Study on Foaming Water-Swellable EPDM Rubber

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ABSTRACT: A foaming ethylene propylene diene terpolymer (EPDM) water-swellable rubber (WSR) was prepared using the multicomponent mechanical blending technology. The morphology of unfilled and silica-filled foaming EPDM WSR was studied from micrographs. The average cell size, maximum cell size, and cell density of the foaming WSR had a peak value with a 4-phr foaming agent loading in both unfilled and silica-filled WSR. The addition of silica made the average cell size and maximum cell size decrease and the cell uniform. With incorporation of silica, the tensile strength of the unfoaming WSR increased three times, while that of the foaming WSR increased about six times before immersing it into water. After water-swelling, the mechanical properties of both the unfilled WSR and silica-filled unfoaming WSR decreased, but that of the silica-filled foaming WSR increased. The silica filler accelerated the water-swelling rate and cut down the water-swelling equilibrium time at the same time. The foaming WSR had a better volume water-swelling ratio than that of the unfoaming WSR in both the unfilled and silica-filled WSR. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3712–3717, 2002

Key words: rubber; swelling; mixing; mechanical properties

INTRODUCTION

Many studies have paid more and more attention to the application of water-swellable rubber (WSR).[1–9] WSR was prepared by blending the rubber matrix, including natural rubber,[10] chlorohydrin rubber,[11,12] nitrile rubber,[13] and EPDM rubber,[14] hydrophilic super-water-absorbent resin containing crosslinking polyacrylate (CPA),[15,16] and some other fillers. By connecting with the WSR, the H_2O molecule came into the WSR by physical actions such as diffusion, capillarity, and surface adsorption, forming a strong affinity with hydrophilic water-absorbent resins. Then, the WSR expanded continuously to the water-swelling equilibrium.

Foaming rubber has excellent properties including low density, a low heat transmitting ratio, good plasticity and compressibility on the basis of the presence of a great many cells, and high elasticity, which is the inherent property of an elastomer.[17–20] Foaming WSR is a new elastic sealing material based on traditional WSR. It possesses not only properties of general rubber such as high resilience and elasticity, but also a better deforming ability during sealing.

The ethylene propylene diene terpolymer (EPDM) has been widely used in the construction and automobile industries. It possesses excellent aging properties and the resistance to deterioration and retains good physical and mechanical properties even at higher temperature and in polar media. CPA, used as a super-water-absorbent resin, has a high water-retention ability and stable structure as it neither decomposes nor denaturalizes below 300°C. Dinitroso pentamethylene tetramine (DNPT) has been used extensively in the plastics and rubber industries. It decomposes irreversibly and exothermically at 130–205°C to give a gas yield of 260 mL/g. The main gaseous decomposition product is nitrogen.

A study on foaming WSR has not been reported yet. To understand the effect of the foaming agent and the precipitated silica filler on WSR in more detail, we prepared foaming WSR using the multicomponent mechanical blending technology and investigated in this article the cell properties, mechanical properties, and water-swelling abilities caused by these two factors.

EXPERIMENTAL

Materials

EPDM 4045 (ethylene content 55–64%, diene content 6.6–9.5%) was manufactured by the Jilin Chemical Industrial Co. Ltd,, (Jilin, China). CPA, with a distilled water absorptivity of 350 g/g, a water-absorbing rate less then 15 s, and a grain size of 74–840 μm, was donated by the Lishu Chemical Factory (Jilin, China). Precipitated silica was purchased from the Tonghua Second Chemical Factory (Jilin, China). Its character-

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TABLE I
Formulation of Unfilled and Silica-filled WSR

	CS1	CS2	CS3	CS4	CF5	CF6	CF7	CF8
EPDM (phr)	100	100	100	100	100	100	100	100
CPA (phr)	30	30	30	30	30	30	30	30
Silica (phr)	0	0	0	0	30	30	30	30
DNPT (phr)	0	2	4	6	0	2	4	6

Basic recipe: ZnO 2 phr; stearic acid: 2 phr; DCP: 2 phr.

istics were as follows: specific gravity, 2.0; BET surface area, 198 m^2/g; and grain size, below 200 mesh. DNPT was manufactured by the Ji City Chemical Factory (Tianjin, China). Dicumyl peroxide (DCP) was purchased from the Shanghai Chemical Co. (Shanghai, China).

