

Preparation and Water-Absorbent Properties of a Water-Swellable Rubber

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ABSTRACT: A water-swallowable rubber was prepared by blending polychloroprene (CR) with crosslinked sodium polyacrylate (CSP), precipitated silica, poly(ethylene oxide) (PEO), and vulcanizing agents. The preparation process was described and the effect of composition of the water-swallowable rubber on its water-absorbent properties such as degree of swelling, swelling rate, and weight loss ratio of CSP was discussed and the optimum composition range was identified: CSP, 25–75 phr; precipitated silica, 10–50 phr; and PEO, 5–30 phr. The reinforcing filler (precipitated silica) and the water-soluble polymer (PEO) were found to improve the water-absorbent properties of water-swallowable rubber. The morphology of CSP and the silica in the rubber was studied by scanning electron microscopy, which showed that they were well dispersed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1219–1225, 1998

Key words: polychloroprene; water-swallowable rubber; silica; water-absorbent resin; poly(ethylene oxide)

INTRODUCTION

Multicomponent polymer systems have been paid great attention in both fundamental and technological fields in the last 20 years.^{1–3} In search of novel properties, of particular combinations of properties or of intermediate properties, two or more polymer materials are combined. Another major driving force for the growth of multicomponent polymer systems is the relative ease of mixing and blending, so that the product cost is usually much lower than that of synthesizing an entirely new polymer.

As a multicomponent product possesses so many advantages, it is widely prepared in industry, like preparing water-swallowable rubber. Wa-

ter-swallowable rubber is a kind of elastomeric material, which can be prepared by blending rubber, water-absorbent resin, and some other fillers, and possesses not only properties of general rubber such as high resilience, good tensile strength, but also water-swallowability. Due to the presence of the crosslinking network of rubber and the water-absorbent material, water-swallowable rubber can be swollen with water several times to its own weight or volume. If the water-swallowable rubber is immersed into water, the water-absorbent material in it absorbs water and an expansion force is exerted. The more the absorbed water, the higher the expansion force. When the expansion force reaches a balance value with that of the crosslinking restriction of the vulcanized rubber, the equilibrium swelling is achieved. The water-swallowable rubber can be widely used in caulking, sealing of gaps, stopping of water in civil engineering and construction works or the like, and the preservation of airtightness in machinery and apparatus. In recent years, many articles about water-swallow-

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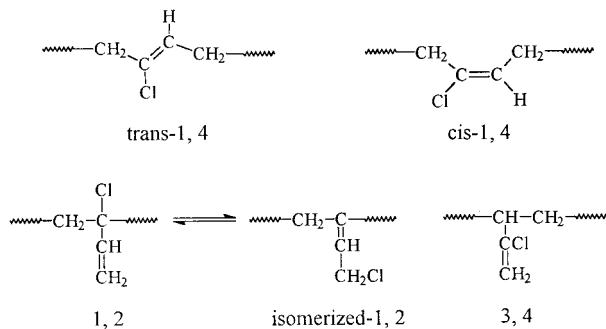


Figure 1 Main structural units in CR chain.

able rubber have been reported, but they have been mainly confined to the patent literature⁴⁻⁶ and data on the relation among the components, structure, and properties of the rubber are scarce. This article reports the preparation and the effect of the composition of a water-swelling rubber on the water-absorbent properties such as degree of swelling by weight and volume, swelling rate, and weight loss ratio of CSP, and the morphology of the blend was studied by SEM.

In this work, polychloroprene (CR) was selected as the rubber matrix of the water-swelling rubber because it is a highly versatile elastomer having a combination of properties suitable for many varied applications and having more advantages than have other rubbers. CR not only exhibits high tensile strength, resilience, and abrasion resistance but also resists deterioration by oils, solvents, weather, oxygen, ozone, heat, and flame. Vulcanization of CR with metal oxides has been well studied.⁷ CR comprises four basic structure units (Fig. 1), in which it is the highly reactive allylic chlorines from the original 1,2 units and isomerized 1,2 units that produce crosslinking via intermolecular dehydrochlorination. The formulation of the vulcanization of CR in this study was ZnO 5 phr and MgO 4 phr, of which ZnO is thought to accelerate crosslinking, yet MgO is thought to retard crosslinking. Compared to other water-absorbent resins like starch or the cellulose system, crosslinked sodium polyacrylate (CSP) possesses many advantages such as a higher degree of absorption and absorbing rate as well as stability, so it was selected as the water-absorbent resin of the water-swelling rubber. To improve the mechanical and water-absorbent properties of the rubber, precipitated silica and PEO were added into the blend system.

