# pH-Induced Crosslinking of Rice Starch *via* Schiff Base Formation

Narudom Srisawang[1]
Saksit Nobsathian[2]
Supa Wirasate[3,4]
Chayanisa Chitichotpanya*[,3,4]

[1] School of Materials Science and Innovation, Faculty of Science, Mahidol University, Bangkok, 10400,Thailand

[2] Nakhon Sawan Campus, Mahidol University, 402 Khao Thong, Phrayuha Khiri District, Nakhon Sawan 60130, Thailand

[3] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok, 10400, Thailand

[4] Center for Surface Science and Engineering, Faculty of Science, Mahidol University, Nakhon Pathom, Thailand

Abstract: Rice starch is an abundant, inexpensive, and biocompatible biopolymer with a wide range of potential applications, particularly in the biomedical field. However, the use of rice starch is limited because of its water-solubility. One way of addressing this is to modify the crosslinking properties. If the degree of crosslinking is sufficiently high, the starch becomes insoluble in water, but it remains swellable. In this study, the first synthesis of pH-induced crosslinking of rice starch without the use of any external chemical crosslinking agent was demonstrated. The crosslinked rice starch was prepared by forming a Schiff base reaction (imine) between the two modified starches: oxidized rice starch (ORS) and amino rice starch (ARS). Here, the ORS and ARS were successfully synthesized, with the content of the glucose units being 32.01 and 27.80 mol%, respectively. Imine bonds were shown to be formed from the aldehyde and amine groups. The relationships between the pH and the degree of crosslinking were also investigated. The chemical structures of the synthesized ORS and ARS and their crosslinked products at different pH levels were determined by ^{1}H NMR, ^{13}C NMR, and FTIR. Furthermore, the effect of pH on swelling behavior was explored. The relationships between the pH and the chemical structure agreed well with the swelling behavior. The swelling ratio was the highest at pH 5 and decreased with increased pH. Under basic conditions, hydrolysis was initiated, reducing the crosslink density and the efficiency of water uptake. The present study suggests that the pH-induced crosslinked rice starch can be a promising biomaterial for controlled release applications.
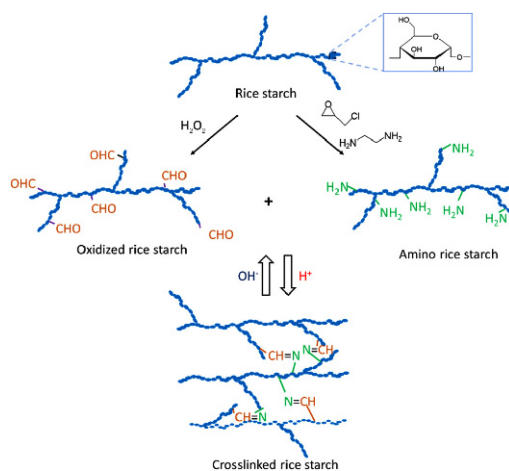
Keywords: rice starch, oxidized rice starch, amino rice starch, crosslinking, imine Schiff base.

1. Introduction

Polysaccharides are unique biopolymers. They are abundant, inexpensive, renewable, stable, hydrophilic, and widely available in many countries. As well, they are modifiable, biological, chemically non-toxic, biocompatible, and biodegradable. Starch is a common polysaccharide. It is abundant as it is sourced from food crops. Rice (*Oryza sativa*) is an important starch resource in Thailand, which is one of the world's largest rice exporters.[1] Thailand's Ministry of Commerce has estimated that Thailand exported approximately 11 million tons of rice, worth 5.62 billion USD, in 2018. Generally, starch is composed of two glucose polymers (glucans): amylose, a low-branched glucan[2] and amylopectin, a hyper-branched glucan, whose molecular weights (Mw) range from 10^4 to 10^6 g/mol and from 10^7 to 10^9 g/mol, respectively. Thai rice starch (RS) contains approximately 15 wt% amylose and 75wt% amylopectin.[3,4]

One of the most important properties of starch is its large number of reactive chemical groups, due to the hydroxy (-OH) present at the 2-, 3- , and 6-positions in the glucose unit. These functional groups can be modified by hydrolysis, oxidation, grafting reactions, esterification, or etherification. One disadvantage of starch is that it is water-soluble, which limits its range of applications. This can be addressed by crosslinking, which occurs when a crosslinking agent is used to introduce bonds between the starch polymer chains. Starch can be crosslinked by the reaction between each hydroxy group in its chain and a crosslinking agent. Crosslinking reduces the mobility of the polymer chains, forming a three-dimensional network. If the degree of crosslinking is sufficiently high, the starch becomes insoluble in water but remains swellable. The degree of crosslinking can be determined by the swelling behavior. Swelling, or expansion in water, is an important characteristic for biomedical applications. The swelling mechanism of polymer films can be determined by measuring swelling behavior through time. This provides important parameters such as swelling kinetics and the swelling ratio at equilibrium.[5,6]

*Corresponding Author: Chayanisa Chitichotpanya
(chayanisa.chi@mahidol.ac.th)

