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Original Article

Water absorption and mechanical properties of water-swellable natural rubber

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Abstract

Water-swellable rubber (WSR) was prepared by blending superabsorbent polymer (SAP) of crosslinked poly (acrylamide-*co*-sodium acrylate) with natural rubber in latex condition. The crosslinked poly(acrylamide-*co*-sodium acrylate) was first prepared by inverse suspension polymerization from acrylamide and sodium acrylate monomers with potassium persulfate initiator and N,N′-methylenebisacrylamide crosslinker. The reaction was carried out at 60°C for 40 mins. Water absorption properties, such as the degree of water absorption, water absorption rate, degree of weight loss, and mechanical properties of WSR were then investigated. It was found that the degree of water absorption, water absorption rate, and the degree of weight loss increased, while tensile strength and elongation at break decreased with increasing quantity of SAP in the blends. However, the degree of water absorption, degree of weight loss, and elongation at break decreased, but tensile strength increased with increasing quantity of the N-*tert*-butyl-2-benzothiazyl sulphenamide (TBBS) accelerator used in the compounds formulation.

Keywords: natural rubber, crosslinked poly(acrylamide-*co*-sodium acrylate), superabsorbent polymer, water-swellable rubber

1. Introduction

Multicomponent polymer systems have attracted much attention in both basic and applied research over the last 20 years as scientists search for novel properties obtained from particular combinations of two or more polymer materials. Another major driving force behind the growth of multicomponent polymer systems is the relative ease of mixing and blending materials, so that the production costs are usually much lower than that of entirely synthesized new polymers (Wang *et al.*, 1998). As multicomponent products possess a number of advantages, they have been widely studied in the industry.

In recent years, the development of water swellable rubber (WSR) has been recognized. WSR is a functional polymer that expands its volume up to more than 1.5 times its original size by absorbing surrounding water. It can be used as a sealing material or in calking applications, preventing water leakage from pipes or blocking connections in civil constructions such as subways and subsea tunnels (Park and Kim, 2001).

WSR is usually prepared by dispersing various kinds of superabsorbent polymer (SAP) particles in common hydrophobic rubbers, such as chloroprene rubber (Wang *et al.*, 1999; Liu *et al.*, 2006), chlorohydrin rubber (Zhang *et al.*, 1999; Zhang *et al.*, 2000; Zhang *et al.*, 2001) and natural rubber (Park and Kim, 2001; Wang *et al.*, 2002). It possesses not only properties of general rubber, such as high resilience and good tensile strength, but also water-swellability. These properties are due to the presence of the crosslinking network

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of rubber and the water-absorbent materials.

In this study, the WSR was prepared by mixing SAP particles with natural rubber latex and compounded with other ingredients. The effect of SAP on water absorption, degree of weight loss, and mechanical properties were then investigated.

2. Materials and Methods

2.1 Materials

High ammonia concentrated NR latex was used as the rubber component, manufactured by Pattani Industry Co., Ltd., Pattani, Thailand. The SAP was prepared by inverse suspension polymerization using an acrylamide : sodium acrylate ratio of 1:1, with distilled water absorptivity of 365 g/g. Sodium lauryl sulfate was used as a surfactant for the preparation of WSR (Ajax Finechem Co., Ltd., Australia). Zinc oxide (ZnO) was used as an activator (Global Chemical Co., Ltd., Thailand). N-*tert*-butyl-2-benzothiazyl sulphenamide (TBBS) was used as an accelerator (Bayer Co., Ltd., Germany). Sulfur was used as a vulcanizing agent (Ciech. S.A. Co., Ltd., Poland)

2.2 Preparation of WSR and compounding

The natural rubber-SAP mixes were prepared in latex state at room temperature. The samples were first prepared by using high ammonia concentrated NR latex with dry rubber content (DRC) of approximately 60%. They were also diluted to various DRCs, as shown in Table 1. The latices were stabilized against coagulation by adding 2% (w/w of SAP) of the surfactant (sodium lauryl sulfate, SDS). The SAP was then added. The mixture was stirred until it reached gel point. The quantity of SAP was varied, as shown in Table 1. Then the rubber sheets were made and after that they were transferred to a hot air oven and dried at 40°C for 4 days.

The mixed materials were then compounded using a two-roll mill adding 3 phr of ZnO (activator) and 0.5 phr of sulfur (vulcanizing agent), 10 phr of carbon black (reinforcing agent) and TBBS (accelerator). Various concentrations of the TBBS were studied at 1, 2, and 3 phr. Properties of various loading levels of SAP were aimed to study, and because of this NR and SAP were formulated according to the values show in Table 1. The compound was then compression molded at 150°C to their respective optimal cure time obtained by using ODR-100s.