EXPERIMENTAL

Materials

CR (M_w 2.0×10^5) was obtained from Da Tong Rubber Factory, Da Tong, Shanxi Province, China. CSP was synthesized by ourselves⁸ (average particle diameter, 17 μm ; water absorptivity, 1200 g/g). Precipitated silica (particle size, below 200 mesh) was obtained from Tong Hua Chemical Inc., Tonghua, Jilin Province, China. PEO (M_w 2000), zinc oxide, and magnesium oxide were all chemical grade.

Blending and Vulcanizing

The samples were first prepared by blending below 50°C and then vulcanized. The details of the preparing process are as follows: CR was first placed in a Banbury mixer with a 50 mL capacity and masticated for 2 min at 30 rpm. The weighed precipitated silica, CSP, and PEO were added one by one for 3, 2, and 1 min, respectively. The other additives like zinc oxide and magnesium oxide were then added over a 2-min period, after which the sample was mixed for a further 10 min at 30 rpm. Then, the sample was removed from the Banbury mixer and passed through a two-roll mill for a few minutes.

The blended materials were vulcanized and compression-molded to thin strips (80 \times 60 \times 1 mm) for the water-absorption studies. The platens of the press were heated to 150°C. The mold cavity was filled with the mixture and covered with the top plate and placed between the two platens of the press; 3 min later, the platens were slowly pressed together until the pressure reached 150 kg/cm². Then, the sample was kept in the mold for a period of 25 min, after which the pressure was relaxed and the mold removed from the press. Thus, the strips of water-swelling rubber were obtained.

Water-absorbent Properties Tests

The vulcanized strips of the water-swelling rubber were cut into sheets with dimensions of 40 \times 20 \times 1 mm, and each was weighed and immersed into ion-exchanged water at room temperature. The samples were removed at specified intervals and gently blotted with tissue paper to remove the excess water on the surface; the weight and the volume of each swollen sample

