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Properties of Spray-dried Rice Starch Microcapsule

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ABSTRACT

This research was conducted to produce rice starch microcapsules from regular rice starches (22-24% solid w/w) with the small amount of each suitable binding agent (0.10-0.30%): acacia, carboxymetylcellulose and gelatin by using spray dryer. Scanning electron microscope (SEM) was used to examine the surface microstructure of the microcapsules. The results revealed that 24% rice starch with 0.30% either carboxymetylcellulose (CMC) or acacia and 22% rice starch with 0.30%gelatin exhibited numerous good appearances of the spherical aggregates. These selected conditions were repeated with glutinous rice starch instead of the regular one. Chemical and physical properties of all products were also investigated, most of which showed a spherical shape under SEM. Concentrations and types of the mixture between starches and binding agents did affect sizes, number and properties of the sphere starch aggregates. The spherical starch aggregates with CMC had a relatively larger in size and number than those with acacia and gelatin. The average sphere diameter of rice starch microcapsules ranged from 15.37-30.19 μm, the particle density was about 1.49-1.55 g/cm^3 and the bulk density was 0.54-0.58 g/cm^3. Flow characteristics of all products showed easy -to-free flowing powder types. The products possessed moisture content less than 10%, water activity (Aw) 0.20-0.41 and water absorption index (WAI) 0.28-0.70. All samples exhibited hygroscopic properties. Among the samples microcapsule with the best physical properties was made from 24% rice starch with 0.30% CMC. However, the rice starch microcapsules especially with 0.30% acacia possessed higher bulk porosity than the others and gave slightly different pasting properties from the native rice starch.

Key words: rice starch, glutinous rice starch, microcapsules, rice starch aggregates

INTRODUCTION

Microencapsulation has been widely applied in the food industry for developing novel food product items which were fitted with the consumer need, since the technology provides many advantages such as offer the food processor a means to protect sensitive food components, ensure nutritional loss, mask or preserve flavors and aromas, and transform liquids into easily handled solid ingredients (Dziezak, 1988).

Encapsulation or microencapsulation is defined as a process by which one material or a mixture of materials is coated or entrapped within another material, or system (Qi and Xu,1999) and can release the inner contents at controlled rate under specific condition. The miniature package or wall material called “microcapsules” have a multitude of shapes depended on the materials and methods used to prepare them, but are ideally spherical, while the coated called the core or fill material. Various substances are reported to be

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used as wall materials such gums, maltodextrin, corn syrup solids, starches, starches derivertives, cyclodextrins, sucrose, common salt, gelatin, waxes, fats and proteins.

Among those materials, starch is abundant, widely distributed in nature and relatively inexpensive as compared with the others. Starch-based microcapsule received greater attention since Zhao and Whistler (1994) reported a novel property of small size starch granules termed "starch aggregate", which provided ability to combine into potentially useful porous sphere when spray dried with small amount of binding agents. The porous structures are retained even after washing with ethanol and subsequent drying. Besides, the ease of production by normal food processing method gives it an added advantage. However, the properties as well as the beneficial effects of starch microcapsule, especially rice starch, as a food ingredient carrier had not been reported. Therefore, in this research a special emphasis on developing rice starch microcapsule was prepared from both regular and glutinous rice varieties combined with various binding agents by using spray dry technology. The properties of the obtained porous structures were also investigated for future application especially as a novel form of rice starch for flavor or other active compound carriers.

MATERIALS AND METHODS

Materials

Native regular and glutinous rice starches were purchased from Bangkok Starch Industries Limited Company. The food grade binding agents were; acacia (Luxara 3A Gum Acacia), the product of Arthur Branwell Co. Ltd, England; sodium carboxymethylcellulose (CMC), from CMC Management Consulting GmbH; gelatin, from Belgium and maltodextrin (DE 10-12), from Tate and Lyle, Staley, USA.

