

Water Swollen Natural Rubber

Sureurg KHONGTONG and Narong FUNGCHONLAJIT

*School of Engineering and Resources Management, Walailak University,
Nakhon Si Thammarat 80161, Thailand*

(E-mail: ksureurg@wu.ac.th)

ABSTRACT

Modification of natural rubber by grafting of maleic anhydride yielded a water absorbable substrate. It was found that water contact angles of treated samples declined as the concentrations of maleic anhydride increased reflecting higher water compatibility in grafted samples. Submergence in water of these samples caused dramatic swelling with the water content up to about 60 wt %.

Keywords: Modified natural rubber, hydrophilicity, water absorption

INTRODUCTION

Natural rubber has been used as a water repellent material for a long time since it consists of hydrophobic repeating units of *cis*-1,4-polyisoprene, very low in polarity. Nowadays, this natural polymer has been used in various applications including in composite materials where it is placed into contact with other substrates, i.e., metal oxides, woods, and polymers [1]. To overcome the poor adhesion at the interface of natural rubber and other substrates owing to the low polarity of rubber, modification of natural rubber is necessary [2]. Grafting of maleic anhydride has been used in order to introduce more polar function groups onto rubber chains [3-8]. This leads to natural rubber becoming more polar and, consequently, more hydrophilic and hence more compatible with water.

In this study, we used maleated natural rubber as a model of hydrophilic modified natural rubber to explore that if it would behave as a hydrogel. We hypothesized that the degrees of hydrophilicity and light crosslinking, a requirement for water absorption by a hydrogel, in maleated natural rubber would play a role in the absorbability of water [9-13]. This may bring about an opportunity for hydrogel innovation from natural rubber which is a cheaper and reproducible natural polymer instead of using very hydrophilic synthetic polymers, the down stream products of petroleum.

MATERIALS AND METHODS

Materials

Natural rubber used in this study is the Standard Thai Rubber, STR 5L, from Thavorn Rubber Industry Co., Ltd., Thailand. Maleic anhydride (99 %, Merck) was used as received.

Grafting of maleic anhydride

Grafting of maleic anhydride onto natural rubber in the molten state was performed by using Thermo Haake Rheomix with Banbury rotors. Fill factor of 0.7, rotors speed of 60 rpm, and a chamber temperature of 135 °C were the conditions used to prepare all grafted samples in this research [7]. Five different amounts of maleic anhydride: 0, 3, 8, 12 and 20 wt %, were mixed with STR 5L that was cut into small pieces of $\sim 2 \times 2 \times 2 \text{ cm}^3$ in the Thermo Haake Rheomix and a mixing time of 12 min was applied to all samples. After mixing, they were left in the dark at room temperature for at least 18 h before use.

Washing of grafted rubber

To ensure that the behavior observed herein is neither due to the unbound portion of maleic anhydride nor that of natural rubber, 50 g of each sample prepared previously were washed by soaking in 500 ml of toluene and occasionally stirred for

48 h [14,15]. The undissolved portion was then filtered and dried in a 50 °C hot air oven to remove the solvent until the sample reached a constant weight. It was kept in the dark at room temperature until required.

Contact angle measurement

The washed samples were passed through a 2 roll mill and they were cut into films measuring $\sim 1.5 \times 3.0 \times 0.1 \text{ cm}^3$. These samples were then placed on glass slides and heated in an oven at 60 °C for 18 h to smoothen the surface. They were then floated on distilled water at room temperature to equilibrate the molecules of grafted maleic anhydride at the surface for another 18 h [14,15]. This step is necessary because during the heating of these surfaces in a hot air oven, some grafted maleic anhydride positioned at the interfacial region of samples would migrate deeply away. This polar moiety would, in turn, migrate back to the surface when samples were placed into contact with water. This behavior is general for all surfaces that consist of polar functional groups in order to minimize the interfacial free energy of the system [14-17]. Therefore, degrees of grafting can be correctly monitored by contact angle measurements when all grafted maleic anhydride at the surface is present. The contact angles of Sessile drops of distilled water on rubber surfaces were recorded at room temperature and ambient humidity with a Tante contact angle meter and the values reported in this paper are an average of at least 10 different measurements. The contact angles of samples with 0 wt % of maleic anhydride were taken on the unwashed films of STR 5L.

