Preparation and Properties of Water-Swellable Elastomer

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ABSTRACT: A series of water-swellable elastomers were prepared by blending chlorinated polyethylene (CPE) with poly(acrylic acid–acrylic amide) [P(AA–AM)]. The effect of component on its water-absorbent properties such as degree of swelling, swelling ratio, and weight loss ratio was discussed. Mechanical behavior of blends was also investigated. The results indicate that swelling rate of CPE/P(AA–AM) was very quick; the blend reached its equilibrium state in only 30 min. The equilibrium swelling ratio increased with increasing amounts of water-absorbent resin, the greater the amount of P(AA–AM), the higher the swelling degree. The effect of temperature on swelling ratio was very interesting, below 30°C, with an increase of temperature, the swelling ratio of blend increased, but above 30°C, with an increase of temperature, the swelling ratio decreased, indicating that this is a temperature-sensitive water-swellable elastomer. The effect of pH of solutions on the swelling behavior showed that water absorption of blends was heavily influenced by pH. The effect of different metal ions on the swelling behavior were also studied and the results showed that the absorption of blends was decreased dramatically with increasing the charge number of the cation, but was not influenced by radius and valence state of the anion. Owing to the compatibility of the amphiphilic graft copolymer (CPE-g-PEG), the equilibrium swelling ratio of the blends increased and the weight loss ratio decreased. Adding CPE-g-PEG can improve the mechanical behavior of blends. But too much grafted copolymer can worsen the tensile strength of blends. Tensile strength of blends decreased with an increase in P(AA-AM). After absorbing water, the material's strength is greater than in the dry state. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1719–1723, 2004

Key words: water-absorbent elastomer; water-absorbent resin; compatibilization; amphiphilic graft copolymer; polyethylene; poly(acrylic acid–acrylic amide)

INTRODUCTION

Water-swellable elastomer (WSE) is a newly developed sealing material that has found broad application in underwater construction.[1–3] It is a new kind of functional elastomer with elastic sealing and water-swelling properties. As a multicomponent product possesses so many advantages, the general methods used to prepare WSE are mechanical mixing[4–8] and chemical grafting.[9–10] The WSE possesses not only properties of general rubber, such as high resilience and good tensile strength, but also water-swellable ability. WSE can be swollen with water several times its own weight or volume. If the WSE is immersed in water, the hydrophilic component in it absorbs water and expansion force is exerted. The greater the absorbed water, the higher the expansion forces. When the expansion force reaches a balance value restriction of elastomer, the equilibrium swelling is achieved. It is obvious that the hydrophilic component will affect many properties of WSE. In WSE that is prepared by simple blending, hydrophilic super water-absorbent resin cannot disperse well in the hydrophobic elastomer, so it can break off from the elastomer network 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 the hydrophilic phase and the hydrophobic phase is expected to be improved greatly. So the water-absorbent and mechanical behavior may be enhanced.

Chlorinated polyethylene (CPE) was selected as the rubber matrix of water-swellable elastomer possessing a combination of properties suitable for many varied applications and having more advantages than other rubbers. Poly(acrylic acid–acrylic amide) [P(AA–AM)] possesses many advantages, such as a higher degree of absorption and absorbing rate as well as stability, so it synthesized by our as the hydrophilic component of the WSE. The amphiphilic graft copolymer (CPE-g-PEG) may serve as a compatibilizer of hydrophobic elastomer and hydrophilic super water-absorbent resin.

In this research, by multicomponent mechanical blending technology, a WSE, which is compatibilized by the graft copolymer, has been prepared using chlorinated polyethylene and poly(AA–AM) as the chief materials and an amphiphilic graft copolymer (CPE-g-PEG) as the compatibilizer. The effect of CPE-g-PEG and P(AA–AM) on water-swelling behaviors was
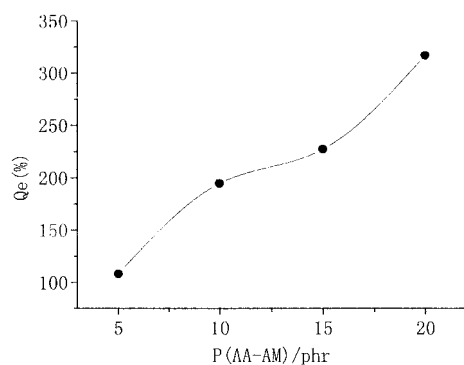
Figure 1 The influence of water-absorbent resin on swelling degree of blends.

studied. The mechanical behaviors were also investigated.

