

# Preparation of Superabsorbent Polymer with Slow-Release Phosphate Fertilizer

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**ABSTRACT:** A superabsorbent polymer with slow-release phosphate fertilizer was prepared by esterification of polyvinyl alcohol (PVA) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ), which was a slow-release fertilizer at the same time. The product's water absorbency (WA) was about 480 times its own weight if it was allowed to swell in distilled water at room temperature for 24 h. WA under various conditions, such as varying the reaction time, the amount of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), the reaction temperature, and the concentration of phosphoric acid ( $[\text{H}_3\text{PO}_4]$ ), were investigated and opti-

mized. The optimal sample of the product was characterized by FTIR and elemental analysis. The results showed that phosphoric groups had grafted on PVA molecule chains, and the content of  $\text{P}_2\text{O}_5$  in the product was 31.2%. The water retention property and phosphate slow-release mechanism of the product were studied as well. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3417–3421, 2004

**Key words:** swelling; esterification; functionalization of polymers; hydrogel

## INTRODUCTION

Application of superabsorbents in agriculture is a growing field of interest. Superabsorbents have been reported as good soil-conditioning materials.<sup>1–4</sup> They can be used in agriculture to improve soil moisture retention capacity; thus, the germination of seeds and plants growth can be promoted.<sup>5</sup> Moreover, it has been found that superabsorbents are effective in increasing soil infiltration and reducing runoff and erosion of soil.

There are many reports about superabsorbents<sup>6</sup> and slow-release phosphate fertilizers,<sup>7</sup> but there is little information on superabsorbent polymers with slow-release phosphate fertilizer. On the basis of our previous studies on the preparation<sup>8–12</sup> and applications<sup>13</sup> of superabsorbents, in this study, we synthesized a superabsorbent polymer with slow-release phosphate fertilizer (SAPSRPF) by grafting phosphoric groups on PVA molecule chains through esterification between PVA and  $\text{H}_3\text{PO}_4$ , which at the same time is a slow-release phosphate fertilizer. Besides water absorbing and retention, the superabsorbent polymer has many advantages over conventional ones, such as a sustained supply of nutrition to plants for a longer time, thus increasing the phosphate fertilizer use efficiency

and decreasing application frequency. Furthermore, it can be used as a soil moisture preservation material.

As is known to us, only about 10–20% of ordinary phosphate fertilizer, which is applied in the farmland, is assimilated by the crops; the other is fixed by soil due to reacting with soil constituents, and thus causes serious waste of phosphate fertilizer and heavy economic losses.<sup>14</sup> It is reported that slow-release technology has done well in increasing the efficiency of phosphate fertilizer utilization, as well as reducing the economic losses.

## EXPERIMENTAL

### Materials

PVA was supplied by the Lanzhou Chemical Corporation. The degree of polymerization and saponification were 1700 and 99%, respectively.  $\text{H}_3\text{PO}_4$  and  $\text{Na}_2\text{CO}_3$  were all analytical reagent grade, and could be available from commercial sources.

### Synthesis procedure

The reaction was conducted in a flask equipped with a mechanical stirrer, condenser, and thermometer.

