Effects of Fillers on Mechanical Properties of a Water-Swellable Rubber

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ABSTRACT: The mechanical properties of the water-swellable rubber prepared by blending polychloroprene with precipitated silica, crosslinked sodium polyacrylate, polyethylene oxide, and vulcanizing agents—such as stress at break, strain at break, modulus, energy at break, and hardness—were studied before and after swelling with water. The results showed that the addition of the reinforcing filler (precipitated silica) increased the mechanical properties, while adding crosslinked sodium polyacrylate decreased the mechanical properties, although it could improve water-absorbent properties of the water-swellable rubber. If some polyethylene oxide was included in the rubber formulation, the water-absorbent properties and the mechanical properties of the rubber both increased; but, with the increase of more polyethylene oxide, the mechanical properties decreased. Wide-angle X-ray diffracting analysis was conducted to study the crystalline behavior of the rubber, which showed that the crystallinity of the vulcanized polychloroprene increased first and then decreased with an increase in the amount of polyethylene oxide. The crosslink density of the rubber was calculated by the Flory–Rehner equation. The mechanical strength of the rubber significantly decreased after swelling with water, compared with that before swelling with water. The morphology of blends was shown by scanning electron microscopy graphs. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 577–584, 1999

Key words: polychloroprene; crosslinked sodium polyacrylate; water-swellable rubber; mechanical properties; crosslink density

INTRODUCTION

Water-swellable rubber is a kind of elastomeric material, which possesses not only properties of general rubber (such as high resilience and good tensile strength), but also the water-swellability. When contacting with water, water-swellable rubber can be swollen, and a good result of sealing can be achieved when used as water-proof sealing material, so it 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.[1–3] In the case of its water-proof applications, it demands that water-swellable rubber should have excellent water-absorbent properties, as well as mechanical properties.

In our laboratory, water-swellable rubber was prepared by blending a rubber matrix, a water-absorbent resin, and some other fillers. Polychloroprene was selected as rubber matrix of the water-swellable rubber, because it is a highly versatile elastomer having a combination of properties suitable for many varied applications and having more advantages than other rubbers. Polychloro-

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prene not only exhibits high tensile strength, resilience, and abrasion resistance, but also resists deterioration by oils, solvents, weather, oxygen, ozone, heat, and flame. Compared with the other water-absorbent resins like starch or 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 water-swellable rubber. To improve mechanical and water-absorbent properties of the rubber, precipitated silica and polyethylene oxide were added into the blend system. In our previous paper,[4] the water-absorbent properties of the rubber was investigated and the results showed that CSP played a critical role in the water-absorbent properties and the addition of precipitated silica and polyethylene oxide could improve swelling rate greatly. This article deals with the effect of fillers on the mechanical properties of the rubber.

EXPERIMENTAL

Materials

Polychloroprene (G type, [η] 1.38) was obtained from Da Tong Rubber Factory, People's Republic of China. CSP was synthesized by ourselves (average particle diameter = 17 μm; water absorptivity = 1200 g g^{-1}).[5] Precipitated silica (particle size: below 200 mesh) was obtained from Tong Hua Chemical, Inc., People's Republic of China. Polyethylene oxide (molecular weight = 2000) and vulcanizing agents (zinc oxide and magnesium oxide) were all chemical grade.

Preparation of Samples

Polychloroprene and the fillers were blended with a Banbury mixer and a two-roll mill. The blend was then vulcanized and compression-molded into thin strips following the method described herein.[4]

Measurement

Degree of Swelling with Water

The vulcanized strips of the water-swellable rubber were cut to sheets with dimensions of 40 $\times$ 20 $\times$ 1 mm, and each was weighed and immersed into ion-exchanged water at room temperature until they reached their equilibrium states. The degree of swelling by weight Ws was calculated by the following equation:

$$W_s = \frac{W_2}{W_1} - 1$$

where W_1 and W_2 are the weights of the sample before immersing into water and after swelling to a equilibrium state with water, respectively.

Scanning Electron Microscopic (SEM) Analysis

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

Mechanical Property

Stress at break, strain at break, modulus and energy at break of the samples were studied using an Instron universal tensile tester (model 1121). Hardness data were obtained from Shore A sclerometer.

Crystalline Behavior

Wide-angle X-ray diffracting (WAXD) patterns of the rubber were recorded on a D/max-rA X-ray diffractometer using CuKα radiation at 50 kV and 150 mA.

