



# Synthesis and characterization of water swellable natural rubber vulcanizates

Charoen Nakason<sup>a</sup>, Yeampon Nakaramontri<sup>a</sup>, Azizon Kaesaman<sup>a</sup>,  
Wiyong Kangwansukpamonkon<sup>b</sup>, Suda Kiatkamjornwong<sup>c,d,\*</sup>

<sup>a</sup> Center of Excellence in Natural Rubber Technology, Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand

<sup>b</sup> National Nanotechnology Center, National Science and Technology Development Agency, 130 Thailand Science Park, Paholyothin Road, Klung Luang Pathumthani 12120, Thailand

<sup>c</sup> Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand

<sup>d</sup> Division of Science, The Royal Institute of Thailand, Sanam Sueapa, Dusit, Bangkok 10300, Thailand

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## ABSTRACT

Cassava starch-g-polyacrylamide superabsorbent polymer (SAP) was prepared by a reactive batch processing. Superabsorbent polymer composites (SAPCs) were prepared by blending the SAP with bentonite. Water swellable natural rubber (WSNR) was then prepared by blending high-ammonia natural rubber latex or dry blending of epoxidized natural rubber (ENR) or maleated natural rubber (MNR) with SAPC, poly(ethylene oxide) (PEO) and trimethylolpropane trimethacrylate (TMPTMA). WSNRs containing 10 phr PEO and 2 phr TMPTMA gave higher mechanical strength and water absorbency. Increasing the PEO loadings (20–40 phr) rendered higher absorbency with lower mechanical strength. A higher scorch time and cure time with a lower crosslinking density and cure rate index were found in the MNR-modified WSNRs compared with the unmodified WSNR or ENR-modified WSNR. ENR- and MNR-modified WSNR exhibited highest water absorbency with lower mechanical strength compared with the unmodified NR-based WSNR. The SAP and vulcanized rubber were thermally degraded under oxygen atmosphere, whereas 11% of the residues were bentonite and ZnO.

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## 1. Introduction

Superabsorbent polymers (SAPs) have been synthesized by modifying the molecular structure of cassava starch, and thus gained in interest since such cassava starch-based SAPs are claimed to be biodegradable products [1,2]. In contrast, most of the current SAPs are synthetic polymers that have a poor biodegradability that then leads to

environmental problems upon their disposal. The development of starch-based SAPs could potentially be used to solve this problem. Potential applications of starch-based SAPs are fairly diverse and include, amongst others, personal care products, fire-fighting gels and agricultural uses [3]. Starch-based SAPs are developed by grafting starch with unsaturated hydrophilic monomers, such as acrylic acid (AA) [4,5], acrylamide (AM) [1–3,6–8] and  $\epsilon$ -caprolactone [9], by a chemical initiated radical chain copolymerization [10,11], or by using  $\gamma$ -ray irradiation [6]. A reactive extrusion process has been used to prepare starch-based graft copolymers [12,13]. Starch-g-polyacrylamide has been successfully prepared using a co-rotating twin screw extruder [8,14], but the maximum water absorbency capacity of the starch-g-superabsorbent polymers obtained

\* Corresponding author at: Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand.

E-mail addresses: [ncharoen@bunga.pn.psu.ac.th](mailto:ncharoen@bunga.pn.psu.ac.th) (C. Nakason), [lmomldao@gmail.com](mailto:lmomldao@gmail.com) (Y. Nakaramontri), [kazizon@bunga.pn.psu.ac.th](mailto:kazizon@bunga.pn.psu.ac.th) (A. Kaesaman), [wiyong@nanotec.or.th](mailto:wiyong@nanotec.or.th) (W. Kangwansukpamonkon), [ksuda@chula.ac.th](mailto:ksuda@chula.ac.th) (S. Kiatkamjornwong).

using this process was relatively low at only approximately 300 times their dry weight [12]. However, our previous work on the reactive blending process [1] with a specially designed batch reactor gave starch-*g*-polyacrylamide/bentonite SAPC with a higher maximum water absorbency capacity at 606 times their dry weight.

Superabsorbent polymer has its own merits in absorbing high amounts of fluid but it does not have enough gel strength while rubber is inherent with good resilience, elasticity and stability but lacks of water absorbency. To mix both materials together with a fine tuned ratio, one can produce a new material called water swellable rubber to meet the need of water absorbency and stability. Water swellable rubber was introduced in the 1970s [15] and Toyoda [16] described an overview of water-swellable rubbers as construction sealants in which superabsorbent polymer and urethane rubber type were described in detail of applications. Theoretically, WSNR is usually composed of a continuous phase of elastomer and a dispersed phase of water absorbing polymer. Any given WSNR is typically prepared by dispersing SAP particles in common hydrophobic rubbers, such as chloroprene rubber [17,18], chlorohydrin rubber [19–21], NR [22,23], and so on. They can be used as a water-stopping material in civil engineering construction such as subways and subsea tunnels [22], building construction, sealing material or in calking applications, preventing water leakage from pipes and blocking connections in many other applications. Thus, WSNRs are functional polymers that their volume is expanded up to more than 1.5 times their original weight by absorbing moisture or surrounding water. This special type of rubber possesses not only the properties of general rubber, such as high mechanical strength, resilience properties, and a low tension set but also has relatively high water absorbency. These properties are resulted in by the presence of an appropriate amount of crosslinking network in the rubber and water absorbing material [24].