Crosslinking of starch is normally achieved through chemical methods using crosslinking agents. The various types of starch such as corn,[7] rice,[8] and potato[9] can be treated with different crosslinking agents, including sodium trimetaphosphate (STMP),[10] sodium tripolyphosphate (STPP),[11] phosphorus oxychloride (POCl$_3$),[12] and carboxylic acid.[13] Rice starch has also been modified using chemical crosslinking with a mixture of STPP and STMP,[14] and epichlorohydrin,[15] resulting in irreversible crosslinking. Recently, novel crosslinking methods that do not require crosslinking agents have been reported, including treatment with various kinds of radiation; for instance, potato starch treated with microwaves[16] and corn starch with electron beams.[17,18] These methods do not require a crosslinking agent and are simple and easy to control.[19] However, they are capital intensive and require high levels of expertise.

The acid condensation reaction between aldehyde and amine is used for chemical crosslinking in polysaccharides such as chitosan and alginate.[20,21] Crosslinking of chitosan with small molecular dialdehydes, such as glyoxal and glutaraldehyde, was reported by Zhang *et al.*.[20] Oxidized alginate can also be used as a crosslinking agent, forming a hydrogel by the introduction of aldehyde groups into the polymer. The chitosan and oxidized alginate form a hydrogel through this reaction,[22] which is known as imine formation or the Schiff base. Current studies are investigating its thermostability,[23] ligand forming ability,[24] and semiconducting properties.[25] Furthermore, the Schiff base reaction produces a reversible condensation between the amines and aldehydes. It is an efficient reaction involving the loss of H$_2$O when an amino (-NH$_2$) and carbonyl group (C=O) react to form an imine (C=N) bond. The bond can be either intra- or intermolecular. The reversible nature of the imine bond allows the reaction to be driven forwards or backwards, as shown in Figure 1. The pH level determines the equilibrium between the imine and its corresponding precursors. This reversibility of imine bonds is part of dynamic covalent chemistry (DCC), in which the formation and cleavage of covalent bonds within the molecule are reversible.[26] One area of current DCC research is the development of stimuli for responsive dynamic functional materials. These play a critical role in the emerging technologies of self-healing systems,[27] sensors,[28] and actuators.[29] Imine formation has the potential to produce a reversible crosslinked polysaccharide.

This study proposed the first pH-induced crosslinking of rice starch synthesized without the use of an external chemical crosslinking agent. The crosslinked starch was prepared by the Schiff base reaction between two modified starches: oxidized rice starch (ORS) and amino rice starch (ARS). The goal of this research was to determine the relationship between the pH value and crosslinking by studying the degree of crosslinking and hydrolysis at different pH levels.
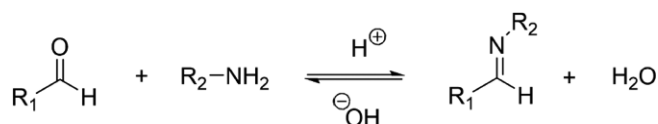

Figure 1. Schiff base formation between the aldehyde and amine.

2. Experimental

2.1. Materials

Native rice starch (RS) was supplied by Nguansoon Co, Ltd (Bangkok, Thailand). Epichlorohydrin was purchased from Sigma-Aldrich (Steinhiem, Germany). Ethylenediamine was purchased from Merck (Hohenbrunn, Germany). Other commercial grade and analytical grade chemicals were purchased from RCI-Lab-Scan (Bangkok, Thailand).

2.2. Synthesis of oxidized rice starch (ORS)

The oxidation procedure was adapted from Zhang *et al.*[30] First, 5 g of RS was suspended in 50 mL of water. The starch slurry was heated at 80 °C for 30 min, then cooled to 60 °C. Next, 18.5 mL of 20% H$_2$O$_2$ was added to the slurry, and kept at 60 °C for 90 min. After the reaction was complete, the ORS solution was precipitated in ethanol. Then, the ORS was filtered and washed with ethanol, and then it was dried in an oven at 40 °C for 24 h.

### 2.3. Synthesis of amino rice starch (ARS)

The synthesis method was adapted from Motte *et al.*[31] First 5 g of RS was reacted in 18 mL of epichlorohydrin at 110 °C for 1 h. The mixture was cooled to 60 °C. Next, 50 mL of 1 M NaOH and 4 mL of ethylenediamine were added. After the reaction was complete, the ARS slurry was precipitated in ethanol, filtered, and washed with ethanol. The ARS powder was then dried in an oven at 40 °C for 24 h.

2.4. Crosslinked starch film preparation

Crosslinked starch films were prepared by the casting technique. The mixture of 2.5 g of ORS and 2.5 g of ARS was dissolved in 50 mL of distilled water. The solution was heated at 90 °C until it was dissolved completely. After that, the starch slurry was cast on a Teflon plate and dried in an oven at 40 °C for 24 h. The schematic for the preparation of pH-induced crosslinked starch is shown in Scheme 1.