Compounding and sample preparation

According to the formulations in Table I, EPDM rubber was masticated on an open mill (160 mm, linear rate of front roll 10.97 m/min, linear rate of front roll to rear roll 1/1.35) for 2 min and then a small amount of zinc oxide, stearic acid, CPA, precipitated silica, the foaming agent DNPT, and the crosslinking agent DCP were added in proper order. These components were mixed continuously to apparent homogeneity. The compounded rubber stock was sheeted out and stabilized to remove the strain overnight (24 h if possible) before being vulcanized and foamed.

Vulcanization and foaming

The mixed compound was put in an $80 \times 60 \times 2\text{-mm}^3$ mold, preheated for 5 min, and cured for 20 min at 140 $\pm$ 1°C to obtain a closed-cell rubber sheet. After the press was over, the mold was taken out and immediately the rubber stock foamed.

Morphology

The micrographs were obtained by an XPS microscope from the Shanghai Optics Instrument Factory.

Test procedures

The mechanical properties, such as tensile strength and elongation at break, of the dumbbell-shaped samples were carried out on a computerized Instron-1121 testing machine. The test was performed at room temperature (25 $\pm$ 2°C). At least five specimens for each analysis were tested and the mean value was considered for the study.

Measurement of the water-swelling abilities

The sample was measured and immersed into ion-exchanged water at room temperature. After a period of time, it was taken out and the volume was measured after removing the surface water until the sample reached the water-swelling equilibrium. The volume water-swelling ratio, Sv %, was calculated using the following expression:

$$Sv\% = (V_2 - V_1)/V_1 \times 100\% \quad (1)$$

where V_1 and V_2 are the volume of a sample before and after swelling with water, respectively.

RESULTS AND DISCUSSION

Morphology of razor-cut surfaces and cell properties

Micrographs of razor-cut surfaces of unfilled and silica-filled foaming WSR are illustrated in Figure 1. These micrographs were analyzed in terms of the average cell size, maximum cell size, and cell density (number of cells per unit volume of the foaming WSR). The values of the average cell size and maximum cell size are shown in Table II. The cell density of foaming WSR was calculated and is plotted in Figure 2 based on the data of the cell size and WSR density. For the foaming rubber system, the relation used for the calculation was given by Wang[21]:

$$N = 6(\rho_s/\rho_f - 1)/\pi d^3 \quad (2)$$

where N is the number of cells per unit volume of foaming rubber; d, the average cell diameter; and ρ_s and ρ_f, the density of the solid rubber (unfoamed rubber) and foamed EPDM rubber, respectively.

For foaming rubber, the ratio of the foaming agent to the crosslinking agent has an essential influence on the cell structure and property. In this article, the crosslinking agent DCP loading was fixed at 2 phr. The variety of the foaming agent loading meant different ratios of the foaming agent to the crosslinking agent. In both the unfilled and silica-filled foaming WSR, the average cell size and maximum cell size

