

Chlorohydrin Water-Swellable Rubber Compatibilized by an Amphiphilic Graft Copolymer. III. Effects of PEG and PSA on Water-Swelling Behavior

ZHILIAO ZHANG, GUO ZHANG, CAIQI WANG, DONG LIU, ZHICHENG LIU, XINFANG CHEN

Institute of Materials Science, Jilin University, Changchun 130023, People's Republic of China

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ABSTRACT: Chlorohydrin water-swellable rubber—composed of chlorohydrin rubber (CHR), crosslinked polyacrylate (CPA), the amphiphilic compatibilizer poly(vinyl alcohol)-*g*-poly(butyl acrylate) (PVA-*g*-PBA), precipitated silica (PSA), and poly(ethylene glycol) (PEG)—was prepared. The dispersion of PEG in the blend was characterized by wide-angle X-ray diffraction (WAXD). The dependence of the water absorbing ratio by weight, the water-swelling ratio by volume, and the percentage loss by weight on PEG and PSA contents were investigated. The effects of PEG and PSA on the second water-swelling behaviors and long-term water-retention behaviors were also studied. Optimums for the water-absorbing and water-swelling abilities within the range of the experiment were obtained. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2509–2516, 2001

Key words: water-swellable rubber; chlorohydrin rubber; crosslinked polyacrylate; poly(ethylene glycol); precipitated silica

INTRODUCTION

The development of water-swellable rubber (WSR) has been investigated in recent years as an area of considerable interest and importance.^{1–5} As a kind of functional elastomer, WSR can both adapt itself to the deformation of structure, stopping water by means of elastic sealing and swell in water and by means of expanding volume. Because of convenient operation, reliable water-proofing, and wide application, WSR has opened vast vistas, especially in tunnel engineering, underground engineering, and civil engineering.

WSR is mainly made up of rubber and water-absorbent resin. The rubber endows it with elasticity and ductility, while the water-absorbent resin supplies it with water absorptivity. The rub-

bers used are often nature rubber, butadiene rubber, isobutylene rubber, chloroprene rubber, acrylonitrile rubber, butyl rubber, or their copolymers. The water-absorbent resins are usually starch grafts, cellulose grafts, poly(ethylene oxide) polymers, poly(vinyl alcohol) polymers, etc.⁶

The pure gum stock of CHR has a very low strength. A strengthening agent has to be added to it in order to improve its strength and other physicomechanical properties. As a kind of strengthening agent of CHR, precipitated silica (PSA) can provide it with higher strength. Moreover, PSA has a lot of isolated hydroxyl groups on its surface⁷ (Fig. 1), which can form hydrogen bonds with water easily and can make water be absorbed on the surface of PSA. Therefore, not only can PSA strengthen the pure gum stock of CHR, but it can also enhance the water absorptivity of WSR.

In WSR, rubber is the continuous phase, while water-absorbent resin is the dispersive phase.

Correspondence to: G. Zhang (mat@mail.jlu.edu.cn).

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The Second Water-Absorbing and Water-Swelling Abilities

The second water-absorbing and water-swelling abilities were estimated by the method described in the previous article.⁹ 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 maximum values of S_{w2} and S_{v2} , respectively.

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

Long-Term Water-Retention Abilities

A sample with the dimensions $40 \times 20 \times 1 \text{ mm}^3$ was weighed and soaked in distilled water at

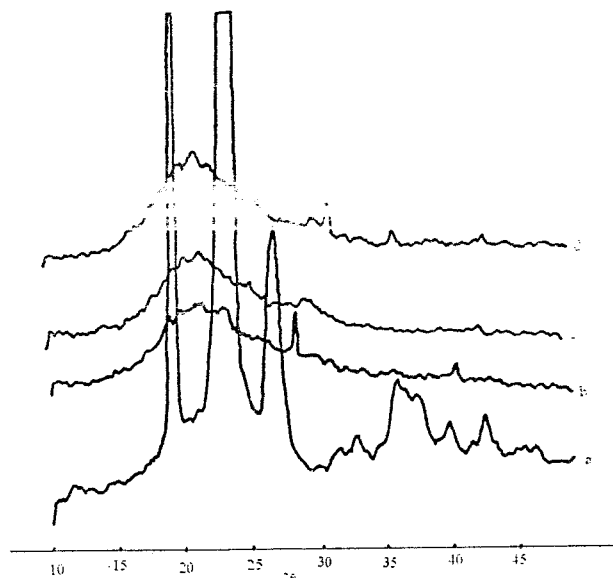


Figure 2 WAXD patterns of (a) PEG; (b) CHR + PEG + CPA, CHR: 100 phr, PEG: 40 phr, CPA: 70 phr; (c) CHR; (d) CHR + PEG, CHR: 100 phr, PEG: 40 phr.