2.5. Determination of aldehyde content

The aldehyde content of ORS was determined following Wing *et al.*[32] First 0.1 g of ORS was dissolved in 10 mL of water. The solution was heated at 80 °C until the ORS was dissolved, then cooled in a water bath to room temperature. Next, 10 mL of standardized 0.1 M HCl, and 15 mL of hydroxylamine hydrochloride solution (25 g of hydroxylamine hydrochloride; 100 mL 0.5 M NaOH diluted to 500 mL using deionized water) were added to the ORS solution. The solution was heated to and kept at 40 °C for 4 h and titrated rapidly with 0.1 M HCl using methyl orange as an indicator. A blank test was performed with the hydroxylamine hydrochloride solution. The aldehyde content was calculated using the following Eq. (1):
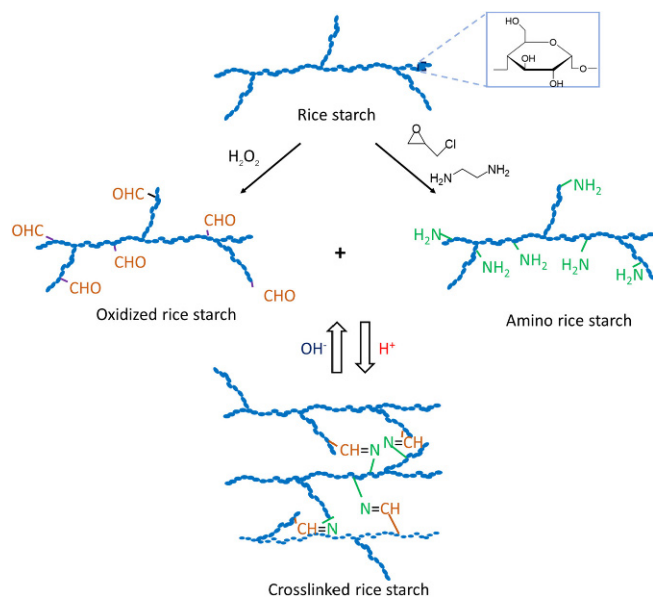
Scheme 1. The schematic of synthetic route of pH-induced cross-linked rice starch (RS).

$$\text{CHO content} = \frac{C_{HCl} \times (V_{blank} - V_{sample})}{\text{wt of dry sample}/162} \times 100 \qquad (1)$$

where C is the concentration (mol/L) and V is the volume of HCl (mL).

2.6. Determination of terminated amine content

To estimate the amine content of the prepared amino starch, the nitrogen content was determined following ASTM E 258-67, using Eq. (2). Briefly, this method consists of three steps: digestion, distillation, and titration. In the digestion step, 0.1 g of sample, 5 g of K_2SO_4, 0.04 g of $CuSO_4$, and 10 mL concentrated H_2SO_4 were placed in a digestion flask. The mixture was heated until the white foam cleared and was then kept at that temperature for 90 min. After that, 250 mL of distilled water was cautiously added and the solution was cooled to room temperature. In the distillation step, the digestion apparatus was connected to the distillation apparatus, and 10 M NaOH was slowly added to the solution. The distillate, NH_3 gas, was collected in a collecting flask containing 100 mL of 0.1 M HCl. The digestion flask and titration flask were removed and the condenser tube was rinsed with DI water. In the titration step, 10 mL of the HCl solution from the previous step was pipetted into a titration flask. This was titrated with standard sodium hydroxide solution, using phenolphthalein as an indicator.

$$\text{NH}_2 \text{ content} = \frac{\frac{\%N}{2} \times 162}{14 \times 10} \qquad (2)$$

2.7. Fourier transform infrared spectroscopy (FTIR)

The chemical structures of RS, ORS, ARS, and imine were determined by using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific: Madison, WI, USA). The measurement was carried out using the KBr pellet technique for the synthesized starch

powders and the Attenuated total reflectance (ATR) technique for starch films with wavelengths in the range of 400-4000 cm^{-1}.

2.8. Nuclear magnetic resonance (NMR)

The chemical structure of the RS, ORS, and ARS were determined by using NMR Bruker DPX 400 MHz (Bruker Biospin Gmbh, Rheinstetten, Germany) for the ^{1}H NMR and ^{13}C NMR spectra. For analysis of the ^{1}H NMR and ^{13}C NMR of the native rice starch, OS and AS were prepared in DMSO-d_6 solvent.

2.9. Swelling measurements

The 0.1 g dry starch films were immersed in buffer solutions at pH 3-11 at 25 °C until the swelling equilibrium was reached. The following equation was used to determine water uptake:

$$M(t) = \frac{W_2 - W_1}{W_1} \qquad (3)$$

where $M(t)$ is the swelling ratio at time t, W_2 is the weight of the wet film, and W_1 is the weight of the dry film.

