Effect of filler water absorption on water swelling properties of natural rubber

J Trakuldee¹, K Boonkerd²
¹Multidisciplinary Program in Petro Chemistry & Polymer Science, Faculty of Science, Chulalongkorn University, Thailand
²Department of Materials Science, Faculty of Science, Chulalongkorn University, Thailand

E-mail: Janyarak_trakuldee@hotmail.com

Abstract. The efficient water swelling rubber can be obtained by using high hydrophilic rubber such as chloroprene rubber. However, chloroprene rubber is synthetic rubber developed from the petroleum. Recently, many researches try to replace the usage of synthetic rubber with natural rubber. This is not only due to the concerning of environment but the cost reduction as well. However, natural rubber is hydrophobic, thus not absorbing water. To develop the water swelling rubber from natural rubber, the addition of water absorption filler is needed. The study was aimed to formulate water swelling rubber from natural rubber filled with sodium polyacrylate (SA)/sodium bentonite clay (SBC) hybrid filler used to water absorbent. The filler loading was kept constantly at 150 phr. The effect of SA/SBC ratio varied from 1:0, 1:1, 1:2 and 1:3 on the water absorption of the hybrid filled natural rubber was determined. The obtained result showed that the water adsorption proportionally increased with increasing SA loading but decreased with increasing SBC loading. The effect of glycidyl methacrylate (GM) and poly ethylene glycol (PEG) on the water absorption was studied later. The result from a scanning electron microscope depicted that the presence of GM can depress the falling out of SA from the rubber matrix while the presence of PEG increased water absorption.

1. Introduction

Water swelling rubber products were used widely as sealing of construction joint, preventing water leakage from pipe or blocking connection in civil construction such as subway and subsea tunnel. In general, a water swelling rubber is installed between concrete joints. When concrete joints are ruptured or leaked, the water swelling rubber will contact with water, and then swells and automatically fills up the void between the two portions of concrete join. Commercially, the effective water swelling rubber are prepared from common hydrophilic rubbers such as chloroprene rubber, chlorohydrins rubber, polyurethane and polyvinyl chloride filled with various kinds of superabsorbent polymer particles [1–4]. However, water swelling rubbers made from synthetic rubber has higher cost than the one made from natural rubber.
Currently, there are many researchers pay attention to develop the water swelling rubber from natural rubber. However, the structure of natural rubber is consisting of carbon and hydrogen atom only, making it has hydrophobic property [5]. Either sodium polyacrylate or sodium bentonite clay generally is used as water absorbent [6, 7]. However, to develop the effective water swelling rubber from natural rubber, the high amount of water absorbent filler is needed. However, when rubber loaded with high amount of filler, it fails under external force easily. Many researches showed that the addition of glycidyl methacrylate and poly ethylene glycol enhanced not only water absorption but also mechanical strength of the water swelling rubber [8].
In this study, it was aimed to develop water swelling rubber with high water absorption efficiency and reasonable mechanical strength from natural rubber. Both SA and SBC are used as water absorbent hybrid filler. The effect of GM and PEG on the water adsorption was investigated.

2. Experiment
2.1. Materials.
Natural rubber grade STR5L was purchased Sakdarungreaungkij Co., Ltd. Sodium polyacrylate (SA) with absorbability 300 g/g was bought from STP Chem Co., Ltd., Thailand. Sodium bentonite clay (SBC) with grade SAC and particle size 200 mesh was obtained from Thai Nippon Chemical Co., Ltd., Thailand. Coupling agents including glycidly methacrylate (GM) and poly ethylene glycol (PEG) with molecular weight 4000 g/gmol were purchased from Sigma-Aldrich Co., Ltd., Singapore. Carbon black with grade N550 and vulcanizing agents were supported from Innovation group, Thailand.

2.2 Sample Preparation.
The rubber formulas used in this study are listed in Table 1. The rubber was orderly mixed with the ingredients in according to Table 1 using an internal mixer (MX500-D75L90) at 60°C and a rotor speed of 60 rpm. Then, the cure characteristic of the obtained compound was characterized using a moving die rheometer at 160°C. The sample was compression molded at 160°C.
Table 1. Composition of natural rubber and mixing step

| Ingredients      | Compound (phr) | 1    | 2    |
|------------------|----------------|------|------|
| Natural Rubber   | 100            | 100  | 100  |
| SA:SBC           | 1:0/1:1/1:2/1:3* | 1:1  | 1:1  |
| GM               | -              | 2.5  |     |
| PEG              | -              | 10   |     |
| Carbon black     | 2              | 2    |     |
| Zinc Oxide       | 3              | 3    |     |
| Stearic acid     | 2              | 2    |     |
| CBS              | 2              | 2    |     |
| DPG              | 1              | 1    |     |
| Sulfur           | 0.8            | 0.8  |     |

*The filler (SA:SBC) loading was kept constantly at 150 phr

2.3 Water Absorbent Properties Tests.
The rubber sample was cut into small pieces with a weight of about 1 g and a volume 2.0×2.0×0.2 cm³ immersed in water for 30 days at room temperature. The weight and volume of swollen samples was checked frequently at the specific time intervals. The swelling by weight and swelling by volume were calculated according to Eq. 1 and 2 respectively.

\[
\text{Swelling by weight (%) } = \frac{W_2 - W_1}{W_1} \times 100
\]

\[
\text{Swelling by volume (%) } = \frac{V_2 - V_1}{V_1} \times 100
\]

W₁, W₂ (unit in gram) is the weight of the sample before and after the swelling, respectively. V₁, V₂ (unit in cm³) is the volume (width x length x high) of the sample before and after the swelling, respectively.