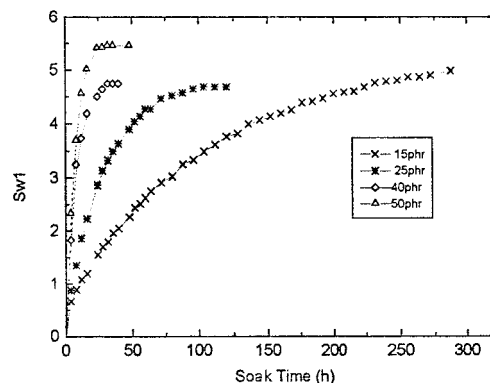


Figure 3 Relationship of S_{w1} to soak time with various PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

room temperature. Then it was taken out, moisture on the surface was eliminated, and its weight and volume were measured every specified time until they did not change for several days.

RESULTS AND DISCUSSION

Effect of PEG

Characterization of Dispersion of PEG by WAXD

The samples with PEG [Fig. 2(a)], CHR [Fig. 2(c)], CHR + PEG [Fig. 2(b)], and CHR + PEG + CPA [Fig. 2(d)] were investigated by means of WAXD in order to analyze the dispersion of PEG in WSR. As seen in Figure 2, the WAXD pattern of PEG shows characteristic diffraction peaks at 19.19, 23.35, and 26.53°C, while the WAXD pattern of CHR has no characteristic diffraction peaks. After PEG was blended with CHR, the characteristic diffraction peaks of PEG disappeared. Similarly, the characteristic diffraction peaks of PEG in PEG, CHR, and CPA ternary blend could not be seen. This shows that in a binary blend of PEG and CHR or a ternary blend of PEG, CHR, and CPA, PEG had a homogeneous dispersion and could not agglomerate by itself to form a crystalline region. The homogeneous dispersion of PEG in WSR played an important role in its increasing water-absorbing, water-swelling abilities.

Effect of PEG on the First Water-Swelling Abilities

R_{w1} , R_{v1} , and S_{w1m} , S_{v1m} . With an increase in PEG content, R_{w1} and R_{v1} dramatically speeded up (Figs. 3 and 4). This may be explained as follows: when WSR with no PEG was soaked in

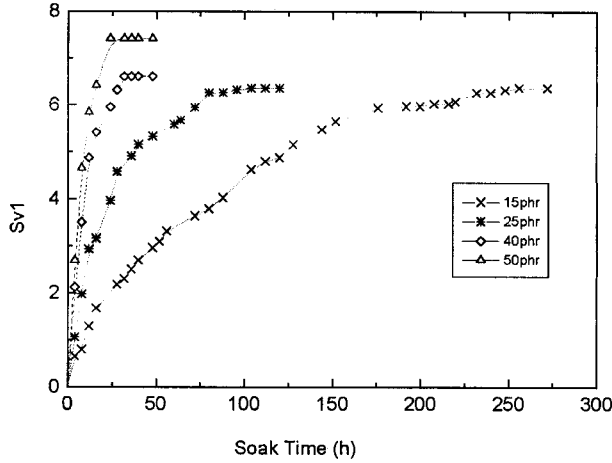


Figure 4 Relationship of S_{v1} to soak time with various PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

water, water molecules could only enter WSR by means of diffusion, capillarity, and surface sorption, so that both R_{w1} and R_{v1} were very slow. It took 23 days for a WSR sample with no PEG to reach maximum water absorption. In WSR, CHR is the continuous phase and CPA grains are the dispersive phase. Each water-absorbent resin grain was isolated from others by a rubber phase and could not give full play to the water-absorbing ability. When PEG was added, it built bridges among water-absorbent resin grains and supplied water-absorbing routes. With an increase in PEG content, the number of water-absorbing routes increased, and the water-absorbing rate speeded up. Figures 3 and 4 also show that although R_{w1} and R_{v1} with smaller PEG content were slower,