3. Results and discussions

3.1. NMR characterization of modified starches

The chemical structure of the ORS synthesized with H_2O_2 was characterized using ^{1}H NMR, as shown in Figure 2. The peak at 2.60 ppm in all the ^{1}H NMR spectra resulted from the process of using the solvent DMSO-d_6. In the spectra of the polymers (Figure 2), a singlet signal as well as a doublet signal were detected at 4.68 and 5.60 ppm and were attributed to the hydroxy protons. The peaks at 5.52 and 5.41 ppm were assigned to C3-OH, the signal at 5.10 ppm to C2-OH, and that at 4.68 ppm to C6-OH. The signal at around 10.2 ppm was assigned to protons of the aldehyde group in the ORS.[30] Figure 3 shows the ^{13}C NMR spectra of RS and ARS. The peaks in the region from 72 ppm to 80 ppm were attributed to C2-5. The signal of C1 appeared at 102 ppm. These are characteristic signals of RS. The ^{13}C NMR spec-
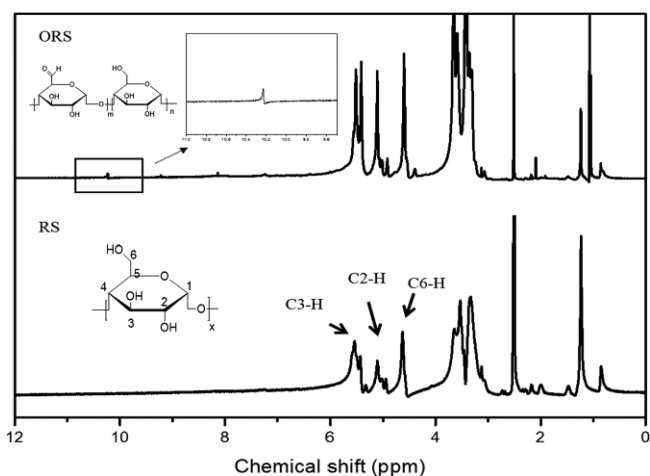

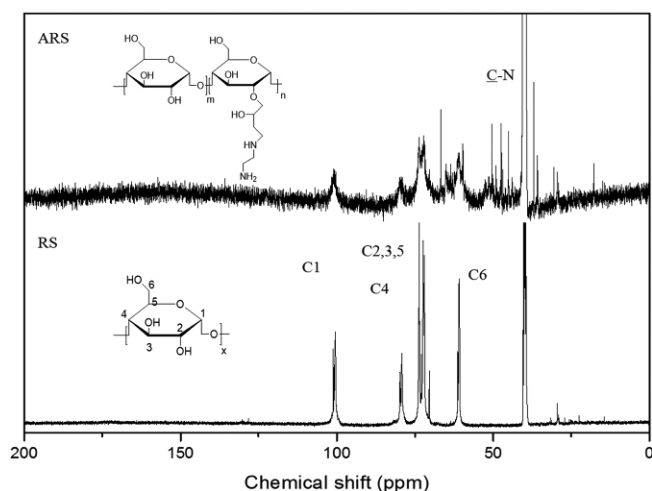**Figure 2.** ^{1}H NMR spectra of the RS and synthesized ORS using oxidation reaction.

Figure 3. ^{13}C NMR spectra of the RS and synthesized ARS by substitution with ethylenediamine.

tra of the amino starch produced a signal at 45 ppm. This was assigned to C-NH$_2$.[33] These spectra suggested that the ORS and ARS starch had been successfully synthesized.

3.2. FTIR characterization of modified starches

Figure 4 shows the FTIR spectra of the RS, ORS, and ARS, in which the existence of a broad band at 3300 cm^{-1}, indicates the -OH group. The peak at 2927 cm^{-1} was assigned to the asymmetric stretching vibration of CH$_2$. The transmittance at 1460 cm^{-1} and 1300 cm^{-1} was attributed to C-H bending vibrations and the peak at 1637 cm^{-1} to deformation vibrations of water molecules absorbed by the rice starch. After complete oxidation, a peak appeared at 1735 cm^{-1}, which is characteristic of the stretching vibrations of the C=O groups of the aldehyde, produced by oxidation of the hydroxy group to aldehyde by H$_2$O$_2$.[30,34,35]

After substitution of ethylenediamine, a peak appeared at 1190 cm^{-1}, which is characteristic of the stretching vibration of the C-N groups of amine. A peak at 2800 cm^{-1} was ascribed to the C-H stretching vibration of the methylene group, which attached to the amino group.[36] The results, therefore, suggested that both ORS and ARS had been successfully prepared.[33,37,38]
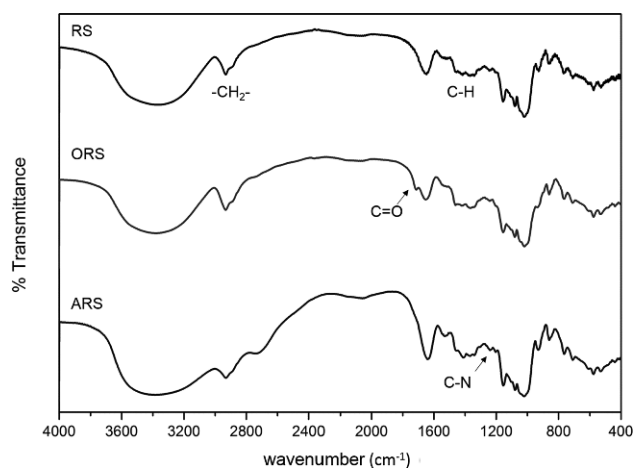

Figure 4. FTIR spectra of the RS, synthesized ORS, and synthesized ARS.

