

# Preparation and Characterization of Water-Swellable Natural Rubbers

JONG HYUN PARK, DUKJOON KIM

Department of Chemical Engineering, Sungkyunkwan University 300, Chunchun-dong, Jangan-gu, Suwon, Kyungki 440-746, Korea

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**ABSTRACT:** Water-swellable rubbers were prepared by dispersing the superabsorbent polymer particles, sodium polyacrylate particles, in natural rubber, and their water absorption properties were investigated. Sodium polyacrylate particles were synthesized using the inverse suspension polymerization technique, and their thermal and water absorption properties were characterized. The equilibrium water uptake in sodium polyacrylate particles was strongly dependent on both the salt concentration of aqueous media and crosslinking density of polymer. The dynamic and equilibrium water-swelling behavior of the prepared rubbers were significantly affected by addition of carbon black, hydrophilic polymer, and coupling agent. Those effects were well explained by microphotographic morphologies obtained using a scanning electron microscope. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 115–121, 2001

**Key words:** superabsorbent polymer; sodium polyacrylate; swelling; rubber; water uptake

## INTRODUCTION

Water-swellable rubbers are functional polymers that expand their volume up to more than 1.5 times original by absorbing surrounding water.<sup>1–10</sup> This functionality provides the materials with sealing or caulking application,<sup>1,11</sup> preventing water leakage from pipe or block connections in civil constructions such as subway and subsea tunnel, etc. Although classical rubbers have been frequently used for this purpose, they have inherent drawbacks in the sealing precision due to their hydrophobicity. As the civil or architectural engineering dealing with surrounding water becomes more detailed and complicated, the needs

for more convenient and efficient sealing materials and techniques are still increased.

Water-swellable rubbers are usually prepared by dispersing so-called superabsorbent polymer particles in common hydrophobic rubbers.<sup>11–13</sup> Superabsorbent polymers (SAP) are hydrogels with three-dimensional network structures absorbing water up to at least 100 times original polymer volume. This high water absorbing capability of SAP provides rubbers with water-swelling functionality. Thus, the water-swellable rubbers prepared by this technique have illustrated successful water absorption properties, but elicited a significant problem regarding their durability. It means that those prepared by the simple dispersion of hydrophilic superabsorbent polymer particles in hydrophobic rubbers do not hold water absorption capacity for long time, as the SAP particles migrates readily into the water phase due to the weak interaction between SAP particles and rubber matrix.

Correspondence to: Dukjoon Kim (E-mail: djkim@yurim.skku.ac.kr).

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Since Weaver and his co-workers<sup>14</sup> reported starch-g-polyacrylate had excellent water-absorbing ability, lots of studies<sup>1</sup> have been performed with respect to the synthesis, characterization, and applications of superabsorbent polymers. Recently, sodium acrylate polymer is reported one of the most prospective materials in view of its strength in synthetic cost and properties.

In this article, sodium polyacrylates were prepared in particle forms, and their properties were characterized. Water-swallowable rubbers were prepared by blending sodium polyacrylate particles with rubber. Glycidyl methacrylate was introduced as a reactive coupling agent for improvement of interaction between hydrophilic particles and hydrophobic rubber matrix. The effects of fillers and modifiers as well as this compatibilizer on thermal, morphological and water absorption properties were characterized. Natural rubber was selected in this study, because it had the widest applications among various commercial rubbers.