A specially designed batch reactor was used to prepare starch-*g*-polyacrylamide SAP via reactive processing, based on the optimum conditions found in Nakason et al. [1]. In the present work, SAP composites (SAPCs) of the starch-*g*-polyacrylamide mixed with bentonite clay were prepared and later blended with NR and other important ingredients. That is, each WSNR was prepared by mixing SAPC particles with the NR or the modified NR, namely, epoxidized natural rubber (ENR) or maleated natural rubber (MNR) in the presence of poly(ethylene oxide) (PEO) and trimethylolpropane trimethacrylate (TMPTMA). The purposes to use PEO and TMPTMA are to increase water absorbency capacity and higher mechanical properties of the swellable rubber, respectively. Each ingredient was then compounded and cured by the sulfur vulcanization system. The effects of the addition of SAPC, PEO and TMPTMA on the water absorbency, curing characteristics, mechanical and morphological properties of the resulting WSNR compounds and vulcanizates were then investigated. The present work uses bio-based polymers of starch and natural rubber as starting materials for preparing superabsorbent polymer composite as the disperse domain and the continuous phase, respectively. Both phases were aimed to be degraded under heat and oxygen environment.

## 2. Experimental

### 2.1. Materials

Table 1 illustrates the raw materials used in this research. Maleated natural rubber (MNR) was prepared in-house by blending the rubber air-dried sheet (manufactured by Khuan Pun Tae Farmer Co-operation, Phattaluang, Thailand) with 8 phr of maleic anhydride at 150 °C using an internal mixer (Brabender Plasticorder, model PLE331, Brabender OHG Duisburg, Germany) at a rotor speed of 60 rpm. Details of the preparation and characterization procedures of MNR were described by Nakason and Saiwari [25]. Sodium lauryl sulfate was prepared in-house by reacting lauric acid with sodium hydroxide (BDH, England).

For preparation of WSNR, TMPTMA was used as a cross-linking co-agent with sulfur vulcanizing agent and as a coupling agent as well to bind the two different phases, whereas PEO was used to enhance water absorbency capacities of SAPC in the rubber phase. Zinc oxide and stearic acid, used as the activators in the sulfur vulcanization system, *N*-tert-butyl-2-benzothiazyl sulphenamide (TBBS), used as an accelerator for sulfur curing agent.

All spectra for the starting materials and the neat natural rubber peaks were not shown here but their main peaks are given as follows: 3224 cm<sup>-1</sup> (w),  $\nu_{\text{O-H}}$  OH (moisture in the rubber); 3037 cm<sup>-1</sup> (s)  $\nu_{\text{C-H}}$ ; 2960, 2916 and 2850 cm<sup>-1</sup>,  $\nu_{\text{C-H}}$ ; 1661 cm<sup>-1</sup>,  $\nu_{\text{C=C}}$ ; 1447 and 1375 cm<sup>-1</sup>,  $\rho_{\text{C-H}}$ ; 826 cm<sup>-1</sup>  $\nu_{\text{C-H}}$  on cis C=C of polyisoprene, or  $\delta_{\text{C-H}}$  polyisoprene. For the neat PEO, the following peaks were found: 3450 cm<sup>-1</sup>,  $\nu_{\text{OH}}$  (hydration of PEO); 2889 cm<sup>-1</sup>,  $\nu_{\text{CH}}$ ; 1632 cm<sup>-1</sup>,  $\nu_{\text{C=O}}$ ; 1467 cm<sup>-1</sup>,  $\delta_{\text{asH-C-H}}$ ; 1360 cm<sup>-1</sup>,  $\delta_{\text{sH-C-H}}$ ; 1149 cm<sup>-1</sup>,  $\nu_{\text{C-O-C}}$ ; 916, 842 cm<sup>-1</sup>,  $\rho_{\text{CH}_2}$  (gauche) [26,27]. For the neat TMPTMA, 2980, 2920, 2900 cm<sup>-1</sup>,  $\nu_{\text{CH}}$  (ali); 1870 cm<sup>-1</sup>,  $\nu_{\text{as C=O}}$  (w); 1720 cm<sup>-1</sup>,  $\nu_{\text{as C=O}}$  (s); 1640 cm<sup>-1</sup>,  $\nu_{\text{C=C}}$  (m); 1480 cm<sup>-1</sup>,  $\delta_{\text{C-H}}$  were found.

### 2.2. Preparation of cassava starch-graft-polyacrylamide superabsorbents (cassava starch-*g*-PAM, SAPs) and associated composites (SAPCs) by reactive blending

Cassava starch-*g*-PAM was prepared by a reactive batch processing using a specially designed batch reactor, with the preparation and characterization as described before [1]. The SAPC loaded with 20 phr of bentonite clay was prepared from the cassava starch-*g*-PAM according to the described procedures below.

### 2.3. Preparation of WSNR

The high-ammonia concentrated NR latex was first mixed with the SAPC (loaded with 20 phr of bentonite clay) and 2% (w/w) of SDS surfactant for 1 h at room temperature, and then the mixture was aged for 24 h to allow it to reach equilibrium. The mixture was then cast into 10 × 10 cm thin films and dried at room temperature for 24 h followed by drying in a hot air oven for over 24 h at 40 °C. The ENR and MNR derived WSNRs or called modified

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