Table 1. The aldehyde and the amine content in the modified starches

Sample	Functionality	Functionality content (unit/100 GU^a)
Oxidized starch	Aldehyde	32.0 ± 2.0
Amino starch	Amine	27.8 ± 2.2

^{a}GU = glucose unit.

3.3. Determination of functional contents of modified starches

The aldehyde and amine content of the modified starches was determined by back titration. The results are presented in Table 1.

3.4. FTIR characterization of crosslinked starches

The imine formation and hydrolysis between aldehyde and amine shown in Figure 5 were confirmed using FTIR and NMR. Figure 6 shows the spectra of oxidized rice starch mixed with amino starch at a weight ratio of 1:1 and stirred in 0.1 M HCl for 1 h. The FTIR peak at 1610 cm^{-1} was assigned to C=N stretching,[27] and disappeared when the mixed starch was stirred in 0.1 M NaOH for 1 h. It was concluded that imine had been successfully formed under acid conditions. As shown in Figure 5, this was reversed under basic conditions.
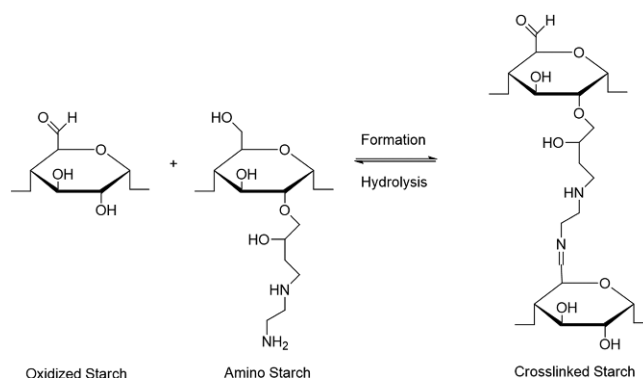

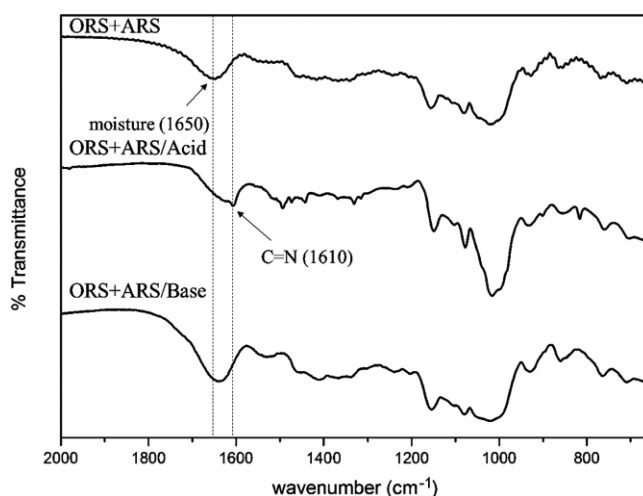**Figure 5.** The reversible formation and hydrolysis of imine.

Figure 6. FTIR spectra confirming the imine formation between ORS and ARS.

3.5. NMR characterization of crosslinked starches

Figure 7 shows the ^{1}H NMR spectra of the imine starch. The peak at 8.3 ppm was assigned to protons at the imine bond (-N=CH-).[39] As shown in Figure 8, the ^{13}C NMR spectra showed a signal at 164 ppm,[33] which was assigned to carbon at the imine bond.

3.6. Swelling behavior

A first-order kinetic model was used to study the swelling behavior associated with the hydrolysis of imine at different pH levels. The model equation is expressed as follows:

$$\frac{dM(t)}{dt} = k(M_\infty - M(t)) \quad (4)$$

where k is the rate constant of gel disintegration, M_∞ is the swelling ratio at equilibrium, and t is time. The corresponding mass $M(t=0)=0$.

This equation was rewritten as:
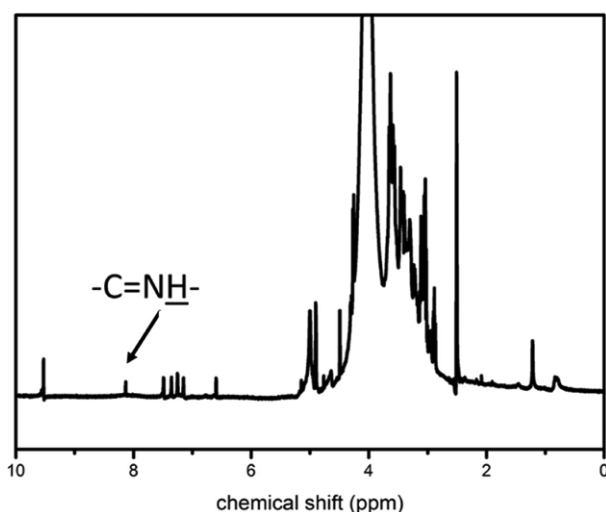
$$M(t) = M_\infty[1 - e^{-kt}] \quad (5)$$

