

# Chlorohydrin Water-Swellable Rubber Compatibilized by an Amphiphilic Graft Copolymer. II. Effects of PVA-*g*-PBA and CPA on Water-Swelling Behaviors

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**ABSTRACT:** A water-swellable rubber (WSR), compatibilized by the amphiphilic graft copolymer, has been prepared by blending chlorohydrin rubber (CHR) with crosslinked polyacrylate (CPA), Poly(vinyl alcohol)-*g*-poly(butyl acrylate) (PVA-*g*-PBA), precipitated silica (PSA), and poly(ethylene glycol) (PEG). The WSR was characterized by scanning electron micrography (SEM). The dependence of the water-absorbing ratio by weight, the water-swelling ratio by volume, and the percentage loss by weight on PVA-*g*-PBA and crosslinked polyacrylate contents was investigated. The effect of PVA-*g*-PBA and crosslinked polyacrylate contents on second water-swelling behaviors and long-term water-retention behaviors were also studied. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3145–3152, 1999

**Key words:** water-swellable rubber; compatibilization; chlorohydrin rubber; crosslinked polyacrylate; amphiphilic graft copolymer; PVA-*g*-PBA

## INTRODUCTION

The water swellable rubber is a new kind of functional elastomer with elastic sealing and water-swelling properties, which is a multicomponent blend composed of a rubber matrix, a super water-absorbent resin, and other hydrophilic ingredients. The general methods used to prepare water-swellable rubber are mechanical mixing and chemical grafting.<sup>1–6</sup> Hydrophilic super water-absorbent resin cannot disperse well in hydrophobic rubber so that it can break off from rubber net-

work easily. This will weaken water-swelling abilities, mechanical properties, long-term water retention, and repeated usage. If an amphiphilic graft copolymer is used in the blend as a compatibilizer, the compatibility of hydrophilic dispersion phase and hydrophobic continuous phase is expected to be improved greatly, and the loss of super water-absorbent resin from the rubber matrix to be reduced. In such a way, the water-swellable properties may be enhanced. But work using this method has seldom been reported.

Chlorohydrin rubber (CHR) is the epichlorohydrin homopolymer obtained by ring-opening polymerization. Because its backbone has plenty of ether bonds, which can readily form hydrogen bonds with water, CHR possesses specific hydrophilicity. At the same time, CHR has better elasticity because of its flexible chains. Moreover,

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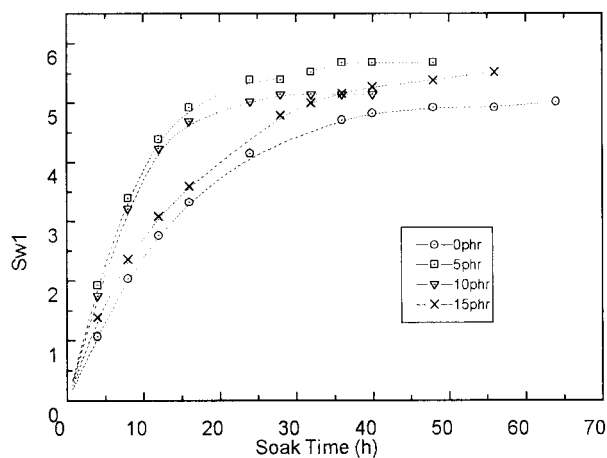
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CHR is a kind of special synthetic rubber with good oil resistance, solvent resistance, heat aging resistance, fire resistance, and ozone resistance properties,<sup>7</sup> and the least air permeability.

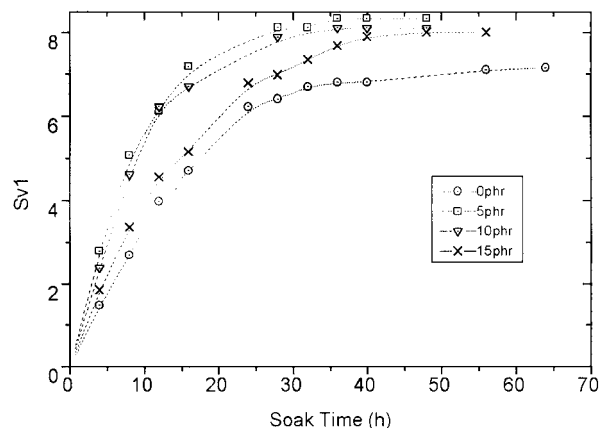
Crosslinked polyacrylate (CPA) used as super water-absorbent resin is of high water-retention abilities, stable structure, and low price. Below 300°C, it does not decompose and denaturalize.