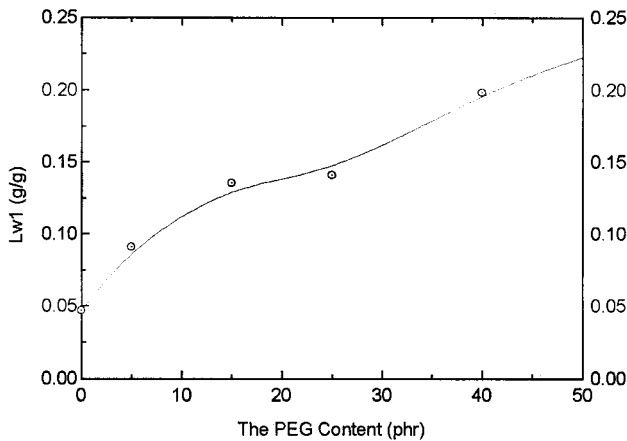


Figure 5 Relationship of L_{w1} to PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

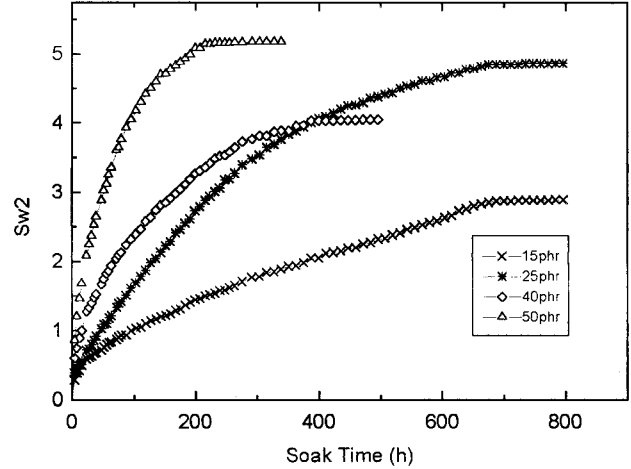


Figure 6 Relationship of S_{w2} to soak time with various PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

S_{w1m} and S_{v1m} of the samples with smaller PEG content obtained from a longer time period were almost equal to those with a larger PEG content. This can be explained by the slower water-absorbing rate because of fewer routes, but maximum values could finally be achieved through a longer term as long as routes existed.

L_{w1} . Figure 5 shows that with an increase in PEG content, L_{w1} increased rapidly. L_{w1} with no PEG was about 5%, while L_{w1} with 50-phr PEG was 23%. Because of this, PEG dissolved easily in water so that PEG was taken out by water in the course of water swelling.

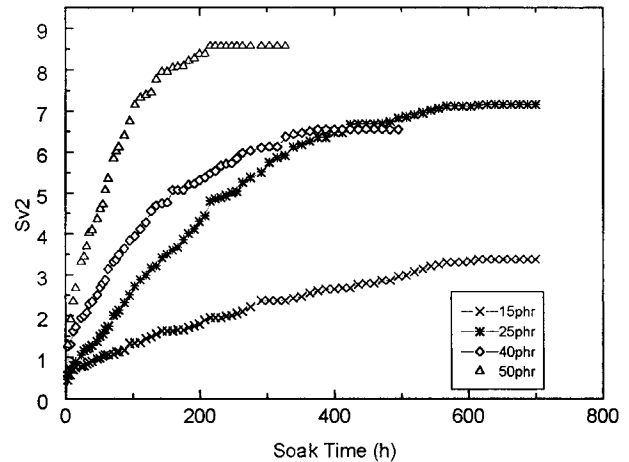


Figure 7 Relationship of S_{v2} to soak time with various PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