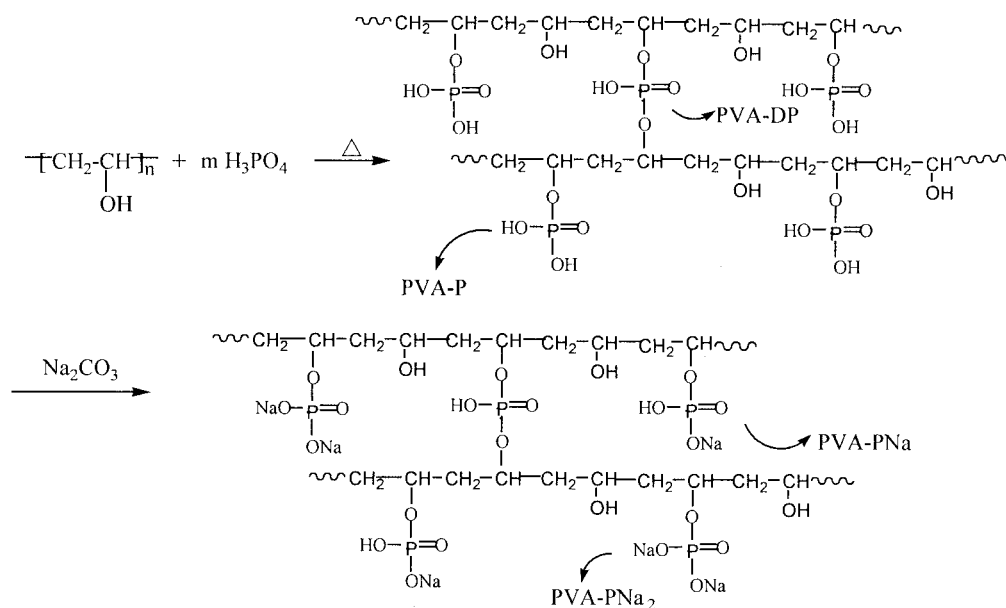
PVA powder (6.6 g), a proper amount of water (8.5 mL), and 15.0 mL of  $\text{H}_3\text{PO}_4$  were added in the flask. The mixture was heated to 80°C under constant stirring until the PVA was dissolved. After 1-h reaction, the resultant was precipitated by adding  $4.25 \times 10^{-2}$  mol of  $\text{Na}_2\text{CO}_3$ , washed, and vacuum dried at 80°C to a constant weight. The resultant was reswollen in an

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excess of water to remove the  $\text{H}_3\text{PO}_4$ , which did not react and other soluble substances. The gel was dried, reweighed, and milled through a 26–45 mesh screen.

The white granular samples with a diameter of 0.18–0.71 mm were obtained. The main scheme of the reaction was as follows.



In this reaction, polyvinyl alcohol phosphate (PVA-P) and polyvinyl alcohol diphosphate (PVA-DP) would be produced. It was considered that the WA of the product was related to the content of PVA-P and PVA-DP in the product: PVA-P acted as a hydrophilic structure; the more its content in the product, the higher the WA of the product. PVA-DP in the resultant acted as a crosslinking structure. Its content in the product should be suitable; when less, it would lead the product to be dissolved; when more, it would result in such a high crosslinked degree that the product could not swell enough in the water. So the factors that affected the degree of esterification would affect the WA. In the present article, the effects of the reaction time, the amount of  $\text{Na}_2\text{CO}_3$ , the reaction temperature, and the concentration of phosphoric acid on WA of SAPSRPF were investigated and optimized.

#### WA of SAPSRPF measurement

A sample of SAPSRPF (0.20 g) was immersed in distilled water at room temperature until equilibrium was reached. The swollen gel was filtered through a silk sieve (aperture 0.076 mm) to remove the nonabsorbed water and then weighed. WA was expressed as the absorbed water per gram of dried product.

#### Water retention of SAPSRPF measurement

Referring to the literature,<sup>15</sup> 100.0 g of dry soil granules (diameter 0.18–0.71 mm) were well mixed with 2.0 g of SAPSRPF, which, along with 200.0 g of dis-

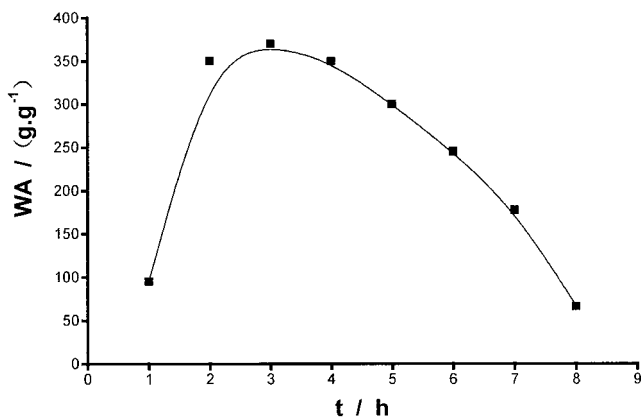
tilled water were added in a 250-mL beaker with a cross-sectional area of 38.5 cm<sup>2</sup>. Then the beaker was placed in our lab, in which the temperature and relative humidity were 25°C and 31%, respectively, and weighed every 5 days. After a period of 30 days, the observation was terminated. At the same time, the controlled experiment, namely, without any SAPSRPF, was also carried out. The evaporation percentage (EP) of the water was calculated using the following equation:

$$\text{EP} (\%) = (m_0 - m_i) / 200.0 \times 100\% \quad (1)$$

where  $m_0$  was the initial weight of the beaker and the mixture mentioned above,  $m_i$  was the weight of that at a different time.

#### Slow release of phosphate in SAPSRPF measurement

Referring to the literature,<sup>16</sup> 0.5 g of SAPSRPF was added into a 500-mL tapered bottle with a plug, then 500.0 mL of distilled water was added. The tapered bottle was put in a constant-temperature oven at 25°C. Then the concentration of P in the aqueous solution was determined by the addition of water for 12, 24, 36, 48, 60, 72, and 672 h (28 days), from which a phosphate release curve could be obtained. The concentration of P was determined by a spectrophotometer. The method was the same as the one that was used to estimate the content of P in the SAPSRPF. The released



**Figure 1** Dependence of WA on reaction temperature (6.6 g of PVA, 8.5 mL of distilled water,  $4.25 \times 10^{-2}$  mol of  $\text{Na}_2\text{CO}_3$ , 15.0 mL of  $\text{H}_3\text{PO}_4$ , reaction temperature =  $80^\circ\text{C}$ , reaction time = 3 h).

percentage (RP) of phosphate in the SAPSRPF was calculated using the following equation:

$$\text{RP}(\%) = 500.0 \times C_{P_i} / 0.5 \times C_P \times 100\% \quad (2)$$

where  $C_{P_i}$  (g/mL) was the concentration of the P in the aqueous solution at different time and  $C_P$  was the content of P in the SAPSRPF.

**Characterization of SAPSRPF by FTIR**

The SAPSRPF was characterized by a Fourier-transform infrared (FTIR) spectrophotometer (American Nicolet Corporation, model 170-SX). The sample of SAPSRPF was extracted using water for 48 h, dried at decompression, and ground with dried KBr powder. The KBr disc was dried again and subjected to FTIR spectrophotometer.

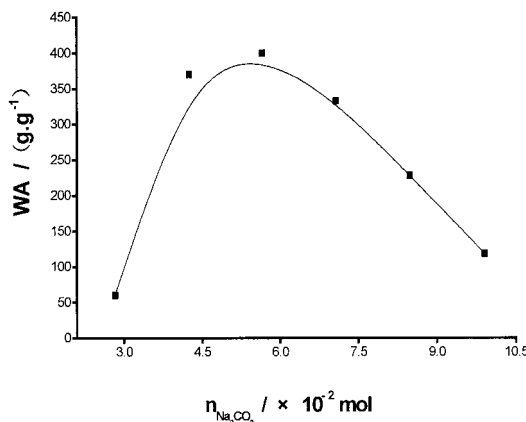
**Content of P estimated in SAPSRPF**

The content of P in the SAPSRPF was determined by a spectrophotometer (The Third Analysis Instrument Corporation of Shanghai, China, model 722).<sup>17</sup> SAPSRPF (0.5 g) was added in a beaker, nitrified with 20.0 mL of concentrated nitric acid over night, boiling the solution until its volume was 10.0 mL, and then adjusting its volume to 250 mL in a 250 mL-volumetric flask, then 2.50 mL was taken out to be determined by the spectrophotometer. The content of P in the SAPSRPF was about 13.6%, namely, the content of  $\text{P}_2\text{O}_5$  was 31.2% (content of nutrition of the phosphate fertilizer was generally expressed as the content of  $\text{P}_2\text{O}_5$ ).