Properties of rice starch

Regular and glutinous rice starches were analyzed for the moisture and protein content according to AOAC (1990), water absorption index (WAI) by Anderson *et al.* (1969) and the pasting viscosities were determined by using a Rapid Visco Analyzer (RVA).

Preparation of rice starch microcapsules

Microcapsules were prepared from regular rice starch as the following process. Rice starch granules were dispersed to about 22-24% solid (w/w) in water containing 0.1-0.3% binding agents such as gelatin, sodium carboxymethylcellulose and acacia individually. The slurry was stirred for 5 min to ensure uniform mixing. Microcapsules were obtained by spraying the solution in the rate of 1 litre/3 min using a commercial spray dry unit with gun spray head type through nozzle, an inlet temperature ranged from 230° to 280°C, and outlet temperature at the range of 75° to 100°C. The experiments were performed in duplicate. Scanning Electron Microscope (SEM) was used to examine and select the sample with high number of the starch aggregate. The whole process was repeated by using glutinous rice starch instead as a miniature package.

Properties analysis of rice starch microcapsules

Chemical properties of the rice starch microcapsules were determined for moisture and protein content according to AOAC (1990) and water activity was analyzed by using an Aw instrumental (Novasiana, Switzerland).

Physical properties of rice starch microcapsules were evaluated for water absorption index (WAI) as described by Anderson *et al.* (1969) and color by using Data Color International. Micro structural observations were also examined by SEM JEOL(model JSM-5600LV, Japan).

Particle size distribution was evaluated by using Mastersizer S (Malvern Instruments Limited) with He-Ne laser source, at λ: 633 nm, beam length 2.40 mm, air dispersing medium and refractive index 1.5300.

Particle density was determined by modified method of Weindorf and Wittie (2003). Rice starch microcapsules were oven-dried at 70° C for 48 h to remove moisture. Dried microcapsule 5 g was placed in a 25 ml volumetric flask and weighed. To replace gases in the microcapsule sample, the volume was made up by hexane, completely submerged the sample and weighed. The flask without sample was again weighed when hexane was added to the volume. The particle density of microcapsule samples were calculated using the following equation.

$$\rho p = \rho h\,(W_c) / [W_c - (W_{ch} - W_h)]$$

where: ρp = Particle density of sample (g/cm^3)

ρh = Density of hexane (g/cm^3)

W_c = Weight of oven-dried microcapsule (g)

W_{ch} = Weight of oven-dried microcapsule and hexane (g)

Wh = Weight of 25 ml of pure hexane (g)

Bulk density (ρb) of rice starch microcapsules was determined from the weight (m) and the bulk volume (Vb). The bulk porosity (ε), defined as the volume fraction of the air or void fraction in the sample, was estimated from the equation illustrated by Marousis and Saravacos (1990)

$$\varepsilon = 1 - (rb / rp)$$

Powder flow ability was evaluated by using texture analyzer model TAXT plus attached with helical blade. The sample about 140 ml (70mm in height) was placed in the beaker then measured for flow characteristic with program Quick Test, and the average value of compaction and cohesion were calculated from the graph plotted between force and time. The cohesive index of each rice starch microcapsule, obtained from the ratio of average cohesion (Av cohesion) to weight of test sample, was expressed as flow behavior by comparing to the cohesive index in the stand table.

Pasting properties of rice starch microcapsule were determined by using a Rapid Visco Analyzer (RVA-super 3, Newport Scientific, New South Wales, Australia). The 3 g sample was weighed and dispersed in 25 ml distilled water prior to performing analysis on the RVA.

Moisture sorption isotherms of the rice starch microcapsules were gravimetrically, by exposing these samples at 29°C in the presence of different salt solutions (approximate range of Aw =0.11-0.89). The 1 g mass of dry microcapsules was put in an open glass tube and placed in desiccators, each of which contained saturated solutions of different salt types. The mass of each sample was measured after 21 days using an analytical balance. Sorption experiments were conducted in duplicate.