Figure 7. ^{1}H NMR spectrum of the crosslinked starch confirming the imine formation between ORS and ARS.
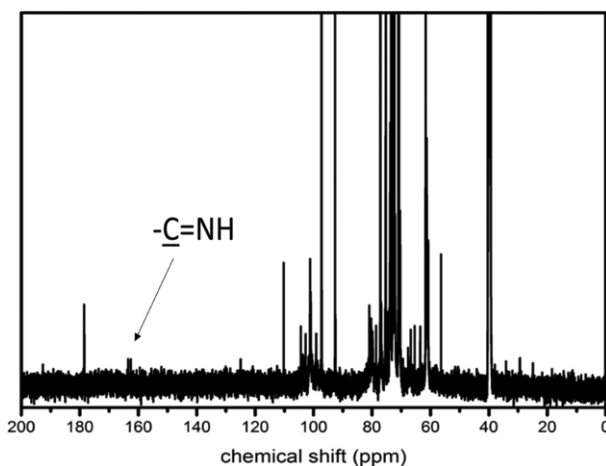

Figure 8. ^{13}C NMR spectrum of the crosslinked starch confirming the imine formation between ORS and ARS.
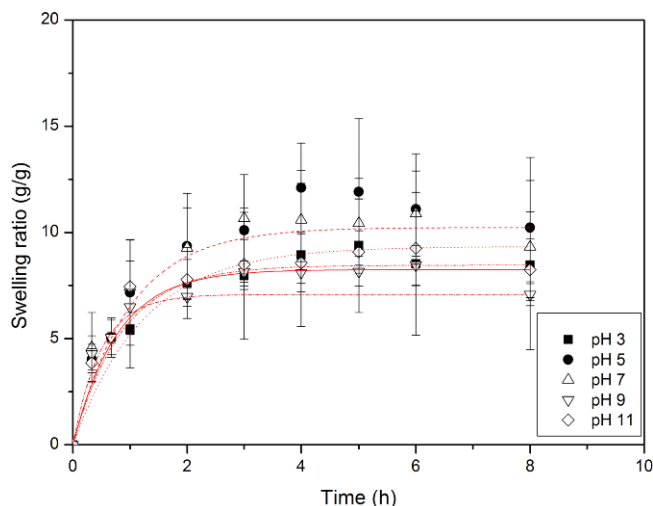

Figure 9. The swelling ratio of the crosslinked starch films as a function of time at different pH levels.

Good exponential fits of the data points were obtained after plotting the swelling ratio and time using the first order kinetic model. The results (Figure 9) showed rapid swelling of all samples in the initial stage, leveling off after at approximately 3 h. After 6 h, the swelling behavior under all conditions slowly decreased. Between 6 h and 8 h, some samples (pH 9 and pH 11) exhibited a small reduction in volume to partial dissolution to water. The first-order kinetic model was used to calculate the values of k and M_∞.

The S-curve profile (Figure 10) reflects the kinetics of hydrolysis at different pH levels. Hydrolysis was inferred from the observation that crosslinking took place only at higher pH values. From pH 3 to 5, the swelling behavior (k) was constant, suggesting that no hydrolysis of imine had occurred. From pH 5 to 9, the k value increased rapidly, in line with the increase in pH. This showed that the speed of hydrolysis increased until the maximum k was achieved at pH 9. In general, imine formation occurred under acidic conditions, whereas hydrolysis took place under basic conditions. The proposed mechanism of hydro-
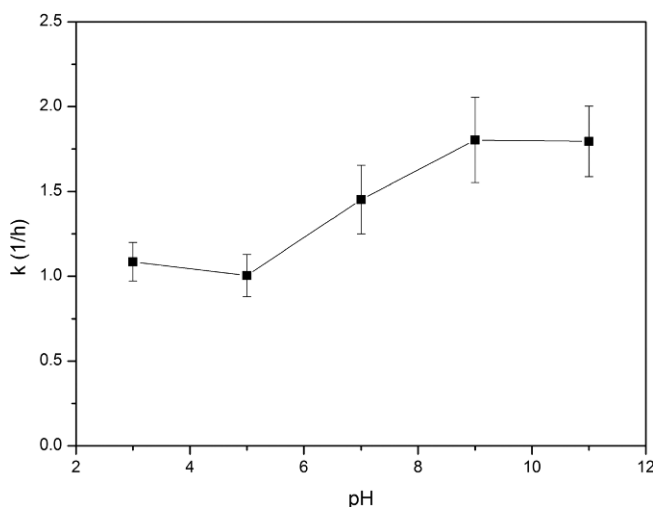