2.4 Morphology of Water Swelling Rubber.
The effect of fillers GM and PEG on the interaction between water absorbent SA and rubber was studied. The fractures surfaces of the sample after swelling were investigated using a scanning electron microscope (JSM 5410LV/JEOL, Japan). Samples were quenched in liquid nitrogen and then broken into section and gold-sputtered onto the rough surface of them to increase the conductivity.

3. Results and Discussion
3.1 Effect of Water Absorbent SA: SBC Ratio on Swelling
Figure 1 shows the effect of SA:SBC ratio on the water adsorption of the rubber. It can be seen
that the rubber filled with SA/SBC at the ratio of 1:0 showed the highest swelling rate. However, after few days the water swelling of the rubber filled with SA/SBC at the ratio of 1:0 clearly decreased. This was due to the falling out of SA from the rubber matrix. For the rubber filled with SA/SBC hybrid filler at the ratios of 1:1, 1:2 and 1:3, the water absorption increased with immersion time and then saturated around day 21. The rubber filled with SA/SBC hybrid filler at the ratio of 1:1 showed the highest water absorption. This was due to the presence of the highest SA content. The water absorption decreased with the increased SBC content. This is because the ability to absorb water of SBC is much lower that of SA. SBC is natural absorbent, it can absorb water 5-10 times from initial weight while SA is synthetic absorbent, it can absorb water about 100-500 times from initial weight [9-10].

![Figure 1. Water swelling by weight (a) and swelling by volume (b) of the rubber filled with various SA:SBC ratios when immersed in water for 30 days](image)

3.2 Effect of GM and PEG.

Figure 2 shows the water swelling of the rubber filled with SA/SBC hybrid filler at the ratio of 1:1 with and without adding GM and PEG. It can be seen that the effect of GM on the water absorption, it was found that GM did enhance the water absorption and no SA falling out of the rubber was observed. Park JH and Kim D (2001) proposed that the increased interaction between SA and rubber by GM occurred via there interaction mechanism that the double bond in GM might react with the unsaturated groups in natural rubbers and the epoxide group with the carboxylic acid in SA [4]. When considering the addition of PEG significantly increased the
water absorption. This is because PEG is hydrophilic material, thus increasing the hydrophilicity of the rubber. However, it was observed during the water absorption testing that the SA in the sample added PEG fell out of the rubber matrix according to Figure 3(c). Therefore, to improve the property of the water swelling rubber, both PEG and GM are needed. Because this has capability to form strong hydrophilic network with rubber to generate highest water absorption [5,8]

![Graph](image)

**Figure 2.** Water swelling by weight (a) and swelling by volume (b) of the rubber filled SA/SBC hybrid filler at the ratio of 1:1 with and without adding GM and PEG

Figure 3 showed SEM photographs of the fractured rubber filled with SA/SBC hybrid filler at the ratio of 1:1 without and with adding GM and PEG after swelling. The result showed that the swollen sample without adding fillers in Figure 3(a) showed a lot of voids due to the falling out of SA. However, when adding GM in Figure 3(b), the swollen sample had less voids. This can confirm that GM enhances the interaction between the SA and rubber, thus preventing the falling out of SA from the rubber. While adding PEG in Figure 3(c) showed a lot of voids without
adding filler due to the falling out of SA. PEG is hydrophilic material, it can increase the hydrophilicity of the rubber but not enhance the interaction between the SA and rubber.

![Figure 3. SEM photographs of the fractured rubber filled with SA/SBC hybrid filler at the ratio of 1:1 after swelling (a) without adding (b) with adding GM and (c) with adding PEG](image)

4. Conclusion

Water swelling rubber was prepared from natural rubber filled SA/SBC hybrid filler. The suitable SA/SBC ratio was at 1:1. Although the higher SA content can lead to the higher water absorption, the SA was prone to fall out of the rubber. GM is necessary to enhance the interaction between SA and rubber while PEG acts as the pathway of water and can strongly enhance the water swellability.

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References

[1] Saijun D et al 2009 Songklanakarin J. Sci. Technol. 31 561.
[2] Wong G, Li M and Chen X 1998 J. Appl. Polym. Sci. 68 1219.
[3] Wong G, Li M and Chen X 1999 J. Appl. Polym. Sci. 7 577.
[4] Park JH and Kim D 2001 J. Appl. Polym. Sci. 80 115.
[5] Nakason C et al 2013 J. Euro. Polym. 49 1098.
[6] Zhang J et al 2007 Mat. Let. 43 316.
[7] Santiago F et al 2009 J. Euro. Polym. 31 1.
[8] Wang C et al 2002 J. Appl. Polym. Sci. 86 3120.
[9] Ozcan As and Ozcan A 2004 J. Colloid, Interface. Sci. 1 276.
[10] Flory PJ and Rehner J 2001 Chem. Phys 11 11.