RESULTS AND DISCUSSIONS

Properties of rice starch

The properties of both regular and glutinous rice starch are presented in Table 1. The moisture content was about 10% and the protein content was not greater than 0.31%. Water absorption index of the glutinous rice starch was slightly greater than the regular one. The results from RVA revealed that regular rice starch had higher in gelatinization temperature, peak viscosity, breakdown, and final viscosity than glutinous rice starch. Therefore, glutinous rice starch could absorb more water and required less cooking time than regular rice starch. Cooked gel also showed less viscosity.

Rice starch microcapsules and its microstructure

Rice starch microcapsules obtained from the spray-dried process were either coarse or fine particles. In this experiment the fine particle was used for property evaluation. SEM morphological examination of the rice microcapsules showed relative sphere and regular in shapes. These

Table 1 Properties of regular and glutinous rice starches used for microcapsule preparation.

Properties	Regular rice starch	Glutinous rice starch
Moisture (%)	10.30	10.19
Protein (%) db.	0.31	0.08
WAI	0.01	0.14
Peak viscosities(RVU)	440.46	304.38
Breakdown(RVU)	310.05	184.42
Setback(RVU)	-234.84	- 130.33
Final viscosity(RVU)	205.63	174.04
Gel.Temp (C°)	71.70	68.23

RVU= Rapid Visco Unit

microstructures exhibited the same finding of Zhao and Whistler (1994), who reported that the spherical aggregate structure contained open spaces in the form of interconnecting cavities that provided extensive porosity, capable of being filled and used to transport materials within the sphere. Besides starch concentrations, various differences in amount and sizes of the starch aggregates were depended on the concentration and types of the binding agents. At 24% starch concentration with either 0.3% CMC or acacia provided better appearances of the starch aggregates than the 22% starch with CMC or acacia at 0.1% and 0.3%, respectively. Gelatin, on the other hand, gave the better result when 22% rice starch and 0.3% gelatin was used. At the same starch concentration (24%), the microcapsule of 0.3% CMC showed relatively larger in sizes as compared to acacia and gelatin under the SEM (Figure 1). However, only three samples which showed good appearances and great number of starch aggregates were selected, namely 24% rice starch with 0.3% acacia, 24% rice starch with 0.3% CMC and 22% rice starch with 0.3% gelatin. Thus the same conditions were repeated by using glutinous rice starch. The results from the SEM revealed the same appearance of the sphere. Physical and chemical properties of all 6 rice starch microcapsules were also determined.

Properties of rice starch microcapsules

The moisture contents of all samples were in the range of 5.43-8.20%, water activity (Aw) exhibited low value (0.20-0.41). Higher protein contents were found in the samples containing gelatin as compared to the others. The WAI values of the spray-dried microcapsule were different among the samples, but the glutinous microcapsules tended to have a greater WAI values than the regular ones, except microcapsule prepared from both types of rice starches with 0.30%acacia. Color values of all samples were slightly different in L*, a* and b*. The particle size distribution of the microcapsule of 24% regular rice starch with 0.30% CMC were in general, larger than the others while 24% glutinous rice starch with 0.30% acacia possessed the smallest size. However, the average sphere diameter of rice starch microcapsules was mainly in the range of 15.37-30.19 μm. The data obtained agree well with the finding of Zhoa and Whistler (1994), who reported that sphere produced were in the range of 10-40 μm. In this experiment, average particle density , bulk density and bulk porosity of the powder also compared (Table 3). The microcapsule of regular rice starch with CMC provided the greatest significant particle density while the 24% glutinous rice starch with acacia showed the lowest bulk density, implied higher in porosity of the powder. The bulk porosity, obtained by calculation, was also showed the same result. Besides said properties, dried powder need to be examined for its flowing ability.

