

Effect of crosslinking agent and starch contents on hydrogel from deproteinized natural rubber latex and starch

Achara Kleawkla^{1,*}, Supinyo Srivipak¹, Ekawit Threenet¹, Pairot Wongputtisin²

¹Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai, 50290 Thailand

²Department of Biotechnology, Faculty of Science, Maejo University, Chiang Mai, 50290 Thailand

*Corresponding Author: achara_kleawkla@yahoo.co.uk

Received: 16 March 2017; Revised: 14 October 2017; Accepted: 16 October 2017; Available online : 1 January 2018
Paper selected from The 8th International Science, Social Sciences, Engineering and Energy Conference (I-SEEC 2017)

Abstract

Natural rubber latex from rubber tree (*Hevea brasiliensis*) is an important natural polymeric resource in Thailand. Natural rubber latex is widely used in several rubber product manufactures especially medical application. However, an allergy is often found when use rubber products. It may cause of an allergen in rubber latex. Then, the objective of this research was prepared hydrogel from deproteinized natural rubber latex (DNRL) with gelatinized starch. Method I, crosslinked deproteinized natural rubber latex (DNRL) was firstly prepared by using zinc mercaptobenzothiazole (ZMBT) as initiator and sulphur as crosslinking agent. Method II, using potassium persulfate as initiator and N,N'-methylenebisacrylamide (MBA) as crosslinking agent. Secondly, the crosslinked DNRL was mixed with gelatinized starch by mechanical stirrer. Finally, the mixture was casted on a glass mould to form thin film via crosslinked reaction at 60 °C in oven for 24 hr. Hydrophilicity properties of hydrogel were determined in term of % swelling and % water content. It was found that hydrogel from DNRL with gelatinized starch crosslinking with MBA provided statistically a greater level of % swelling and % water content. Furthermore, hydrogel from DNRL with gelatinized starch are able to developed for use as wound dressing in medical application.

Keywords: deproteinized natural rubber latex; hydrogel; wound dressing

©2018 Sakon Nakhon Rajabhat University reserved

1. Introduction

Hydrogel refers to a broad class of polymeric materials which swell extensively, but do not dissolve in water. They include many natural material of both plant and animal origin. Because of the similarity between synthetic and natural hydrogels, these gels have been used in a wide variety of medical application. An application of hydrogels such as wound dressing, suture, contact lenses and artificial organs [1]. Hydrogels, or water containing gels, consist of polymeric networks characterized by hydrophilicity and insolubility in water. In water, they swell to an equilibrium volume but preserve their shape. The hydrophilicity is due to the presence of water solubilizing groups, for example –OH, –COOH, –CONH₂, –CONH–, SO₃H [1]. The insolubility and stability of shape are due to the presence of a three dimensional network. The swollen state results from a balance between the dispersing forces acting on hydrated chains and cohesive force that do not prevent the penetration of water into the network. There are several factors, favorable and inhibitive, which influence the degree of hydrogel swelling. Some of the favorable influences on swelling are osmotic potential, strong interactions with water, high free volume, high chain flexibility and low crosslink density. Conversely, the inhibitive factors affecting swelling are weak interactions with water, low free volume, low chain flexibility, and

high crosslink density. When dehydrated polymer is placed in water, there will be an osmotic driving force for the water to enter the water free region within the polymer. As water enters the polymer, the chains extend and exert a resistive force because swelling places the chains into less entropically desired configurations. The entrance of water into the system will necessitate its expansion and a consequent ordering of the polymer chain. Since the chains will be elongated into less entropically desirable configurations, they exert a resistive force. When this resistive force balances the osmotic force driving water into the polymer, at that point, the equilibrium degree of swelling will have been achieved.

Natural rubber or para rubber (*Hevea Brasiliensis*) is an important natural polymeric resource in Thailand. The outstanding mechanical properties of natural rubber, such as elasticity and tear resistance, are more than synthetic rubber from petrochemical industry [2]. Natural rubber is a hydrophobic polymer and high elasticity with structure has unsaturated double bonds which can be degraded from UV, heat, oxygen and ozone. However, the modification of natural rubber can be performed via double bond on main chain of natural rubber such as hydrogenated natural rubber and grafted copolymer onto natural rubber. Many researcher have interested to improve hydrophilicity of natural rubber that is a popularly elastic material and uses to widely applications such as tire, glove, drug delivery [3] and also promote angiogenesis which is helpful for wound healing process [4].

