A STUDY ON THE PREPARATION OF MODIFIED STARCH FROM BROKEN RICE

Htet Htet Aung[1], Khin Hla Mon[2], Ohnmar Kyi[3], Mon Mon Maung[4],Aye Aye Aung[5]

Abstract

This research was emphasized on the preparation of modified broken rice starch using both acid treatment method and cross-link method. Broken rice (Paw Hsan Hmwe) was collected from Bago Township, Bago Region. The most suitable parameters for the preparation of native starch were 1:8 (w/v) ratio of broken rice to water at 4 hr settling time. The optimum conditions for the preparation of modified broken rice starch by acid treatment were 1 mL of 10% HCl, 1mL of 1% NaOH at reaction temperature 65°C for 15 min of reaction time. In cross-link method, the optimum parameters were 5mL of 2.5% sodium tripolyphosphate,5mL of 1% NaOH, 5mL of 5 % HCl at 45°C for 10 min. The characteristics of modified starch such as ash, moisture, pH and gelatinization temperature, solubility, swelling power, amylose and amylopectin content were determined. The morphology properties, molecular components and structures of native and modified broken rice were determined with Scanning Electron Microscopy (SEM) and FT-IR Analysis.

Keywords: Native starches, acid treatment method, cross-link method

Introduction

Starch is a basis of food and plays a major role in industrial economy. The most abundant substance in nature is starch. Starch consists of semi crystalline carbohydrate synthesized in plant roots, seeds, rhizomes and tubers. It is a polymer of glucose and consists of two types of glucose polymers such as amylose and amylopectin. These polymers have different structures and properties. Starch can be converted into many diverse products such as paper, beverages, pharmaceuticals, plastics, textiles and confectioneries either through chemical or biological process depending on the physical and chemical characteristics of the starch (Tester et al. 2004; Nand et al. 2008). Native starches are pure forms of starch. They can be obtained from the source such as corn, wheat, potato, rice, cassava and tapioca. The native starches are modified physically, enzymatically, or chemically to enhance their performance in different applications. Modified starches are better than native starches due to their functional properties.(Kavlani N et al, 2012).

Rice (*Oryza sativa* L.) is an important cereal grain which feeds nearly half of the world's population. Broken rice is fragments of rice grains obtained during drying, during transport or by milling. It is nutritious like the unbroken rice. Broken rice is used to make starch which is used as laundry starch and in foods, cosmetics and textile manufacture. Due to economic reasons the rice starch is extracted preferably from broken rice which is most valuable for numerous industries like food and cosmetic industry. It is also favourable because of its unusual characteristics like small particle size, white color and neutral taste. The objectives of this research work are-to investigate the different chemical modification reactions of starch and to determine the characteristics of modified broken rice starches.

[1] Dr, Lecturer, Department of Industrial Chemistry, Dagon University.
[2] Dr, Professor and Head, Department of Industrial Chemistry, Dagon University.
[3] Dr, Assistant Lecturer, Department of Industrial Chemistry, Dagon University.
[4] Dr, Assistant Lecturer, Department of Industrial Chemistry, Dagon University.
[5] Dr, Assistant Lecturer, Department of Industrial Chemistry, Dagon University.

Materials and Methods

Raw Materials

Broken rice (Paw Hsan Hmwe) was collected from Bago Township, Bago Region. The chemicals used were Analar grade hydrochloric acid (HCL), sodium hydroxide (NaOH), sodium tripolyphosphate ($Na_5P_3O_{10}$).

Methods

Preparation of Broken Rice Starch

Broken rice (100 g) was thoroughly washed with water to remove impurities such as dirt, girt and dust. Then, broken rice was ground in a grinder and the resulting broken rice paste was soaked in water in the ratio of 1:4(w/v %) for 60 min at room temperature by stirring with a constant rate of 150 rpm. The broken rice starch slurry was filtered through a nylon cloth to obtain the starch solution. The settling of starch solution was taken about 4 hr. The supernatant layer of water was decanted to remove out the starch. Water washing of native starch was carried out two times to obtain pure starch. Then, the starch was sundried and then ground in mortar and pestle to get fine powder. Effect of broken rice to water ratio (1:5), (1:6), (1:7), (1:8) and (1:9) (w/v) and effect of setting time (1, 2, 3, 4, 5) hr on the yield of broken rice starch were conducted according to the above procedure.