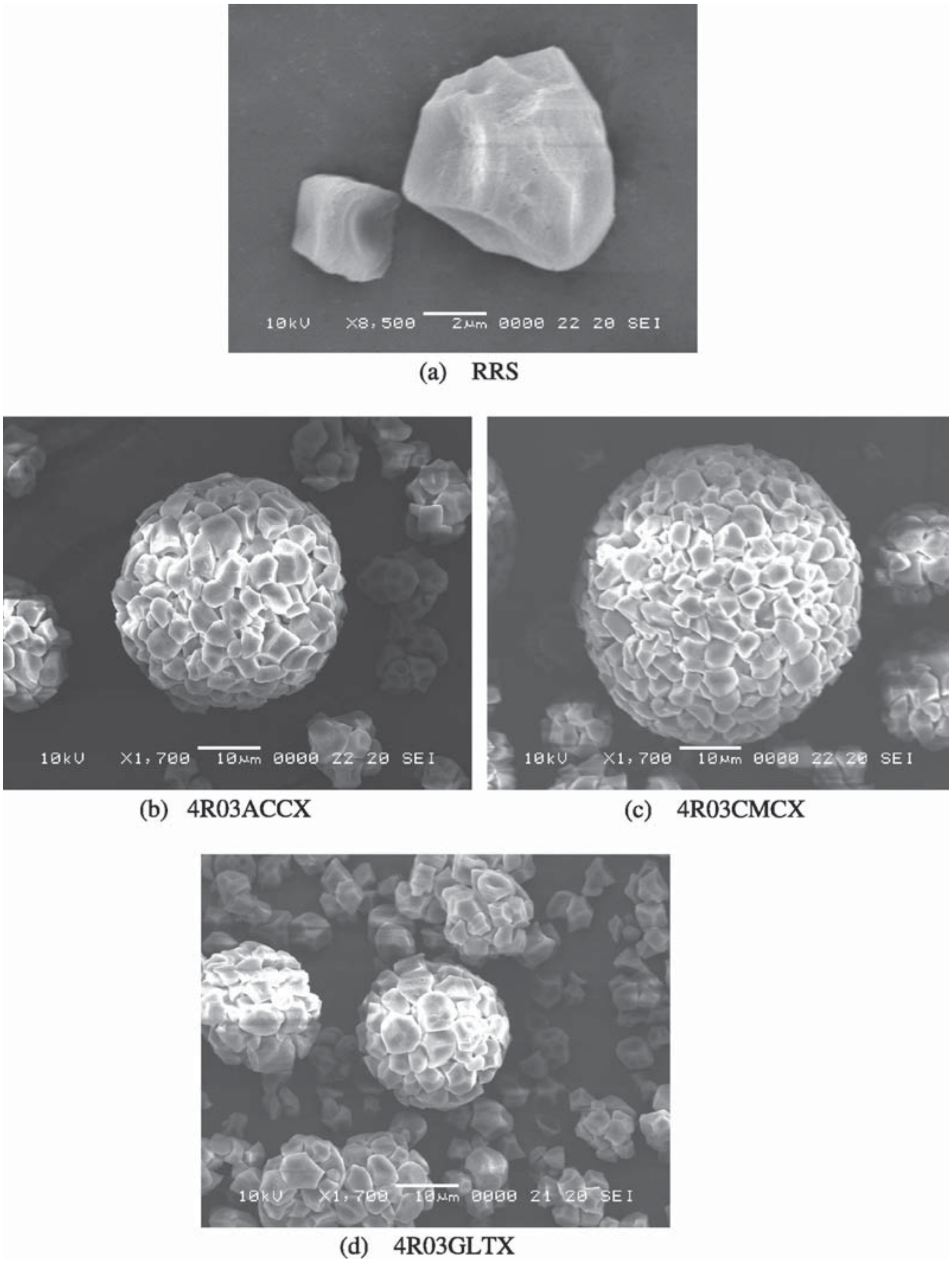

Figure 1 Comparison of surface microstructure of rice starch and rice starch microcapsulesby using SEM.

