Synthesis and Swelling Properties of Grafting-Type and Crosslinking-Type Water-Swellable Elastomers

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ABSTRACT: A grafting water-swellable elastomer (WSE) that is, chlorinated polyethylene (CPE)-*graft*-poly(ethylene glycol) (PEG), was synthesized by a grafting reaction. The synthesis was based on the reaction between chlorine in CPE and sodium salt of PEG. PEG with molecular weights of 600 and 1000 were used. The maximum grafting percentage of the resulted copolymers after purification was 9.79%. The structure of the copolymer was confirmed by an IR spectrum. The grafting degree and PEG content increased with increasing reaction time and reaction temperature. The equilibrium swelling degree of the grafting copolymer was very small, only 16.94%. However, for the crosslinking WSE, the swelling degree was influenced by the absorbency temperature and absorbency time. The absorbency rate was faster than that of the grafting WSE, and the swelling degree in the equilibrium state was higher than that of the grafting WSE, too. The maximum swelling degree of the crosslinking WSE was 70%. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2637–2642, 2007

Key words: water-swellable elastomer; graft copolymers; chlorinated polyethylene (CPE); swelling

INTRODUCTION

Water-swellable elastomers (WSEs) are a new kind of functional product with elastic sealing and water-swelling properties. They can absorb large quantities of water, several times and even several hundred times their own weights. After absorbing water, the material still retains its peculiar elasticity and intensity and can keep water under a pushing situation. These materials are widely used in dams, the underground parts of building, tunnels, and subways.[1,2] The main component of water-absorbent elastomers are rubber, elastomer, and an absorbent resin. According to different preparation methods, rubber meeting material, solvent, and so on can be added to the materials.

WSE is usually prepared by two methods.[3–5] One is physical blending, which is the mixing of rubber with water-absorbent materials by the proper method. The other is graft modification, that is, the grafting of a hydrophilic segment onto the rubber macromolecule. The advantages of water-absorbent elastomers prepared by blending are that the preparation course is simple, easy, and cheap and that the first absorbency ratio and the absorbing speed of the materials are high. However, hydrophilic super water-absorbent resin cannot disperse well in a hydrophobic elastomer, so it can break off from the elastomer network easily. This will weaken its water-swelling abilities,

mechanical properties, long-term water retention, and repeated usage. The advantages of water-swelling elastomers prepared by chemical modification are that the materials have microcompatibility and good intensity. The mechanical behavior and expanding behavior are steady after water is absorbed, even in repeated courses. However, the disadvantage is that water absorbency ratio is very low and the preparation course is tedious.

Chlorinated polyethylene (CPE) has a saturated molecular chain without double bonds. It has exhibited excellent resistance to heat, ozone, oil, and chemicals. Its flexibility and resistance to ozone are valuable in outdoor applications.[6] CPE is a highly versatile elastomer with a combination of properties suitable for many varied applications, and it has more advantages than other rubbers. So we used CPE as a hydrophobic backbone. In this study, chemically grafted crosslinking water-swelling elastomers were prepared by chemical modification. The synthesis was based on the reaction between chlorine in CPE and sodium salt of poly(ethylene glycol) (PEG). By adjusting the molar ratio of PEG to Na, we prepared grafting-type and crosslinking-type WSEs. The influence of the reaction conditions on the PEG content was investigated, and the swelling properties of the copolymers were also investigated.

EXPERIMENTAL

Reagents

Industry-pure CPE (135A) was supplied by ShanDong WeiFang Chemical Factory (Shandong, China). PEG600

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was a Japanese import (Sanyo-Chemical Industries, Ltd., Japan). PEG1000 was supplied by Beijing Chemical Factory (Beijing, China). Analytical-reagent-grade toluene was supplied by Hubei University Chemical Factory (Hubei, China). Toluene was dried over sodium with stirring and was distilled before use. Analytical-reagent-grade methyl alcohol was supplied by Hubei University Chemical Factory.

Synthesis of CPE-*g*-PEG (the grafting WSE)

All reactions were carried out through the following procedure. Water was separated as toluene azeotrope from the solution of PEG in toluene. When some toluene was removed, sodium was added to this solution. The metallation of the hydroxyl group in PEG was carried out under reflux with stirring for 12 h under nitrogen at 115°C. This reaction mixture was used in the next procedure.

In a 250-mL, four-necked, round-bottom flask, the solution of CPE in toluene was added. Water was separated as toluene azeotrope in the same way. A solution of a sodium alkoxide derivative of PEG was added dropwise, and the reaction mixture was stirred vigorously at 80, 90, 100, and 110°C in oil bath under nitrogen for a prescribed time. The reaction mixture was poured into a large amount of methanol and reprecipitated from toluene solution with methanol to remove the unreacted PEG. Soxhlet extraction with methanol was carried out for 48 h. The resulted polymer was dried *in vacuo* at ambient temperature.