Poly(vinyl alcohol) (PVA) has plenty of hydroxyl groups, which form strong intramolecular and intermolecular hydrogen bonds; therefore, it crystallizes very easily<sup>8</sup> and weakens its hydrophilicity obviously. Poly(butyl acrylate) (PBA) has longer flexible side chains so as to possess quite good elasticity. Grafting BA onto a PVA backbone can improve backbone hydrophilicity through destroying crystallizability of PVA. At the same time, the PBA branched chains have hydrophobicity. The amphiphilic graft copolymer PVA-*g*-PBA may serve as a compatibilizer of hydrophobic rubber and hydrophilic super water-absorbent resin.

In this research, by multicomponent mechanical blending technology, a water-swallowable rubber, which is compatibilized by the graft copolymer, has been prepared through choosing chlorohydrin rubber and crosslinked polyacrylate as chief materials, and an amphiphilic graft copolymer PVA-*g*-PBA as the compatibilizer. The effects of PVA-*g*-PBA and crosslinked polyacrylate on water-swelling behaviors were studied. The morphological structure of the fractured surface of WSR was characterized by SEM.



**Figure 1** Relationship of  $S_{w1}$  to soak time at various PVA-*g*-PBA contents. CPA: 70 phr; PEG-2000: 40 phr; PSA: 40 phr.



**Figure 2** Relationship of  $S_{v1}$  to soak time at various PVA-*g*-PBA contents. CPA: 70 phr; PEG-2000: 40 phr; PSA: 40 phr.

## EXPERIMENTAL

### Materials

Chlorohydrin rubber, the epichlorohydrin homopolymer, industrial product, with Mooney viscosity  $ML_{1+4}$  (100°C) 60–70, was produced in the Cangzhou Synthetic Rubber Factory, Hebei Province, China. Crosslinked polyacrylate salt with distilled water absorptivity 316.48 g/g, water absorbent rate less than 15 s, gel strength 8 g/cm<sup>2</sup>, and fineness 20–200 mesh (grain size 74–840  $\mu$ m) was purchased from Pujiang Plastic Factory, Gaoqiao Petrochemical Co. Ltd., Shanghai, China. PVA-*g*-PBA with a percentage of grafting of 151.68% was prepared by us.<sup>9</sup> Poly(ethylene glycol) (PEG) with an average molecular weight of 2000 was provided by Tiantai Chemical Co.Ltd., Tianjin, China. Precipitated silica (PSA) with a grain size below 200 mesh was supplied by Tonghua's Second Chemical Factory, Jilin Province, China.

### Blending

Chlorohydrin rubber was masticated on a open mill ( $\Phi$ 160 mm, linear rate of front roll 10.97

**Table I** Effect of Amount of PVA-*g*-PBA on Maximum Water-Swelling Properties

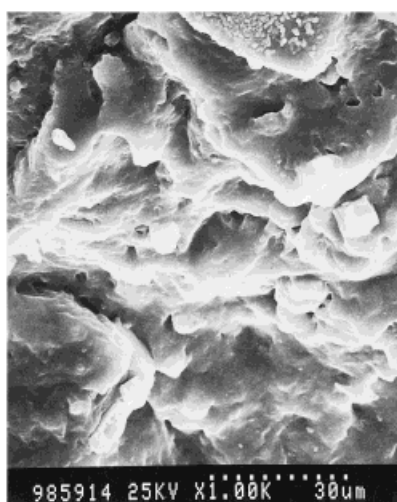
	0 phr	5 phr	10 phr	15 phr
$S_{w1m}$	5.06	5.68	5.14	5.51
$S_{v1m}$	7.15	8.34	7.88	8.01
$S_{w2m}$	3.46	4.76	—	3.68
$S_{v2m}$	4.59	6.13	—	5.11