In general, hydrogels were prepared from synthetic polymers so they were expensive. Hydrogels from natural rubber are an alternative for use as wound dressing. Natural polymer has many advantages such as non-toxic in environment and biodegradable. However, natural rubber in medical applications must eliminate the protein allergens by using protease to remove proteins but it cannot used as a rubber material to absorb water, which is an important feature of the wound because rubber is a polymer of hydrophobic. Natural rubber, which is required to resolve this disadvantage by improving the properties of a natural hydrophilicity. At this point, Khongtong *et al.* [5] prepared water swollen natural rubber by grafting maleic anhydride onto natural rubber chains and Kiyajan *et al.* [6] grafted the modified cassava starch onto natural rubber to improve the hydrophilicity and biodegradation of natural rubber. This method could change the hydrophobicity to hydrophilicity of natural rubber. Starch is a nutritional polysaccharide and the major storage carbohydrate in plant. It is a hetero polysaccharides composed of two polysaccharides, amylose and amylopectin. They related to swelling and water absorption properties which are useful for exudates absorption from injury [7]. The objective of this research was prepared hydrogel from deproteinized natural rubber latex (DNRL) with gelatinized starch by casting in thin films. The effects of starch contents and crosslinking agent on hydrophilicity of hydrogel were investigated.

2. Materials and Methods

Materials

Natural rubber latex (NRL, 60% natural rubber content) was obtained from Thai Rubber Latex Corporation Public Company Limited, Thailand. Starch was purchased from E.T.C. Eaib Tong Chan Company Limited, Thailand. Sulphur and N,N'-methylene bisacrylamide (MBA, 99%) were used as crosslinking agent. Zinc mercaptobenzothiazole (ZMBT) and potassium persulfate were used as initiator. Potassium hydroxide (KOH, 85%) (Carlo Erba Co., Ltd., Italy) and Tween® 80 were also used in this study.

Preparation of DNRL

Natural rubber latex (NRL, 60% natural rubber content) and protease were mixed in ratio 500:100 unit ml⁻¹ to incubated at 45 °C with 150 rpm shaking for 6 hour.

Preparation of hydrogels from sulphur-pretreated DNRL with starch

60% DNRL (100 parts per hundred rubber, phr) was mixed with 50% dispersion of 1.50 phr sulfur solution, 50% dispersion of 1.80 phr zinc oxide solution, 50% dispersion of 1 phr zinc

mercaptobenzothiazole (ZMBT) solution and 50% dispersion of 1 phr lowinox® CPL solution incubated for 24 hour. Then gelatinized starch was mixed gently to DNRL mixture in ratio of DNRL:Starch; 1:2 at 60 °C for 24 hour.

Preparation of hydrogels from MBA polymerization DNRL with starch

60% DNRL (100 phr) polymerization was made by 10% KOH 5 phr, Tween® 80 5 phr at 70 °C and 1 phr of K₂S₂O₈ was continually added while stirring for 15 minute and then added 1 phr of MBA. The reaction was then allowed to proceed for 2 hour under continuous stirring and then the reaction was stopped by cooling down at room temperature to mix with gelatinized starch were added and mixed gently to DNRL mixture by ratio of DNRL: Starch; 1: 2 at 60 °C for 24 hour.

Mass swelling and water content (WC) studies

Hydrogel samples were cut into (2 × 2 cm²) pieces. Then, they were immersed in distilled water at room temperature. Remove the excess media on the surface with tissue paper. The weight of swollen sample would be calculated following equation 1 and 2.

$$\% \text{ Mass swelling} = \frac{\text{weight of swollen polymer} - \text{weight of initial polymer}}{\text{weight of initial polymer}} \times 100 \quad (1)$$

$$\% \text{ WC} = \frac{\text{weight of swollen polymer} - \text{weight of initial polymer}}{\text{weight of swollen polymer}} \times 100 \quad (2)$$

Chemical characterization

In this research project, the functional groups of hydrogels were investigated by Fourier Transform Infrared Spectrometer (Perkin Elmer model Spectrum RX I, Perkin Elmer, England). The spectra were recorded in the range 400 – 4,000 cm⁻¹. The FTIR spectra were obtained from samples prepared in thin film.