Preparation of Acid Treated Modified Broken Rice Starch

(5) g of native broken rice sample was mixed thoroughly with 1mL of 10% (w/v) hydrochloric acid in a 250 mL beaker and stirred for 15 min at 30°C. The slurry was neutralized with 1 mL of 1 % of sodium hydroxide. The slurry was washed with water and settled for one day. After that, it was separated by decantation of water. The starch was sun-dried for 3 hr and then ground in motor and pestle to obtain fine powder. Effect of volume of 10% hydrochloric acid (0.5, 1, 1.5,2 ,2.5)ml, effect of concentration of 1 mL of hydrochloric acid(5, 10, 15, 20 , 25)(v/v %) , effect of reaction time(5, 10, 15, 20 ,25) min and effect of reaction temperature (35, 45, 55, 65 , 75) °C on the yield of modified broken rice starch were determined according to the above procedure.

Preparation of Cross-Linked Modified Broken Rice Starch

(5) g of native broken rice sample was mixed thoroughly with 10mL of water for 10min. 5mL of 2.5% sodium tripolyphosphate and 5mL of 1% sodium hydroxide were added into the starch slurry and stirred with small scale batch type mixer for 30min at 30˚C. The pH of the obtained slurry was adjusted to 6-7 using 5mL of 5% hydrochloric acid. The slurry was washed two times with water and settled for one day. Then, water was decanted to separate out the starch. The starch was sun-dried for 90min and ground in motor and pestle to obtain fine powder. The yield percent of modified broken rice starch were determined by varying the effect of volume of 2.5% sodium tripolyphosphate (1, 3, 5, 7 and 9) mL, effect of concentration of 5mL of sodium tripolyphosphate (0.5, 1, 1.5, 2, 2.5 and 3)% (w/v) ,effect of reaction temperature (35, 45, 55, 65 and 75) ˚C and effect of reaction time (5, 10, 15, 20 25) using according to the above procedure.

Determination of the Physicochemical Properties of Native and Modified Broken Rice Starch

The p**hysicochemical properties** of native and modified broken rice starch such as, ash, gelatinization temperature, moisture, pH, solubility, swelling power, amylose and amylopectin content were determined.

Results and Discussion

Figure (1) shows the results of the effect of ratio of broken rice to water on the yield percent of broken rice starch. Although the ratio of broken rice to water was increased from 1:8 (w/v) to 1:9 (w/v), the yield percent of broken rice starch does not apparently increased. So, 1:8 (w/v) ratio of broken rice to water was chosen as the most suitable ratio from the economic point of view. The yield percent of modified broken rice starch were determined by varying the effect of settling time in the range of 1,2,3,4 and 5 hr. Among them, 4 hr settling time was selected as the most suitable condition from the economic point of view. The results are shown Figure (2).