Synthesis of crosslinking-type WSE

The molar ratio of PEG to Na was adjusted to 1 : 2; the other prepared measure was the same as the grafting-type WSE.

Sample sheet preparation

The samples of the grafting WSE and crosslinking polymer were weighed on an electric balance, put in a mold, preheated for 5 min, and cured at 140 ± 1°C in a press vulcanizer at 15 MPa for some time. After that, the mold was cooled to below 100°C and removed and cut into a standard sample sheet.

IR test

The IR spectrum was recorded on Shimadzu IR-440 spectrometer (Shimadzu, Japan).

PEG content and grafting degree tests

Chlorinate content was based oxygen bomb burning:[7]

$$\text{Grafting degree(\%)} = (\text{Weight of grafted PEG} / \text{Weight of CPE backbone}) \times 100$$

$$\text{PEG content (\%)} = (\text{Weight of grafted PEG} / \text{Weight of copolymer}) \times 100$$

Water-absorbency tests of the copolymers

The copolymer was weighed and immersed in ion-exchanged water at a prescribed temperature. At regular intervals, the swollen samples were removed from the ion-exchanged water, and the superficial moisture was removed; the weight of sample was measured immediately. The swelling degrees (S) of the polymers were calculated by the following equation:

$$S(\%) = (W_2 - W_1)/W_1 \times 100$$

where W_1 and W_2 are the weights of the sample before immersion in water and after swelling for the prescribed time, respectively.

Water-retention testing of the copolymers

The copolymer at the swelling equilibrium state was weighed. Then, it was put at room conditions. At regular intervals, the weight of the sample was measured. We weighed the copolymer at the prescribed time. The water-retention ratio (R) was calculated by the following equation:

$$R(\%) = W_3/W_4 \times 100$$

where W_4 and W_3 are the weight of the equilibrium state and the weight of the polymer at regular intervals, respectively.

RESULTS AND DISCUSSION

Characterization of CPE-*g*-PEG

The molecular structure of the copolymer (CPE-*g*-PEG) was evaluated by IR spectroscopy. The IR spectrum of CPE-*g*-PEG is shown in Figure 1. The absorption band due to the aliphative C—O—C stretching vibration of the ether group was detected at 1100 cm^{-1}, the O—H stretching vibration of the hydroxyl group of PEG was detected at 3400 cm^{-1}, and the C—Cl stretching vibration was detected at 930 cm^{-1}. For the mixture of CPE and PEG prepared by precipitation in toluene with methanol, the stretching vibration band
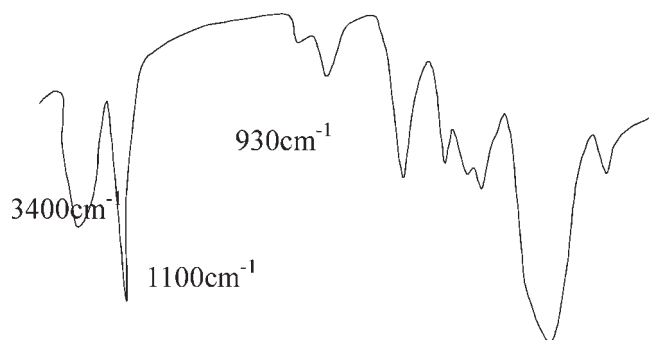
Figure 1 IR spectrum of CPE-*g*-PEG.

of neither the hydroxyl group nor that of the ether group was detected in the IR spectrum. From the previous analysis, the proposed molecular structure of graft copolymers was confirmed.

Influence of the PEG/Na molar ratio on the remaining chlorine content

Because the synthesis was based on the reaction between chlorine in CPE and sodium salts of PEG, the degree of reaction, grafting degree, and PEG content in the copolymers was estimated by measurement of the weight percentage of chlorine element in the resulting copolymers. Controlling the molar ratio of Na to PEG decreased the crosslinking degree and improved the solubility of the resulting copolymers. The crosslinking extent of the polymer could be seen through remaining chlorine content. Table I shows the influence of the match of PEG to Na on the remaining chlorine content.