Testing of water absorption

A piece, 5.0 g, of the washed samples was passed through a 2 roll mill in order to make a rubber sheet with a thickness of $\sim 0.1 \text{ cm}$. (For one with 0 wt % of maleic anhydride, the unwashed sample was used.) As a result, all samples would be expected to have about the same surface area. Sheets of each sample were soaked in 300 ml of distilled water and, after each interval, they were then retrieved from the water. These samples were subsequently blown dry under a stream of nitrogen before changes in weight were monitored. The values of water content (%) were calculated from the weight of absorbed water divided by that of a whole swollen sample [18].

RESULTS AND DISCUSSION

Increasing the hydrophilicity of grafted natural rubber

The modification of natural rubber was conducted by mixing 5 different amounts of maleic anhydride (0, 3, 8, 12 and 20 wt %) with STR 5L. The grafted samples were washed in toluene to ensure that no free maleic anhydride and rubber chains influenced the results observed herein. After washing, it is found that the dry residue of these samples reveals difference in weights. Samples with 0 wt % of maleic anhydride show no residue while those with 3, 8, 12 and 20 wt % increasingly display residue weight (**Figure 1**). The dramatic difference in the weights of the residue from

samples with 0 wt % of maleic anhydride and that with 3, 8, 12 and 20 wt % of maleic anhydride shown in this figure reflects an undissolved portion in the grafted samples. This is expected since cross-linking of unsaturated rubber chains due to coupling of free radicals, enhanced during the grafting procedure of maleic anhydride in a Thermal Haake Rheomix, may occur [19]. Additionally, the high levels of residue weight (~80 - 90 %) found in samples with 3, 8, 12 and 20 wt % of maleic anhydride observed here also ruled out the possibility that the residue weight is due to free maleic anhydride in the washed samples. The dry residue was then transformed to rubber films for contact angle measurements. **Figure 2** shows the values of contact angles of distilled water on the films that had been grafted with different amounts of maleic anhydride. We found that the contact angles fell sharply from about 90 - 55 degree as the amount of maleic anhydride increases indicating that greater hydrophilicity of grafted natural rubber is achieved. The values of contact angles observed here likely reflect the amount of grafted maleic anhydride since the unbound portions were already extracted as stated earlier.

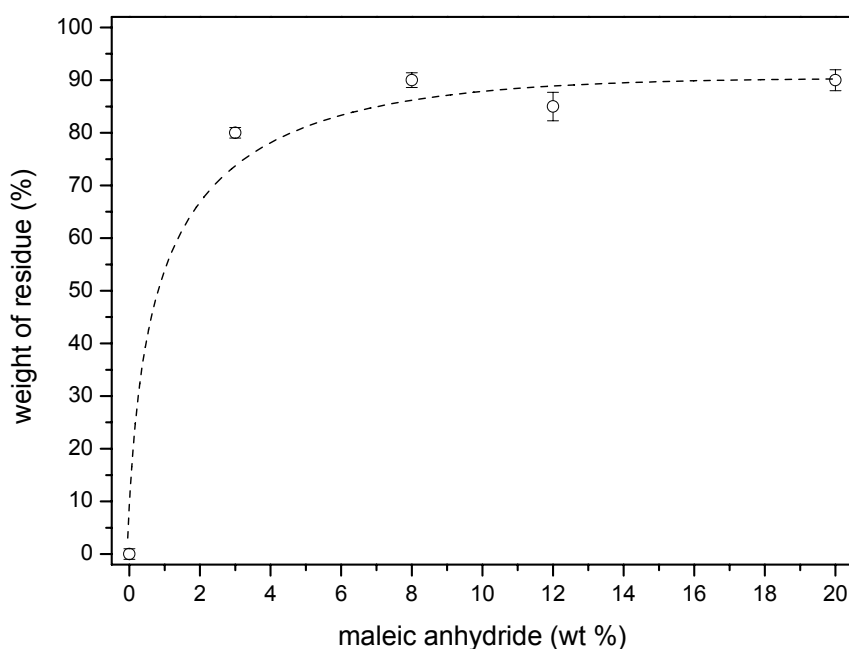


Figure 1 An increase in the weight of residue for grafted samples with different amounts of maleic anhydride: 0, 3, 8, 12 and 20 wt %. The dashed line shows the tendency of the data and the error bars indicate twice standard deviation for each point.