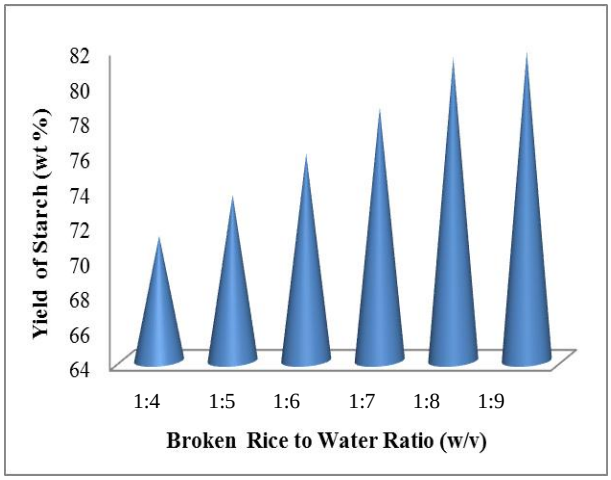


Figure 1 Effect of Broken Rice to Water Ratio on the Yield of Broken Rice Starch

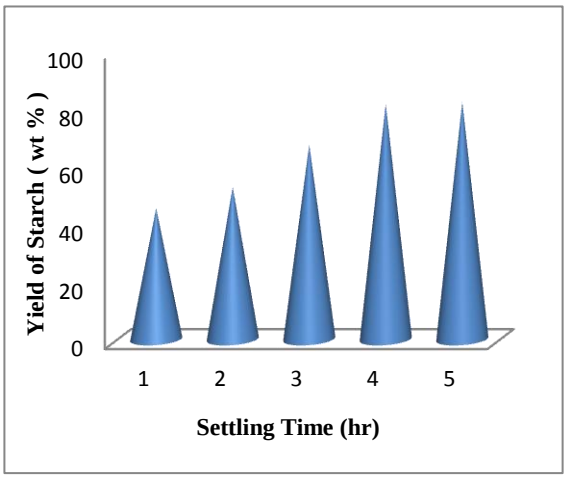


Figure 2 Effect of Settling Time on the Yield of Broken Rice Starch

The results of Table (1) show the effect of volume of 10 % hydrochloric acid on the yield of acid treated modified broken rice starch The volume of 10 % hydrochloric acid beyond 1 mL caused slightly rough texture and the yield percent of modified broken rice starch was decreased. When higher concentration of hydrochloric acid was used in the treatment of starch, non-starchy materials were broken down from slurry. Therefore, 1 mL of 10% hydrochloric acid was chosen as the most suitable condition.

The effect of concentration of 1 mL of hydrochloric acid on the yield of modified broken rice starch is shown in Table (2).The lower the acid concentration, the higher the yield percent of rice broken starch was obtained. Moreover, lower concentration of hydrochloric acid gave a smooth texture of modified broken rice starch and it was more economic. It can also reduce the side effect of the application of high concentration of hydrochloric acid. Therefore 10% of 1 mL hydrochloric acid was selected as the most suitable condition.

Table 1 Effect of Volume of 10% Hydrochloric Acid on the Yield of Acid Treated Modified Broken Rice Starch

Weight of Native Starch Sample - 5 g
Volume of 1%(w/v) NaOH - 1 mL
Reaction Time - 15 min
Reaction Temperature - Room Temp

Sr. No.	Volume of 10% HCl (mL)	Yield (w/w%)	Colour	Texture
1	0.5	84.0	White	Smooth
2	1*	84.8	White	Smooth
3	1.5	84.1	White	Slightly Rough
4	2	83.2	Odd-White	Slightly Rough
5	2.5	83.0	Odd-White	Slightly Rough

*Most suitable condition

Table 2 Effect of Concentration of 1mL Hydrochloric Acid on the Yield of Acid Treated Modified Broken Rice Starch

Weight of Native Starch Sample - 5 g
Volume of HCl - 1 mL
Volume of 1(w/v)% NaOH - 1 mL
Reaction Time - 15 min
Reaction Temperature - Room Temperature

Sr. No.	Concentration of 1mL HCl (v/v%)	Yield (w/w%)	Colour	Texture
1	5	83.8	White	Smooth
2	10*	84.8	White	Smooth
3	15	83.4	White	Slightly Rough
4	20	83.2	Odd-White	Slightly Rough
5	25	83.1	Odd-White	Slightly Rough

*Most suitable condition

Table (3) shows the effect of reaction time on the yield of acid treated modified broken rice starch. The highest yield percent (87.6%) of modified rice broken starch was obtained on the reaction time of 15 min. The yield percent of modified broken rice starch was also investigated by varying the effect of reaction temperature in the range of (35, 45, 55, 65 and 75 °C). The results are shown in Table (4). Among them, 65°C reaction temperature gave the highest yield percent of modified broken rice starch (92.8%) than others. Beyond this temperature, it can be seen that the texture was slightly rough and the yield percent of modified broken rice starch was decreased.