3. Results and Discussion

Mass swelling studies

The effect of starch contents and crosslinking agent on water absorption in term of % mass swelling is presented in Fig. 1. It was found that, hydrogels with 2 – 3% cassava starch were higher % mass swelling than DNRL due to the presence of crosslink network including high amylose content of cassava starch in hydrogel. Similarly, the percentage of mass swelling and water absorption increased with increasing amylose content [8]. The results as shown in Fig. 1 that when concentration of starch increased, the mass swelling of hydrogels increased. When comparison of type of crosslinking agent used in experimental, it was found that method II, using potassium persulfate as initiator and N,N'-methylenebisacrylamide (MBA) as crosslinking agent gave higher mass swelling than method I, using zinc mercaptobenzothiazole (ZMBT) as initiator and sulphur as crosslinking agent.

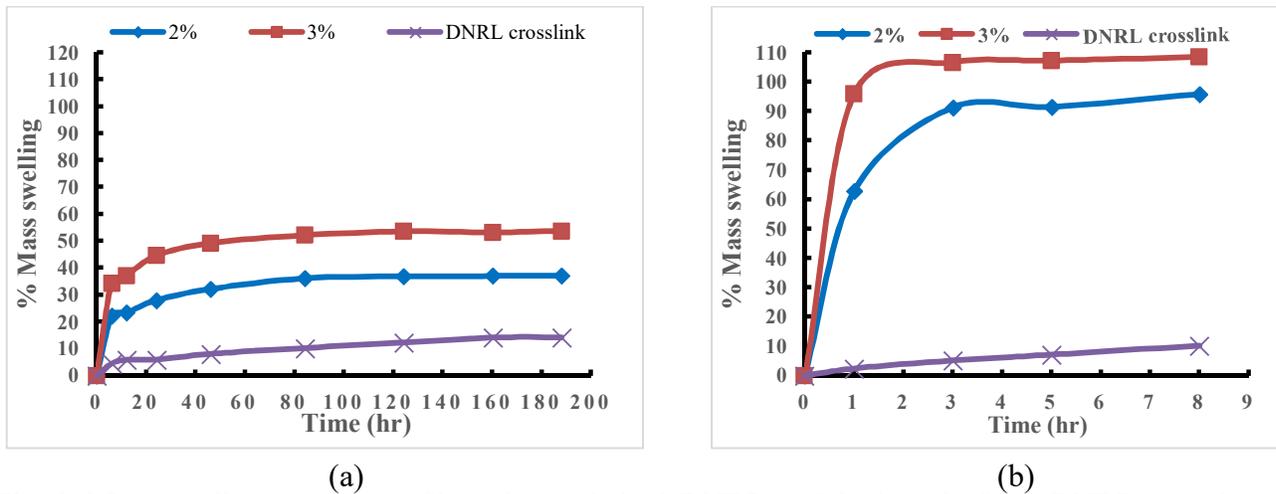


Fig. 1 Mass swelling - time profiles of crosslinked DNRL and hydrogels from DNRL mixed with gelatinized cassava starch on DNRL: Starch ratio 1:2 using method I (a) and method II (b)

Water content

The effect of starch contents and crosslinking agent on water absorption in term of % water content is presented in Fig. 2. The result of hydrogels from DNRL mixed with gelatinized cassava starch shown 2 – 3% gelatinized cassava starch were higher % water content than pure rubber (DNRL). The reason due to the presence of crosslink network including high amylose content of cassava starch in hydrogel. Similarly, the percentage of mass swelling and water absorption increased with increasing amylose content. When increased concentration of starch, % water content of hydrogels increased. When comparison of type of crosslinking agent use in experimental, it was found that method II, using potassium persulfate as initiator and N,N'-methylenebisacrylamide (MBA) as crosslinking agent gave higher % water content than method I, using zinc mercaptobenzothiazole (ZMBT) as initiator and sulphur as crosslinking agent.