EXPERIMENTAL

Materials

CPE (Cl% = 35) was obtained from Shandong Wei-Fang Chemical Factory, Shandong Province, China. P(AA–AM) and CPE-g-PEG was synthesized according to a previous publication.[11]

Blending

CPE, P(AA–AM), and the compatibilizer, CPE-g-PEG, were masticated on an open mill at 140°C for 15 min.

The first water-absorbing and weight loss ratio

The strips of the WSE were cut out into sheets and each was weighed and immersed in distilled water at some temperature. The samples were removed at specified intervals and gently blotted with tissue paper to remove the excess water on the surface. The weight of each swollen sample was dried at 50°C to constant weight. The degree of swelling by weight Ws
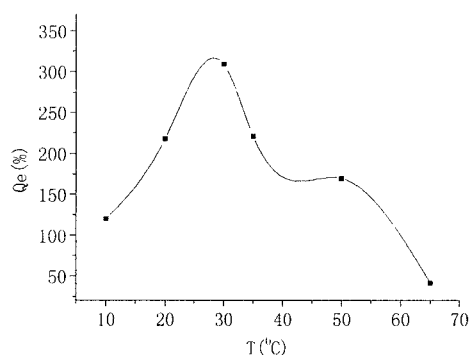
Figure 2 The influence of temperature on swelling degree of blends.
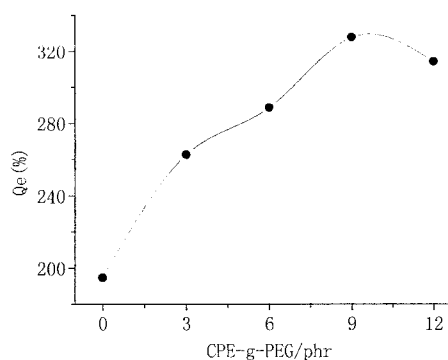
Figure 3 Effect of compatibilizer on swelling ratio of blends [CPE/P(AA–AM) (100/10)].

and the weight loss ratio WL of WSE in the sample were calculated using the following equations:

$$Q1 = (W2 - W1)/W1 \quad WL = (W1 - W3)/W1$$

Here $W1$ and $W2$ are the weights of the sample before immersing in water and after swelling to a state, respectively. $W3$ is the weight of the dried swollen sample, which has reached its equilibrium state.

The second water-absorbing and the third water-absorbing

After the first water-swelling test, the dried sample was soaked in distilled water at a given temperature. At specified time, it was taken out, the moisture on the surface was removed, and the weights was recorded until it reached the second and the third maximum water-swelling abilities.

$$Q2 = (W4 - W3)/W3 \quad Q3 = (W6 - W5)/W5$$

Where $W3$ and $W4$ were the weights of a sample before and after the second water absorption. $W5$ and $W6$ were the weights of a sample before and after the third water absorption.

Mechanical properties test

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

The standard sample was tensile tested using the standard GB1040–79 and a tensile rate of 20 mm/min.

RESULTS AND DISCUSSION

Effect of water-absorbent resin

The water-absorbent resin [P(AA–AM)] plays an important role in the degree of swelling of the water-absorbent elastomer. The curves in Figure 1 reveal that the degree of swelling increased with increasing amounts of P(AA–AM). The greater the water-absorbent resin, the higher the expansion force and the more water the water-absorbent resin can soak up.

Effect of absorbent temperature

From Figure 2 we can see, when the temperature is below 30°C, with an increase in temperature, the degree of swelling of blends increases, with the largest equilibrium swelling of 308.85%, but when the temperature is above 30°C, the degree of swelling is decreased with an increase in temperature. The temperature sensitivity of blends is related to water molecule interaction and chain segment movement. With the increase in temperature, the movement of water molecules is faster, and the hydrophobic action between chains is strengthened, thus, the degree of swelling is decreased.

Influence of the compatibilizer PEG-g-PEG on the degree of swelling

Figure 3 shows the influence of compatibilizer on the equilibrium degree of swelling. From Figure 3, we can see that, after adding CPE-g-PEG, the degree of swelling of the blend was increased. The degree of swelling increased with the increasing amount of CPE-g-PEG. This can be explained as follows: when it was added, the graft copolymer compatibilized the CPE/P(AA–AM) 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 CPE was improved and the water-absorbing and water-swelling abilities were enhanced.