Table 3 Effect of Reaction Time on the Yield of Acid Treated Modified Broken Rice Starch

Weight of Native Starch sample - 5 g
Volume of 10 (v/v) %HCl - 1 mL
Volume of 1(w/v)% NaOH - 1 mL
Reaction Temperature - Room Temperature

Sr. No.	Reaction Time(min)	Yield (w/w%)	Colour	Texture
1	5	86.0	White	Smooth
2	10	86.6	White	Smooth
3	15*	87.6	White	Smooth
4	20	85.6	White	Smooth
5	25	84.8	White	Slightly Rough

*Most suitable condition

Table 4 Effect of Reaction Temperature on the Yield of Acid Treated Modified Broken Rice Starch

Weight of Native Starch Sample - 5 g
Volume of 10% (v/v) HCl - 1 mL
Volume of 1% (w/v) NaOH - 1 mL
Reaction Time - 15 min

Sr. No.	Reaction Temperature (°C)	Yield (w/w%)	Colour	Texture
1	35	87.6	White	Smooth
2	45	89.8	White	Smooth
3	55	91.2	White	Smooth
4	65*	92.8	White	Smooth
5	75	92.9	White	Slightly Rough

*Most suitable condition

By varying the volume of 2.5(w/v)% sodium tripolyphosphate such as 1,3,5,7 and 9 mL, the effect of volume of 2.5 (w/v)% of sodium tripolyphosphate on the yield of modified rice broken starch was studied. It was found that 5mL of 2.5% sodium tripolyphosphate gave 90.0 wt% of modified rice broken starch, which is the highest yield among them. The results are shown in Table (5). Highest concentration of sodium tripolyphosphate gave white and smooth texture of modified rice broken starch. 2.5 % and 3 % of sodium tripolyphosphate gave the 94.6 % and 93.8 % of modified rice broken starch respectively. Between them, 2.5 % of sodium tripolyphosphate was selected as the most suitable condition due to its higher yield percent .The results of the effect of concentration of sodium tripolyphosphate on the yield percent of cross-linked modified broken rice starch are shown in Table (6).

The yield percent of modified rice broken starch was investigated by varying the effect of reaction temperature on in the range of (35, 45, 55, 65 and 75)˚C. Among them, 45˚C of reaction temperature gave the highest yield percent of modified rice broken starch 99.6% than the others.

Beyond this temperature modified rice broken starch absorbed water to form gel. The results are shown in Table (7).The longer the reaction time, the lower the yield % of modified rice broken starch and also the colour of modified rice broken starch was found to be the odd white colour. So, reaction time 10 min was selected as the most suitable condition. The results are shown in Table (8).

Table 5 Effect of Volume 2.5% (w/v) of Sodium Tripolyphosphate on the Yield of Cross-Linked Modified Broken Rice Starch

Weight of Native Starch Sample - 5g
Water - 10 mL
Volume of 1% (w/v) NaOH - 5 mL
Volume of 5% (v/v) HCl - 5 mL
Reaction Temperature - 38˚C
Reaction Time - 10 min

Sr. No.	Volume of 2.5% (w/v) of Sodium Tripolyphosphate (mL)	Yield (wt %)	Colour	Texture
1	1	86.8	White	Smooth
2	3	89.2	White	Smooth
3	*5	94.6	White	Smooth
4	7	86.8	White	Slightly Rough
5	9	84.8	Odd White	Slightly Rough

*Most suitable condition

Table 6 Effect of Concentration of 5mL of Sodium Tripolyphosphate on the Yield of Cross-Linked Modified Broken Rice Starch

Weight of Native Starch Sample - 5g
Water - 10 mL
Volume of 1% (w/v) NaOH - 5 mL
Volume of 5% (v/v)HCl - 5 mL
Reaction Temperature - 38˚C
Reaction Time - 10 min

Sr. No.	Concentration of 5mL of Sodium Tripolyphosphate (%)	Yield (wt %)	Colour	Texture
1	0.5	84.2	White	Smooth
2	1	90.6	White	Smooth
3	1.5	91.0	White	Smooth
4	2	91.2	White	Smooth
5	*2.5	94.6	White	Smooth
6	3	93.8	White	Slightly Rough