(a)



(b)



(c)

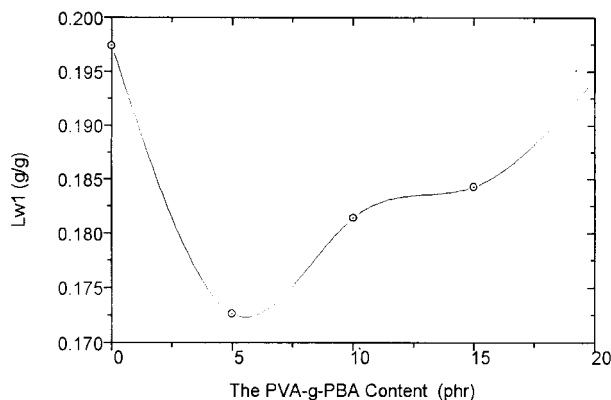
**Figure 3** Scanning electron micrographs of (a) CHR + CPA + PEG. CHR: 100 phr; CPA: 70 phr; PEG: 40 phr; PSA: 40 phr. (b) PVA-*g*-PBA; (c) CHR + CPA + PEG + PVA-*g*-PBA. CHR: 100 phr; CPA: 70 phr; PEG: 40 phr; PVA-*g*-PBA: 10 phr; PSA: 40 phr.

m/min, linear rate ratio of front roll to rear roll 1/1.35) for 2 min, and then a small amount of zinc stearate, compatibilizer PVA-*g*-PBA, water-absorbent resin CPA, PEG-2000, lead tetraoxide, precipitated silica, surplus zinc stearate, and NA-22 were added in proper order, mixing continuously until apparent homogeneity. The compounded rubber stock was laid up on a dry and

clear place at room temperature for over 4 h and then remilled and passed through the open mill seven times. A mixed compound with better dispersion was obtained.

#### Vulcanization

The mixed compound was put in a  $80 \times 60 \times 1$  mm<sup>3</sup> mold, preheated for 5 min, and cured for 45



**Figure 4** Relationship of  $L_{w1}$  to the PVA-g-PBA contents. CPA: 70 phr; PEG-2000: 40 phr; PSA: 40 phr.

min at  $151 \pm 1^\circ\text{C}$  in a press vulcanizer of 16 ton. After that, the mold was taken out and cooled down at room temperature.

### Morphology

Scanning electron micrographs were obtained by an X-650 scanning electron microscope. Samples were cryogenically fractured in liquid nitrogen and coated the broken surface with gold in a sputter machine prior to the installation in the SEM chamber.

### The First Water-Absorbing and Water-Swelling Abilities

The sample of size  $40 \times 20 \times 1 \text{ mm}^3$  was weighed and soaked in distilled water at room tempera-

ture. At a specified time it was taken out, the moisture on the surface removed, and weight and volume were measured until they reached the first maximum water-absorbing and water-swelling abilities, after which weight and volume of the sample did not increase for 12 h. After that, the sample was dried below  $50^\circ\text{C}$  until it achieved a constant weight. The first water-absorbing ratio by weight,  $S_{w1}$ , the first water-swelling ratio by volume,  $S_{v1}$ , and the first percentage loss by weight,  $L_{w1}$ , were calculated using the following expression:

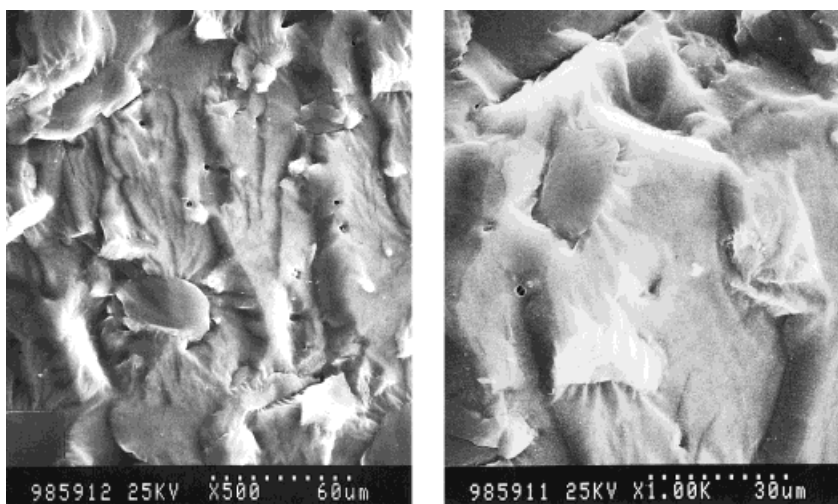
$$S_{w1} = W_2/W_1 - 1$$

$$S_{v1} = V_2/V_1 - 1$$

$$L_{w1} = 1 - W_3/W_1$$

where  $W_1$  and  $W_2$  were the weights of a sample before and after the first water absorbing;  $V_1$  and  $V_2$ , the volumes of a sample before and after the first water swelling;  $W_3$ , the dried weight of a sample after the first water absorbing.

The first maximum water-absorbing ratio by weight,  $S_{w1m}$ , and the first maximum water-swelling ratio by volume,  $S_{v1m}$ , were  $S_{w1}$  and  $S_{v1}$  at the first maximum water-absorbing and water-swelling condition, respectively. The first water-absorbing rate by weight,  $R_{w1}$  was indicated by the slope of  $S_{w1}$  vs. soak time, the first water-



**Figure 5** Scanning electron micrographs of CHR + CPA + PEG. CHR: 100 phr; CPA: 70 phr; PEG: 40 phr; PSA: 40 phr.

swelling rate by volume,  $R_{v1}$ , by the slope of  $S_{v1}$  vs. soak time.

### The Second Water-Absorbing and Water-Swelling Abilities

After the first water-absorbing and water-swelling test, the dried sample was soaked in distilled water at room temperature. At specified time, it was taken out, the moisture on the surface was removed, and weight and volume were measured until they reached the second maximum water-absorbing and water-swelling abilities, after which weight and volume of the sample did not increase for 24 h. The second water-absorbing ratio by weight,  $S_{w2}$ , and the second water-swelling ratio by volume,  $S_{v2}$ , were calculated using the following expression:

$$S_{w2} = W_4/W_3 - 1$$

$$S_{v2} = V_4/V_3 - 1$$

where  $W_3$  and  $W_4$  were the weights of a sample before and after the second water absorbing;  $V_3$  and  $V_4$ , the volumes of a sample before and after the second water swelling.

The second maximum water-absorbing ratio by weight,  $S_{w2m}$ , and the second maximum water-swelling ratio by volume,  $S_{v2m}$ , were  $S_{w2}$  and  $S_{v2}$  at the second maximum water-absorbing and water-swelling condition, respectively.

The second water-absorbing rate by weight,  $R_{w2}$ , was indicated by the slope of  $S_{w2}$  vs. soak time, the second water-swelling rate by volume,  $R_{v2}$ , by the slope of  $S_{v2}$  vs. soak time.

### The Long-Term Water-Retention Abilities

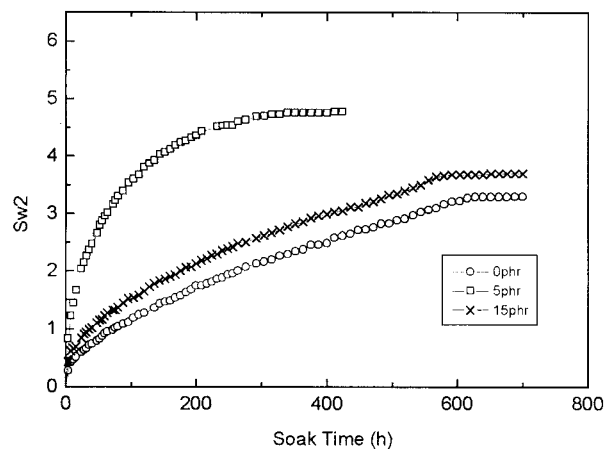
The sample of size  $40 \times 20 \times 1 \text{ mm}^3$  was weighed and soaked in distilled water at room temperature. Then it was taken out, the moisture on the surface removed, and weight and volume were measured every specified time until they did not change for several days.