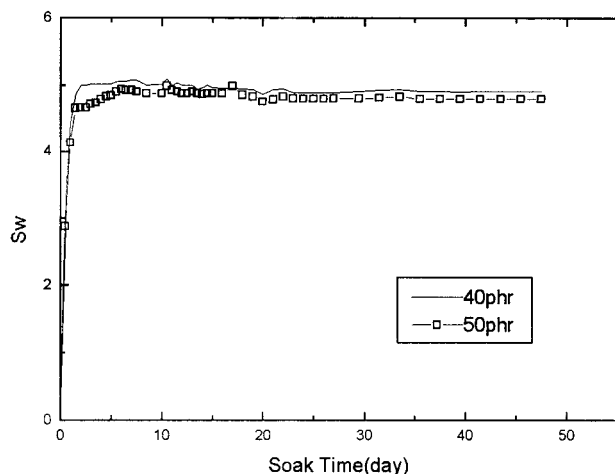


Figure 8 Relationship of S_w to soak time at various PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

Effect of PEG on the Second Water-Swelling Abilities

Figures 6 and 7 show that the effect of PEG on the second water-absorbing and water-swelling abilities was similar to that on the first water-swelling abilities. With an increase in PEG content, the impact of the water-absorbing accelerant also increased, so that both R_{w2} and R_{v2} speeded up. However, R_{w2} and R_{v2} were less than R_{w1} and R_{v1} . Except for the sample with 15 phr PEG, the addition of 25 phr, 40 phr, and 50 phr PEG made S_{w2m} and S_{v2m} of the samples equal to or higher than S_{w1m} and S_{v1m} , respectively. Compared

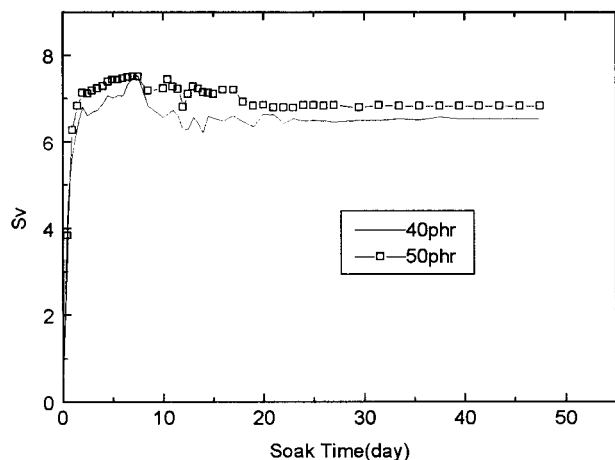


Figure 9 Relationship of S_v to soak time at various PEG-2000 contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PSA: 40 phr.

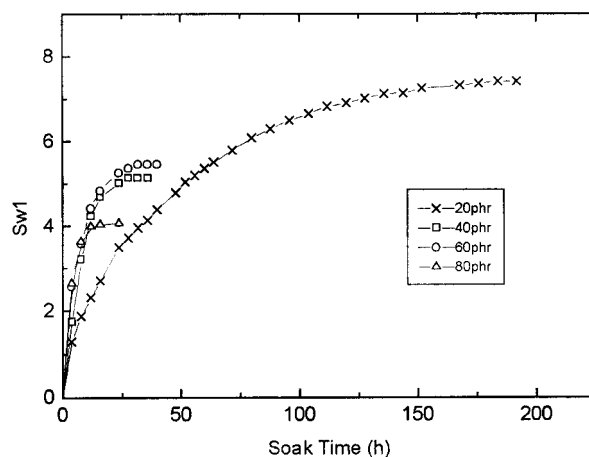


Figure 10 Relationship of S_{w1} to soak time at various PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

with S_{v1m} with 50 phr PEG, S_{v2m} increased by more than 10%. This may be explained by the fixing of the route volume occupied by PEG molecules when the mixed compound was cured during preparation of WSR. After PEG was taken out by water, the routes fixed by the crosslinked networks still existed and would allow water to pass through.

Effect of PEG on Long-Term Water-Retention Abilities

After long-term soaking in water, S_w and S_v of the sample with 40 phr PEG were almost equal to those of the sample with 50 phr PEG (Figs. 8 and 9), which indicates 40 phr PEG could meet the need of our WSR.