## EXPERIMENTAL

### Preparation of Sodium Polyacrylate Particles

Sodium polyacrylate particles were prepared using an inverse suspension polymerization method<sup>3,4</sup> via free radical reaction mechanism. The amount of 20 wt % of aqueous solution including 0.58 mol of acrylic acid (Daejung Chemical) was neutralized with 25.4 wt % sodium hydroxide aqueous solution. After cooling down the neutralization heat with cold water, a crosslinking agent of *N,N'*-methylene bisacrylamide (Arcous Organics) and an initiator of potassium persulfate (Duksan Chemical) were added and dissolved in the prepared aqueous solution. The amount of 1.9 g of SPAN 60 (Daejung Chemical) and the same amount of ethyl cellulose (EC) (Junsei Chemical) as surfactants were completely dissolved in 220 mL of cyclohexane (Daejung Chemical) at 60°C by agitation. The aqueous solution (dispersed phase) was added in cyclohexane solution (continuous phase) using a dropping funnel at the same temperature. Polymerization reaction was conducted for 2 h with mechanical agitation in a three-neck flask filled with nitrogen gas. After completion of polymerization reaction, sodium polyacrylates particles were precipitated. The precipitates were washed with methanol in vigorous agitation and

then filtered. The products were vacuum-dried at 60°C for 2 days.

### Preparation of Water-Swallowable Rubbers

Sodium polyacrylates particles were blended with the natural rubber (SMR-L) supplied from Kukdong Electrical Company. Pelletized natural rubber was roll-rotored with superabsorbent particles at 30 rpm using a Rheometer (600 P, Hakke). The amount of 1 phr of ZnO and 0.5 phr of sulfur were added as vulcanization agents, 1.65 phr of 2-mercaptobenzothiazole as an accelerator, and carbon black as a reinforcing agent. The amount of 3 phr of KD-250 was also added, as it was compounded with thermal, oxygen, and ozone stabilizers. Glycidyl methacrylate (Aldrich Chemical) in Figure 1(a) was added as a reactive coupling agent between the dispersed particles and rubber matrix by the reaction mechanism that the double bond in glycidyl methacrylate might react with the unsaturated groups in natural rubbers and the epoxide group with the carboxylic acid in acrylate polymers as shown in Figure 1(b). Natural rubbers were placed in the mixer. Glycidyl methacrylate, polyacrylate particles, poly(ethylene oxide) (PEO; MW = 100,000 g/gmol, Aldrich Chemical), and carbon black were then added and blended in series at 95°C, followed by sulfur and ZnO at 60°C. Detailed blending procedures and conditions are summarized in Figure 2.

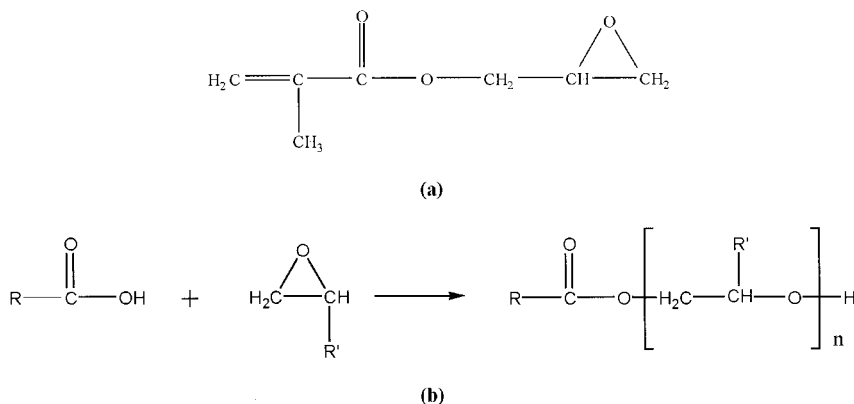
The SAP-dispersed natural rubbers were placed in a mold, and then pressed at 150°C and 220 kg/cm<sup>2</sup> for about 5.5 min for which the curing extent reached to 90% of complete cure. The cured rubber sheets were in the thickness of 2 mm.

### Characterization

Size distribution of the prepared sodium polyacrylate particles was analyzed using a Mastersizer (Malvern Instruments) and their images were observed using an optical microscopy.

Thermal properties were analyzed using the differential scanning calorimetry (DSC; Perkin Elmer, DSC7) and thermogravimetric analyzer (TGA; Perkin Elmer, TGA7). DSC and TGA measurements were performed at the scanning rates of 10 and 30°C/min, respectively, in the presence of nitrogen gas.

