การศึกษาความหนืดและคุณสมบัติเชิงกลของไฮโดรเจลโครงร่างตาข่ายแบบแทรกสอดจากยางธรรมชาติและแป้ง

จตุพร ประทุมเทศ[1], วริษฎา ศิลาอ่อน[1], ชัยวุฒิ วัดจัง[2], อุษณา พัวเพิ่มพูลศิริ[1*]

บทคัดย่อ

การศึกษาความหนืดและคุณสมบัติเชิงกลของไฮโดรเจลโครงร่างตาข่ายแบบแทรกสอดจากยางธรรมชาติและแป้ง
จตุพร ประทุมเทศ[1], วริษฎา ศิลาอ่อน[1], ชัยวุฒิ วัดจัง[2], อุษณา พัวเพิ่มพูลศิริ[1*]

บทนำ: คุณสมบัติการไหลและคุณสมบัติเชิงกลของไฮโดรเจลมีผลต่อการเตรียม การขึ้นรูปแผ่นฟิล์ม และการประยุกต์ใช้งานของไฮโดรเจล ดังนั้นการศึกษานี้มีวัตถุประสงค์เพื่อศึกษาผลของแป้งดัดแปรต่อความหนืดและคุณสมบัติเชิงกลของไฮโดรเจลโครงร่างตาข่ายแบบแทรกสอดจากยางธรรมชาติและแป้ง (แป้งข้าวเจ้าและแป้งกล้วย) **วิธีการดำเนินการวิจัย:** เตรียมยางด้วยวิธีฟรีแรดดิคอลพอลิเมอไรเซชัน โดยมี N,N-Methylenebisacrylamide (MBA) เป็นสารเชื่อมขวางยางธรรมชาติ จากนั้นผสมกับแป้งที่เชื่อมขวางด้วยกรดมาเลอิค (maleic acid) ที่อุณหภูมิห้อง และศึกษาความหนืดของแป้งดัดแปรแต่ละชนิดและคุณสมบัติเชิงกลของไฮโดรเจล **ผลการศึกษาวิจัย:** ที่อุณหภูมิ 25 องศาเซลเซียส พบว่าน้ำยางธรรมชาติมีความหนืดต่ำกว่าแป้งพรีเจลาติไนซ์จากแป้งข้าวเจ้าและแป้งกล้วยอย่างมีนัยสำคัญ (22.09 $\pm$ 12.86, 2957.67 $\pm$ 807.51 เซ็นติพอยต์ และ 19253.33 $\pm$ 5173.6 เซ็นติพอยต์ ตามลำดับ $p < 0.05$) เมื่อผสมแป้งกับยางธรรมชาติเพื่อเตรียมไฮโดรเจลจะทำให้ระบบมีความหนืดเพิ่มขึ้น พบว่า ไฮโดรเจลจากแป้งกล้วย ที่ปริมาณสารเชื่อมขวาง 2 phr อัตราส่วนยางต่อแป้ง 1:2 ให้ค่าความหนืดมากกว่าจากแป้งข้าวเจ้าอย่างมีนัยสำคัญ (9607.33 $\pm$ 5965.21 เซ็นติพอยต์ และ 1667 $\pm$ 844.88 เซ็นติพอยต์ ตามลำดับ $p < 0.05$) เนื่องจากแป้งกล้วยมีปริมาณอะไมโลสสูงกว่าแป้งข้าวเจ้าทำให้ต้องใช้พลังงานในการเคลื่อนสายโซ่ในอะไมโลสมาก อย่างไรก็ตามไฮโดรเจลจากแป้งกล้วยมีความสามารถในการขึ้นรูปเป็นแผ่นต่ำ ดังนั้นไฮโดรเจลจากแป้งข้าวเจ้าจึงมีความเหมาะสมในการเตรียม จากการศึกษาคุณสมบัติเชิงกลของไฮโดรเจลจากแป้งข้าวเจ้า พบว่าเมื่อปริมาณสารเชื่อมขวางเพิ่มขึ้น ความแข็งแรงของไฮโดรเจลจะเพิ่มขึ้นและมีความยืดหยุ่นน้อยเนื่องจากเกิดการเกาะกลุ่มกันของแกรนูลแป้ง **สรุปผลการวิจัย:** ไฮโดรเจลจากยางธรรมชาติและแป้งข้าวเจ้าเป็นวัสดุที่มีความหนืดที่สามารถขึ้นรูปได้และเป็นวัสดุที่มีความแข็งแรงแต่มีความเปราะ ดังนั้นควรพัฒนาคุณสมบัติเชิงกลของไฮโดรเจลต่อไป

คำสำคัญ: ไฮโดรเจลโครงร่างตาข่ายแบบแทรกสอด ยางธรรมชาติ แป้ง ความหนืด คุณสมบัติเชิงกล

Abstract

Apparent Viscosity and Mechanical Properties Studies of Interpenetrating Network Hydrogel from Natural Rubber and Starch