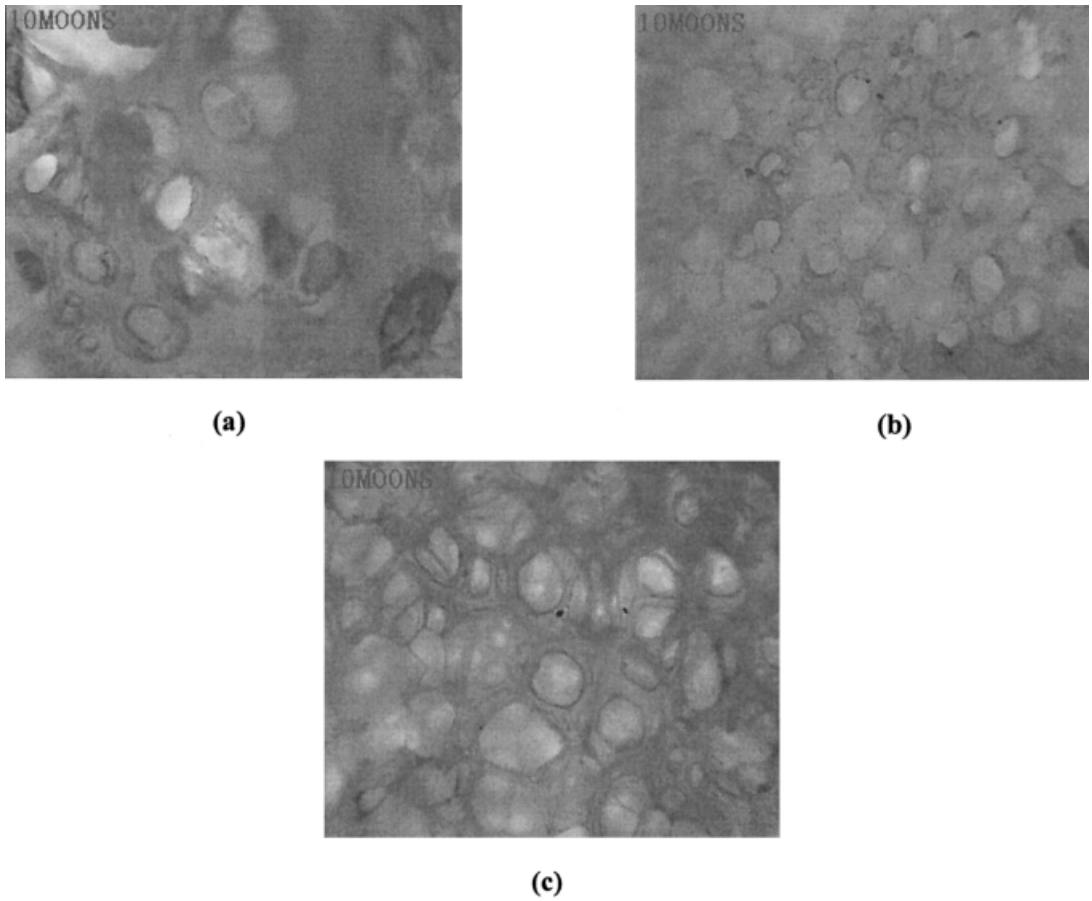

Figure 1 Photographs of razor-cut surfaces of foaming WSR (×40): (a) CS3, (b) CF7, (c) CF8.

decreased with increasing foaming agent loadings from 2 to 4 phr. But when the foaming agent was 6 phr, the average cell size and maximum cell size increased. The cell density had the trend of increasing first and then decreasing. According to the peak value in Figure 2, the optimum value of the foaming agent loading was 4 phr, which is also a suitable ratio of the foaming agent to the crosslinking agent. When the foaming agent loading was less than 4 phr, the decomposing rate of the crosslinking agent was a little faster than that of the foaming agent, so a stable cell structure was formed. When the foaming agent loading was more than 4 phr, the decomposing rate of the crosslinking agent was much slower than that of the foaming agent. Cell walls with weak intension were easily broken. Two or more cells combined to one, so the cell size increased [Fig. 1(b, CF7) and Fig. 1(c, CF8) were compared] and the cell density decreased. It is noticeable in Figure 2 that rate of the cell density increase or decrease was more remarkable in silica-filled WSR as compared with unfilled WSR. This was because silica caused an increase of the melting viscosity. The cell growth is retarded by a high melting viscosity. Micrographs demonstrated that the presence of silica made the cell size smaller and uniform [Fig. 1(a, CS3) and Fig. 1(b, CF7) were compared].

Physical properties

The physical properties involved the relative density, tensile strength, and elongation at break. In Figure 3, the relative density (ρ_f/ρ_s) decreased with an increasing foaming agent loading for both the unfilled and silica-filled WSR. The relative density decreased more

TABLE II
Cell Properties of Unfilled and Silica-filled WSR

	CS1	CS2	CS3	CS4	CF5	CF6	CF7	CF8
Cell size (μm)	—	390	200	300	—	320	166	249
Maximum cell size (μm)	—	420	270	330	—	350	250	300

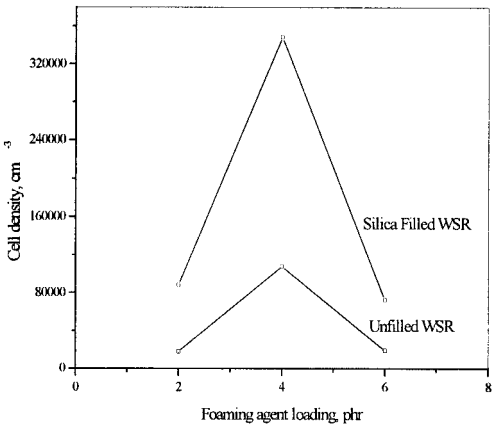

Figure 2 Relationship of cell density (N) of EPDM-foaming WSR and foaming agent loading.

obviously in the silica-filled WSR for the same foaming agent loading. This was affected by more decomposition of the foaming agent and diffusion of those decomposed inert gases.