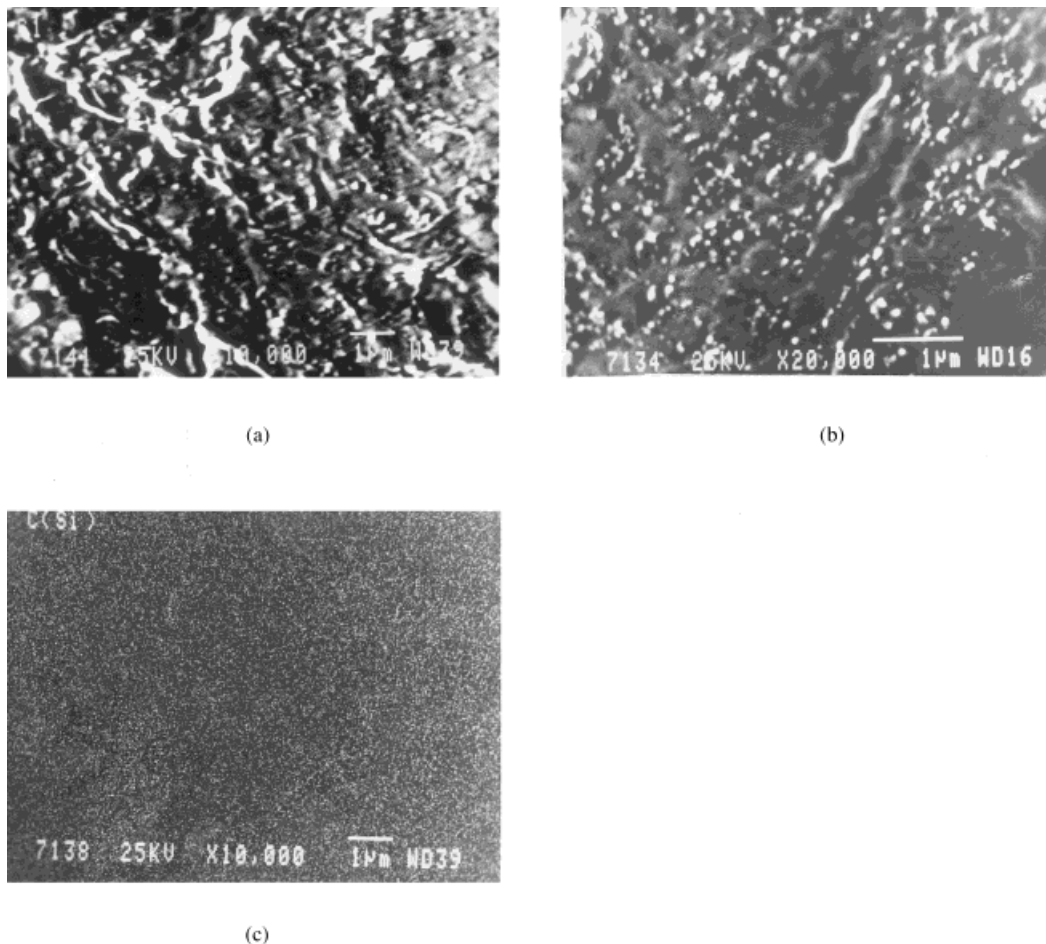


Figure 2 SEM micrographs showing dispersion for precipitated silica in the rubber: (a) unvulcanized; (b) vulcanized; (c) scanning of the element Si in the vulcanized rubber. CSP, 50 phr; silica, 30 phr; PEO, 30 phr.

were recorded. This process was repeated at several time intervals until they reached their equilibrium states and the time of swelling to the equilibrium state (T_s) indicated the swelling rate, after which the samples were dried at 50°C in a vacuum to a constant weight. The degree of swelling by weight W_s and by volume V_s and the weight loss ratio W_L of CSP in the sample were calculated by the following equations:

$$W_s = \frac{W_2}{W_1} - 1 \quad V_s = \frac{V_2}{V_1} - 1 \quad W_L = \frac{W_1 - W_3 - W_{PEO}}{W_{CSP}}$$

where W_1 and W_2 are the weights and V_1 and V_2 are the volumes of the sample before immersing into water and after swelling to a equilibrium state with water, respectively; W_3 is the weight of the dried swollen sample, which has reached its

equilibrium state; and W_{PEO} and W_{CSP} are the weights of PEO and CSP of the sheet sample.

SEM Analysis

SEM observations of water-swellaable rubber were performed on a JXA-840 scanning electron microscope. The samples were quenched in liquid nitrogen and then broken into sections and gold-sputtered onto their rough surface to increase the conductivity.

RESULTS AND DISCUSSION

Effect of Precipitated Silica

To increase hardness, tensile strength, tear resistance, abrasion resistance, and other application

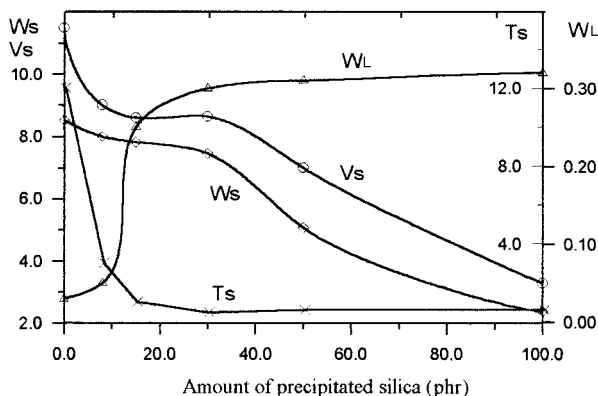


Figure 3 Plots of degree of swelling by weight (W_s) and by volume (V_s), weight loss ratio (W_L), and swelling rate (T_s : days) versus the loading precipitated silica. CSP, 50 phr; PEO, 30 phr.

properties of rubber, reinforcing fillers are commonly used.⁹ Carbon black is unquestionably the most universal reinforcing filler, both in regard to the diversity of its physicochemical characteristics and to the level of performance which its use results in. However, nonblack filler such as silica has received great attention and a better knowledge of reinforcement phenomena has been achieved in recent years.¹⁰⁻¹³ Precipitated silica can improve not only mechanical properties but also the water-absorbent properties of the water-swallowable rubber, because of its highly polar and hydrophilic surface due to the existence of numerous silanol groups, and it was chosen as the reinforcing filler of the water-swallowable rubber in our work.