Figure 10. The calculated rate constant of the swelling behavior of starch films as a function of pH.
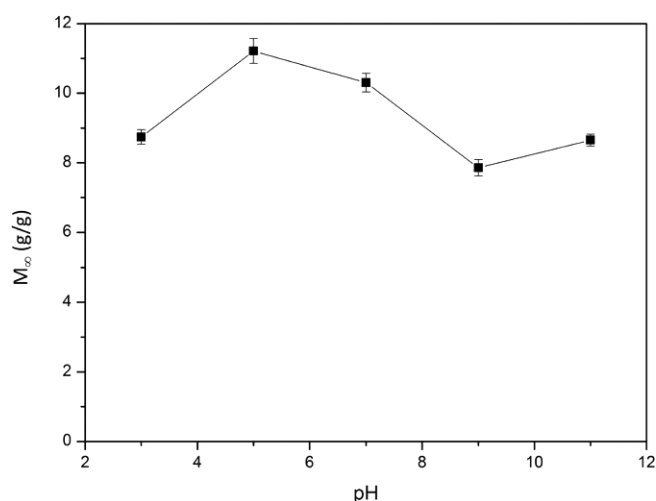
Figure 11. The calculated swelling ratio at the equilibrium of the starch films as a function of pH.

lysis of the imine involves the attack of H_2O and OH^- at the aldimine carbon or carbon at the imine bond, resulting in its protonated form in base media.[40,41] Such a result suggests that hydrolysis of imine involves base catalysis. It could be described that hydroxy groups in starch were deprotonated by the base to generate alkoxy anions.[42] These anions formed intermediates with H_2O molecules. The intermediate was then hydrolyzed to the corresponding amine and aldehyde compounds.[43] This was confirmed by the FTIR results, and the mechanism is shown in Figure 6. It can be inferred that hydrolysis occurred at the bonds between the oxidized starch and amino starch under basic conditions. Therefore, the crosslink density of the starch was lower under basic conditions than acidic conditions. Thus, water was absorbed into the crosslinked starch more quickly under basic conditions than acidic conditions.

Figure 11 shows the swelling ratio (M_∞) as a function of pH. The maximum M_∞ was observed at a pH level of 5, then decreased as the pH level increased or decreased. This was attributed to the presence of imine in the crosslinked starch at pH 5. The results agreed well the rate constant of swelling, suggesting that hydrolysis of imine occurred in the neutral and basic solutions. This confirmed the hydrolysis of the imine group of the starch in the basic aqueous solutions.

It is worth noting that our pH-induced crosslinked rice starch has great potential as wound dressing material because the pH range of infectious skin (pH 6.5-8.5)[44] is the same as that of the hydrolysis of the imine group of the starch, which occurs at a pH range of 7-11 (Figure 10). This could lead to the controlled release of a drug loaded within a wound dressing.

4. Conclusions

The ORS and ARS were successfully synthesized with glucose unit contents of 32.0% and 27.8%, respectively. Their chemical structures were characterized using ^{1}H NMR, and FTIR techniques. The crosslinked starch between ORS and ARS was prepared using the casting technique. A pH-induced crosslinked reaction was demonstrated, in which crosslinking occurred under acidic conditions, whereas hydrolysis occurred under basic conditions. The chemical structures and their crosslinking were confirmed using FTIR, ^{1}H NMR, and ^{13}C NMR. The effect of pH on the crosslinked starch was determined from the swelling behavior. The pH effect on chemical structure agreed well with the swelling behavior. The maximum swelling ratio was found at pH 5 and decreased as the pH value increased further. Under basic conditions, hydrolysis occurred, resulting in a lower crosslink density, which reduced the efficiency of water uptake. In addition, the swelling kinetics of these crosslinked starches showed that swelling was slower at a pH level lower than 5 then increased in line with pH, reaching a maximum at pH 9. Normal pH on the human skin surface is in the range of 5.4-5.9. When skin is infected, the skin pH shifts from an acid range (pH 5.4-5.9) to a basic range of pH 6.5-8.5. Therefore, these pH-induced crosslinked rice starches are promising biomaterials for controlled release application.