The equilibrium water uptake of sodium polyacrylate was measured. The amount of 0.1 g of superabsorbent particles were placed in 200 mL distilled water, and then mildly agitated for about



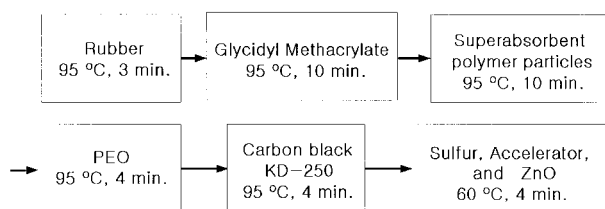
**Figure 1** (a) Chemical structure of glycidyl methacrylate and (b) coupling reaction mechanism with carboxylic acid group.

20 min to absorb sufficient amount of water. The weight of water-swollen particles was measured after free (unabsorbed) water was eliminated by filtration. The water uptake ratio  $Q$  was determined as the water absorption amount (weight) divided by the initial polymer weight as in

$$Q = \frac{W_t - W_o}{W_o}$$

where  $W_t$  and  $W_o$  are weights of polymer samples at time  $t$  and initial state, respectively.

Dynamic swelling experiments were conducted to investigate the swelling kinetics of the prepared rubbers in water with different salinity. Samples in the dimension of  $30 \times 30 \times 2$  mm ( $L \times W \times T$ ) were placed in the saline water, and then their weights were periodically measured until no weight change was observed. Before measuring each sample weight, the sample surface was blotted dry using clean tissues. The same measurements were repeated three times, and the average value was taken for the determination of water uptake ratio. Saline aqueous solutions were prepared at different NaCl concentrations up to 1.6 wt %.



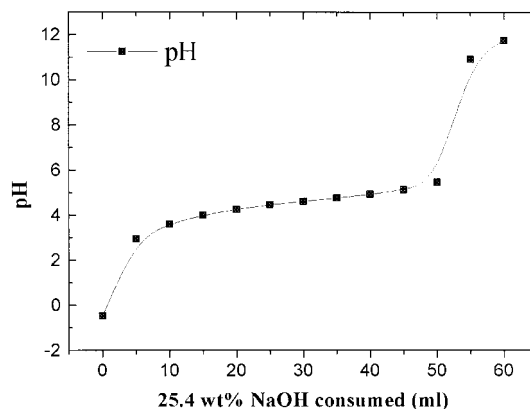
**Figure 2** Blending procedures and conditions for the preparation of water-swelling natural rubbers.

The morphology of SAP-dispersed rubbers was investigated using a scanning electron microscope (SEM; Hitachi, S-2400). The fractured or nonfractured surfaces of SAP dispersed rubbers were microphotographed both before and after water absorption experiments and the results were compared. The loading effects of carbon black, PEO, and coupling agent on the rubber morphology were investigated.