SEM analysis was employed to characterize the compatibility of the blends. Figure 2 shows SEM morphology micrographs of vulcanized and unvulcanized water-swallowable rubber. The white points of micrograph (c) correspond to the silica, which was demonstrated by surface silicon scanning measurement. The morphological study shows that the silica dispersed well in the rubber matrix.

Figure 3 shows the effects of precipitated silica on the degree of swelling, the swelling rate, as well as the weight loss ratio of CSP. From curves W_s and V_s , it is clear that the more silica, the less the degree of swelling by weight and volume, which may be caused by the interaction between precipitated silica and CR. The more silica, the greater the interaction, the more the number of elastically effective entanglement points, and the higher the crosslinking density and the crosslink-

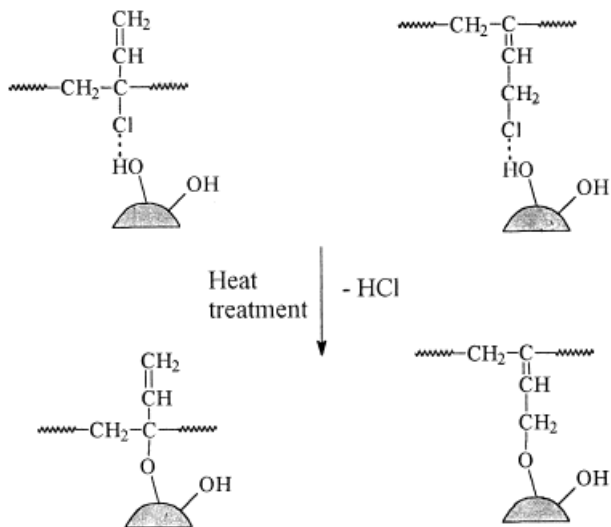


Figure 4 Probable mechanism of interaction between CR and silica surface.

ing restriction force, resulting in a lower degree of swelling. Precipitated silica, which has many highly polar and hydrophilic silanol groups on its surface, can bond with a polar polymer such as CSM¹³ and NBR,¹⁴ so it is believed that the silica surface may provide sites for bonding with polar rubber like CR through allylic chlorines. The probable mechanism for this interaction is given in Figure 4. Curve T_s shows the relationship between the amount of silica and the time of swelling to the equilibrium state. The swelling rate increased significantly with increasing silica when the amount of silica was below 20 phr, and the swelling rate changed little when it was over

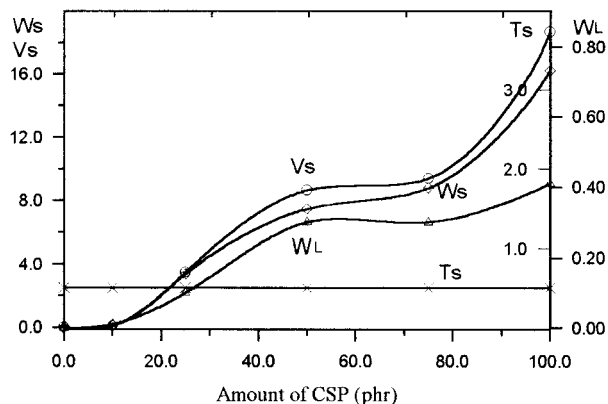


Figure 5 Plots of degree of swelling by weight (W_s) and by volume (V_s), weight loss ratio (W_L), and swelling rate (T_s : days) versus the loading CSP. Silica, 30 phr; PEO, 30 phr.