References

(1) P. Rodsamran and R. Sothornvit, *Int. J. Food Sci. Technol.*, **50**, 1953 (2015).
(2) Y. Takeda, T. Shitaozono, and S. Hizukuri, *Carbohydrate Research*, **199**, 207 (1990).
(3) P. Noosuk, S. E. Hill, I. A. Farhat, J. R. Mitchell, and P. Pradipasena, *Starch - Stärke*, **57**, 587 (2005).
(4) P. Noosuk, S. E. Hill, P. Pradipasena, and J. R. Mitchell, *Starch - Stärke*, **55**, 337 (2003).
(5) J. Liu, X. Zheng, and K. Tang, *Rev. Adv. Mater. Sci.*, **33**, 452 (2013).
(6) P. Ashtaputrey and S. Ashtaputrey, *J. Drug Deliv. Ther.*, **8**, 218 (2018).
(7) H. J. Chung, K. S. Woo, and S. T. Lim, *Carbohydr. Polym.*, **55**, 9 (2004).
(8) P. Chatakanonda, S. Varavinit, and P. Chinachoti, *LWT - Food Sci. Technol.*, **33**, 276 (2000).
(9) G. Wang, M. R. Thompson, and Q. Liu, *Ind. Crop Prod.*, **36**, 299 (2012).
(10) M. Seker and M. A. Hanna, *Ind. Crop Prod.*, **23**, 249 (2006).
(11) H.-J. Chung, D. Min, J.-Y. Kim, and S.-T. Lim, *J. Appl. Polym. Sci.*, **105**, 2280 (2007).
(12) J. A. Han and J. N. BeMiller, *Carbohydr. Polym.*, **73**, 532 (2008).
(13) S.-Y. Chang and H.-M. Lai, *Food Hydrocolloid*, **56**, 254 (2016).
(14) P. Deetae, S. Shobsngob, W. Varanyanond, P. Chinachoti, O. Naivikule, and S. Varavinit, *Carbohydr. Polym.*, **73**, 351 (2008).
(15) O. S. Kittipongpatana and N. Kittipongpatana, *Food Chem.*, **141**, 1438 (2013).
(16) H. Staroszczyk, *Carbohydr. Polym.*, **77**, 506 (2009).
(17) H. L. A. El-Mohdy, *J. Appl. Polym. Sci.*, **104**, 504 (2007).
(18) M. Zhai, F. Yoshii, and T. Kume, *Carbohydr. Polym.*, **52**, 311 (2003).
(19) N. Pekel, F. Yoshii, T. Kume, and O. Güven, *Carbohydr. Polym.*, **55**, 139 (2004).
(20) Y. Zhang, L. Tao, S. Li, and Y. Wei, *Biomacromolecules*, **12**, 2894 (2011).
(21) J. Shi, W. Guobao, H. Chen, W. Zhong, X. Qiu, and M. M. Q. Xing, *Polym. Chem.*, **5**, 6180 (2014).
(22) J. Shi, N. M. Alves, and J. F. Mano, *Macromol. Biosci.*, **6**, 358 (2006).
(23) D. Sek, B. Jarzabek, E. Grabiec, B. Kaczmarczyk, H. Janeczek, A. Sikora, A. Hreniak, M. Palewicz, M. Lapkowski, K. Karon, and A. Iwan, *Synthetic Met.*, **160**, 2065 (2010).
(24) M.-F. Zaltariov, M. Cazacu, C. Racles, V. Musteata, A. Vlad, and A. Airinei, *J. Appl. Polym. Sci.*, **132**, 41631 (2015).
(25) İ. Kaya and E. Kılavuz, *J. Fluoresc.*, **25**, 663 (2015).
(26) Y. Jin, C. Yu, R. J. Denman, and W. Zhang, *Chem. Soc. Rev.*, **42**, 6634 (2013).

(27) F. Ding, S. Wu, S. Wang, Y. Xiong, Y. Li, B. Li, H. Deng, Y. Du, L. Xiao, and X. Shi, *Soft Matter*, **11**, 3971 (2015).

(28) A. Ramdass, V. Sathish, M. Velayudham, P. Thanasekaran, S. Umapathy, and S. Rajagopal, *Sensor Actuat. B: Chem.*, **240**, 1216 (2017).

(29) Y. Li, O. Rios, J. K. Keum, J. Chen, and M. R. Kessler, *ACS Appl. Mater. Interfaces*, **8**, 15750 (2016).

(30) S.-D. Zhang, Y.-R. Zhang, X.-L. Wang, and Y.-Z. Wang, *Starch - Stärke*, **61**, 646 (2009).

(31) H. de la Motte, M. Hasani, H. Brelid, and G. Westman, *Carbohydr. Polym.*, **85**, 738 (2011).

(32) R. E. Wing and J. L. Willett, *Ind. Crop. Prod.*, **7**, 45 (1997).

(33) R. J. Anthony and R. C. Sims, *Carbohydr. Polym.*, **98**, 1409 (2013).

(34) X. Yi, S. Zhang, and B. Ju, *Starch - Stärke*, **66**, 115 (2014).

(35) Y.-R. Zhang, X.-L. Wang, G.-M. Zhao, and Y.-Z. Wang, *Carbohydr. Polym.*, **87**, 2554 (2012).

(36) X. Lian, W. Zhu, Y. Wen, L. Li, and X. Zhao, *Int. J. Biol. Macromol.*, **59**, 143 (2013).

(37) Q. Bian, Y. Xiao, C. Zhou, and M. Lang, *J. Colloid Interface Sci.*, **392**, 141 (2013).

(38) A. Dong, J. Xie, W. Wang, L. Yu, Q. Liu, and Y. Yin, *J. Hazard. Mater.*, **181**, 448 (2010).

(39) İ. Kaya, İ. E. Orta, E. Özdemir, and D. Şenol, *J. Iran. Chem. Soc.*, **15**, 35 (2018).

(40) W. Bruyneel, J. Charette, and E. De Hoffmann, *J. Am. Chem. Soc.*, **88**, 3808 (1966).

(41) E. Cordes and W. Jencks, *J. Am. Chem. Soc.*, **84**, 832 (1962).

(42) S. de M. Fontes, M. T. Cavalcanti, R. A. Candeia, and E. L. Almeida, *Food Sci. Technol.*, **37**, 224 (2017).

(43) A. C. Dash, B. Dash, and S. Praharaj, *J. Chem. Soc., Dalton Trans.*, 2063 (1981).

(44) S. L. Percival, S. McCarty, J. A. Hunt, and E. J. Woods, *Wound Repair Regen.*, **22**, 174 (2014).