Crosslink Density

The Flory–Rehner equation[6] was used to calculate crosslink density from V_r, the volume fraction of rubber in the swollen gel measured by swelling the rubber in benzene following the procedure described by Elise and Welding.[7] The benzene polychloroprene interaction of 0.4284 was calculated from the literature data.[8]

RESULTS AND DISCUSSION

Effect of Precipitated Silica

To increase hardness, tensile strength, tear resistance, abrasion resistance, and other application properties of rubber, reinforcing fillers are commonly used.[9] Carbon black is unquestionably the most universal reinforcing filler, both with regard to the diversity of its physicochemical character-

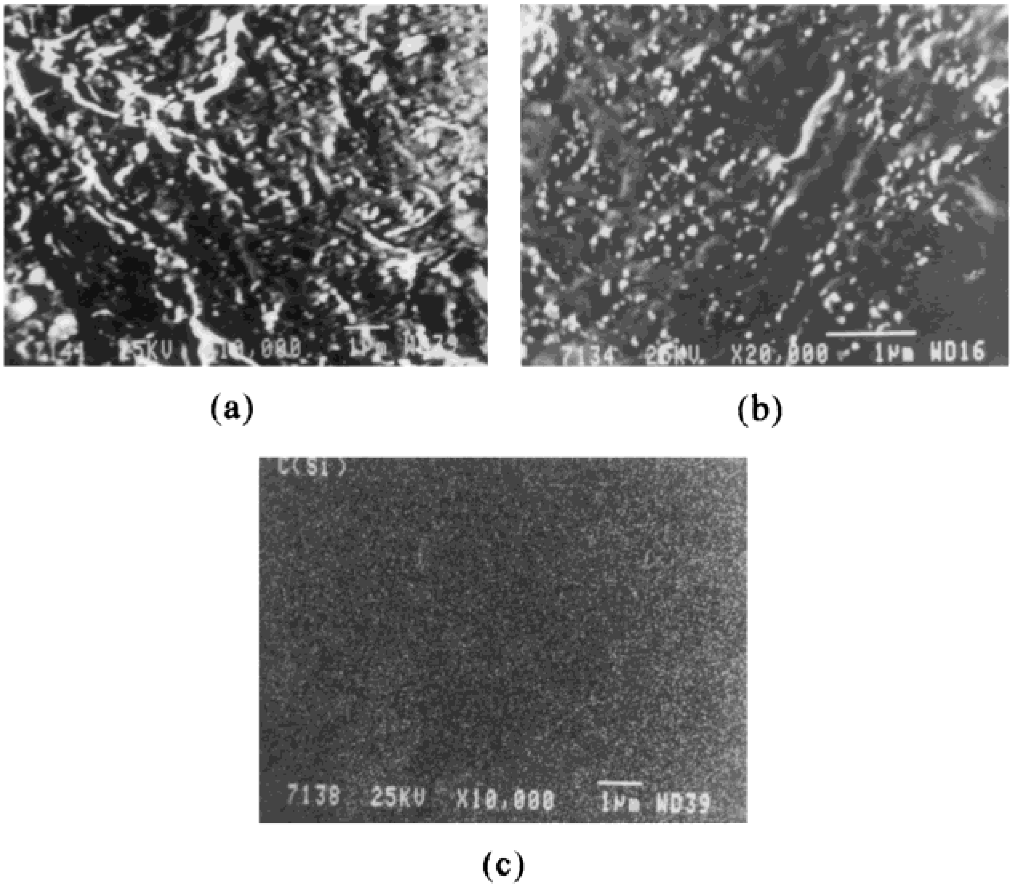

Figure 1 SEM micrographs showing dispersion of precipitated silica in the rubber. (a) Unvulcanized; (b) vulcanized; and (c) scanning of the element Si in vulcanized rubber. CSP, 50 phr; silica, 30 phr; polyethylene oxide, 30 phr.

istics, and to the level of performance that its use results in. However non-black 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 water-absorbent properties of the water-swellable rubber, because of the highly polar and hydrophilic surface due to the existence of numerous silanol groups, and was chosen as the reinforcing filler of the water-swellable rubber in our work.