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Introduction: Viscosity and mechanical properties of interpenetrating network (IPN) hydrogel are important for preparation process, film forming/molding and application. This work aims to the study the effects of different types of starch on apparent viscosity and mechanical properties on IPN hydrogel characteristic. **Materials and Method:** IPN hydrogel was prepared by the free-radical polymerization and was evaluated apparent viscosity before casting at 25ºC. Crosslink density and mechanical properties were also determined for IPN hydrogel. **Results:** At temperature 25 ºC, natural rubber provides statistically a lower apparent viscosity than pre-gelatinized rice starch and pre-gelatinized banana starch (22.09 ± 12.86, 2957.67 ± 807.51 and 19253.33 ± 5173.60 cP, respectively, $p < 0.05$). The viscosity of natural rubber mixture increased after starch into mixture. IPN hydrogel with MBA 2 phr comprising of natural rubber and banana starch provides statistically a higher apparent viscosity than IPN hydrogel from rice starch (9607.33 ± 5965.21 cP and 1667 ± 844.88 cP, respectively $p < 0.05$). It may be due to banana starch has a higher % amylose content than rice starch which lead to require more energy to move. In addition, a higher MBA amount enhanced higher crosslink density and tensile strength as well as lower elongation at break due to the agglomeration of starch granule that show rigid or stiffer. **Conclusion:** IPN hydrogel comprising of natural rubber and banana starch is not suitable for this work because discontinuous film was appeared during film forming. Rice starch is applicable to use for IPN hydrogel from natural rubber by this method. IPN hydrogel from natural rubber and rice starch is strong but brittle. Thus, it should be develop the mechanical properties in further study.

Keywords: Interpenetrating network (IPN) hydrogel, natural rubber, starch, apparent viscosity, mechanical properties

Introduction

Hydrogel is alternatively developed as a pharmaceutical material. The disadvantages of hydrogel are poor mechanical properties. The formation of interpenetrating network (IPN) structure is the way for enhancing the mechanical properties (Yue *et al*., 2009). Natural rubber (NR) and starch (S) (rice starch and banana starch) were employed for IPN hydrogel assembly. Natural rubber was extracted from the bark of the *Hevea Brazilliensis* tree. Natural rubber has been reported to provide poor swelling and water absorption properties (Puapermpoonsiri *et al*., 2014). Also they can show good elasticity. Starch consists of amylose and amylopectin. In the recently has been reported that the different of amylose content affect on the viscosity such as corn starch (Xie *et al*., 2009). And also amylose content is related to swelling and water absorption properties (Zou *et al*, 2012). These properties can be useful for use as pharmaceutical material.

Aim of this study is to investigate the effects of different type of starch on apparent viscosity and mechanical properties on IPN hydrogel characteristic.

Materials and Method

Materials

Natural rubber latex (NRL, 60% natural rubber content) (Luck Four Co., Ltd., Bangkok, Thailand) and modified starch (prepared from lab) were used for IPN-hydrogel frabrication. Potassium persulphate (KPS, 97%) (Ajax Finechem Pty Ltd., Aucland New Zealand) and *N,N′*-methylenebisacrylamide (MBA, 99%) (Sigma-Aldrich, Missouri, USA) were used for natural rubber latex polymerization. Maleic acid (Sigma-Aldrich,, MO, Austria) was used as starch crosslinker. Potassium hydroxide (KOH, 85%) (Carlo Erba Co., Ltd., Italy) and Tween 80 (Sigma-Aldrich, MO, United Kingdom) were also used in this study.

Methods

1. Preparation of IPN hydrogel

Natural rubber latex (NRL) polymerization was made by KOH, Tween 80, KPS and MBA with 1 and 2 parts per hundred rubber (phr). Following polymerization of NRL, pre-gelatinized starch with maleic acid were added and mixed gently to NRL mixture by ratio of NRL: S 1:2.

2. Viscosity study

One millilitre of sample was determined the apparent viscosity at 25 ºC by rheometer (HAAKE MARS III). Cone plate model P35TiL and the shear rate over the range of 0.1-1,000 s^{-1} was used.

3. Crosslink density measurement

Samples 0.1 g were immersed in toluene 50 ml at room temperature for one week and dried in hot air oven at 70°C until constant weight was obtained and calculated by Flory-Rehner equation.

4. Mechanical properties

The tensile strength and elongation at break (%EB) were measured using universal machine (M350-5 AT, Testometric, UK). Samples were cut via dye in the dumbbell shape (25×160 mm^2) with gage length 25 mm and test at a cross head speed of 10 mm/min. All data shows mean ± standard deviation (SD). One – way ANOVA analysis of the variance followed by post hoc analysis was used to test the statistical significant of the results at ($p < 0.05$).

Results

Apparent viscosity study

Natural rubber provides the lowest apparent viscosity as shown in Figure 1. A higher MBA amount, a greater viscosity of natural rubber mixture was seen. It was clearly supported by the crosslink density value. The different types of starch also provides the significant different of viscosity ($p < 0.05$) in Figure 2. As the results, banana starch provides a higher apparent viscosity than rice starch because the percentage of amylose content of banana starch is higher than rice starch (16.71 %, and 15.36 % respectively). Similarly, Xie and colleagues (2009) also reported that the apparent viscosity of starch increased with increasing amylose content (Xie *et al.*, 2009) due to long linear chains in amylose have the higher energy to move. When starch was added into natural rubber, the apparent viscosity was increased in this system (data not shown) (Sila-On *et al.*, 2014).