*Most suitable condition

Table 7 Effect of Reaction Temperature on the Yield of Cross-Linked Modified Broken Rice Starch

Weight of Native Starch Sample - **5g**
Water - 10 mL
Volume of 1(w/v)% NaOH - 5 mL
Volume of 5(v/v)% HCl - 5 mL
Volume of 2.5% STPP - 5mL
Reaction Time - 10 min

Sr. No.	Reaction Temperature (˚C)	Yield (wt %)	Colour	Texture
1	35	96.6	White	Smooth
2	*45	99.6	White	Smooth
3	55	95.2	White	Slightly Rough
4	65	94.8	White	Slightly Rough
5	75	90.0	White	Slightly Rough

*Most suitable condition

Table 8 Effect of Reaction Time on the Yield of Cross-Linked Modified Broken Rice Starch

Weight of Native Starch Sample - 5g
Water - 10 mL
Volume of 1(w/v)% NaOH - 5 mL
Volume of 5(v/v)% HCl - 5 mL
Volume of 2.5(w/v)% $Na_5P_3O_{10}$ - 5mL
Reaction Temperature - 45°C

Sr. No.	Reaction Time (hr)	Yield (wt %)	Colour	Texture
1	5	96.2	White	Slightly Rough
2	*10	96.6	White	Smooth
3	15	92.6	White	Smooth
4	20	92.4	White	Smooth
5	25	92.2	White	Smooth

*Most suitable condition

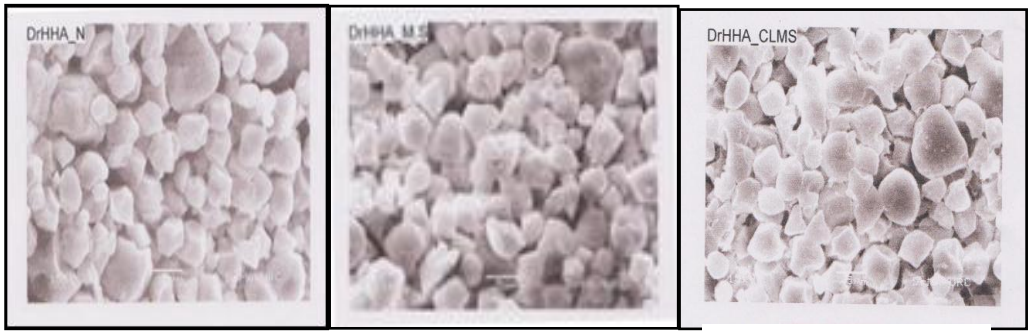
The physicochemical properties of native and modified broken rice starch such as amylose and amylopectin content, ash, gelatinization temperature, moisture, pH, solubility and swelling power, were determined and the results are shown in Table (9). Amylose was the major factor influencing the physico-chemical properties of starch. Starch swelling was property of amylopectin content whereas higher amylose content limited it. During modification, the amylose content was increased due to hydrolysis of amylopectin. Among the two methods of modification of starch, cross –link modification generated significant changes in starch behavior, gelatinization capacity, solubility and paste properties than acid treatment method.

Table 9 Characteristics of Native and Modified Broken Rice Starches

Characteristics	NS		AMS		CMS	
	E.V	***LV**	**E.V**	***LV**	**E.V**	***LV**
Ash (wt %)	1.57	-	1.53	-	1.52	-
Gel.Temp. (^{o}C)	60	-	68	-	65	-
Moisture (wt %)	8.66	-	8.36	-	8.41	-
Solubility	4.0	-	4.8	-	6.0	-
Swelling Power	1.12	-	1.00	-	0.89	-
pH	6.4	-	6.32	-	6.46	-
Amylose Content (wt%)*	24	15-35	32	38.62±0.6	40	48.41±0.6
Amylopectin Content (wt%)	76	65-85	68	61.39±0.6	60	51.59±0.6

NS- Native Starch
AMS- Acid Treated Modified Starch
CMS- Cross-Link Modified Starch
E-V- Experimental Value
*L-V – Literature Value
Source: www.scielo.br
www.onlinelibary.wiley.com

The native broken rice starch granules are polygonal shape with well-defined edges and smooth surface. The acid treated and cross link modified broken rice starch granules are oval, spherical and irregularly shaped with slightly rough surface and pores. The SEM photomicrograph of native and modified starches of broken rice is shown in Figure (3). SEM images of the granules of native and modified starches showed difference in their appearance.