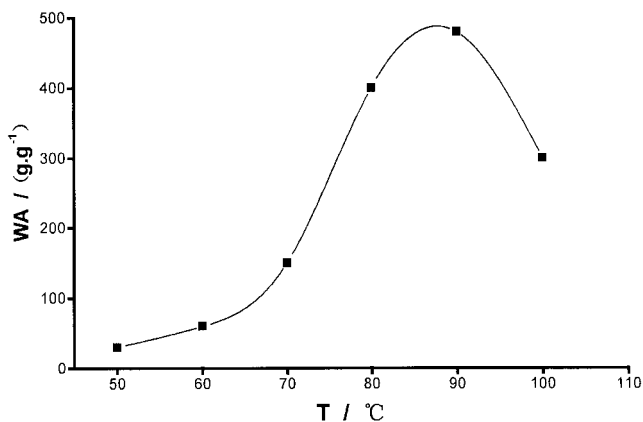
**RESULTS AND DISCUSSION**

Figure 1 represented dependence of WA on the reaction time. Changing the reaction time and fixing other conditions, we obtained the curve of reaction time vs WA. The reaction in this system was an esterification between the macromolecule and the small molecule. The time was a significantly impact factor on the esterification degree of the product, namely on WA. Figure 1 showed that the WA of the product was increased at first and then decreased along with the prolonged reaction time. WA of the product reached maximum when the time was 3 h. When reaction time was shorter than 3 h, the content of PVA-P in the resultant was low, and there were many crystal structures in PVA molecules;<sup>18</sup> thus, WA was low. When the time was more than 3 h, the result might be more and more PVA-DP, which acted as a crosslinking structure in the product so that the crosslinking densities of the product were gradually enhanced; thus, interspace of the polymer networks diminished. The volume of water that could be held in the networks was lessened, and the WA of the product also decreased. Therefore, the optimal reaction time was about 3 h.

Figure 2 represented the dependence of WA on the amount of sodium carbonate. Reaction time was 3 h, and the altered amount of  $\text{Na}_2\text{CO}_3$ , and other conditions were the same as above. The curve of the amount of  $\text{Na}_2\text{CO}_3$  vs WA was obtained. From Figure 2, it could be known that there existed a suitable quantity of  $\text{Na}_2\text{CO}_3$ , at which WA of the product was tip top. The reasons might be as follows:  $\text{Na}_2\text{CO}_3$  could react with PVA-P and produced PVA-PNa<sub>2</sub> or PVA-PNa, and the groups started to ionize when they came into with water, and caused PVA molecule chains, producing negative charges. The charge number in the three-dimensional network of the resultant would go up in pace with the amount of increased  $\text{Na}_2\text{CO}_3$ , and it



**Figure 2** Dependence of WA on amount of sodium carbonate ( $5.66 \times 10^{-2}$  mol of  $\text{Na}_2\text{CO}_3$ , other conditions same as in Fig. 1).

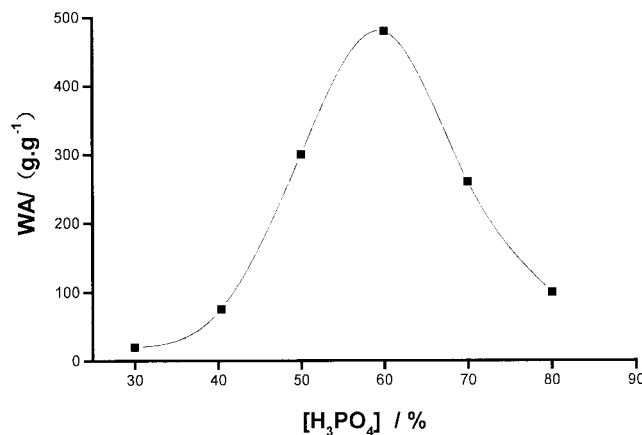


**Figure 3** Dependence of WA on reaction temperature (reaction temperature = 90°C, other conditions same as in Fig. 2).

could be conferred from the P. J. Flory formula<sup>19</sup> that the WA of the product should go up also. When the amount of Na<sub>2</sub>CO<sub>3</sub> was more; on the one hand, it would lead PVA-DP to hydrolyzing and decreasing the crosslinked densities of the product; on the other hand, the charge number on the molecule chains would accumulate so much that the three-dimensional network structures were broken while the product swelled in water, so WA of the product decreased when the amount of Na<sub>2</sub>CO<sub>3</sub> was too much. The suitable quantity of Na<sub>2</sub>CO<sub>3</sub> was  $5.66 \times 10^{-2}$  mol.