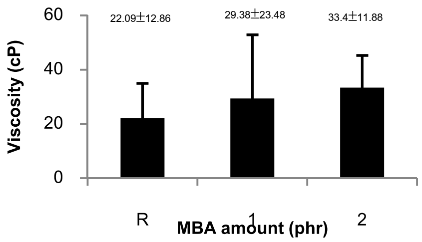

Figure 1 Apparent viscosity of pure rubber (R) and crosslinked rubber with different MBA amount (1 and 2 phr) (n=3, mean±SD)

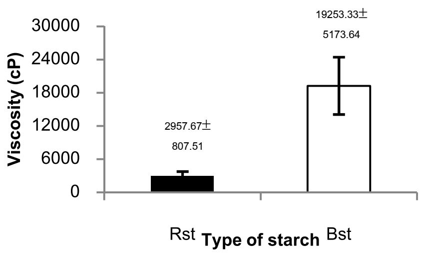

Figure 2 Apparent viscosity of pre-gelatinized rice starch (rst) and banana starch (bst) (n=3, mean±SD)

Crosslink density

Natural rubber with 0, 1 and 2 phr MBA amount provides the significant crosslink density value 0.18 ± 0.01, 0.24 ± 0.02 and 0.46 ± 0.05 mol/m^3, respectively ($p < 0.05$). Crosslink density increased with increasing MBA amount due to the higher degree of crosslinking network. Jagadish and Vishalakshi (2012) also report that crosslink density is related to mechanical properties.

Mechanical properties

The effect of MBA amount of pure rubber and IPN hydrogel comprising of natural rubber and rice starch on the tensile strength are shown as Figure 3 and 4 (Banana starch was excluded since it produced discontinuous film). Pure rubber has the higher strength comparing with crosslinked rubber (Figure 3) due to capable of crystallization in high strain state (Saijun *et al*., 2009). In Figure 3 and 4, it illustrates that natural rubber and IPN hydrogel provides a greater tensile strength with increasing MBA amount ($p < 0.05$) because of increasing crosslinked network. The tensile strength of IPN hydrogel increased but elongation at break decreased due to the agglomeration of starch granule resulted for the rigidity (Hoque *et al*., 2013) whereas natural rubber provides a higher elongation at break than IPN hydrogel as shown in Figure 5 and 6. It demonstrates that natural rubber is ductile material and IPN hydrogels is brittle material which shows plastic deformation or irreversible.

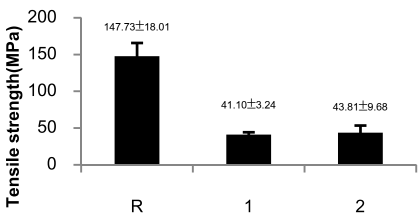

Figure 3 Tensile strength of pure rubber (R) and crosslinked rubber with different MBA amount (1 and 2 phr) (n=3, mean±SD)

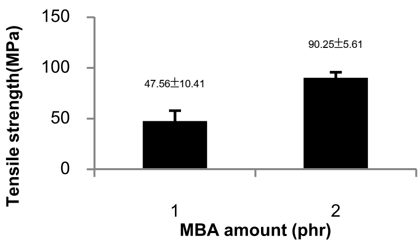

Figure 4 Tensile strength of hydrogel from natural rubber and rice starch with different MBA amount (1 and 2 phr) on ratio NRL:S 1:2 (n=3, mean±SD)

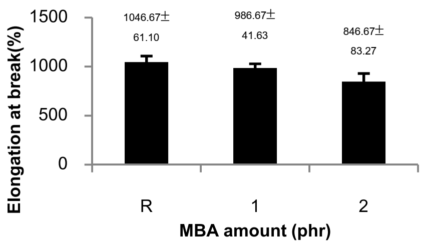

Figure 5 Elongation at break of pure rubber (R) and crosslinked rubber with different MBA amount (1 and 2 phr) (n=3, mean±SD)

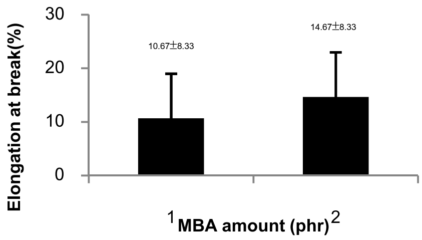

Figure 6 Elongation at break of hydrogel from natural rubber and rice starch with different MBA amount (1 and 2 phr) on ratio NRL:S 1:2 (n=3, mean±SD)

Conclusion

Different type of starch affect to apparent viscosity. The apparent viscosity increased at higher amylose content of starch. As MBA amount increasing, crosslink density of IPN hydrogel also increased and produced the increasing of tensile strength with the lower elongation at break due to the agglomeration of starch granule. Therefore, IPN hydrogel from natural rubber and rice starch at MBA amount 2 phr on NRL:S ratio 1:2 is rigid material. In further study, it would be enhanced this properties for use as pharmaceutical material.

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