2.3 Measurements

2.3.1 Water absorbent properties tests

The vulcanized strips of the WSR were cut into small pieces of approximately 1 g. They were later immersed in distilled 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 of each swollen sample was recorded. The sample was then dried at 40°C until it achieved a constant weight, degree of water absorption (S_w), and degree of weight loss (L_w). These two quantities were calculated using the following expressions (Zhang *et al.*, 2001; Wang *et al.*, 2002; Liu *et al.*, 2006)

$$S_w = \frac{W_2 - W_1}{W_1}$$

$$L_w = \frac{W_1 - W_3}{W_1} \times 100$$

where W_1 and W_2 are the weights of the sample before and after the water absorption respectively, and W_3 is the dried weight of a sample after water absorption.

Table 1. Blend compositions of natural rubber and SAP.

Blend codes	DRC of NR (%)	Quantity of SAP (phr)
A	60	10
B	30	20
C	20	40
D	15	60

2.3.2 Crosslink density

Samples weighing approximately 0.8 g were cut from cured sheets and immersed in 100 ml of toluene in the dark for one week at room temperature. The crosslink density of WSR was calculated by using the Flory-Rehner Equation (Hamed and Rattanasom, 2002)

$$\rho_c = -\frac{1}{2V_s}\frac{\ln\left(1 - V_r^o\right) + V_r^o + \chi\left(V_r^o\right)^2}{V_r^{o^{1/3}} - \frac{V_r^o}{2}}$$

where ρ_c is the crosslink density (mol/m^3), V_s is the molar volume of toluene (1.069x10^{-4}) m^3/mol at 25°C, V_r^0 is the fraction of rubber in the swollen gel, and χ is the interaction parameter (0.39 for NR).

2.3.4 Mechanical properties

The instrument used was a Hounstield tensometer, H10KS (Hounsfield Test Equipment Co. Ltd, UK). The test was performed according to ASTM D412.

3. Results and Discussion

3.1 Water absorption properties

The degree of water absorption of WSR with different quantities of SAP and TBBS are presented in Figure 1. It can be seen that the water absorption increased with increasing

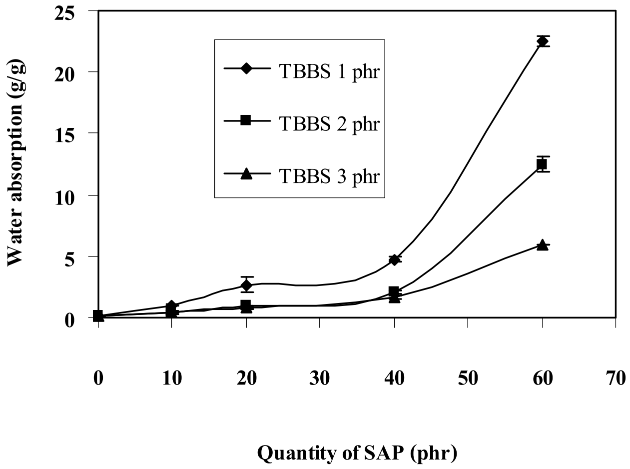

Figure 1. Influence of SAP and TBBS quantities on water absorption of WSR, using ZnO 3 phr, S 0.5 phr, carbon black 10 phr, and a soaking time of 91 days.

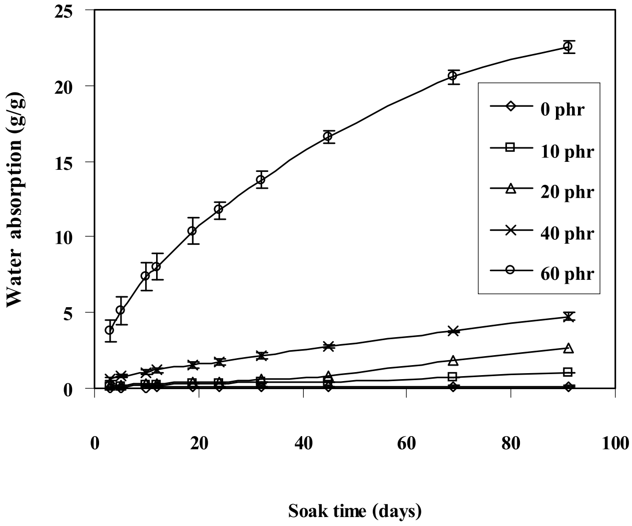

Figure 2. Influence of soaking time and SAP quantity on water absorption of WSR, using ZnO 3 phr, TBBS 1 phr, S 0.5 phr, and carbon black 10 phr.

quantity of SAP but decreasing level of TBBS accelerator. The amount of SAP plays an important role in the degree of water absorption of the WSR. WSR showed minimal water absorption when the quantity of SAP was 40 phr or less. At 60 phr of SAP the degree of water absorption was much higher and showed the highest values for all 3 levels of TBBS. The water absorption of the WSR decreased with increasing quantity of TBBS. This could be due to the crosslink network of WSR. Figure 6 shows that the effect of TBBS on the crosslink density properties of the WSR increased with increasing TBBS content. This is related to the degree of water absorption properties. A higher crosslink density, a lower free volume and flexibility of rubber molecules, and a lower water absorption were obtained when the TBBS content in WSR increased.