(a) native rice starch (X 8500 at 2mm)

(b) 24%rice starch +0.3% acacia (X 1700 at 10mm)

(c) 24% rice starch + 0.3% CMC (X 1700 at 10mm)

(d) 24% rice starch + 0.3% gelatin (X 1700 at 10mm)

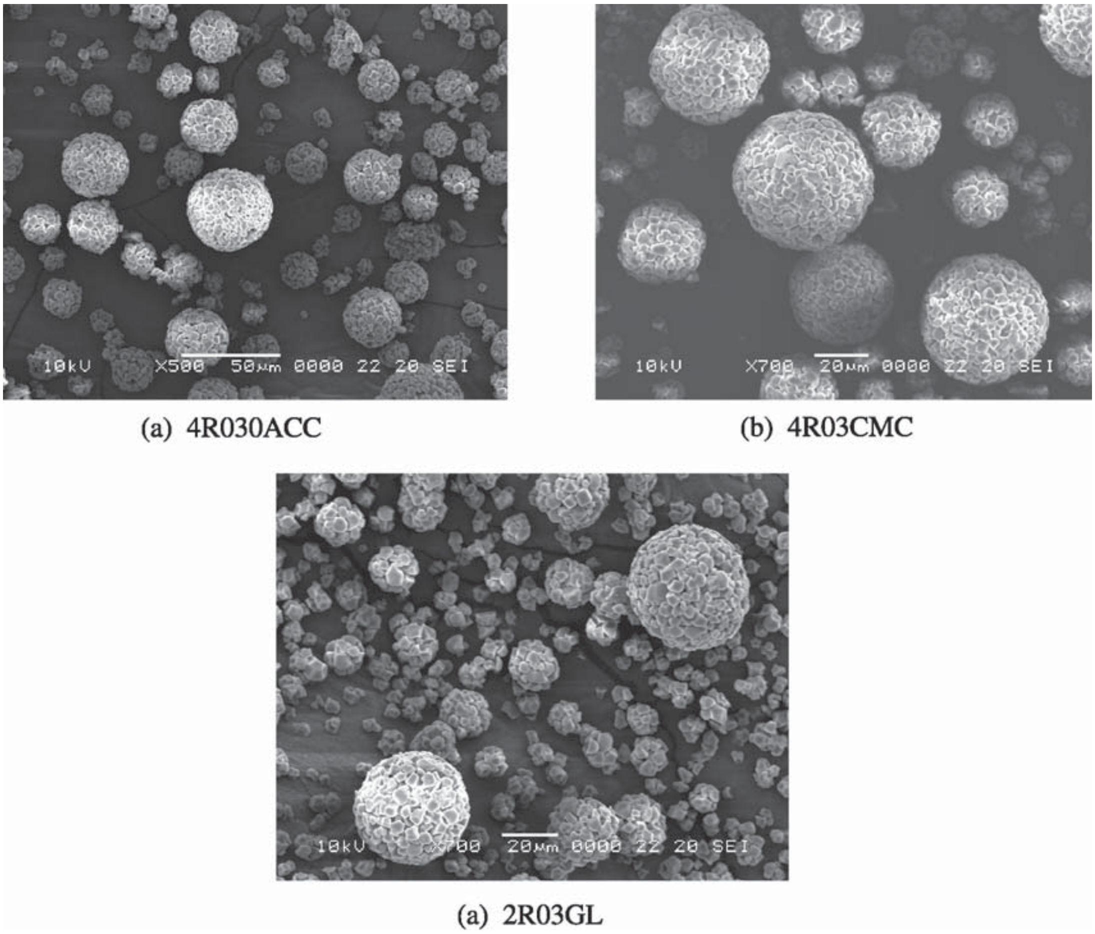

Figure 2 Surface microstructure of selected rice starch microcapsules examined under SEM.
(a) 24%rice starch +0.3% acacia (X 500 at 50mm)
(b) 24% rice starch + 0.3% CMC (X700 at 20mm)
(c) 22% rice starch + 0.3% gelatin (X700 at 20mm)

Table 2 Properties of regular and glutinous rice starch microcapsules.