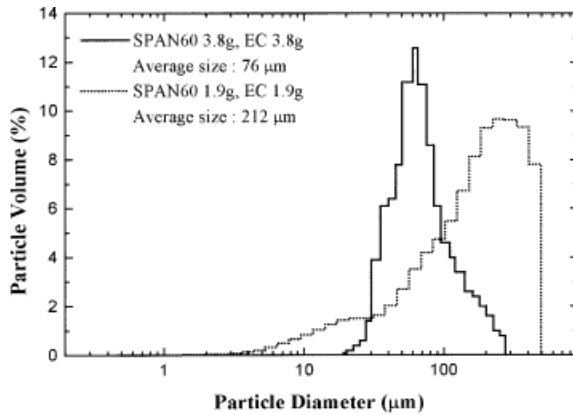
## RESULTS AND DISCUSSION

### Characterization of Sodium Polyacrylate Particles

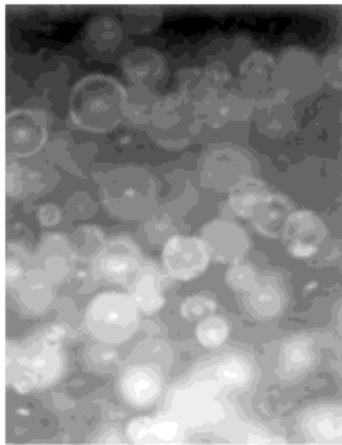
As shown in Figure 3, the neutralization degree of sodium acrylate polymers was controlled to be 75% in their preparation, as the pH of neutralized polymer gels was 5.7. Higher neutralization than this value made the particles so



**Figure 3** Neutralization degree of acrylic acid as a function of NaOH solution consumed.



(a)



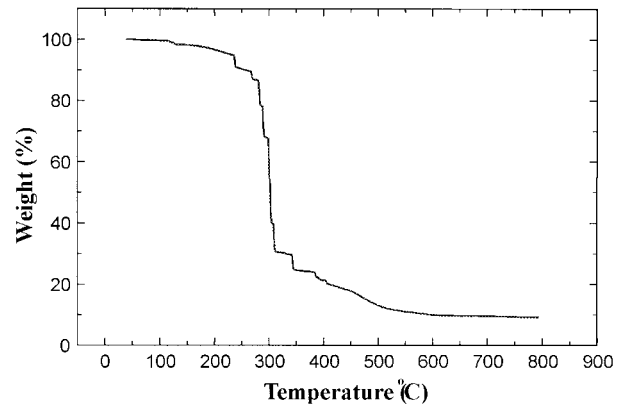
(b)

**Figure 4** (a) Size distribution and (b) optical photographs of the sodium polyacrylate particles prepared.

brittle that they could not be manipulated for further processing.

Figure 4(a) shows the size distribution of the sodium polyacrylate particles prepared. Their sizes were distributed in the range from ten to hundreds micrometers. Increase in the amount of surfactants of SPAN 60 and EC reduced the mean particle diameters from 212 to 76  $\mu\text{m}$ , because more micelles were stabilized in their dispersion. The optical photograph in Figure 4(b) shows that the particles are in spherical forms well established.

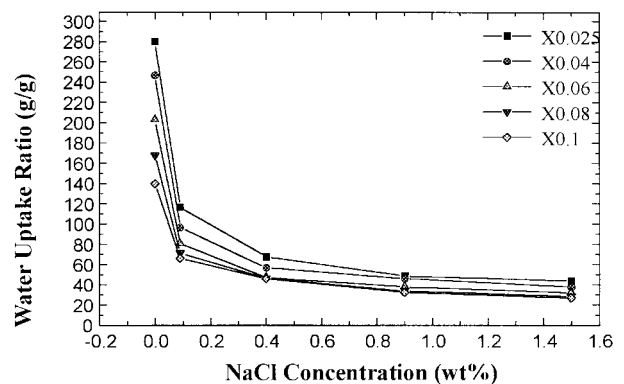
Figure 5 shows the thermogravimetric analysis of sodium polyacrylates. There was no significant weight loss up to 200°C, and thus no degradation was assured in the blending and curing processes conducted at 65 and 150°C, respectively.



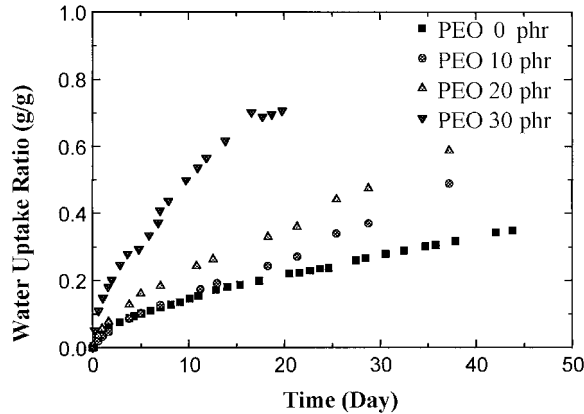
**Figure 5** Thermogravimetric results of sodium polyacrylates.