As shown in Table I, when the same amount of PEG was used but the amount of Na was increased, the remaining chlorine content decreased. The dissolution of the polymer became bad. This was because with the increasing Na, the two hydroxyls of PEG had more chances to react with Na, and the more double sodium salt of PEG was formed. When CPE

reacted with PEG/Na, those two sodium atoms reacted with the chlorine atom. Thus, the crosslinking degree of the copolymer increased. The dissolution became bad, too. As shown in Table I, when the amount of Na was very small (PEG/Na molar ratio = 5 : 1), the remaining chlorine content was close to the chlorine content of CPE. This means that the graft reaction had not taken place. When the molar ratio of PEG to Na was 5/2, the copolymer not only had good dissolution but also a high grafting degree.

Influence of the reaction temperature on the grafting degree and PEG content of the graft copolymers

The influence of the reaction temperature on the grafting degree and PEG content of the graft copolymers are shown in Table II. The grafting percentage and PEG content increased with increasing reaction temperature. The higher the reaction temperature was, the larger the grafting degree and PEG content were. Under the conditions of the same reaction time and temperature but with a different graft chain length, that is, a different molecular weight of PEG, the grafting degree for grafting of a short-side chain onto CPE was higher than that for long-side-chain grafting. When the molecular weight of PEG was 600, the grafting degree and PEG content were larger than the molecular weight of PEG, which was 1000. This showed that the short chain was easily grafted onto CPE. This was because the hindrance of the short chain molecule was smaller than the long chain molecule in the polymer–polymer grafting reaction.

Influence of the reaction time on the grafting degree and PEG content of the graft copolymers

The influence of the reaction time on the grafting degree and PEG content of the graft copolymers are given in Table III. As shown in Table III, the grafting degree and PEG content of the graft copolymers

TABLE I
Influence of the Match of PEG to Na on the Reaction

| CPE (g) | PEG | | Na (g) | PEG/Na | Reaction temperature (°C) | Reaction time (h) | Chlorine content (%) |
	M_n	Weight (g)					
5	600	15	0.115	5 : 1	90	8	35.45
5	600	15	0.23	5 : 2	90	8	32.35
5	600	15	0.345	5 : 3	90	8	30.80
5	600	15	0.460	5 : 4	90	8	27.99
5	600	15	0.575	5 : 5	90	8	25.61
5	1000	25	0.115	5 : 1	90	8	34.33
5	1000	25	0.230	5 : 2	90	8	32.68
5	1000	25	0.345	5 : 3	90	8	29.83
5	1000	25	0.460	5 : 4	90	8	26.01
5	1000	25	0.575	5 : 5	90	8	24.10

M_n, number-average molecular weight.

TABLE II
Effect of the Reaction Temperature on the Grafting Degree and PEG Content

Sample	CPE (g)	PEG M_n	PEG Weight (g)	Na (g)	Reaction temperature (°C)	Reaction time (h)	Chlorine content (%)	Grafting degree (%)	PEG content (%)
1	5	600	15	0.23	110	10	31.59	9.79	8.78
2	5	600	15	0.23	100	10	31.89	8.73	8.02
3	5	600	15	0.23	90	10	32.07	8.15	7.54
4	5	600	15	0.23	80	10	32.16	7.90	7.32
9	5	1000	25	0.23	110	10	31.75	9.53	8.65
10	5	1000	25	0.23	100	10	32.12	8.36	7.72
11	5	1000	25	0.23	90	10	32.48	7.24	6.75

M_n, number-average molecular weight.

increased with increasing reaction time. However, when the reaction time was above 8 h, the increases in grafting degree and PEG content were very small. So, prolongation of time had little influence on the grafting degree and PEG content of the graft copolymers.

Influence of the reaction temperature on the PEG content of the crosslinking WSE

Table IV shows the variation tendency of PEG content of the crosslinking WSE. As shown in Table IV, with increasing reaction temperature, the PEG content of the crosslinking WSE increased. The PEG content of the crosslinking WSE was the highest when the reaction temperature was 110°C.

Influence of the reaction time on the PEG content of the crosslinking WSE

As shown in Table IV, with increasing reaction time, the PEG content of the crosslinking WSE increased. However, after the reaction time reach 8 h, the increase in PEG content leveled off. When the reaction time was prolonged, the PEG content did not change distinctly. So. one should not rely on a longer reaction time to improve the PEG content of the crosslinking WSE.

Swelling properties of the CPE-*g*-PEG graft copolymer

Table V shows the swelling properties of the graft copolymer. As shown in Table V, the graft copolymer had a higher PEG content; the equilibrium swelling degree (S_e) was also higher.