Native Broken Rice Starch | Acid Treated Modified Broken Rice Starch | Cross-Link Modified Broke Starch

Figure 3 SEM Photomicrograph of Native and Modified Broken Rice Starches

FT-IR spectroscopy was used to verify the structural changes of native and modified broken rice starch. Figures (3 and 4) show the FT-IR spectra of native and modified broken rice starches. In native and modified broken rice starch, the IR spectrum of starch samples was described by seven main modes, with maximum absorbance peaks near 3500, 2900, 1600, 1400, 1000, 800, and 500 cm^{-1}. The peaks at 3664 cm^{-1} and 2929 cm^{-1} in native starch and 3630 cm^{-1} and 2933 cm^{-1} in modified starches could be attributed to O-H and C-H bond stretching , while the peaks in native starch at 1672 cm^{-1} and 1373 cm^{-1} and the bonding modes of H-C-H ,C-H and O-H attributed to the peaks in modified starches at 1645 cm^{-1} and 1413 cm^{-1}. C-O-H stretching in both native and modified starches attributed to the peaks at 1300~1000 cm^{-1} .The bands at 763±10 cm^{-1} were attributed to

D-glucopyranosyl ring stretching. The 1645~1600 cm^{-1} bands were assigned to H_2O bending vibrations.

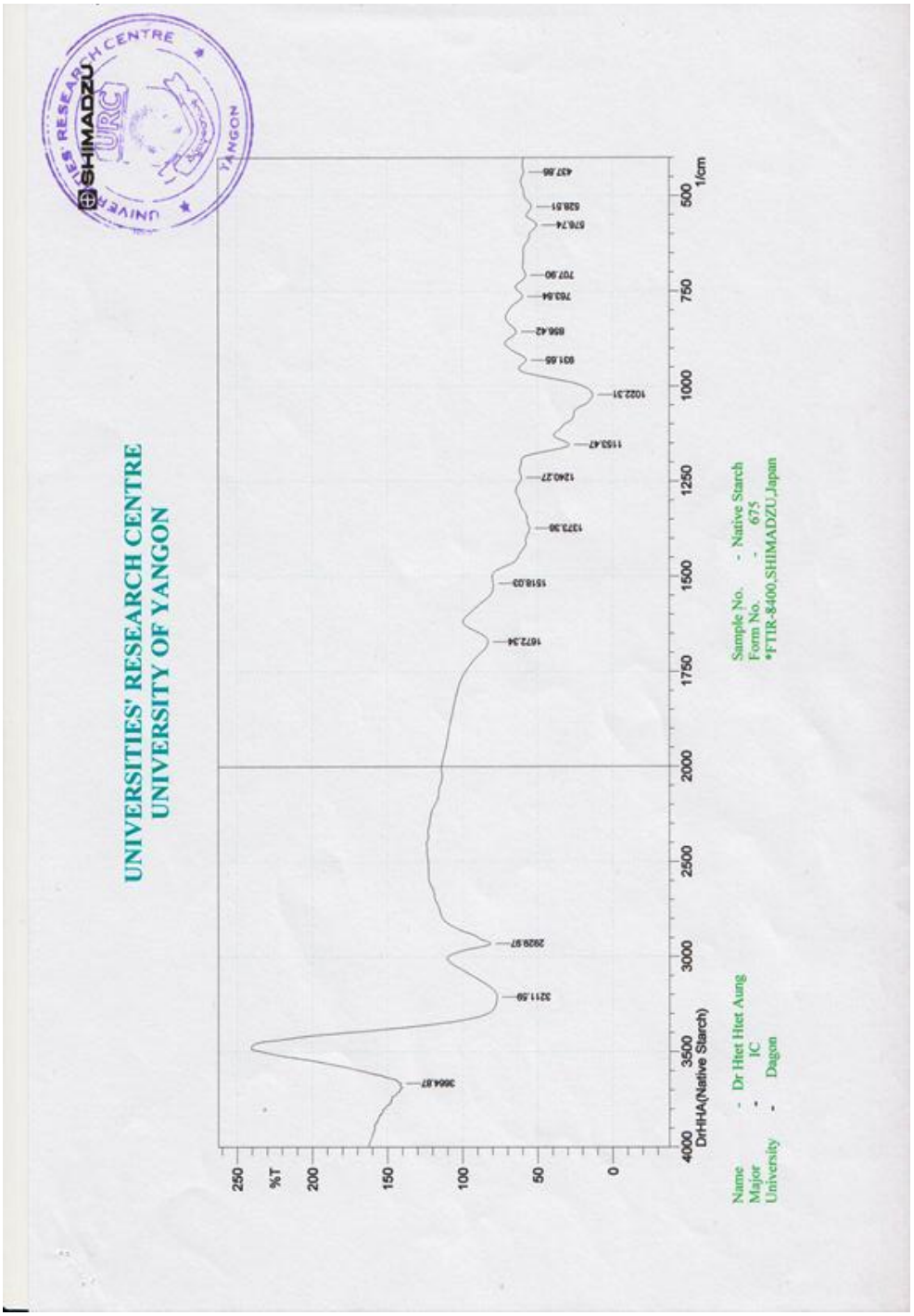


Figure 4 FT-IR Spectrum of Native Broken Rice Starch