Table I Effect of Precipitated Silica on Mechanical Properties of Rubber Before Swelling (CSP, 50 phr; Polyethylene Oxide, 30 phr)

	Precipitated Silica Loading (phr)				
Properties	0	15	30	50	100
Stress at break (Mpa)	4.5	5.1	5.6	5.9	8.5
Strain at break (%)	1267	826	640	484	15
Modulus (Mpa)	9.6	20.4	25.0	62.3	132.4
Energy at break (MJm^{-3})	2.4	2.5	2.2	2.1	0.1
Hardness (Shore A)	72	80	84	88	96
Crosslink density ($\times 10^{-5}$ mol mL^{-1})	4.82	6.38	10.16	12.20	19.09

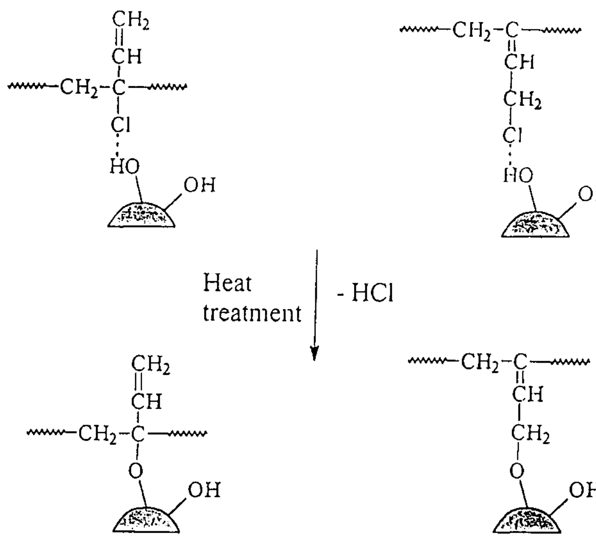

Figure 2 Probable mechanism of interaction between polychloroprene and the silica surface.

SEM analysis was used to characterize the compatibility of blends. Figure 1 shows the SEM morphology micrographs of vulcanized and unvulcanized water-swellable rubber. The white points of the micrograph [Fig. 1(c)] correspond to the silica, which was demonstrated by the surface silicon scanning measurement. The morphological study shows that the silica dispersed well in the rubber matrix.

Mechanical properties of the water-swellable rubber with a different content of precipitated silica before swelling are presented in Table I. With an increase of the content of precipitated silica from 0 phr to 100 phr, the stress at break increased from 4.5 MPa to 8.5 MPa; modulus increased from 9.6 MPa to 132.4 MPa, in which there was a significant increase when the precipitated silica loading was >50 phr; hardness increased from 72 to 96. Energy at break varied little when the content of precipitated silica was <50 phr, but there was a sharp decrease to 0.1 MJm^{-3} when it increased to 100 phr, where the rubber sample was too brittle to need much energy to be broken. Similarly, the strain at break decreased a lot when the precipitated silica loading was >50 phr.

From previously described data, it can be seen that the strength of the rubber increased with an increase in the amount of precipitated silica, which could be caused by the interaction between polychloroprene and precipitated silica. Precipitated silica, which has many highly polar and hydrophilic silanol groups on its surface, can bond with polar polymer, such as chlorosulfonated polyethylene[13] and acrylonitrile-butadiene rubber,[14] so it is believed that the silica surface may provide sites for bonding with polar rubber-like polychloroprene through allylic chlorines. The probable mechanism for this interaction is given in Figure 2. The more the amount of precipitated silica, the stronger the interaction between polychloroprene and precipitated silica, and the greater the strength of the rubber. The interaction was verified by the crosslink density calculated by the Flory–Rehner equation. The crosslink density of the rubber increased with an increase of the amount of precipitated silica, as observed in Table I.

Table II shows the effect of precipitated silica on the mechanical properties of the swollen samples. Stress at break, strain at break, modulus, energy at break, and hardness all increased with an increase of the content of precipitated silica. This is related to the degree of swelling. The more the precipitated silica, the less the absorbed water, the better the mechanical properties. It is noticeable that the mechanical properties of the

Table II Effect of Precipitated Silica on Mechanical Properties of the Rubber After Equilibrium Swelling (CSP, 50 phr; Polyethylene Oxide, 30 phr)

	Precipitated Silica Loading (phr)				
Properties	0	15	30	50	100
Stress at break (Mpa)	0.35	0.40	0.45	0.80	1.45
Strain at break (%)	305	320	332	390	524
Modulus (Mpa)	0.14	0.16	0.16	0.21	0.37
Energy at break (MJm^{-3})	0.08	0.10	0.12	0.26	0.55
Hardness (Shore A)	8	10	11	20	35
Degree of swelling	8.5	7.8	7.5	5.1	2.4