### Swelling Properties of Sodium Polyacrylate Particles

Figure 6 shows the equilibrium swelling capacities of sodium polyacrylate particles in saline water. The equilibrium water uptake ratio decreased with increasing polymer crosslinking densities due to higher diffusional resistance in the tighter network structures. It also decreased with increasing saline concentrations. The presence of fixed charges on sodium polyacrylate polyelectrolyte gels and the requirement of neutralization in the bulk systems led to higher mobile ion concentrations in gel phase than those in solution phase. This unequal distribution of mobile ion concentrations between gel and solution phases made an ionic contribution to the total swelling pressure.<sup>15–19</sup> Thus the increase in the NaCl concentration in the solution phase reduced ionic contribution to swelling pressure, resulting in less water absorption.



**Figure 6** Equilibrium swelling capacities of cross-linked sodium polyacrylate particles in saline water.



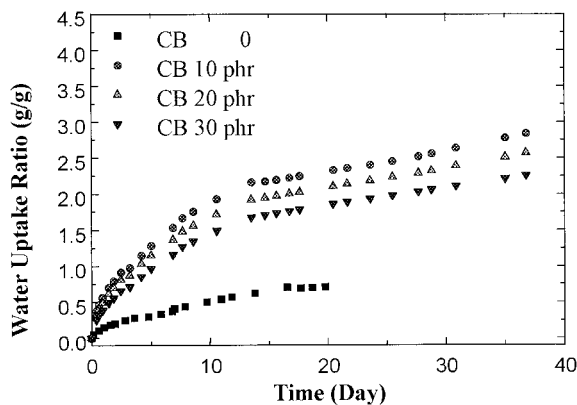
**Figure 7** PEO effect on the water uptake kinetics of SAP-dispersed natural rubbers.

**Effect of Hydrophilic Polymers**

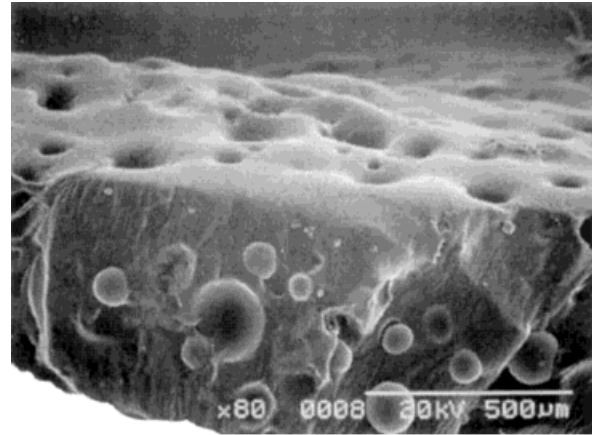
Incorporation of a hydrophilic polymer of PEO might enhance the water swelling kinetics of rubbers by acting as waterways between SAP particles embedded in hydrophobic rubbers. Figure 7 shows its effect on the swelling kinetics in which the water absorption rate increases with increasing amount of PEO loaded.

**Effect of Carbon Black**

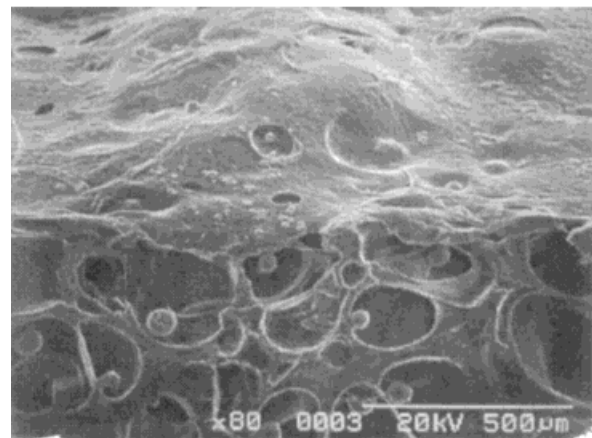
The presence of carbon blacks in the polymer molecules generally resulted in the increase of moduli due to the strong adsorption or covalent bonding of macromolecules on/to carbon black surfaces.<sup>20</sup> The strong interaction between carbon blacks and polymer molecules induced tighter molecular structure bridged by carbon black ag-