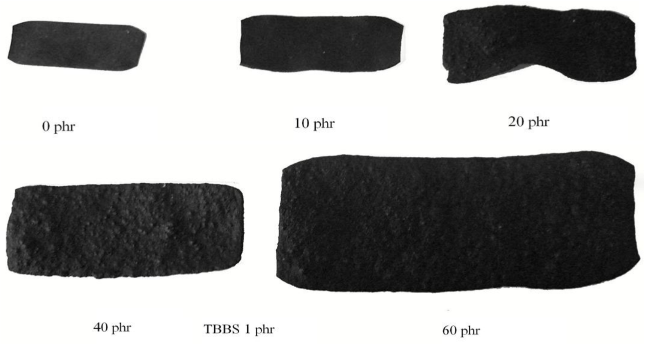

Figure 3. Photogaphs of WSR at various SAP contents with ZnO 3 phr, TBBS 1 phr, S 0.5 phr, carbon black 10 phr, and a soaking time of 91 days.

Figure 4. Photographs of WSR at various TBBS contents with SAP 40 phr, ZnO 3 phr, S 0.5 phr, carbon black 10 phr, and a soaking time of 91 days.

Figure 2 shows the effect of soaking time on water absorption of WSR for different contents of SAP. It can be seen that the water absorption of WSR increased with increasing soaking time and level of SAP. The water absorption of WSR increased obviously when the amount of SAP was 60 phr compared with $\leq$ 40 phr due to water diffusion through WSR, which depends on the SAP contents.

Figure 3 and 4 show photographs of WSR at various SAP contents. The size of the samples corresponds to the levels of SAP and TBBS. The photographs show that the addition of the SAP increased the water absorption, while adding TBBS decreased water absorption. If the WSR was immersed in water, the SAP in it absorbs the water and then an expansion force is exerted. When the expansion force reaches a balance value of crosslinking restriction of the vulcanized rubber, equilibrium swelling is achieved. Therefore, the equilibrium swelling of WSR decreases with increasing TBBS content.

Figure 5 illustrates the effect of SAP on the degree of weight loss after water absorption. It was found that the degree of weight loss of WSR increased with increasing level of SAP. This may be due to the low interaction between the hydrophilic SAP and hydrophobic natural rubber. Insufficient adhesion at the interface may cause the SAP to separate from the natural rubber. At a higher SAP content, a higher degree of weight loss was obtained. Moreover, it can be seen that the degree of weight loss of WSR corresponds to the

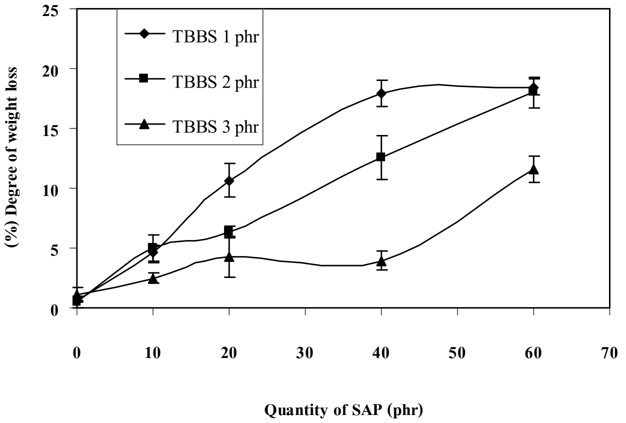

Figure 5. Influence of SAP and TBBS quantities on the degree of weight loss of WSR, using ZnO 3 phr, S 0.5 phr, and carbon black 10 phr after a soaking time of 91 days.