Figure 3 represented the dependence of WA on the reaction temperature. Reaction time: 3 h, Na<sub>2</sub>CO<sub>3</sub>:  $5.66 \times 10^{-2}$  mol, changed reaction temperature; the other conditions were the same as above. The curve of reaction temperature vs WA was obtained. Figure 3 showed that the reaction temperature had a dominant influence on WA. As the temperature rose from 50 to 90°C, WA rose quickly also; when the temperature exceeded 90°C, WA drastically reduced with temperature rising. This was because the PVA could not be dissolved completely when reaction temperature was low, and most of the hydroxyls in the PVA molecules were not activated due to hydrogen bonds; moreover, the esterification between PVA and H<sub>3</sub>PO<sub>4</sub> was carried out on the surface of PVA powders, so the probability of the reaction was low. Therefore, esterification degrees of the product were low, and WA was low correspondingly; when the temperature was 90°C, WA was up to the maximum (480 g/g), while at a higher temperature, it might produce more PVA-DP, and crosslinked densities of the product were higher; thus, WA decreased.

Figure 4 represented dependence of WA on the phosphoric acid mass concentration. Reaction time: 3 h, Na<sub>2</sub>CO<sub>3</sub>:  $5.66 \times 10^{-2}$  mol, reaction temperature: 90°C, PVA: 6.6 g, fixed the total mass of H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>O and changed their mass ratio, a series of phos-

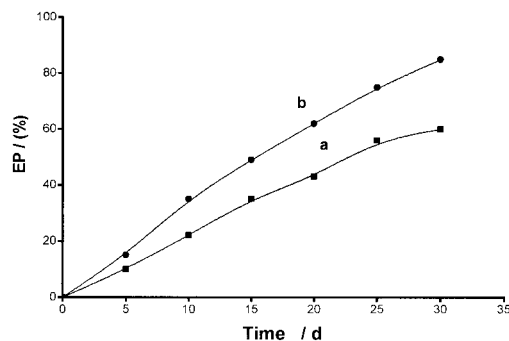


**Figure 4** Dependence of WA on phosphoric acid mass concentration (6.6 g of PVA, 8.5 mL of distilled water,  $5.66 \times 10^{-2}$  mol of Na<sub>2</sub>CO<sub>3</sub>, 15.0 mL of H<sub>3</sub>PO<sub>4</sub> reaction temperature = 90°C, reaction time = 3 h).

phoric acid solution with different concentrations were obtained. Figure 4 showed that as the phosphoric acid concentration increased, WA increased in the concentration range of 30–60%, but decreased when the phosphoric acid concentration was higher than 60%. There existed an optimal concentration of about 60%, at which WA reached its maximum. The thermodynamics equilibrium equation of this reaction was  $K = \frac{[\text{H}_2\text{O}][\text{PVA-P}][\text{PVA-DP}]}{[\text{H}_3\text{PO}_4][\text{PVA}]}$ . The equilibrium constant  $K$  of this reaction system was an invariable value under constant temperature and pressure, because it was only a function of the temperature and pressure for a given reaction system.<sup>20</sup> Therefore, when [H<sub>3</sub>PO<sub>4</sub>] in the system increased, [PVA-P] increased also, and the content of PVA-P in the product was enhanced at the same time. WA increased, along with [H<sub>3</sub>PO<sub>4</sub>] increasing as a result. The decrease of WA as [H<sub>3</sub>PO<sub>4</sub>] was higher than 60%, and could be attributed to the content of PVA-DP in the increased product.