**Figure 8** Carbon black effect on the water swelling kinetics of SAP-dispersed natural rubbers when PEO was loaded at 30 phr.



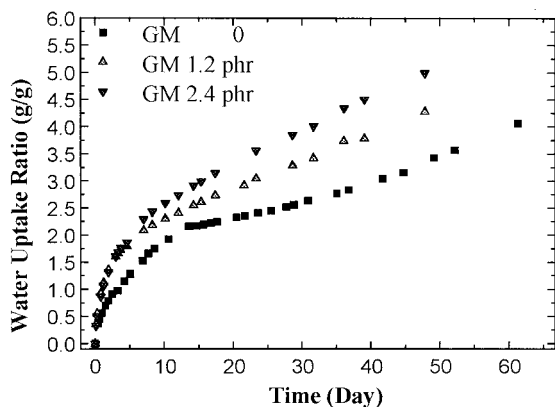
(a)



(b)

**Figure 9** SEM microphotographs of SAP-dispersed natural rubbers dried after swelling (a) when carbon black was unloaded, and (b) when carbon black was loaded.

gregates. This bridging effect of carbon blacks contributed competitive effects on the overall swelling ability of rubbers. The positive swelling effect was to inhibit the migration of SAP particles from rubber surface to surrounding bulk water prolonging the swelling capacity, but the negative one was to reduce the swelling tendency of SAP particles attributed to the decreasing mobility of rubber molecular networks followed by the reduction of free volume in systems. These two competitive effects on the swelling behavior of rubbers are well illustrated in Figure 8. The swelling ratio increased with increasing amounts of carbon blacks up to 10 phr, but then decreased beyond this concentration. This means that the carbon blacks acted more likely as preventing agents for particle migration when they were



**Figure 10** Coupling agent effect on the water uptake kinetics of SAP-dispersed natural rubbers when PEO and carbon black were loaded at 30 and 10 phr, respectively.

loaded less than 10 phr, but more likely as the immobilizing agents for rubber molecules when they were loaded more than 10 phr. This presumption was well supported by the microphotographs measured by SEM. Figure 9(a) and (b) illustrate the microphotographs of carbon black unloaded and loaded rubber surfaces, respectively. Microphotographs were taken for the samples dried after swelling to equilibrium. After swelling experiments, the carbon black unloaded rubber surface illustrates quite considerable vacancies where SAP particles originally located have been migrated to contacting water, but the carbon black loaded rubber surface does not illustrate such vacancies.