Strain–stress behaviors of the unfilled and silica-filled WSR are shown in Figures 4 and 5, respectively. With the foaming agent loading increasing, there was a decreasing trend in the curves of the tensile strength and elongation at break. The decreasing trend can be explained partly on the basis of the number of cells increased and the rubber density decrease with increasing foaming agent loading. Aa analyzed from Table III, for the unfoaming WSR before immersing it into water, the tensile strength was increased three times, contrasting the silica-filled CF5 sample with the unfilled CS1 sample. For the foaming WSR, comparing CF6 with CS2 and CF7 with CS3, which, separately, had the same foaming agent loading, the tensile strength was increased about six times (from 0.40 to 2.48 and from 0.33 to 1.86). Therefore, silica enhanced the strength of the WSR, especially for the foaming

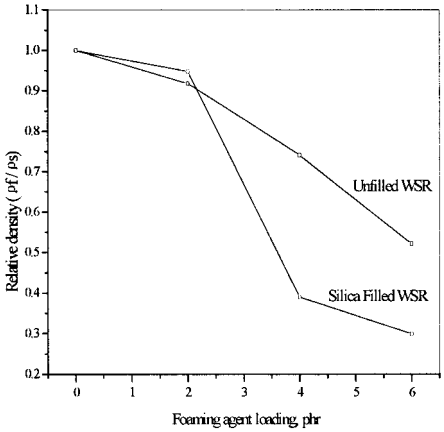

Figure 3 Effect of foaming agent loading on relative density.

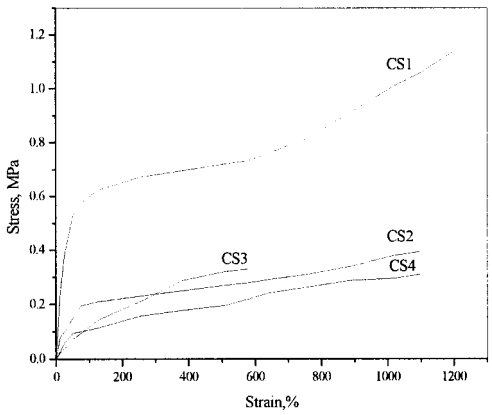

Figure 4 Stress–strain curve of unfilled foaming WSR.

WSR. It is well known that the water-absorbent resin was rigid; it did not deform with the motion of the EPDM rubber under the effect of external force. The compatibility was very poor between the water-absorbent resin phase and the EPDM rubber phase. So, the water-absorbent resin was easy to collect in the rubber matrix. Well-dispersed silica prevented the CPA from getting together. Therefore, the stress concentration caused by the congregation of the water-absorbent resin was avoided and the tensile strength was enhanced.

Table III shows a comparison of the mechanical properties of the WSR before and after the water-swell. The tensile strength and elongation at break of the unfilled EPDM WSR decreased after the water-swell (samples CS1, CS2, CS3, and CS4). For the silica-filled unfoaming WSR, the mechanical properties decreased (sample CF5). However, both the tensile strength and elongation at break increased for the silica-filled foaming WSR (samples CF6, CF7 and CF8). This was likely the result of the silica causing the water-absorbent resin to disperse well and the WSR to swell regularly after the water-swell.

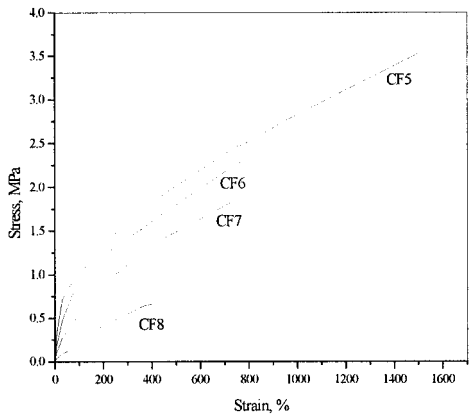

Figure 5 Stress–strain curve of silica-filled foaming WSR.