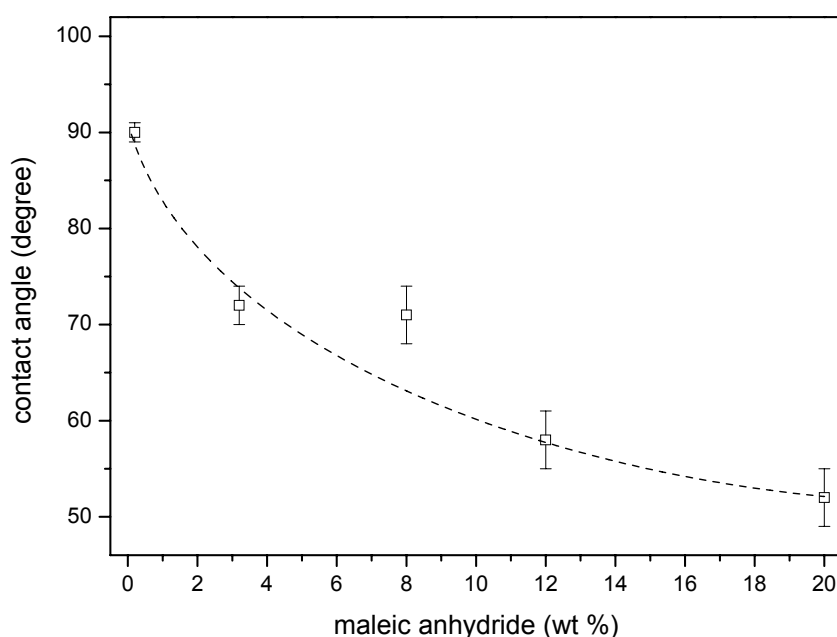


Figure 2 Contact angles on the surface of natural rubber grafted with different amounts of maleic anhydride: 0, 3, 8, 12 and 20 wt %. The dashed line shows the tendency of the changes and the error bars indicate twice standard deviation for each point.

Water absorbability of grafted natural rubber

To test that grafted natural rubber would take water into its hydrophilic network, samples were soaked in water. After monitoring changes in weight for 30 days, we found that untreated natural rubber (with 0 wt % of maleic anhydride) shows a slight weight gain (**Figure 3**) indicating that only a little water could be absorbed (less than 10 wt %), while grafted natural rubber, especially one with 20 wt % of maleic anhydride, reveals a dramatic increase in water content up to ~60 wt %. Obviously, samples with higher amounts of maleic anhydride, thereby containing more hydrophilicity, display larger magnitudes of water absorption. The small amount of water absorbed in the untreated samples may reflect some polarity added to natural rubber due to autoxidation during the experiment [2]. To support the result of water absorption displayed in **Figure 3**, the appearance of representative samples with 20 wt % of maleic anhydride is also shown in **Figure 4**. It was found that a light brown thin sheet of rubber became red and swollen after 30 days of soaking in red colored water. The results observed in **Figure 3** and **4** imply that water absorbing materials from nature rubber could possibly be prepared.