Comparing Table V to Tables II and III, we could see that the influence of reaction temperature and reaction time on the grafting degree of the graft WSE was equal to the influence of reaction temperature and reaction time on S of the WSE. The higher reaction temperature and the longer reaction time were, the higher grafting degree, the higher the hydrophilic content in grafting copolymer, and the larger S were. In the beginning stage, the swelling ratio of the CPE-*g*-PEG copolymer was slow. After they were soaked in water for 7 days, the materials reached the equilibrium state. This was because the hydrophilic-segment PEG was circulated by hydrophobic CPE, which hindered water molecules from entering the network. Thus, S of CPE-*g*-PEG was very small.

Influence of the absorbency time on S of the crosslinking WSE

Figure 2 indicates that S of the crosslinking copolymer rose with increasing absorbency time. The crosslinking copolymer reached the equilibrium state after

TABLE III
Effect of the Reaction Time on the Grafting Degree and PEG Content

Sample	CPE (g)	PEG M_n	PEG Weight (g)	Na (g)	Reaction temperature (°C)	Reaction time (h)	Chlorine content (%)	Grafting degree (%)	PEG content (%)
3	5	600	15	0.23	90	10	32.07	8.15	7.54
6	5	600	15	0.23	90	8	32.35	7.82	7.26
7	5	600	15	0.23	90	5	32.79	6.03	5.69
11	5	1000	25	0.23	90	10	32.48	7.24	6.25
13	5	1000	25	0.23	90	5	33.02	5.62	5.31

M_n, number-average molecular weight.

| Sample | CPE (g) | PEG | | Na (g) | PEG/Na | Reaction temperature (°C) | Reaction time (h) | PEG content (%) |
		M_n	Weight (g)					
S-1	4	600	12	0.92	1 : 2	110	10	13.52
S-2	4	600	12	0.92	1 : 2	100	10	11.04
S-3	4	600	12	0.92	1 : 2	90	10	7.98
S-4	4	600	12	0.92	1 : 2	80	10	7.19
S-5	4	600	12	0.92	1 : 2	90	2	6.66
S-6	4	600	12	0.92	1 : 2	90	5	7.30
S-7	4	600	12	0.92	1 : 2	90	8	7.87

M_n, number-average molecular weight.

5 days. After 6 days, S had not changed much, so we thought the crosslinking copolymer could reach equilibrium state in 5 days. S_e of the crosslinking WSE rose with increasing PEG content. This was because the crosslinking copolymer was mainly made up of CPE and PEG chain sections. CPE had a hydrophobic group, but PEG had a hydrophilic group. Therefore, the amount of hydrophilic groups was the main influential factor on S of the polymer, thus, with increasing PEG content, S_e increased.

Comparing S of the crosslinking WSE to that of the graft copolymer, we found that the crosslinking copolymer had higher S_e than the graft copolymer, even though they had the same PEG content. For example, for sample 2 of the graft copolymer, the PEG content was 8.02%, and the equilibrium swelling ratio was 16.02% under 35°C, but for sample 3 of the crosslinking copolymer, the PEG content was 7.98%, and the equilibrium swelling ratio increased to 77.35%. This was because the configuration of the crosslinking copolymer was a network. However, the graft copolymer was line type. Network polymers can hold more water molecules, whereas the line-type graft copolymer cannot.

Influence of the absorbency temperature on the equilibrium swelling ratio of the crosslinking WSE

Some temperatures let the crosslinking WSE absorb water fully at some temperatures. The influence of absorbency temperature on the absorbency ratio is given in Figure 3.

Figure 3 indicates that the equilibrium absorbency degree of the crosslinking copolymer increased with increasing absorbency temperature. For sample 1, at 25°C, S_e was 142.3%; at 35°C, S_e was 165.7%; and at 45°C, S_e was 208.2%. This was because with increasing temperature, water molecules moved rapidly, the network of crosslinks expanded, and the liquid amount that could be held increased. This, combined with the result from Table I, showed that the PEG content of the copolymer increased, and the equilibrium absorbency ratio increased, too. In addition, the equilibrium absorbency ratio was related to the reaction time (e.g., S-6, S-5, S-7). When the reaction time was increased to 5 h from 2 h, the PEG content increased, and S_e increased, too. However, with increasing reaction time, although the PEG content increased, S_e decreased. This phenomenon could be explained by the fact that with increasing reaction time, the crosslink density increased and the inflation ability of the network decreased. As shown in Figure 3, when the reaction time was 5 h, S_e reached a maximum value.