Sample	Moisture%[1]	Protein%[1]	Aw[1]	WAI [1]
22%RRS+0.30%Gelatin	6.28	0.16	0.25	0.28
24%RRS+0.30%Acacia	8.20	0.03	0.41	0.57
24%RRS+0.30%CMC	6.45	0.02	0.26	0.29
22%GRS+0.30%Gelatin	7.52	0.17	0.35	0.70
24%GRS+0.30%Acacia	6.93	0.01	0.26	0.57
24%GRS+0.30%CMC	5.43	0.01	0.20	0.60

[1] Averages were based on duplicate measurements of moisture free sample.
Note: RRS = regular rice starch and GRS = glutinous rice starch

All microcapsule powder samples obtained from the experiments showed easy flowing and free flowing while native glutinous rice starch exhibited poorer flowing (very cohesive). Among these samples, the 24% regular rice starch with 0.3%CMC showed the best flowing properties. The Cv compaction of the 22% regular rice starch with 0.30% gelatin had the highest value which was great different from 1 as compared to the other samples, interpreting that said sample possessed the lowest stability under compression condition while the 24% regular rice starch with 0.30% CMC showed the best stability.

Table 5 presented the pasting properties of different rice starch microcapsules. It revealed that types of starch and binding agent affected the paste viscosities. The glutinous samples gave lower values in gelatinization temperature (GT), peak viscosity, trough, breakdown and final viscosity than the microcapsules prepared from the

Table 3 Color value, particle size and particle density of native rice starch, regular andglutinous rice starch microcapsules.

Sample	Color value[1] L*	a*	b*	Particle size (μm)[1]	Particle[1,2] density g/cm[3]	Bulk density g/ cm[3]	Bulk porosity
22%RRS+0.30%Gel	99.36	0.01	0.38	17.70±0.42	1.52ab	0.57	0.63
24%RRS+0.30%Acacia	98.58	0.03	0.37	24.73±0.13	1.52ab	0.57	0.63
24%RRS+0.30%CMC	98.93	0.08	0.84	30.19±0.07	1.55a	0.57	0.63
22%GRS+0.30%Gel	99.28	0.00	0.37	27.35±0.83	1.49bc	0.58	0.61
24%GRS+0.30%Acacia	99.32	0.01	0.31	15.37±0.18	1.50ab	0.54	0.64
24%GRS+0.30%CMC	99.14	0.05	0.44	25.39±0.07	1.52ab	0.58	0.62
RRS	99.58	0.02	0.35	-	1.47c	-	-
GRS	99.54	-0.01	0.36	-	1.47c	-	-

1 Averages were based on three measurements of each sample.

2 In a column, means followed by the same superscript are not significantly different (p>0.05) by DMRT

\- not determined.

Table 4 Comparison of flow-ability of microcapsule powder prepared from regular and glutinous rice starch.

Sample	Av Compaction coef 50mm/s (g.mm)	Cv Compaction	Av Cohesion coef 50mm/s (g.mm)	Cohesive index	Flow behavior
22%RRS+0.30%Gel	3168.83	3.315	-699.29	11.46	Easy flowing
24%RRS+0.30%Acacia	3181.26	1.117	-695.48	11.31	Easy flowing
24%RRS+0.30%CMC	3173.52	0.965	-510.89	8.38	Free flowing
22%GRS+0.30%Gel	3737.71	1.276	-649.08	10.64	Free flowing
24%GRS+0.30%Acacia	2293.58	1.088	-510.80	10.22	Free flowing
24%GRS+0.30%CMC	3328.04	0.649	-582.22	9.54	Free flowing
RRS	3599.19	1.911	-814.43	13.35	Easy flowing
GRS	3683.80	0.789	-898.92	17.98	Very cohesive

Averages were based on three measurements of each sample.