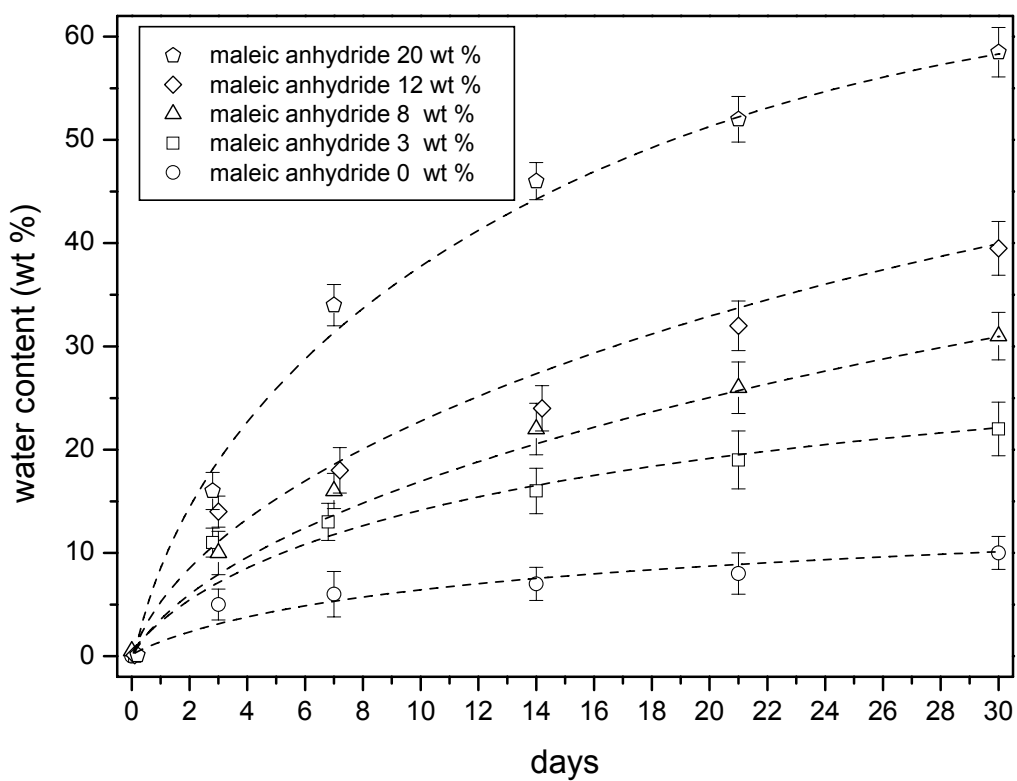


Figure 3 Water content in grafted natural rubber as a function of soaking time in water. The dashed lines show the tendency of increasing water content in each sample and the error bars indicate twice standard deviation for each point.



(a)



(b)

Figure 4 Illustration of the grafted natural rubber (20 wt % of maleic anhydride): (a) before soaking and (b) after soaking in red colored water.

CONCLUSIONS

Grafting of maleic anhydride onto natural rubber in the molten state provides a water absorbing material. We found that grafted rubber could take greater amounts of water when more maleic anhydride was incorporated. This result is consistent with the degrees of hydrophilicity of samples when monitored by contact angle measurement.

ACKNOWLEDGEMENTS

We gratefully acknowledge the Thailand Research Fund for the support of this research. We also thank the Molecular Technology Research Unit, Walailak University, for providing us with the contact angle meter.

REFERENCES

- [1] Examples of the products made of natural rubber composites are showed in the following patents. Method and apparatus for treatment of snoring, hypopnea and apnea, United States Patent: 4,761,925 August, 9, 1998. Polymer composition imparting low surface energy, United States Patent: 5,110,667 May, 5, 1992. Reciprocating gas valve for pulsing a gas, United States Patent: 6,818,094 November, 16, 2004. Anti-seismic rubber bearing, United States Patent: 4,761,925 August, 9, 1988. Available at: <http://61.19.225.243/DIPSearch/SearchSimple.aspx>, accessed June 2008.
- [2] AF Halasa, JM Massie and RJ Ceresa. *Science and Technology of Rubber*. In: Eirich FR (ed.). Academic Press, New York, 1978, p. 513-41.
- [3] H Ismail, A Rusli and AA Rashid. Maleated natural rubber as a coupling agent for paper sludge filled natural rubber composites. *Polym. Test.* 2005; **24**, 856-62.
- [4] C Nakason, S Saiwaree, S Tatum and A Kaesaman. Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate). *Polym. Test.* 2006; **25**, 656-67.
- [5] C Nakason, A Kaesaman and P Supasanthitkul. The grafting of maleic anhydride onto natural rubber. *Polym. Test.* 2004; **23**, 35-41.
- [6] C Nakason, A Kaesaman, Z Samoh, S Homsin and S Kiatkamjornwong. Rheological properties of maleated natural rubber and natural rubber blends. *Polym. Test.* 2002; **21**, 449-55.
- [7] C Nakason, A Kaesaman, S Homsin and S Kiatkamjornwong. Rheological and curing behavior of reactive blending. I. maleated natural rubber-cassava starch. *J. Appl. Polym. Sci.* 2001; **81**, 2803-13.
- [8] E Carone Jr, U Kopcak, MC Goncalves and SP Nunes. *In situ* compatibilization of polyamide 6/natural rubber blends with maleic anhydride. *Polymer* 2000; **41**, 5929-35.