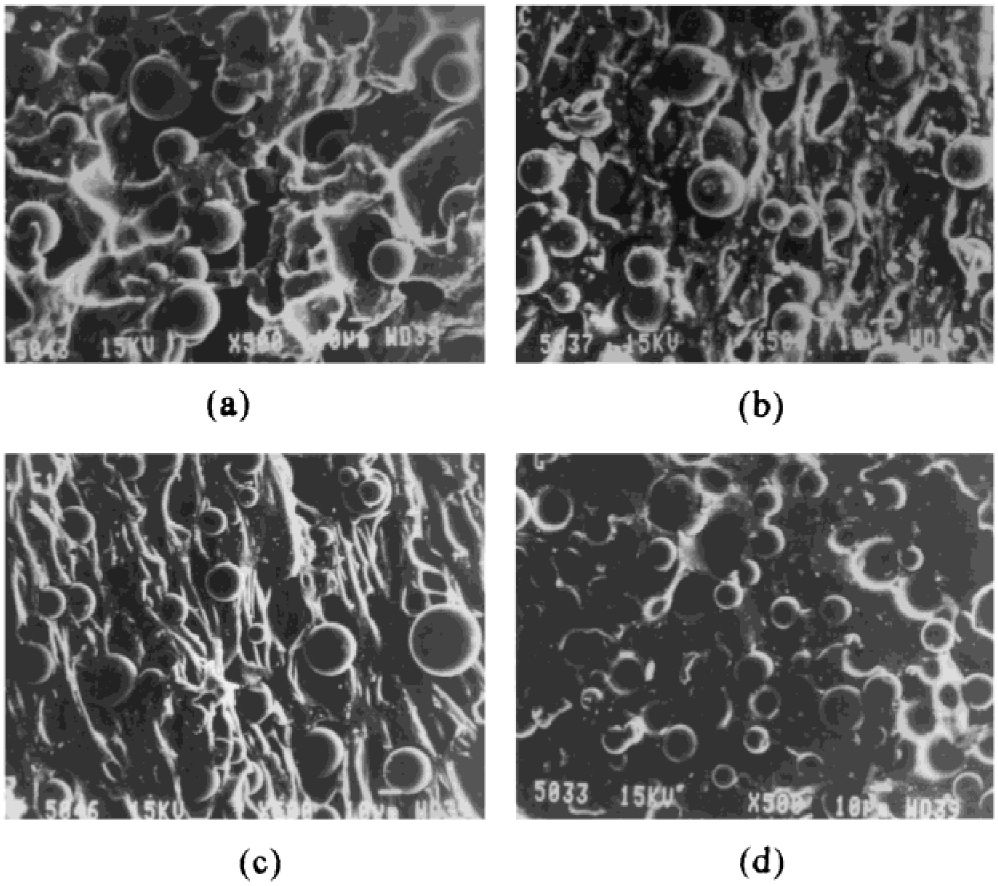

Figure 3 SEM micrographs showing dispersion of CSP in rubber. (a) Unvulcanized and (b) vulcanized (CSP, 50 phr; silica, 30 phr; polyethylene oxide, 30 phr). (c) Unvulcanized and (d) vulcanized (CSP, 50 phr; silica, 30 phr; polyethylene oxide, 0 phr).

swollen sample decreased a lot, compared with that before swelling. In the swollen sample, water served as a plasticizer and weakened the intermolecular forces between polychloroprene chains; thus, the mechanical strength decreased. The higher the degree of swelling, the lower the mechanical strength.

Effect of CSP

Figure 3 shows the morphology micrographs of water-swellable rubber with different compositions. It can be seen that CSP particles dispersed well in the rubber, and no aggregation occurred.