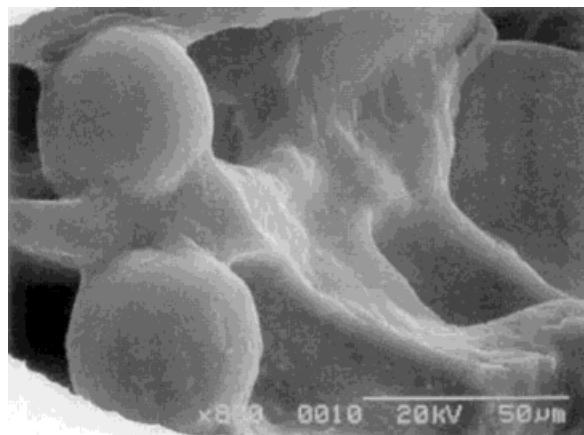
#### Effect of Coupling Agent

Figure 10 shows the coupling agent effect on the water uptake kinetics of the prepared rubbers. The introduction of glycidyl methacrylate enhanced water absorption kinetics and equilibrium water uptake. This might be caused by more effective prevention of SAP particles from migration to water, since SAP particles and rubber molecules were strongly bonded by the coupling agent via the reaction mechanism mentioned in Figure 1. This coupling effect is more clearly shown by the SEM microphotographs in Figure 11. In Figure 11(b), where glycidyl methacrylate was incorporated, there was a strong bond between SAP particles and polymer molecules, but in Figure 11 (a), where no glycidyl methacrylate was incorporated, no such a strong bond was generated. This coupling agent effect is also illustrated when microphotographs of frac-

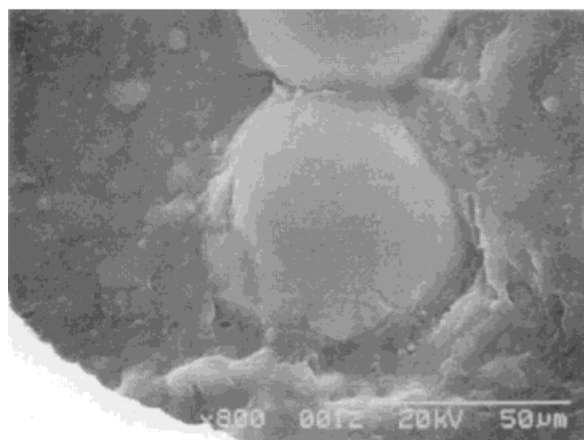
tured surfaces of the two systems were compared. As shown in Figure 12(a), the fractured surface of rubbers without glycidyl methacrylate has lots of voids from which SAP particles have been eliminated during the fracturing process due to the weak interaction between particles and rubber molecules. In Figure 12(b), on the other hand, the fractured surface of rubbers with glycidyl methacrylate does not show so many voids as in Figure 12(a) due to higher interaction between particles and matrix molecules.

#### CONCLUSIONS

Water-swallowable natural rubbers were prepared by blending hydrophilic sodium polyacrylate par-

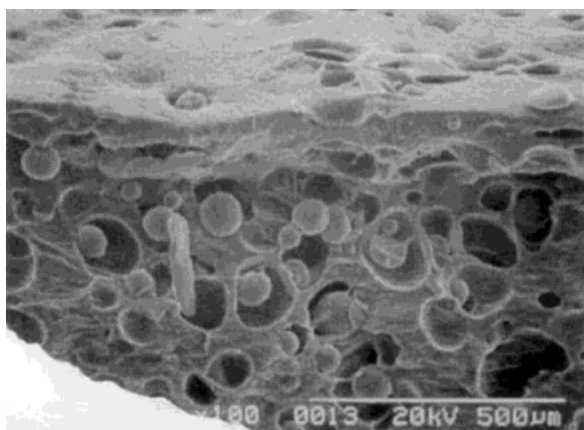


(a)

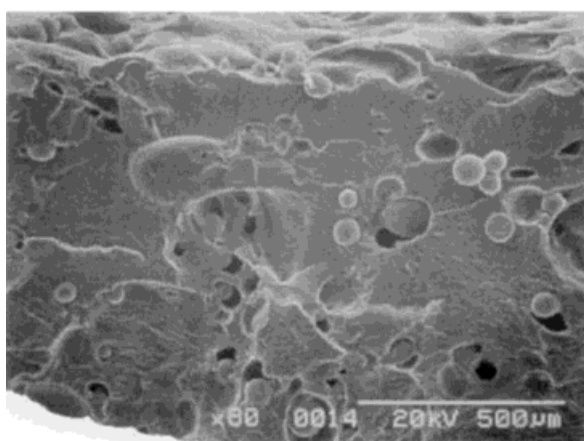


(b)

**Figure 11** SEM microphotographs of the SAP particles: embedded natural rubbers before swelling (a) when no glycidyl methacrylate was incorporated, and (b) when glycidyl methacrylate was incorporated.