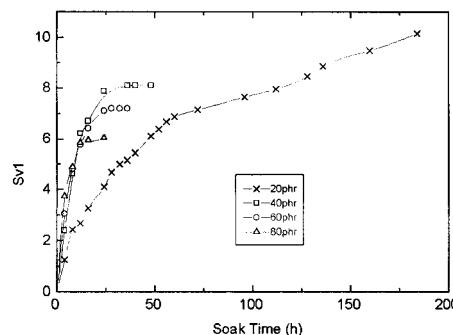


Figure 11 Relationship of S_{v1} to soak time at various PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

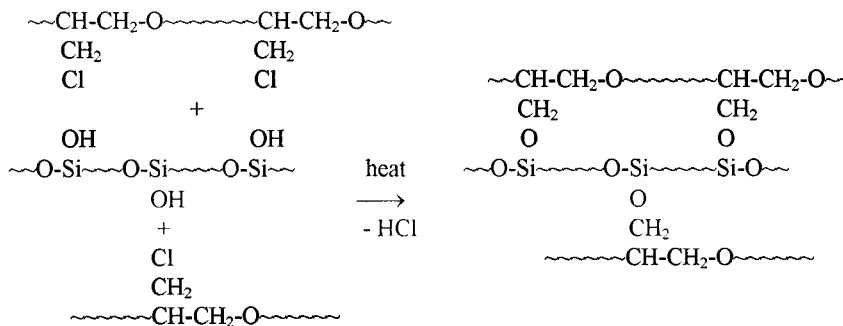


Figure 12 Reaction scheme between PSA and CHR.

Effect of PSA

Effect of PSA on the First Water-Swelling Abilities

R_{w1} , R_{v1} , and S_{w1m} , S_{v1m} . Figures 10 and 11 show that S_{w1m} and S_{v1m} decreased with increasing PSA content. It is probable that when PSA content was modest, the chloromethyl side group of CHR reacted with the hydroxyl groups of PSA during vulcanization to form ether bonds and made the crosslinked networks of WSR smaller (Fig. 12), this is similar to G. J. Wang's work.⁵ With an increase in PSA content, the size of the crosslinked networks decreased, which set a limit to the expansion of WSR and absorption of water. However, with an increase in PSA content, R_{w1} and R_{v1} sped up. Presumably this is because the free PSA that didn't form ether bonds interacted with water to form hydrogen bonds, so that PSA could absorb water upon its surface and speed up R_{w1} and R_{v1} . When PSA content was equal to or higher than 40 phr, R_{w1} and R_{v1} tended to be constant.

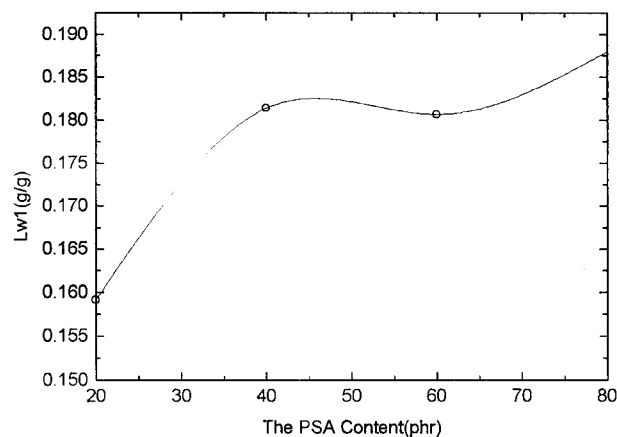


Figure 13 Relationship of L_{w1} to PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

L_{w1} . With an increase in PSA content, L_{w1} increased (Fig. 13). When PSA content was high enough to consume almost all chloromethyl groups, the free PSA whose hydroxyl groups reacted with no chloromethyl groups might be taken out easily by water. The higher the PSA content, the more the free PSA was taken out.