- [9] Wikimedia Foundation, Inc. Wikipedia Encyclopedia: Hydrogels, Available at: <http://en.wikipedia.org/wiki/Gel>, accessed April 2008.
- [10] M/S Nichi-In Bio Sciences Co., Ltd. Sky-gel for agriculture use, Available at: <http://nichiin.com/skygel/index.htm>, accessed April 2008.
- [11] The Hindu Republication. Hydrogel to promote plant growth, Available at: <http://www.hinduonnet.com/seta/2003/04/10/stories/2003041000200300.htm>, accessed April 2008.
- [12] CNET Networks, Inc. When to use hydrogel dressing, Available at: http://findarticles.com/p/articles/mi_qa3689/is_199909/ai_n8855996, accessed April 2008.
- [13] D Hou, X Tong, H Yu, A Zhang and Z Feng. A kind of biodegradable hydrogel made from copolymerization of gelatin with polypseudorotaxanes based on alpha-CDs. *Biomed. Mater.* 2007; **2**, 147-52.
- [14] S Khongtong and GS Ferguson. The integration of bulk and interfacial properties in a polymeric system: elasticity at a polybutadiene/water interfaces. *J. Am. Chem. Soc.* 2001; **123**, 3588-94.
- [15] S Khongtong and GS Ferguson. The integration of bulk and interfacial properties in a polymeric system 2: elasticity at a polyisoprene/water interfaces. *Macromolecules* 2002; **35**, 4023-29.
- [16] DH Carey and GS Ferguson. Synthesis and characterization of surface-functionalized 1,2-polybutadiene bearing hydroxyl or carboxylic acid groups. *Macromolecules* 1994; **27**, 7254-64.
- [17] GM Whitesides and GS Ferguson. Organic chemistry in two dimensions: surface-functionalized polymers and self-assembled monolayer films. *Chemtracts* 1988; **1** 171-3.
- [18] W Li, F Xue and R Cheng. States of water in partially swollen poly(vinyl alcohol) hydrogels. *Polymer* 2005; **46**, 12026-31.
- [19] J Saelao and P Phinyocheep. Influence of styrene on grafting efficiency of maleic anhydride onto natural rubber. *J. Appl. Polym. Sci.* 2004; **95**, 28-38.

บทคัดย่อ

สุฤกษ์ คงทอง และ ณรงค์ ฝั่งชลจิตต์
ยางธรรมชาติที่เกิดการพองตัวในน้ำ

การปรับปรุงโมเลกุลยางธรรมชาติโดยการทำกิ่งต่อด้วยโมเลกุลมาลิกแอนไฮไดรด์ สามารถเปลี่ยนยางธรรมชาติให้เป็นวัสดุที่ดูดซับน้ำได้ ยางตัวอย่างดังกล่าวให้ค่ามุมสัมผัสลดลงตามการเพิ่มขึ้นของความเข้มข้นของมาลิกแอนไฮไดรด์ที่ใช้ สะท้อนให้เห็นว่ายางตัวอย่างที่ผ่านการทำกิ่งต่อมีความสามารถเข้ากับน้ำได้ดีขึ้น และพบว่าเมื่อนำยางตัวอย่างดังกล่าวไปแช่น้ำจะทำให้ยางเกิดการบวมพองในน้ำได้ โดยมีปริมาณน้ำที่ถูกดูดซับอยู่ถึงประมาณ 60 % โดยน้ำหนัก