## RESULTS AND DISCUSSION

### Effect of PVA-g-PBA

#### Effect of PVA-g-PBA on the First Water-Swelling Abilities

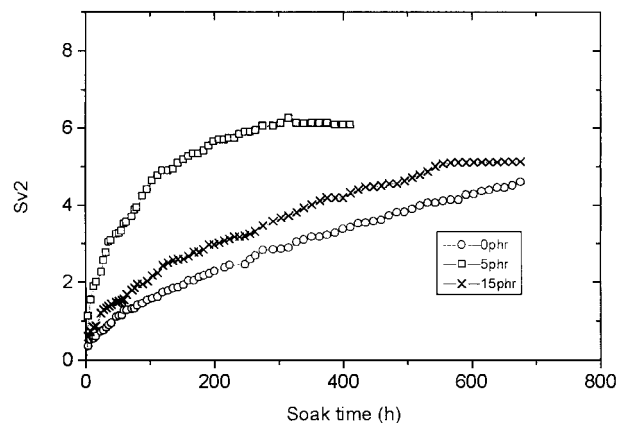
$R_{w1}$ ,  $R_{v1}$ , and  $S_{w1m}$ ,  $S_{v1m}$ : Figures 1 and 2, and Table I show that  $R_{w1}$  and  $R_{v1}$  speeded up, and



**Figure 6** Relationship of  $S_{w2}$  to soak time at various PVA-g-PBA contents. CPA: 70 phr; PEG-2000: 40 phr; PSA: 40 phr.

$S_{w1m}$  and  $S_{v1m}$  increased after the compatibilizer was added. This can be explained as follows: when it was added, the graft copolymer compatibilized the CHR/CPA blend system, so that the interfacial tension between the two phases decreased and the cohesive force between them increased. As a result, the dispersion of water absorbent resin in CHR was improved and the water-absorbing and water-swelling abilities were enhanced. It can also be seen from Figures 1 and 2 that with an increase in PVA-g-PBA content,  $R_{w1}$  and  $R_{v1}$  slowed down, and  $S_{w1m}$  and  $S_{v1m}$  slightly decreased. When a large amount of PVA-g-PBA was added, it not only compatibilized the blend system but also agglomerated by itself to form a new phase. Branched chain PBA aggregated to form a thin layer of continuous paste so as to hinder water from passing well through and reaching the water-absorbent resin grains. As shown in Figure 3, the fractured surface of the sample with compatibilizer was smooth thin layer made up of the graft copolymer.

$L_{w1}$ : The  $L_{w1}$  of the samples with compatibilizer were less than that of the sample with no compatibilizer. The addition of PVA-g-PBA prevented CPA from coagulating with time and dropping out of crosslinked network (Fig. 4). But it is clearly seen from morphological structure of fractured surface of the sample with no compatibilizer that there was a certain combined interaction between CHR and CPA (Fig. 5). Water absorbent resin grains could be broken by brittle fracture force, but could not be dragged out as a whole from CHR to form cavities. So  $L_{w1}$  with a



**Figure 7** Relationship of  $S_{v2}$  to soak time at various PVA-g-PBA contents. CPA: 70 phr; PEG-2000: 40 phr; PSA: 40 phr.

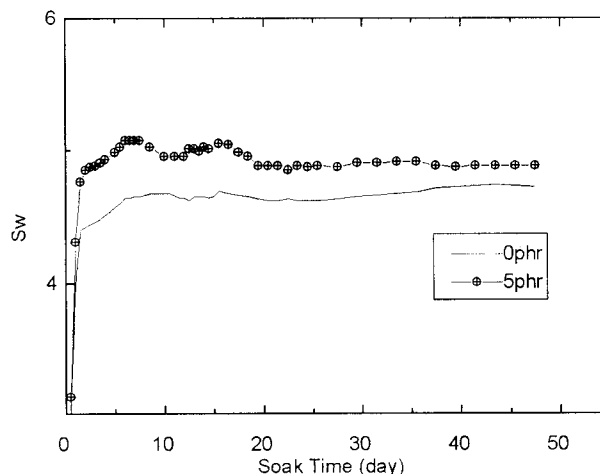
compatibilizer could not further decrease. Another factor was that water-absorbent resin grains were far larger (74–840  $\mu\text{m}$ ), and they did not have a homogeneous dispersion and so easily dropped out of rubber matrix after water absorption, for it has been reported that fine water-absorbent resin powder below 20  $\mu\text{m}$  had a better dispersion<sup>1,10</sup>