Effect of PSA on the Second Water-Swelling Abilities

Figures 14 and 15 illustrate that the effect of PSA on the second water-absorbing and water-swelling abilities was different from that on the first ones. With an increase in PSA content, R_{w2} and R_{v2} slowed down because loss of free PSA, PEG, and CPA in higher PSA content samples was more than those in lower ones in the course of the first water absorbing and the first water swelling. In addition, S_{w2m} and S_{v2m} decreased with in-

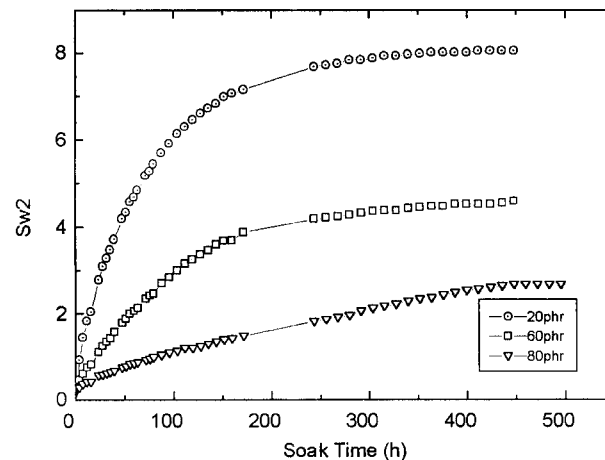


Figure 14 Relationship of S_{w2} to soak time at various PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

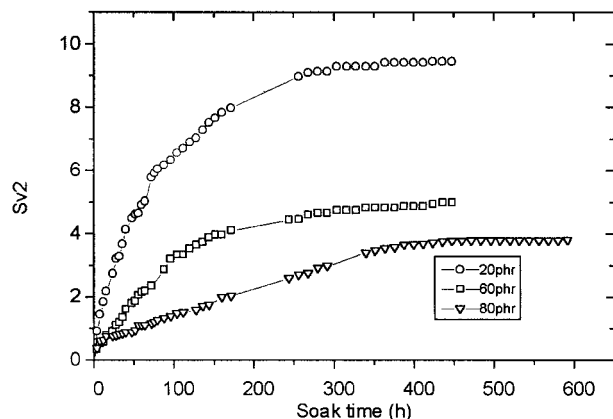


Figure 15 Relationship of S_{w2} to soak time at various PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

creasing PSA content, just as those in the first water-absorbing and -swelling test did. Except for the sample with 20 phr PSA, the second water-absorbing and water-swelling abilities were poorer than the first ones; this may be due to the loss of free PSA, CPA, and PEG. That the second maximum water-absorbing ratio of the sample with 20 phr PSA was more than the first one may be attributed to the proper size of crosslinked networks and the lower loss of free PSA, PEG, and CPA.

Effect of PSA on Long Term Water Retention Abilities

After long-term soaking in water, the S_w and S_v of the sample with 80 phr PSA were less than

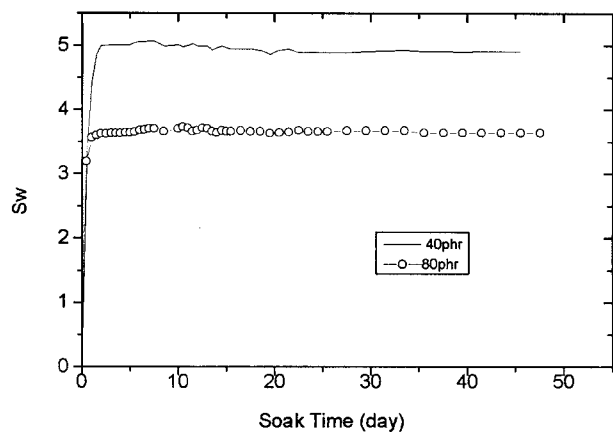


Figure 16 Relationship of S_w to soak time at various PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

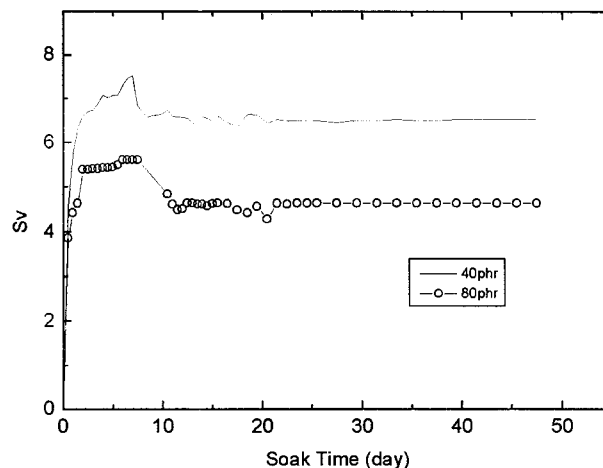


Figure 17 Relationship of S_v to soak time at various PSA contents; PVA-g-PBA: 10 phr; CPA: 70 phr; PEG-2000: 40 phr.

those of the sample with 40 phr PSA (Figs. 16 and 17) because the size of crosslinked networks of the former was smaller than those of the latter.