TABLE III
Mechanical Properties of WSR Before and After Water-swell

	Before water-swell		After water-swell	
	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)
CS1	1.14	1200	0.81	565
CS2	0.40	1100	0.28	810
CS3	0.33	580	0.32	550
CS4	0.31	1100	0.14	680
CF5	3.53	1500	1.60	795
CF6	2.48	770	3.37	980
CF7	1.86	750	1.94	950
CF8	0.68	420	0.70	590

Water-swelling abilities

Figures 6 and 7 show the relationship of the volume water-swelling ratio (*Sv* %) of unfilled and silica-filled WSR samples with the soak time, respectively. The slope of the curve represents the water-swelling rate. For the unfilled EPDM WSR, the *Sv* % of the unfoaming CS1 sample is 171%. With an increasing amount of the foaming agent up to 6 phr, the *Sv* % increased from 314 to 384 and 1138%, that is, the *Sv* % was enhanced two to six times. So, in contrast to unfoaming WSR, a high *Sv* % is one of the advantages of foaming WSR. Because the water-swelling rate is an important factor for WSR as sealing and waterproofing materials, foaming WSR has another advantage. For unfilled WSR, the soak time to a water-swelling equilibrium was quite long. The introduction of the silica filler improved the water-swelling rate of the WSR (Fig. 7), so the water-swelling equilibrium time was reduced considerably. Also, this was more evident in the high foaming agent loading WSR. The existence of silica increased the *Sv* % of the unfoaming CF5 sample with a slow water-swelling rate, which could be explained by that the silica filler acted, more likely, as a water-absorbing bridge between the CPA particles in the hydrophobic rubber matrix.

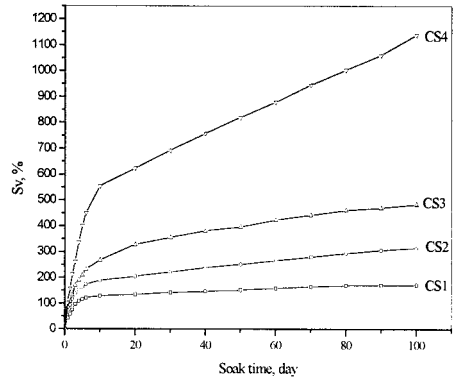

Figure 6 Relationship of *Sv* % of unfilled foaming rubber to soak time.

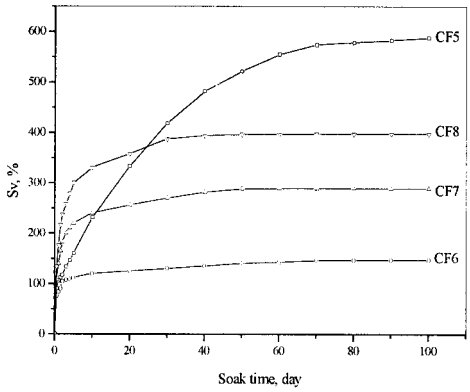

Figure 7 Relationship of *Sv* % of silica-filled foaming rubber to soak time.

CONCLUSIONS

1. In both the unfilled and silica-filled EPDM WSR, the average cell size and maximum cell size of the foaming WSR decreased, the cell density increased before the amount of the foaming agent loading increased to 4 phr, but the cell size increased and the cell density decreased beyond this amount. At this amount, the ratio of the foaming agent to the crosslinking agent was suitable.
2. The relative density and mechanical properties decreased with an increasing foaming agent loading for both the unfilled and silica-filled WSR. The incorporation of silica made the tensile strength of the unfoaming WSR increase three times, while that of the foaming WSR increased about six times before immersing it into water. After water swelling, the mechanical properties of both the unfilled WSR and the silica-filled unfoaming WSR decreased, but that of the silica-filled foaming WSR increased. The silica filler imparted good intension to the foaming WSR.
3. In contrast to the traditional WSR, the foaming WSR improved the *Sv* % two to six times and improved the water-swelling rate. With the existence of silica, the water-swelling rate was accelerated and the water-swelling equilibrium time was decreased considerably.

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