**Effect of PVA-g-PBA on the Second Water-Swelling Abilities**

Figures 6 and 7 and Table I indicate that effect of PVA-g-PBA on the second water-swelling abilities was similar to that on the first ones. Upon addition of PVA-g-PBA, compatibilization made water-absorbent resin disperse well and WSR enhanced water-absorbing and water-swelling abilities. However, compared with the first water-absorbing and water-swelling abilities,  $R_{w2}$  and  $R_{v2}$  slowed down, and  $S_{w2m}$  and  $S_{v2m}$  decreased. Because water-absorbent resin CPA and water-absorbent accelerant PEG had lost to a certain extent.

**Table II** Effect of Amount of CPA on Maximum Water-Swelling Properties

	15 phr	40 phr	70 phr	100 phr
$S_{w1m}$	0.68	2.71	5.45	8.77
$S_{v1m}$	0.86	3.94	7.51	11.95
$S_{w2m}$	0.73	2.43	4.67	9.31
$S_{v2m}$	1.18	3.74	6.76	11.02



**Figure 8** Relationship of  $S_w$  to soak time at various PVA-g-PBA contents. CPA: 70 phr; PEG-2000: 40 phr; PSA: 40 phr.

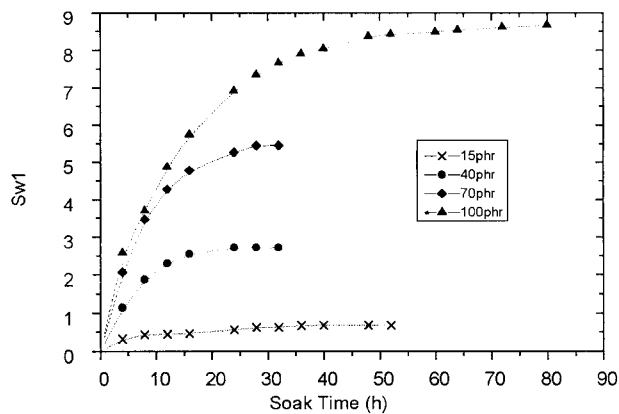
**Effect of PVA-g-PBA on Long-Term Water-Retention Abilities**

After long-term soaking in water,  $S_w$  of the sample with 5 phr PVA-g-PBA was more than that with no PVA-g-PBA (Fig. 8). This was because compatibilizer decreased the loss of CPA.

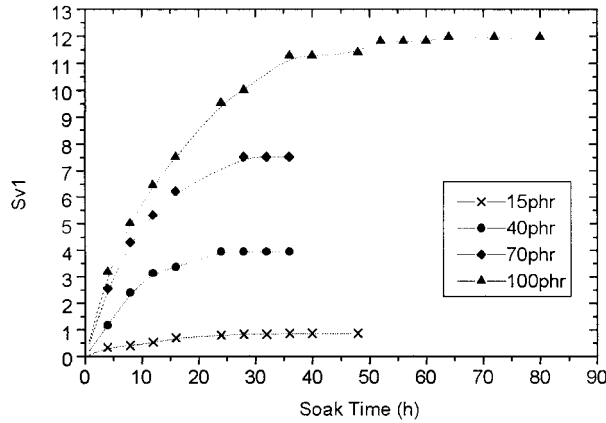
**Effect of CPA**

**Effect of CPA on the First Water-Swelling Abilities**

$R_{w1}$ ,  $R_{v1}$ , and  $S_{w1m}$ ,  $S_{v1m}$ : Figures 9, 10, and Table II illustrate that with an increase in CPA content,  $R_{w1}$  and  $R_{v1}$  speeded up, and  $S_{w1m}$  and  $S_{v1m}$  increased. Because water-absorbent resin plays a



**Figure 9** Relationship of  $S_{w1}$  to soak time at various CPA contents. PVA-g-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.