Effect of absorbence time

With regard to the degree of swelling of blends, according to absorbence time, all blends swelled rapidly, reaching equilibrium within 30 min (Fig. 4). Therefore, this material can be used as a quick, high expansion
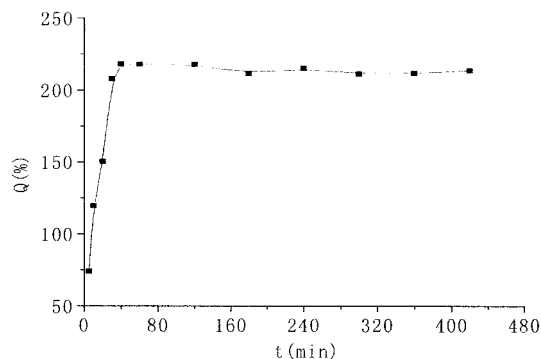

Figure 4 The influence of absorbent time on swelling degree of blends.

mealing material. The water-absorbent resin has an ion group acrylic acid and a neutral group acrylic amide. These two absorbent groups have an additive property, thus, the swelling rate is high.

Effect of salt

Table I shows the effect of different metal ions on swelling behavior. Table I shows that the degrees of swelling of blends were heavily influenced by salt aqueous solutions. The swelling degree was very small, smaller than 100%. Comparing the swelling behavior of different salts, we can see that the swelling degree in different electrolytes changed with the cation's charge number, but had nothing to do with radius and charge number of the negative ion. The Q_e of the blend was decreased dramatically with the increase in the cation's charge number. This is because the –COONa chain of the hydrophilic component P(AA–AM) produces the same ion effect in salt aqueous solution, thus making the swelling number decrease.

Influence of pH

The sample was soaked in aqueous solutions of different pH (the pH was regulate by HCl and NaOH) and the swelling abilities after soaking for 30 min by turns in different pH solutions were measured. From Figure 5, we can see by examining the range of pH values, the swelling degree varied very clearly with the change of pH. When the pH values were 0 and 14, the degree of swelling was smaller, only 50%; when

TABLE I
Effects of Ions of Electrolytes on Swelling Ratio[a]

Electrolytes	NaCl	KCl	NH$_4$Cl	(NH$_4$)$_2$SO$_4$	CaCl$_2$	Al(Cl)$_3$	Distilled water	Tap water
Swelling ratio	69.76	67.08	70.69	72.05	54.61	36.41	231.71	135

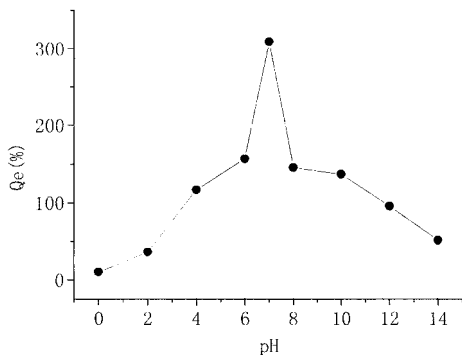[a] Concentration of electrolytes, 0.09mol/l.

Figure 5 The effect of pH on swelling ratio of blends.

the pH value was 6, the degree of swelling was 160.5%; and when the pH value was 8, the degree of swelling was 145.2%, showing greater absorption ability. Compared to soaking in distilled water; the difference was very great.

Effect of water-absorbent resin on weight loss ratio

Table II shows the weight loss ratios of blends at different water-absorbent use levels. From Table II we know that blends of different water-absorbent resins [P(AA–AM)] have weight loss. The more absorbent the resin, the greater the weight loss ratio. From this we can conclude that with only simple blending water-absorbent resin and elastomer, it is difficult to get water-absorbent elastomers that exhibit stable behavior.

Recycled use of blends

Table III indicates that the effect of CPE-g-PEG on the second and the third water-swelling abilities was similar to that on the first. Upon addition of CPE-g-PEG, compatibilization made water-absorbent resin [P(AA–AM)] disperse well and WSE enhanced water-absorbing abilities. However, compared to Qe1, Qe2 and Qe3 decreased in both the CPE/P(AA–AM) and the CPE/P(AA–AM)/CPE-g-PEG systems. This is because, after the first and the second water-swelling tests, water-absorbent resin breaks off from the blends network to a certain extent. A remainder of P(AA–AM) could still

TABLE II
Relation between Absorbent Resin and Weight Loss Ratio of Blends

Sample no.	P(AA–AM)	WL
1	5	0.734
2	10	1.228
3	15	2.217
4	20	3.678

TABLE III
Recycle Use of Blends

Sample	Qe1	Qe2	Qe3
CPE/P(AA–AM)	262.46	67.32	43.38
CPE/P(AA–AM)/CPE-g-PEG	327.49	155.66	75.91

guarantee water-absorbent abilities after loss in the first and the second water-swellable test.

Mechanical behavior

The multiple component polymer material's properties, especially mechanical behavior, is related to the blending material's components. Figure 6 shows the stress–strain curve of CPE/P(AA–AM) blends of different amounts in a dry state.

From Figure 6 and Table 4 we know that, by adding P(AA–AM) to CPE, (1) the properties of the material are simplified, belonging to soft and tough types; (2) the modulus of material is low, has greater deformation, and higher tensile strength; (3) its breakage elongation is high, all greater than 600%; and (4) after absorbing water, its tensile strength is greater than in the dry state.