In Table III, mechanical properties of the rub-

Table III Effect of CSP on Mechanical Properties of the Rubber Before Swelling (Precipitated Silica, 30 phr; Polyethylene Oxide, 30 phr)

	CSP Loading (phr)				
Properties	0	25	50	75	100
Stress at break (Mpa)	7.8	6.6	5.6	5.0	4.2
Strain at break (%)	808	695	640	601	583
Modulus (Mpa)	20.2	22.4	25.0	27.0	27.5
Energy at break (MJm^{-3})	3.6	3.1	2.2	1.9	1.5
Hardness (Shore A)	78	80	84	86	87
Crosslink density ($\times 10^{-5}$ mol mL^{-1})	7.67	8.86	10.16	10.16	10.30

Table IV Effect of CSP on Mechanical Properties of the Rubber After Equilibrium Swelling (Precipitated Silica, 30 phr; Polyethylene Oxide, 30 phr)

Properties	CSP Loading (phr)				
	0	25	50	75	100
Stress at break (Mpa)	7.4	1.2	0.45	0.35	0.10
Strain at break (%)	1333	450	332	304	150
Modulus (Mpa)	0.55	0.28	0.16	0.14	0.10
Energy at break (MJm^{-3})	3.3	0.44	0.12	0.08	0.02
Hardness (Shore A)	71	29	11	8	4
Degree of swelling	0	3.4	7.5	8.8	16.2

ber with different contents of CSP before swelling are presented. The stress at break decreased with an increase in CSP loading. Like stress at break, strain at break and energy at break also followed the same trend, showing a decrease with an increase in the content of CSP, which was the result of an increase in flaws in the vulcanizate. The more the amount of CSP (nonadhering filler), the more the flaws in the rubber, and the lower the strength of the rubber. Correspondingly, the crosslink density should decrease with an increase in CSP; but, in the experiment, it increased, which is shown in Table III. This is caused by the method of measuring crosslink density. Because CSP is a hydrophilic polymer and heavily repels nonpolar solvent (benzene), the absorbed benzene in the rubber reduced with an increase in the amount of CSP and the apparent crosslink density increased. The modulus and hardness increased with an increase in CSP, because of the high rigidity and hardness of the crosslinked polymer. However, the trend was not as significant as that of precipitated silica.

The effect of CSP on mechanical properties of the swollen samples is also different from that of the samples before swelling. Table IV shows that the more the amount of CSP, the higher the degree of swelling and the worse the mechanical properties. The stress at break, strain at break, modulus, energy at break, and hardness all considerably reduced with an increase in the content of CSP.

Effect of Polyethylene Oxide

The mechanical properties of the water-swellable rubber with a different content of polyethylene oxide before swelling are shown in Table V. The stress at break and strain at break decreased with an increase of polyethylene oxide and decreased a lot when it was >10 phr. When there was no polyethylene oxide in the sample, the modulus was only 12.2 MPa, whereas when 10 phr polyethylene oxide was added into the blend, it increased considerably to 26.2 MPa, and when polyethylene oxide increased more, it decreased.

Table V Effect of Polyethylene Oxide on Mechanical Properties of the Rubber Before Swelling (CSP, 50 phr; Precipitated Silica, 30 phr)

Properties	Polyethylene Oxide Loading (phr)			
	0	10	30	50
Stress at break (Mpa)	9.4	9.0	5.6	3.2
Strain at break (%)	1206	1070	640	591
Modulus (Mpa)	12.2	26.2	25.0	20.1
Energy at break (MJm^{-3})	4.6	4.7	2.2	1.2
Hardness (Shore A)	76	86	84	80
Crosslink density ($\times 10^{-5}$ mol mL^{-1})	13.64	13.64	10.16	7.9