CONCLUSIONS

1. The WAXD patterns show that in the binary blend of PEG and CHR or the ternary blend of PEG, CHR, and CPA, PEG dispersed homogeneously and could not agglomerate by itself to form a crystalline region.
2. With PEG content increasing, R_{w1} , R_{v1} , R_{w2} , and R_{v2} sped up and L_{w1} increased, but evidently S_{w1m} and S_{v1m} did not increase. For the sample with the same PEG content, R_{w2} and R_{v2} were less than R_{w1} and R_{v1} . But compared with S_{v1m} with 50 phr PEG, S_{v2m} increased by more than 10%.
3. R_{w1} and R_{v1} sped up, but R_{w2} and R_{v2} decreased when PSA content increased.

Table I Effect of Amount of PEG on Maximum Water-Swelling Properties

	15 phr	25 phr	40 phr	50 phr
S_{w1m}	5.03	4.68	4.74	5.46
S_{v1m}	6.57	6.36	6.61	7.41
S_{w2m}	2.87	4.85	4.03	5.16
S_{v2m}	3.48	7.17	6.56	8.17

Table II Effect of Amount of PSA on Maximum Water-Swelling Properties

	20 phr	40 phr	60 phr	80 phr
S_{w1m}	7.42	5.45	5.45	4.07
S_{v1m}	10.14	7.51	7.2	6.03
S_{w2m}	8.05	4.67	4.59	2.72
S_{v2m}	9.45	6.69	4.99	3.82

Moreover, S_{w1m} , S_{v1m} , S_{w2m} , and S_{v2m} decreased with an increase in PSA content. For the sample with the same PSA content, R_{w2} and R_{v2} were less than R_{w1} and R_{v1} . However, S_{w2m} with 20 phr PSA was more than S_{w1m} .

4. Various component contents have an influence on R_{w1} , R_{v1} , S_{w1m} , S_{v1m} , L_{w1} , R_{w2} , R_{v2} , S_{w2m} , S_{v2m} , R_{w2} , S_w , and S_v . As far as water-absorbing and -swelling abilities are concerned, the optimums within the range of the experiment were: CHR, 100 phr; CPA, 70 ~ 100 phr; compatibilizer PVA-g-PBA, 5 ~ 10 phr; PEG, 40 ~ 50 phr; and PSA, 40 ~ 60 phr. The first maximum water-swelling ratio by volume was 11.95,

and the second maximum water-absorbing ratio by weight was 9.31.

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REFERENCES

1. Namba, T. et al. In *Advances in Superabsorbent Polymer*; American Chemical Society: Washington, DC, 1994.
2. Satoda, H. *Jpn Kokai Tokkyo Koho JP* 1993, 05, 179,066.
3. Satoda, H. *Jpn Kokai Tokkyo Koho JP* 1994, 06, 136,005.
4. Itabashi, K.; Sugiyama, K.; Waki, H. *Jpn Kokai Tokkyo Koho JP* 1997, 09,48,965.
5. Wang, G. J.; Li, M.; Chen, X. F. *J Appl Polym Sci* 1998, 68, 1219.
6. Zhou, X. X. *Superabsorbent polymer*; Chemical Industry Press: Beijing, 1991.
7. Chen, Y. B. *Inorganic Chemicals Industry (Chinese)* 1993, 25, 39.
8. Zhang, G.; Zhang, Z. H.; Xie, F. C.; Hu, X. Q.; Chen, X. F. *J Appl Polym Sci*, to appear.
9. Zhang, Z. H.; Zhang, G.; Li, D. F.; Liu, Z. C.; Chen, X. F. *J Appl Polym Sci*, to appear.