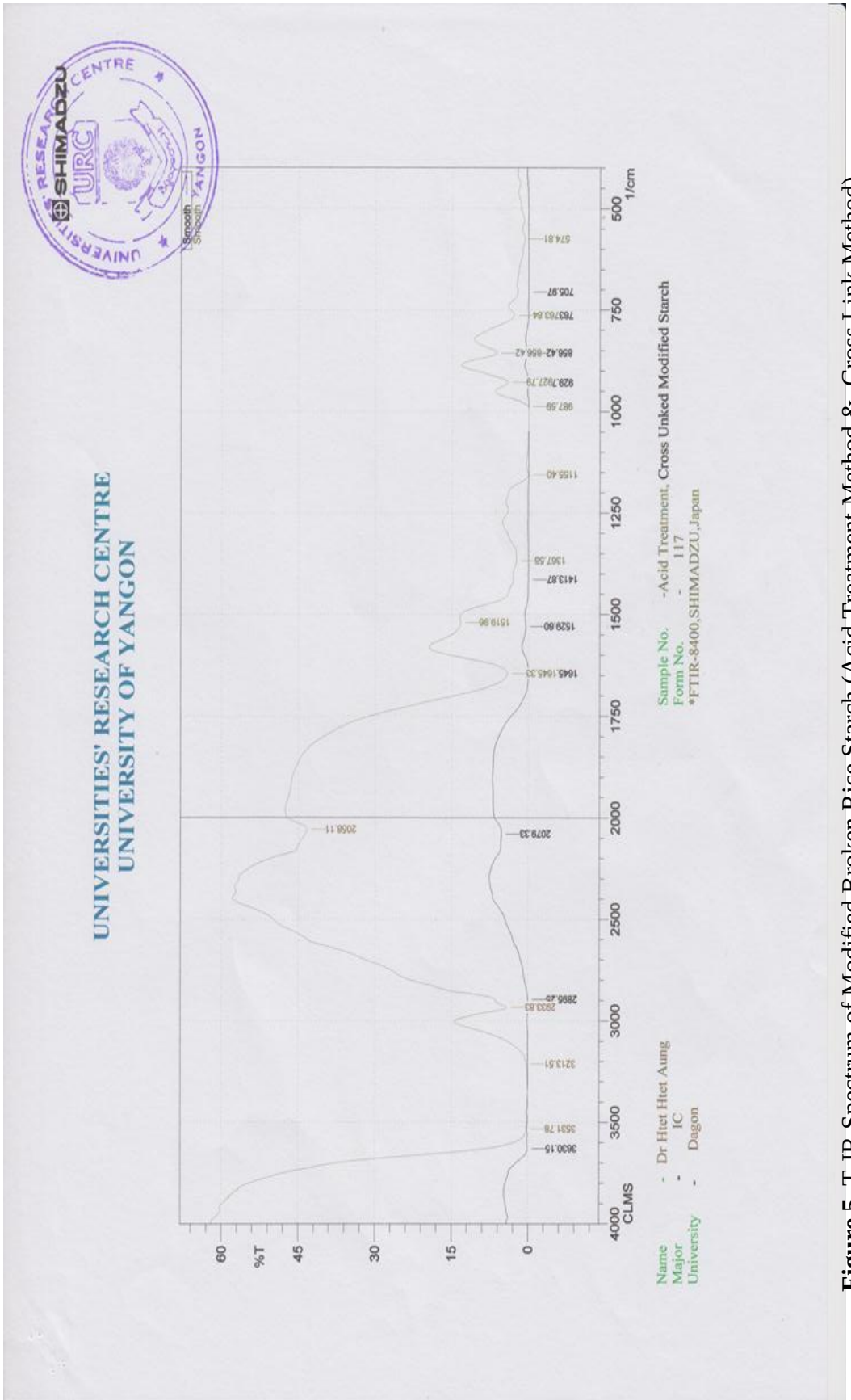


Figure 5 T-IR Spectrum of Modified Broken Rice Starch (Acid Treatment Method & Cross Link Method)

Conclusion

Native starch was prepared from broken rice and then it was modified using both acid treatment method and cross linked method. The most suitable conditions of the preparation of native starch were found to be 1:8 of the ratio of raw to water and 4 hr of settling time. The most favorable conditions for the preparation of modified starch by acid treatment were 1 mL of 10% HCl, 1mL of 1% NaOH at reaction temperature 65^{o}C for 15 min of reaction time and 5ml of 2.5% $Na_5P_3O_{10}$, 5mL of 1% NaOH, 5mL of 5 % HCl at 45^{o}C reaction temperature for 10 min of reaction time for cross-link method. The characteristics of native and modified starch were investigated. The morphology properties, molecular components and structures of native and modified broken rice were determined with Scanning Electron Microscopy (SEM) and FT-IR Analysis. . According to the results of the characteristics and yield % of modified starch using two different methods, the quality of cross-linked modified starch is better than the acid treated modified starch.

Acknowledgements