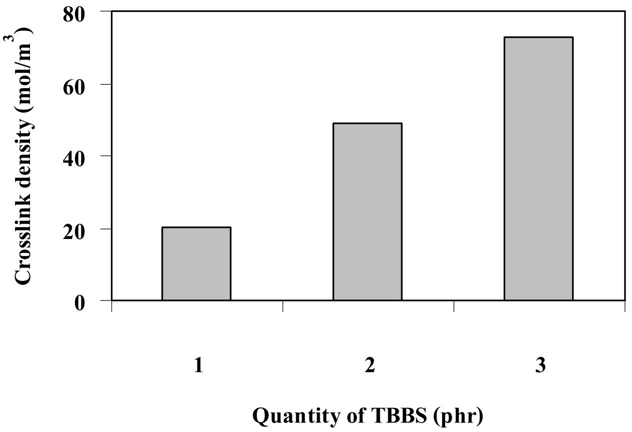

Figure 6. Effect of TBBS quantity on crosslink density of WSR, compounding with 40 phr SAP, 3 phr ZnO, 0.5 phr S, and 10 phr carbon black.

crosslink density of the rubber phase. The higher the quantity of TBBS, the greater the crosslink density, and therefore the higher adhesion at the interface resulted in a lower degree of weight loss.

3.2 Mechanical properties

Figure 6 shows the effect of TBBS quantity on the crosslink density of the WSR. It is seen that the crosslink density increased with increasing level of TBBS. A higher accelerator/sulfur ratio usually means that the vulcanization is more efficient; resulting in shorter crosslinks, predominantly of the monosulfidic type (Hagen *et al.*, 1996). This is related to the crosslinked density of WSR. The higher the TBBS content, the greater the monosulfidic crosslink and a higher crosslink density were observed.

Figure 7 and 8 show that the tensile strength and elongation at break of WSR decreased with increasing SAP content. This is due to an increase in flaws in the vulcanizate. The higher the SAP content (nonadhering filler) the more

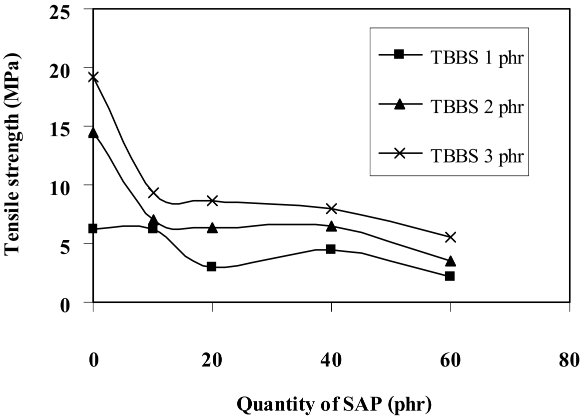

Figure 7. Influence of SAP and TBBS quantities on the tensile strength of WSR, using ZnO 3 phr, S 0.5 phr, and carbon black 10 phr.

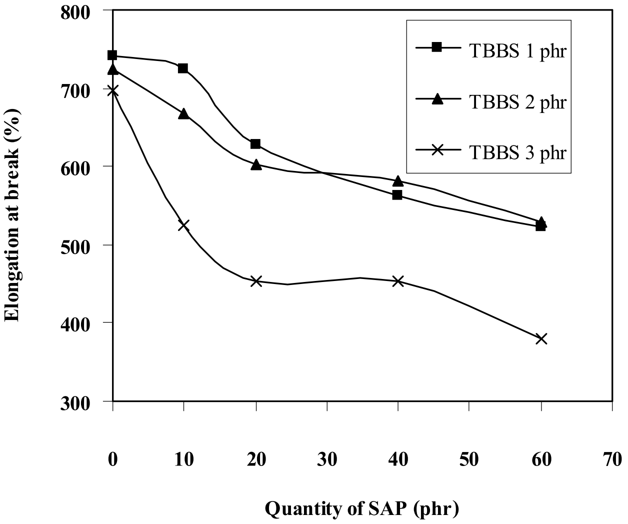

Figure 8. Influence of SAP and TBBS quantities on the elongation at break of WSR, using ZnO 3 phr, S 0.5 phr, and carbon black 10 phr.

flaws in the rubber and the lower the strength of the rubber were found (Wang *et al.*, 1999). Moreover, natural rubber is capable of crystallization in a high stain state. Thus, natural rubber has higher strength. When SAP was added, it obstructed the crystallization of the rubber molecules. Therefore, the strength of WSR decreased with increasing quantity of SAP content. The result shows that the addition of TBBS increased the tensile strength, while elongation at break decreased. This is related to the crosslink density. The higher the amount of TBBS content the greater the crosslink density and the higher the strength obtained.

4. Conclusion

The WSR was prepared by blending SAP with natural rubber in latex condition. The degree of water absorption, water absorption rate, and degree of weigth loss of WSR increased with increasing SAP content. However, the degree of water absorption and degree of weight loss decreased with increasing loading level of the TBBS. Moreover, the addition of SAP decreased the tensile strength, while adding TBBS increased the tensile strength. Elongation at break decreased with increasing of SAP and TBBS content.

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