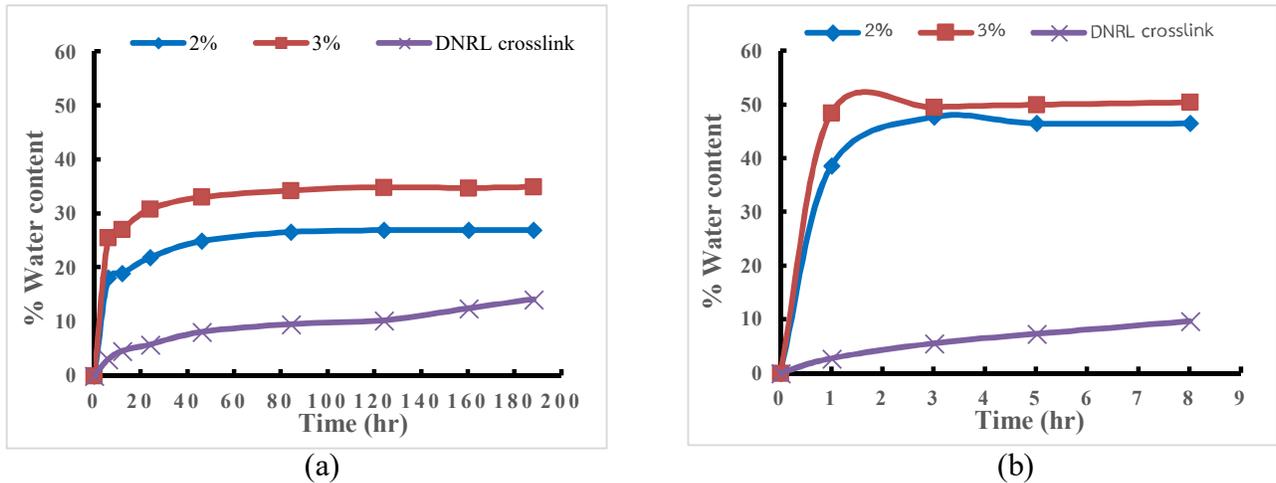


Fig. 2 Water content - time profiles of crosslinked DNRL and hydrogels from DNRL mixed with gelatinized cassava starch on DNRL: Starch ratio 1 : 2 using method I (a) and method II (b)

From the results, the effect of starch contents and crosslinking agent on water absorption in term of % mass swelling and % water content as shown in Fig. 1 – 2. When concentration of starch increased, the % mass swelling and % water content of hydrogels increased. It was anticipated that the hydroxyl group of starch with high starch contents would promote the superior water absorption of hydrogel

owning to the abundance hydroxyl groups which are available for interaction with the water molecules [9]. When comparison of type of crosslinking agent use in experimental, it was found that method II, using potassium persulfate as initiator and N,N'-methylenebisacrylamide (MBA) as crosslinking agent gave higher % mass swelling and % water content than method I, using zinc mercaptobenzothiazole (ZMBT) as initiator and sulphur as crosslinking agent. The reason was because after the hydroxyl groups of starch absorbed water molecules into hydrogel, the chains could easily expanded and retained volumes of water molecules. Guilherme *et al.* [10] reported that hydrogel presented high water absorption because of the flexibility and hydrophilicity of the polymer structure.

Chemical characterization

FTIR spectra of DNRL, DNRL crosslinked, DNRL with 3% cassava starch crosslinked with sulphur and cassava starch as shown in Fig. 3.

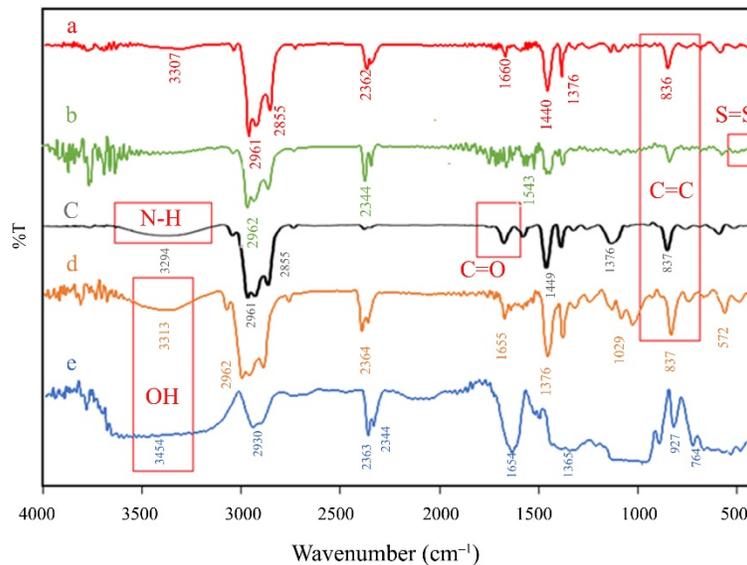


Fig. 3 FTIR spectra of (a) DNRL (b) DNRL crosslinked with sulphur (c) DNRL crosslinked with MBA (d) DNRL with 3% cassava starch crosslinked with sulphur and (e) cassava starch