R of the crosslinking WSE

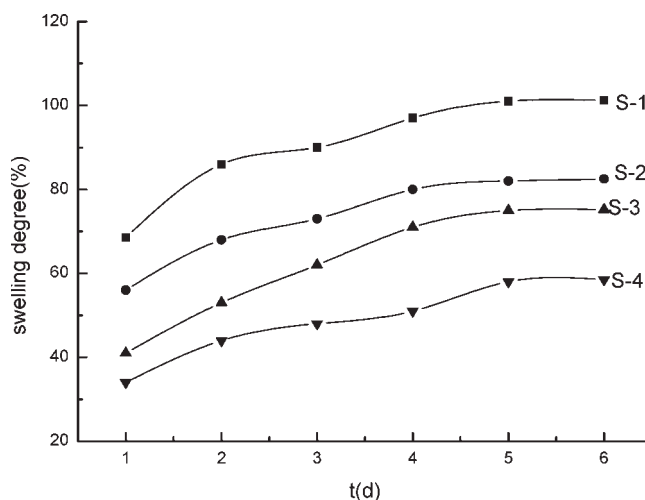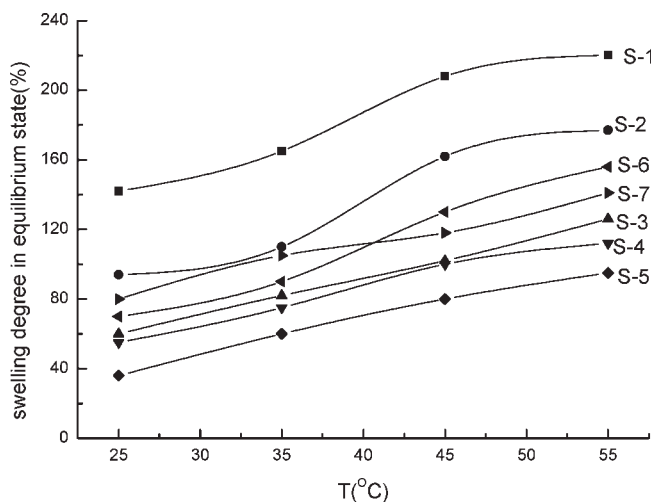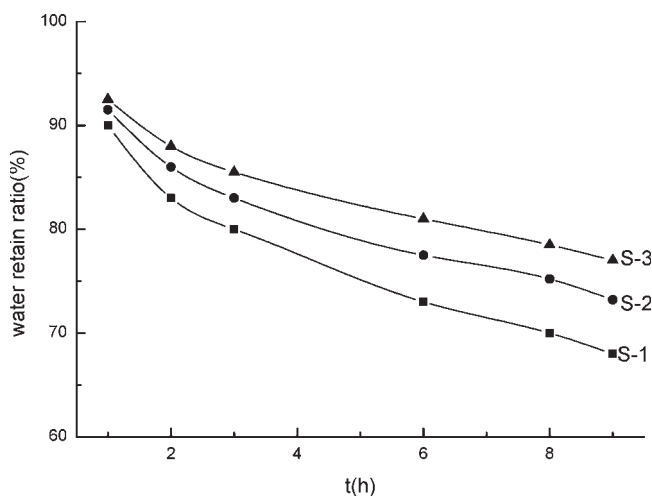Figure 4 show R of the crosslinking WSE. With increased time, R decreased. For different polymers,

TABLE V
Absorbency of CPE-*g*-PEG

| | Sample | | | | |
	1	2	3	6	7
PEG content (%)	8.78	8.02	7.54	7.26	5.69
S_e (%)	16.94	16.02	15.45	14.12	11.08

Figure 2 Influence of the absorbency time (t) on S of the crosslinking WSE.

Figure 3 Effect of absorbency temperature (T) on the equilibrium swelling ratio of the crosslinking WSE.

R of the crosslinking WSE was heavily influenced by PEG content. The higher the PEG content was, the smaller R was. For sample 1, the PEG content was 13.52%; after 3 h, R was 80.17%. However, for sample 2, the PEG content was 11.04%, and R was 83.62%. This was because the higher PEG content was, the higher the water absorbency was; therefore, more water was lost at the same temperature.

CONCLUSIONS

1. In both the grafting and crosslinking WSEs, the PEG content increased with increasing reaction time and increasing reaction temperature.
2. When the PEG content of the grafting WSE was the same as that of the crosslinking WSE, the equilibrium absorbency ratio was small, only 16.94%, but S_e of the crosslinking WSE was high, 70%.
3. The absorbency rate of the grafting WSE was slow and reached an equilibrium state after 7 days. However, for the crosslinking WSE, after only 5 days, S reached the maximum.
4. The absorbency ratio of the crosslinking WSE was influenced by the absorbency temperature; with increasing absorbency temperature, S_e increased.

Figure 4 Effect of time (t) on R of the crosslinking WSE.

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