### Structure analysis of SAPSRPF

The infrared spectrum of SAPSRPF was shown as peaks corresponding to the groups attached to PVA,



**Figure 5** Water retention curve of SAPSRPF. (a) Water + SAPSRPF + dry soil; (b) water + dry soil.

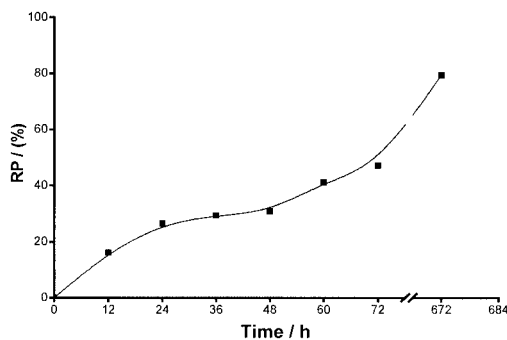


Figure 6 Release curve of phosphate in SAPSRPF in water.

additionally, the peaks observed at 1172, 1076, and 925  $\text{cm}^{-1}$  corresponded to  $\text{P}=\text{O}$ ,  $\text{C}-\text{O}-\text{P}$  and  $\text{O}-\text{P}-\text{O}$ ,<sup>21</sup> respectively. Therefore, we might confirm that phosphoric groups were grafted on the PVA molecule chains.

### Water retention of SAPSRPF

The experimental result of water retention was shown in Figure 5, where it could be found out that the water evaporation rate obviously decreased after the addition of SAPSRPF in the soil. This was because the SAPSRPF had excellent water absorbency, so the water evaporation rate decreased. Therefore, if the SAPSRPF was applied in the farmland, it would be like a subminiature reservoir to retain and supply moisture to crops over time as the soil underwent alternate wet and dry periods. In this way, it would enhance efficiency of water utilization, prolong irrigation cycles and reduce irrigation frequencies, and strengthen ability of crops to fight a drought. At the same time, it was observed that, after addition of SAPSRPF to soil, lots of granular structures were formed in the soil, the content of which in the soil could increase 24.8% compared to the controlled sample. It had been reported in the literature<sup>22</sup> that these clay granules would help to stabilize the soil structure, improve soil aeration and permeability, and prevent soil from becoming harder. Thus, a good environment for crops to grow would be created.

### Release of phosphate in SAPSRPF

The experimental result for phosphate release in the SAPSRPF was shown in Figure 6. As showed in Figure 6, about 26.5% of phosphate in SAPSRPF was released out within 24 h; on the 72th hour, the total amount of phosphate released out was about 47%. The phosphate released out in this period mainly existed in the SAPSRPF surface layer, because it would go into water without diffusing as soon as it was dissolved, so the release rate was fast, and on the (672th hour) 28th day, the total amount of phosphate released out had gradually increased to 79%. During this time, the phosphate released

out was mainly encapsulated inside of the SAPSRPF, because it not only need to be dissolve but also to diffuse out of hydrogel granule before it went into water, so the release rate was slow. The release behavior of phosphate in SAPSRPF mentioned above was the same as the behavior of other conventional slow-release fertilizer.<sup>1</sup> Regarding the slow release mechanism of phosphate in SAPSRPF synthesized by our work, SAPSRPF started to swell when it was immersed into water, and gradually became a hydrogel; then the phosphoric groups that grafted on the PVA molecule chains were dissolved because of hydrolyzing, the dissolved phosphate went out of the hydrogel along with water due to the existing concentration gradient inside and outside of the gel granules. But, for one thing, the swollen hydrogel compressed the diffusion channels of phosphate encapsulated in the SAPSRPF,<sup>23</sup> for another thing, the hydrogel could absorb the phosphate.<sup>24</sup> Thus, the product was endowed with a slow-release property. As mentioned above and illustrated herein, we found that the course of SAPSRPF swelling, diffusion of the phosphate, and absorption of the hydrogel were the primary factors that affected and controlled phosphate release rate.

In fact, we reported a new method to prepare a slow-release phosphate fertilizer in this article. This type of slow-release phosphate fertilizer has many advantages over the conventional ones because of its water absorbing and excellent water retention capacity.

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