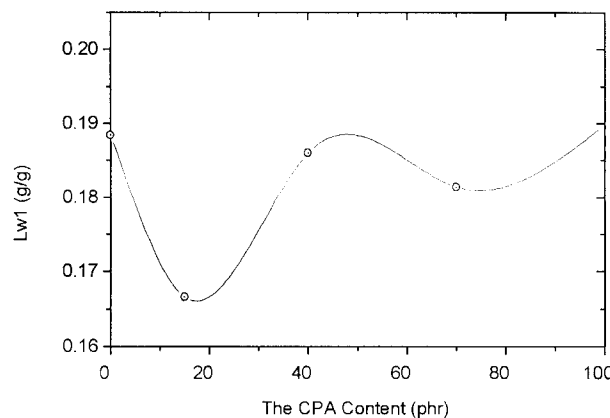
**Figure 10** Relationship of  $S_{v1}$  to soak time at various CPA contents. PVA-*g*-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.

leading role in WSR, the more the water-absorbent resin was used, the stronger the water-absorbing abilities were. Therefore, the crosslinked networks of cured CHR were forced to expand largely and the volume of WSR to expand more rapidly.

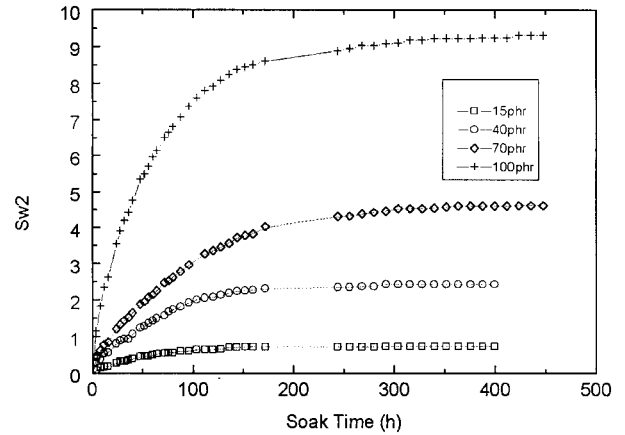
$L_{w1}$ : unlike other WSR, whose  $L_{w1}$  showed a trend towards increasing dramatically with an increase in CPA content,<sup>10</sup>  $L_{w1}$  of this WSR varies within a very narrow range (16.5–19%) with an increase in CPA content from 0 to 100 phr (Fig. 11). It could have something to do with compatibilization of PVA-*g*-PBA.

**Effect of CPA on the Second Water-Swelling Abilities**

As shown in Figures 12, 13, and Table II, the effect of CPA on the second water-absorbing and



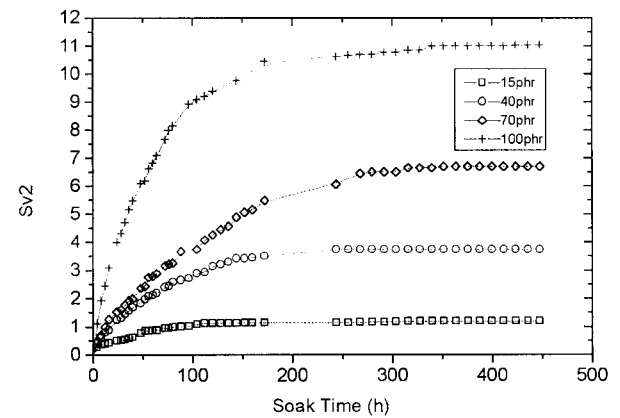
**Figure 11** Relationship of  $L_{w1}$  to the CPA content. PVA-*g*-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.



**Figure 12** Relationship of  $S_{w2}$  to soak time at various CPA contents. PVA-*g*-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.

water-swelling abilities was similar to that on the first ones. With an increase in CPA content,  $R_{w2}$  and  $R_{v2}$  speeded up,  $S_{w2m}$  and  $S_{v2m}$  increased as the first water-absorbing and swelling test did.