Note: RRS= regular rice starch, GRS= glutinous rice starch regular rice starch. Therefore, the glutinous rice starch microcapsule was easier to cook, and gave softer gel as compared to the rice starch microcapsules. Rice starch microcapsules with 0.3% CMC provided higher final viscosity than with gelatin or acacia. Among the samples either regular or glutinous rice starches with 0.30% acacia showed nearly the same pasting properties as its native starch.

The results of sorption isotherm revealed that all products showed hygroscopic properties (Figure 3). An increase in Aw, resulted in an increase in water content of the products, and water sorption was quite noticeably sharp at Aw = 0.70. Therefore, environmental condition should be considered since it has an effect on the properties of the sphere starch powder, which might forming a glutinous texture or aggregate during storage or transportation.

CONCLUSIONS

Microcapsule could be produced from either regular or glutinous rice starches with the small amount of suitable binding agents by using a spray dryer. Most of the products exhibited a spherical shape which contained open spaces in the form of interconnecting cavities that provided extensive porosity within the sphere. Variation in sizes, number and properties of the starch

Table 5 RVA peak viscosities[1] of different rice starch microcapsules.

Samples	GT(°C)	Peak vis.(RVU)	Trough (RVU)	Breakdown (RVU)	Final vis. (RVU)	Setback (RVU)
22%RRS+0.30%Gelatin	70.95	395.08	130.92	264.17	197.80	-197.30
24%RRS+0.30%Acacia	70.93	404.79	125.88	278.92	203.33	-201.34
24%RRS+0.30%CMC	71.73	397.71	154.21	243.50	244.96	-152.75
22%GRS+0.30%Gelatin	67.65	291.83	124.50	167.34	169.29	-122.54
24%GRS+0.30%Acacia	66.53	303.46	118.50	184.96	166.46	-137.00
24%GRS+0.30%CMC	68.58	311.46	113.38	198.09	179.92	-131.54

Averages were based on duplicated determination.

[1] RVU = Rapid Visco Unit.

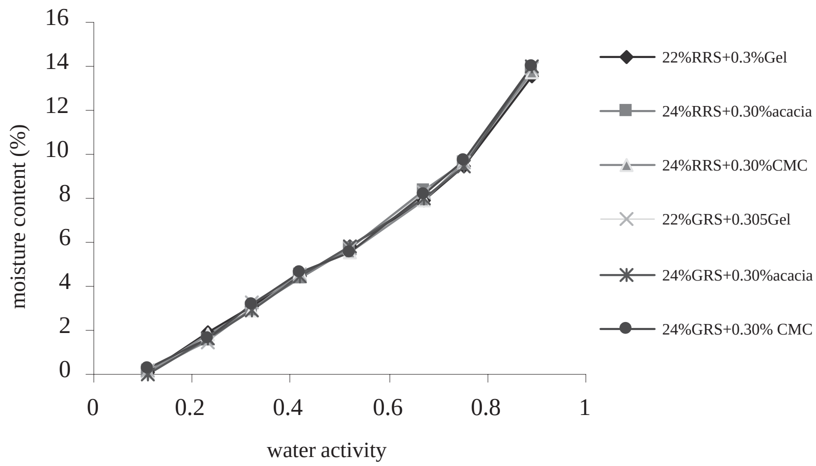

Figure 3 Sorption curve for rice starch microcapsules under various water activity at 29 °C.

aggregates were depended on types and concentration of the starches and the binding mixtures. The average sphere diameter of all rice starch microcapsules was in the range of 15.37-30.19 μm, the particle density and bulk density was about 1.49-1.55 g/cm^3 and 0.54-0.58 g/cm^3, respectively. Flow characteristics of all products showed easy -to-free flowing powder types. However, these products exhibited hygroscopic properties.

Because of its porous structure, the microcapsules can be filled up with food ingredients such as flavor.

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