Comparing Table 4, it is clear that, with an increase of P(AA–AM), tensile strength is quickly decreased. This is because CPE and P(AA–AM) are incompatible, water-absorbent resins and CPE has no linkage, dispersion is irregular, particle size is large, and phase separation is clear.

Influence of CPE-g-PEG on the mechanical behavior of blend system

After adding the compatibilizer, the tensile strength of the blend system was increased. By adding 6 phr CPE-g-PEG, tensile strength was increased to 9.30 MPa compared to 8.55 MPa (without added compatibilizer). This is obviously because the graft copolymer
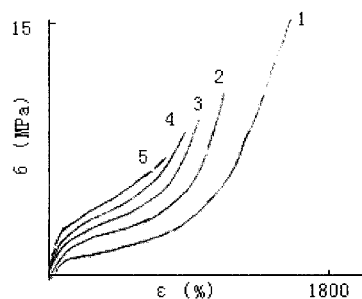

Figure 6 Stress–strain curve of CPE/P(AA–AM) in the dry state. 1, CPE; 2, CPE/P(AA–AM) (100/5); 3, CPE/P(AA–AM) (100/10); 4, CPE/P(AA–AM) (100/15); 5, CPE/P(AA–AM) (100/20).

TABLE IV
Effect of CPE/P(AA–AM) on Tensile Strength, Breakage Elongation of Blends

CPE/P(AA–AM)	100/0	100/5	100/10	100/15	100/20
Dry state σ (MPa)	13.72	9.96	8.55	7.86	6.45
ε (%)	1,613.6	1177.9	1007.6	911.3	785.2
Wet state σ (MPa)	13.98	12.26	11.66	10.72	8.80
ε (%)	1465.1	956.3	867.4	785.2	669.3

increased the cohesive force between CPE and P(AA–AM). Adding CPE-g-PEG to the blends can change the morphological structure of the fracture surface of the sample and cause an interaction between CPE and P(AA–AM). The interaction between the two phases changed the chemistry key compared to the original physical action. So the burden that the material suffer can deliver between two phases increased the suffer loading ability of the material.

From Table V, we can see the tensile strength was increased with the increase in CPE-g-PEG. But when it was excessive far beyond saturation, the change in interaction between the two phases was not clear, so the compatibilzation effect was also unclear. This is because adding excessive amounts of CPE-g-PEG causes the interface layer to become thicker and causes its constitution to change. The interaction becomes lax, the delivery stress weakens, therefore, the tensile strength decreases. The compatibilization was decided by the saturation degree of compatibilizer on the phase interface. Before reaching saturation, compatibilization was increased with the increase of graft copolymer. So the usage of the graft copolymer CPE-g-PEG as a compatibilizer should be controlled in scope. In this research, when the amount of compatibilizer (CPE-g-PEG) was 6 phr, the compatibilization effect was best.

CONCLUSION

The WSE was prepared by blending chlorinated polyethylene and water-absorbent resin [P(AA–AM)]. The influence of water-absorbent resins on its water-absorbent properties, such as degree of swelling, swelling rate, and weight loss ratio was discussed. The results indicate that the swelling rate of CPE/P(AA–AM) was very rapid, the blend reached its equilibrium state after only 30 min. The equilibrium swelling ratio increased with increasing amounts of water-absorbent resin; the greater the amount of P(AA–AM), the higher the swelling degree. According to the absorbent temperature, the degree of swelling of blends increases below 30°C, as the temperature increases, the swelling ratio of blends increases, but above 30°C, as the temperature increases, the swelling ratio decrease. The water absorption of blends was heavily influenced by pH. The effect of different metal ions on the swelling behavior was also studied and the results showed that the absorption of blends was decreased dramatically with the increasing of charge number of the cation, but was not influenced by the radius and the valence state of the anion. Generally speaking, the first water-absorbing abilities were stronger that the second and the third ones. Adding amphiphilic graft copolymer to the system can enhance the Qe1. For the compatibilization of CPE and P(AA–AM), after adding compatibilizer, Qe2, Qe3 were larger than the blend without the added CPE-g-PEG compatibilizer. Mechanical behavior of blends was also investigated. Tensile strength of blends decreased with an increase in P(AA–AM). After absorbing water, the material's strength is greater than in the dry state.

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TABLE V
Influence of CPE-g-PEG Use Level on Tensile Strength of CPE/P(AA–AM) Blends

CPE-g-PEG	0	3	6	9	12
Tensile strength in dry state σ (MPa)	8.55	8.65	9.30	8.78	8.22