After the first water-absorbing and swelling test, the second water-absorbing and swelling abilities declined slightly (Table II). Similarly, this is due to the loss of CPA and PEG. But the sample containing 100 phr CPA had a bigger  $S_{w2}$  than  $S_{w1}$  and a  $S_{v2}$  approximate to  $S_{v1}$ . This was probably because a large amount of CPA was used, and a remainder of CPA could still guarantee water-absorbing and water-swelling abilities after loss in the first water-absorbing and swelling test.



**Figure 13** Relationship of  $S_{v2}$  to soak time at various CPA contents. PVA-*g*-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.

### Effect of CPA on Long-Term Water-Retention Abilities

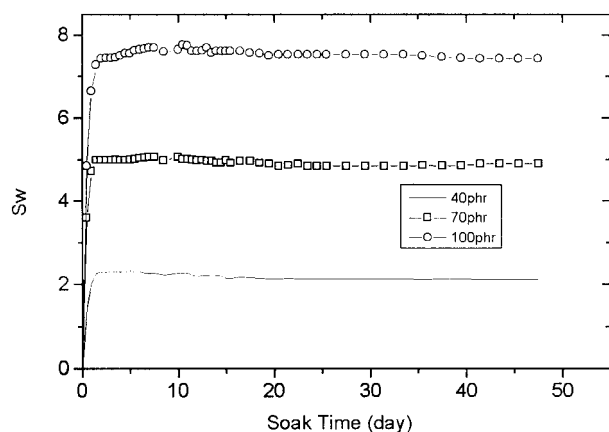
After long-term soaking in water,  $S_w$  and  $S_v$  increased with an increase in CPA content (Figs. 14 and 15). The reasons are also the same as in the first water-absorbing and water-swelling test.

### CONCLUSIONS

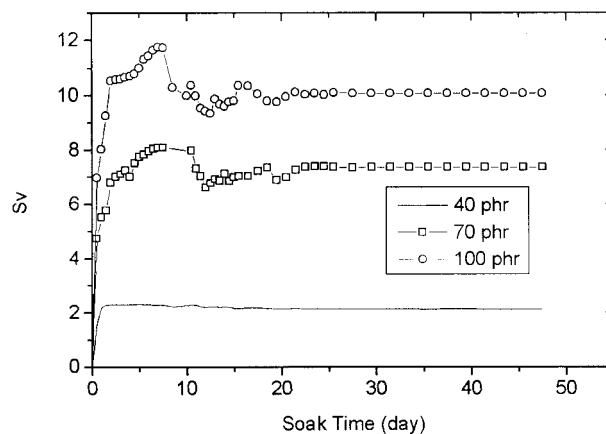
The CHR/CPA blend system compatibilized by the amphiphilic graft copolymer PVA-g-PBA has higher  $R_{w1}$ ,  $R_{v1}$ ,  $S_{w1}$ , and  $S_{v1}$ , less  $L_{w1}$ , higher  $R_{w2}$ ,  $R_{v2}$ ,  $S_{w2}$ , and  $S_{v2}$ , and better long-term water retention property than the system not compatibilized. However, with a further increase in PVA-g-PBA content,  $R_{w1}$ ,  $R_{v1}$ ,  $S_{w1}$ , and  $S_{v1}$  declined. From SEM photographs, we could observe a thin continuous layer of paste agglutinated by hydrophobic PBA branched chains. Probably the paste obstructed the contact of water with the CPA grains.

With CPA content increasing,  $R_{w1}$ ,  $R_{v1}$ ,  $S_{w1}$ ,  $S_{v1}$ ,  $S_{w2}$ , and  $S_{v2}$  became larger. Owing to the compatibilization of the amphiphilic graft copolymer,  $L_{w1}$  did not increase greatly, while CPA increased (e.g., 0–100 phr).

Generally speaking, the first water-absorbing and swelling abilities were stronger than the second ones. Nevertheless, the sample with 100 phr



**Figure 14** Relationship of  $S_w$  to soak time at various CPA contents. PVA-g-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.



**Figure 15** Relationship of  $S_v$  to soak time at various CPA contents. PVA-g-PBA: 10 phr; PEG-2000: 40 phr; PSA: 40 phr.

CPA possessed a bigger  $S_{w2m}$  than  $S_{w1m}$ , and a  $S_{v2m}$  nearly as much as  $S_{v1m}$ .

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