The structure of DNR, DNRL crosslinked with sulphur, DNRL crosslinked with MBA, DNRL with 3% cassava starch crosslinked with sulphur and cassava starch were confirmed by FTIR spectroscopy. Both DNRL, DNRL crosslinked and DNRL with 3% cassava starch crosslinked with sulphur spectra show the absorption peak at 836 – 837 cm^{-1} which can be assigned to the vibration of double bond in backbone of rubber molecules. The peak at 3,313 – 3,454 cm^{-1} is the stretching of O-H in starch. The peaks at 3,294 and 1,660 cm^{-1} are the stretching of N-H and C=O, respectively, that can be attributed to acrylamide functional group in MBA. From the results, it indicates that the successful preparation of hydrogel from deproteinized natural rubber latex and starch used sulphur and MBA as crosslinking agent respectively.

4. Conclusion

This research was successfully prepared hydrogels from deproteinized natural rubber latex (DNRL) with gelatinized starch, using sulphur and N, N'-methylenebisacrylamide (MBA) as crosslinking agent to study the effect of starch contents and crosslinking agent on water absorption in term of % mass swelling and % water content. It was found that, % mass swelling and % water content increase with increase starch contents. MBA crosslinking agent showed % mass swelling and % water content higher than using sulphur as crosslinking agent. The reason because the hydroxyl group of starch after

absorption of water molecules into hydrogel resulted in the expansion of chains and can retained volumes of water molecules. Thus, hydrogels from deproteinized natural rubber latex and starch are able to develop for using in medical application in further study.

5. Acknowledgements

This research is financially supported by Thailand Research Fund (TRF). The authors gratefully acknowledge the Department of Chemistry, Faculty of Science and Department of Rubber and Polymer Technology, Faculty of Engineering and Agro-Industry, Maejo University for provide laboratory facilities.

6. References

- [1] M. Kurecic, M. Sfiligoj-Smole, K. Stana-Kleinschek, UV polymerization of poly (N-isopropylacrylamide) Hydrogels, *MTAEC9*. 46(1) (2012) 87 – 91.
- [2] S. Kongparakul, Natural Rubber Modification Technology and Its Applications, *KKU Sci.J.* 41(3) (2013) 567 – 581.
- [3] R.D. Herculano, G.C. Belmonte, A. Kinoshita, O N. Oliveira Jr, C. Fo Graeff, On the release of metronidazole from natural rubber latex membrances, *Mater Sci Eng.* 31(2) (2011) 272 – 275.
- [4] G. Gallego Ferrer, M. Monleon Pradas, J.L. Gomez Ribelles, F Romero Colomer, I. Castilla-Cortazar, A. Vidaurre, Influence of the nature of the porous confining network on the sorption, diffusion and mechanical properties of hydrogel IPNs, *Eur Polym J.* 46(4) (2010) 774 – 782.
- [5] S. Khongtong, N. Fungchonlajit, Water swollen natural rubber, *Walailak J Sci & Tech.* 5(1) (2008) 67 – 75.
- [6] S. Riyajan, Y. Sasithornsonti, P. Phinyocheep, Green natural rubber-g-modified starch for controlling urea release, *Carbohydr Polym.* 89 (2012) 251 – 258.
- [7] W. Zou, L Yu , X Lin, L. Chen, X. Zhang, D Qiao, Effects of amylose/amylopectin ratio on starch-based superabsorbent polymers, *Carbohydr Polym.* 87(2) (2012) 1583 – 1588.
- [8] J. Pratoomted, S. Sila-on, U. Puapermpoonsiri, High Dose Cefazolin for Entrapment in Interpenetrating Network Hydrogel Comprising of natural rubber and rice starch, *Isan J. Phar. Sci.* 9 (2014) 1 – 5.
- [9] G.H. Yew, A.M.M. Yusof, Z.A.M. Ishak, U.S. Ishiaku, Water absorption and enzymatic degradation of Poly (lactic acid)/rice starch composites, *Polym. Degrad. Stab.* 90 (2005) 488 – 500.
- [10] M.R. Guilherme, A.V. Reis, S.H. Takahashi, A.F. Rubira, J.P.A. Feitosa, E.C. Muniz, Synthesis of a novel superabsorbent hydrogel by copolymerization of acrylamide and cashew gum modified with glycidyl methacrylate, *Carbohydr Polym.* 61 (2005) 464 – 471.