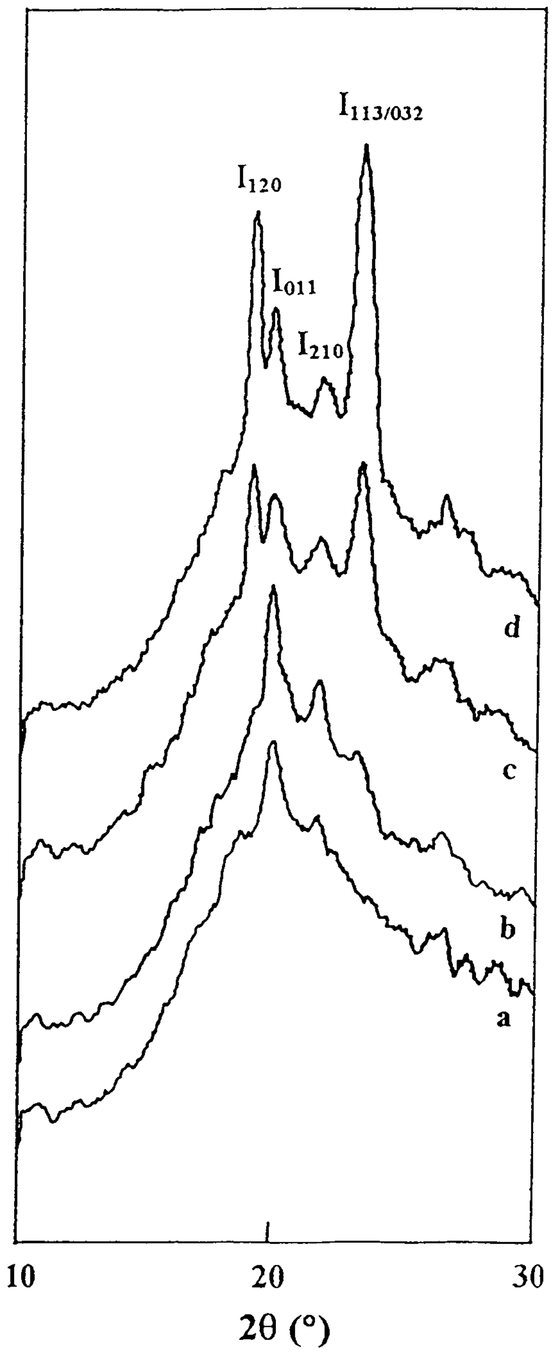

Figure 4 WAXD patterns of water-swellable rubber with 50 phr CSP, 30 phr precipitated silica, and different amounts of polyethylene oxide: (a) 0 phr, (b) 10 phr, (c) 30 phr, and (d) 50 phr.

The energy at break and hardness had the same trend that they increased to a maximum value at 10 phr polyethylene oxide and then decreased. As a result of the change of the crystallinity of the rubber due to the addition of polyethylene oxide: the higher the crystallinity, the higher the mechanical strength of the rubber. Figure 4 shows the WAXD patterns of the samples with a different amount of polyethylene oxide. The crystalline peaks at 20.0° and 21.8° correspond to the 011 and 210 planes of the vulcanized polychloroprene[15,16] and the crystalline peaks at 19.1° and 23.4° correspond to the 120 and 113/032 planes of polyethylene oxide,[17] respectively. It can be seen from Figure 4 that the addition of polyethylene oxide had a significant effect on the crystallinity of the vulcanized polychloroprene. The crystallinity of the rubber increased a lot when 10 phr polyethylene oxide was added and then decreased some with increasing more polyethylene oxide into the blend, as can be seen from the changes of the crystalline peaks of the vulcanized polychloroprene. They became more intense and sharper, and then weaker with an increase in the amount of polyethylene oxide. But, when more polyethylene oxide was loaded, it could not only decrease the intermolecular forces of the rubber acting as a plasticizer, but also led to more flaws in the rubber and lower crosslink density, so the mechanical properties decreased, which coincided with the decrease of crosslink density shown in Table V.

Table VI shows the effect of polyethylene oxide on the mechanical properties of swollen samples. Like that of precipitated silica and CSP, mechanical properties of the swollen samples decreased with an increase in the amount of polyethylene oxide, due to a increase of the absorbed water.

CONCLUSIONS

Precipitated silica had a marked effect on the mechanical properties and degree of swelling of the water-swellable rubber. Considering mechanical properties of the samples before swelling and after equilibrium swelling, the content of precipitated silica is preferred to 15–50 phr. The amount of CSP in the sample played a critical part in swellability of the water-swellable rubber, but the mechanical properties of the rubber reduced with an increase in the amount of the water-absorbent resin. To obtain a useful water-swellable rubber, the content of CSP is preferred to 25–50 phr. According to the effect of polyethylene oxide on the mechanical properties and degree of swelling of the water-swellable rubber, the content of polyethylene oxide is preferred to $\sim$ 10 phr.

Table VI Effect of Polyethylene Oxide on Mechanical Properties of the Rubber After Equilibrium Swelling (CSP, 50 phr; Precipitated Silica, 30 phr)

	Polyethylene Oxide Loading (phr)			
Properties	0	10	30	50
Stress at break (Mpa)	0.90	0.55	0.45	0.43
Strain at break (%)	395	350	332	380
Modulus (Mpa)	0.22	0.18	0.16	0.16
Energy at break (MJm^{-3})	0.28	0.14	0.12	0.13
Hardness (Shore A)	21	13	11	10
Degree of swelling	4.8	6.8	7.5	7.6

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