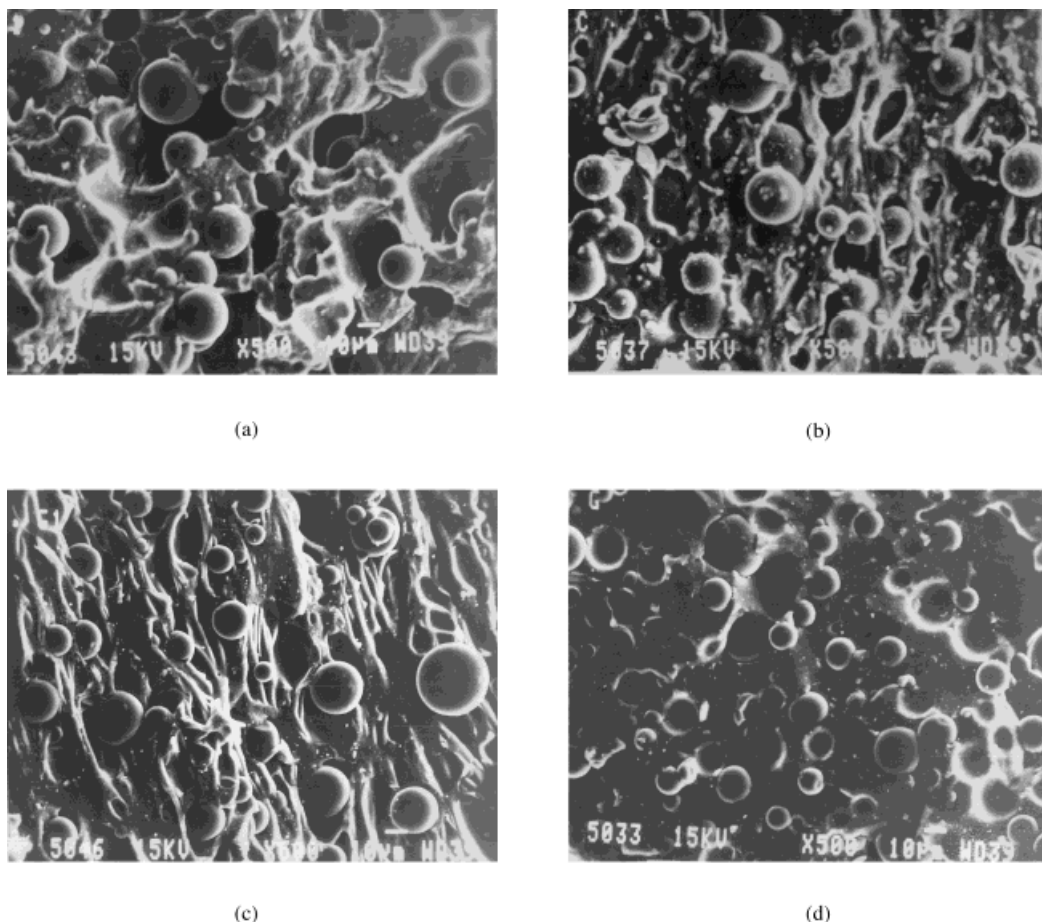


Figure 6 SEM micrographs showing dispersion for CSP in the rubber: (a) unvulcanized; (b) vulcanized (CSP, 50 phr; silica, 30 phr; PEO, 30 phr); (c) unvulcanized; (d) vulcanized (CSP, 50 phr; silica, 30 phr; PEO, 0 phr).

20 phr. Silica has numerous hydrophilic silanol groups and it accelerates the entry of water into the rubber, so the time of swelling to the equilibrium state decreases until the effect of the silanol groups reaches its limit. It can be seen from curve W_L that the weight loss ratio of CSP increased with increasing silica. Water may enter into the rubber along the hydrophilic silica which acts as a waterway, from which CSP molecules can easily separate off from the rubber.

Effect of CSP

The water-absorbent resin CSP plays an important role in the degree of swelling of the water-swelling rubber. The curves W_s and V_s of Figure 5 reveal that the degree of swelling increased with increasing the amount of CSP. The more the CSP,

the greater the water-absorbent force and the higher the degree of swelling. On the other hand, as the particle size of CSP was comparatively large ($17 \mu\text{m}$), it could weaken the vulcanization and the mesh width of the rubber network became wider and the degree of swelling increased. Curve W_L shows that the weight loss ratio increased with an increasing amount of CSP. The more loading of CSP, the more absorbed water and the higher the expansion force and the more CSP molecules expanded into the water. Curve T_s reveals that the amount of CSP had little effect on the swelling rate in the studied range, for the amount of precipitated silica (30 phr) and PEO (30 phr) in the mixture was so large that the effect of CSP could be negligible. The samples all swelled to their equilibrium states in 0.5 day.

