, 1229.
- Kim, J. W.; Kim, S. G.; Choi, H. J.; Jhon, M. S. *Macromol Rapid Commun* 1999, 20, 450.
- Park, J. H.; Lim, Y. T.; Park, O. O. *Macromol Rapid Commun* 2001, 22, 616.
- Kim, J. W.; Kim, S. G.; Choi, H. J.; Suh, M. S.; Shin, M. J.; Jhon, M. S. *Int J Mod Phys B* 2001, 15, 657.
- Sung, J. H.; Choi, H. J.; Jhon, M. S. *Mater Chem Phys* 2002, 77, 778.
- Bay-Smidt, A. M.; Wischmann, B.; Olsen, C. E.; Nielsen, T. H. *Starch/Stärke* 1994, 46, 167.
- Arslanov, S. S.; Rakhmenderdiev, G. R.; Mirkamilov, T. M.; Abidova, F. *Russian J Appl Chem* 1996, 68, 444.
- Kim, S. G.; Kim, J. W.; Jang, W. H.; Choi, H. J.; Jhon, M. S. *Polymer* 2001, 42, 5005.
- Zobel, H. F.; Stephen, A. M. *Starch: Structure, Analysis and Application*; Marcel Dekker: New York, 1995.
- Sung, J. H.; Hyun, Y. H.; Kwon, D. H.; Choi, H. J. *J Ind Eng Chem* 2002, 8, 28.
- Lim, S. T.; Choi, H. J.; Jhon, M. S. *J Ind Eng Chem* 2003, 9, 51.
- Sitohy, M. Z.; Ramadan, M. F. *Starch/Stärke* 2001, 53, 27.
- Waly, A.; Abdel-Mohdy, F. A.; Higazy, A.; Hebeish, A. *Starch/Stärke* 1994, 46, 59.
- See, H.; Kawai, A.; Ikazaki, F. *Colloid Polym Sci* 2002, 280, 24.
- Sim, I. S.; Kim, J. W.; Choi, H. J.; Kim, C. A.; Jhon, M. S. *Chem Mater* 2001, 13, 1243.
- Choi, H. J.; Cho, M. S.; Kim, J. W.; Kim, C. A.; Jhon, M. S. *Appl Phys Lett* 2001, 78, 3806.
- Atten, P.; Foulc J.-N.; Gonon, P. *Int J Mod Phys B* 2002, 16, 2662.
- Choi, H. J.; Cho, M. S.; To, K. *Phys A* 1998, 254, 272.
- Jhon, M. S.; Kwon, T. M.; Choi, H. J.; Karis, T. E. *Ind Eng Chem Res* 1996, 35, 3027.
- Lim, S. T.; Cho, M. S.; Choi, H. J.; Jhon, M. S. *J Ind Eng Chem* 2003, 9, 336.
- Aubry, T.; Lagenton, B.; Moon, M. *Langmuir* 1999, 15, 2380.