We would like to express our special thanks of gratitude to Dr Win Naing, Rector, Dr Nu Nu Yi and Dr Nay Thwe Kyi, Pro-Rectors, Dagon University for their permission to submit this article. We would like to extend our deepest appreciation to Dr. Khin Hla Mon, Professor and Head of Department of Industrial Chemistry, Dagon University, for her invaluable suggestions, advice, encourages during this research.

References

Akhilesh V Singh et al., (2010), Pharmaceutical, Food and Non-Food Applications of Modified Starches: A Critical Review, EJEAFChe, 9 (7).

Hoover, R. and Sosulski, F.W., (1985), Studies on the Functional Characteristics and Digestibility of Starches from Phaselous Vulgaris Biotypes. Starch.

Kavlani N, et al., (2012), Various Techniques for the Modification of Starch and the Applications of its Derivatives, International Research Journal of Pharmacy.

Leach, H. W., McCowen, L. D., & Schoch, T. J. (1959). Structure of the starch granule. I. Swelling and solubility patterns of various starches. Cereal Chemistry.

Mohan (2000) Organic Spectrocopy Principle and Narasa Publishing House.

Tester, R.F., Karkalas, J. and Qi, X. (2004). Starch structure and digestibility: Enzyme substrate relationship. World's Poultry Science Journal.

Saleh, M. and Meullenet, J.F., Effect of Broken Rice Kernels on Cooked- RiceTexture and Rice-Flour Pasting Properties.