Figure 6 shows the morphology micrographs of water-swelling rubber with different composi-

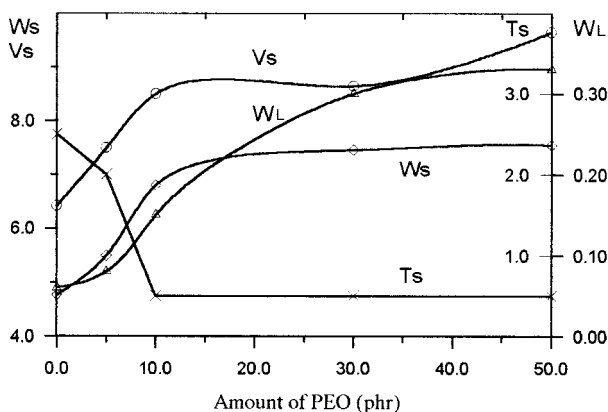


Figure 7 Plots of degree of swelling by weight (W_s) and by volume (V_s), weight loss ratio (W_L), and swelling rate (T_s ; days) versus the loading PEO. CSP, 50 phr; silica, 30 phr.

tions. It can be seen that CSP particles dispersed well in the rubber and no aggregation occurred.

Effect of PEO

Although the water-swallowable rubber prepared from rubber and water-absorbent resin possesses water-swallowability, its swelling rate is usually low and no satisfactory results can be obtained. If some PEO is included in the rubber formulation, the water-absorbent properties can be much improved. The effects of PEO on the water-absorbent properties are given in Figure 7. From the curves W_s and V_s , it can be seen that the degree of swelling by volume or weight increased with increasing PEO when it was 0–30 phr, yet when it was over 30 phr, the degree of swelling changed little with increasing PEO. The effect of PEO on the degree of swelling was much less than that of CSP, but PEO could significantly influence the swelling rate, which is shown in curve T_s . The time of swelling to the equilibrium state decreased from 4.5 to 0.5 day as the amount of PEO increased from 0 to 10 phr. After that, the swelling rate was improved little with increasing PEO. As can be understood by the diffusion process of the swelling, PEO is a water-soluble polymer and can act as a waterway of the water-swallowable rubber, so PEO made it favorable for water to diffuse into the rubber, and the degree of swelling and the swelling rate both increased until they reached maximum values. On the contrary, with increasing PEO, the loss weight ratio of CSP increased,

as CSP molecules could easily be lost along the waterway, as shown in curve W_L in Figure 7.

From the micrographs of SEM in Figure 6, it is obvious that there is a great difference between the micrographs of the sample with PEO and those of the one without PEO. The vulcanization can much reduce the extent of crystallization of CR,⁹ but it has little effect on that of PEO. The difference between the micrographs of (c) and (d) may result from the change of crystallinity of CR due to the vulcanization. The difference between the micrographs of (a) and (b) is not yet obvious, as may result from the presence of crystalline PEO.

CONCLUSIONS

The preparation procedure for the water-swallowable rubber by a Banbury two-roll mill is practically useful, with the additives like precipitated silica and CSP having a good dispersion in the blend, which was shown from the micrographs of SEM. A probable mechanism for the interaction between precipitated silica and CR was proposed: that the silanol groups of the silica should bond with the allylic chlorines of CR as a result of heat treatment. The water-absorbent properties of the rubber are influenced not only by the loading water-absorbent resin (CSP) but also by the reinforcing filler (precipitated silica) and the water-soluble polymer (PEO) in it. Precipitated silica and PEO can increase the swelling rate of the rubber significantly. In considering the degree of swelling, swelling rate, and weight loss ratio, the optimum composition was CSP, 25–75 phr; precipitated silica, 10–50 phr; and PEO, 5–30 phr. In the application of the water-swallowable rubber, its mechanical properties before and after swelling with water and its reuse are also important features, as will be discussed later.

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