(a)



(b)

**Figure 12** SEM microphotographs of the fractured surface of natural rubbers dried after swelling (a) when no glycidyl methacrylate was incorporated, and (b) when glycidyl methacrylate was incorporated.

ticles and hydrophobic natural rubber. Seventy-five percent neutralized sodium polyacrylate particles were synthesized using an inverse suspension polymerization method and the products were mean sized in the range from 76 to 225  $\mu\text{m}$ . The equilibrium water uptake in particles decreased with increasing saline concentration due to the decreasing ionic concentration difference between gel and bulk phases. It also decreased with increasing crosslinking density of polymers due to the decreasing molecular mobility. Water absorption properties of SAP dispersed natural rubbers were significantly affected by incorporation of additives or fillers. Incorporation of linear hydrophilic polymer of PEO-enhanced swelling kinetics by acting as waterway to SAP particles. Incorporation of carbon blacks up to 10 phr in-

creased the equilibrium water uptake by preventing SAP particles from migration to water phase, and that of glycidyl methacrylate enhanced its effect more considerably by acting as a reactive coupling agent between SAP and rubbers. These effects on water absorption properties were well explained by the microphotographs taken before and after swelling experiments using SEM.

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## REFERENCES

1. Shimomura, T.; Namba, T. In *Superabsorbent Polymers: Science and Technology*, ACS Symposium Series 573; Buchholz, F. L. Peppas, N. A., Eds.; The American Chemical Society: Washington DC, 1994.
2. Buchholz, F. L.; Graham, A. T. *Modern Superabsorbent Polymer Technology*, Wiley—VCH: New York, 1998.
3. Mathur, A. M.; Moorjani, S. K.; Scranton, A. B. *Rev Macromol Chem Phys* 1996, C36(2), 405.
4. Wang, G.; Li, M.; Chen, X. *J Appl Polym Sci* 1997, 65, 789.
5. Askari, F.; Nafisi, S.; Omidian, H.; Hashemi, S. A. *J Appl Polym Sci* 1993, 50, 1851.
6. Buchholz, F. L. *J Chem Edu* 1996, 73(6), 512.
7. Liu, X. X.; Tong, Z.; Hu, O. *Macromolecules* 1995, 28, 3813.
8. Shioyama, T. *Jpn Patent* 05,32,0426, 1993.
9. Kondo, T.; Watanabe, Y. *Jpn Patent* 06,57,237, 1994.
10. Kosuge, H.; Hashimoto, H. Ezaki, A. *Jpn Patent* 07,41,606, 1995.
11. Wang, G.; Li, M. Chen, X. *J Appl Polym Sci* 1998, 68, 1219.
12. Vondracek, P.; Lopour, P.; Sulc, J. *U.S. Patent* 5,384,370, 1995.
13. Hron, P.; Vymazalova, Z.; Lopour, P. *Angew Makromol Chem* 1997, 245, 203.
14. Weaver, F.; Bagley, E. B.; Fanta, G. F. M. Doane, W. *U.S. Patent* 3,981,100, 1976.
15. Okay, O.; Sariisik, S. B.; Zor, S. D. *J Appl Polym Sci* 1998,70, 567.
16. Lee, W.-F. Yeh, P. *J Appl Polym Sci* 1998, 68, 1597.
17. Hooper, H. H.; Baker, J. P.; Blanch, H. W. Prausnitz, J. M. *Macromolecules*, 23, 1096 (1990).
18. Baker, J. P.; Hong, L. H.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* 1994, 27, 1446.
19. Baker, J. P.; Blanch, H. W.; Prausnitz, J. M. *Polymer* 1995, 36, 1061.
20. Donnet, J.-B. *Carbon Black*; Marcel Dekker: New York, 1976.