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Thermal characteristics and state diagram of extruded instant artificial rice

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ABSTRACT

Instant artificial rice was developed by extrusion method using corn flour, glycerol monostearate (GSM), and glucomannan and guar gum. Moisture sorption isotherm and thermal characteristics of the artificial rice with glucomannan and guar gum were measured and modeled to develop different regions of a state diagram. The freezing point, glass transition, and solids-melting were measured and modeled by Chen's model, modified Gordon–Taylor model, and Flory–Huggins model, respectively. The ultimate maximal-freeze-concentration conditions were found as $(T_m')_u$ (i.e., annealed end glass transition temperature for the sample with moisture 0.40 g/g sample) equal to −8.3 °C and $(T_g''')_u$ (i.e., annealed onset glass transition temperature for the sample with moisture 0.40 g/g sample) equal to −8.4 °C, and the characteristic solids content, X_s' as 0.76 g/g sample (i.e., un-freezable water, X_w' equal to 0.24 g/g sample). Similarly the characteristic glass transition temperature, T_g^{iv} (i.e., intersection of vertical line passing through T_m' and glass transition line above X_s') was estimated as 29.8 °C.

1. Introduction

Artificial rice could be developed as a new value added product using different types of grains with added nutrients and functionalities. The terms of artificial rice, enriched rice, rice analogs or reformed rice were introduced by several authors [1–4]. The developed products could avoid deficiency in nutrients as compared to the natural rice without major changes in consumers' dietary habits. The main advantages could be the easy process of developing instant rice and the possibility of incorporating different nutrients with desired textural characteristics. In addition, it could be developed using wastes or byproducts with low cost and utilizing energy efficient process, such as extrusion [5]. A number of studies are reported on the development of artificial rice [4–13].

Instant rice can be prepared quickly within 2–15 min with simple procedures or steps. Luh et al. [14] stated that quick cooking could take only 5–15 min, however good ones should take only 5 min. Roberts [15] stated that a quick cooking rice is expected to be ready to serve within 5–15 min. Once prepared (i.e., cooked) the rice must comply with the characteristics of paddy rice in terms of its taste, aroma, and texture. Wang et al. [5] developed extrusion-cooked instant rice with emulsifiers (glycerol monostearate, soybean lecithin, sodium stearoyl lactylate), gums (gum Arabic, sodium alginate) and sticky rice. They assessed their quality parameters (i.e., bulk density, water soluble index, α-amylase sensitivity, water hydration rate and water soluble carbohydrate) in order to optimize the processing conditions. Mishra et al. [6] reviewed formulations (i.e., ingredients) of instant artificial rice and their processing methods. The important aspect of formulation is the fortifications of color, flavors, vitamins, nutrients, and antioxidant in order to ensure its value addition; and it is important to determine the stability of fortified components in the artificial rice matrix during processing and its storage. Recently, a great deal of research has been reported on the utility of glass transition to determine foods' stability and their ingredients [16–18]. The glass transition was also related to the molecular mobility, chemical reaction and shelf life of foods [16,17,19,20]. The possible regions of extrusion, drying and freezing process can be easily visualized in the state diagram (i.e., a map presents different phases and states as a function of solids or water content and temperature) [16]. The effect of aging on the glass transition and enthalpy relaxation of waxy rice starch [21,22] and native and

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gelatinized starch [23] was reported in the literature. Sablani et al. [18] measured the glass transition and freezing point of rice by modulated DSC and cooling curve methods, respectively. In the literature, relatively low information is available on the thermal characteristics of starch based products, such as rice and instant artificial rice. Thus the objectives of this research were to study thermal characteristics (i.e., freezing, glass transition, solids-melting and maximal-freeze-concentration condition) using different types of DSC as initial data to develop state diagram of extruded artificial rice. Finally different components of the state diagram were also developed in order to visualize different phases and states of the artificial instant rice as a function of temperature and solids contents (i.e., moisture) so that it could be used to determine the stability of artificial rice during its processing and storage. In addition the isothermal protocol proposed by Rahman and Al-Saidi [24] was also tested for measuring glass transition of biomaterial consisting stiff molecular polymer.

2. Materials and method

2.1. Materials

Corn flour was made from corn (i.e., White Srikandi variety) released by IAARD (Indonesia Agency for Agricultural Research and Development, Bogor, Indonesia). In order to produce the artificial rice, corn flour, tapioca starch (Tapioca Gunung Agung Merck, Indonesia), guar gum (Type V-62, Spectrum, Pakistan), glycerol monostearate (GMS) (Type EN 38098, Danisco Malaysia, Penang, Malaysia) were used. Indonesian commercial rice (i.e., Purnama, Cianjur, Indonesia) were purchased from the local super market. Sodium hydroxide (NaOH), magnesium chloride ($MgCl_2$), magnesium nitrate $Mg(NO_3)_2$, sodium chloride (NaCl), and potassium sulfate (K_2SO_4) were purchased from Merck, Darmstadt, Germany. Potassium chloride (KCl) was purchased from Cica Kanto Chemical Co., Tokyo, Japan and barium chloride ($BaCl_2$) from Showa Chemical Co., Tokyo, Japan.

2.2. Sample preparation

Corn flour was prepared by dry mill method according to Johnson [25]. In preparing artificial rice, 2 kg of dough was prepared with 1.74 kg corn flour, 200 g tapioca starch, 40 g GMS, 19.2 g glucomannan and 0.8 g guar gum. First dough was prepared by mixing 1 kg of distilled water to guar gum followed by addition of other ingredients and mixed for 5 min. The dough was then fed into twin screw extruder (Twin Screw Bex 225-6, Berto Industries, Jakarta, Indonesia) and run at 96 °C and 168 rpm. The extruded rice was then treated with steam (Tea Steaming Machine, Terada Seisakusho, ED-4K-SP, Shizuoka, Japan) in a closed chamber (5 min) followed by convection air drying (Tea Drier Oven, Terada Seisakusho, Shizuoka, Japan) at 70 °C for 6 h. In order to decrease the cooking time of artificial rice, the extruded rice was further treated with steam to increase the degree of gelatinization. The artificial rice was then ground into powder and desiccated over calcium chloride. The samples containing different levels of unfreezable water were prepared by adsorption over saturated salt solutions in desiccators. The samples with freezable water were prepared by adding predetermined amount of water into the dry powder and equilibrated at 4 °C for 24 h.

2.3. Chemical analysis

The chemical analysis of the samples for moisture, ash, fat and protein were performed according to the AOAC [26], while carbohydrate was determined by difference (i.e., total mass fraction and mass fractions of water, ash, fat and protein). The fiber was determined by enzymatic method as proposed by Asp et al. [27].

2.4. Moisture sorption isotherm

The moisture sorption isotherm was measured by isopiestic method [28–30]. The ground artificial rice flour and the commercial rice flour were placed in a desiccator maintained dry environment with calcium oxide. The samples were equilibrated for two weeks at 30 °C. 2 g of dry samples were stored in different desiccators maintained at different relative humidity environments at 30 °C. The specific relative humidity in the desiccators were created using saturated salt solution placed at the bottom of the desiccators (i.e., under the metal mesh). The saturated condition was created by maintaining a layer of salt crystals at the bottom. The salts used to prepare solution for maintaining relative humidity were: sodium hydroxide (NaOH), magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3), magnesium nitrate $Mg(NO_3)_2$, sodium chloride (NaCl), potassium chloride (KCl), barium chloride ($BaCl_2$), and potassium sulfate (K_2SO_4). The water activity values of the above saturated salt solutions are presented in Table 1. Samples were equilibrated at 30 °C until a constant mass was achieved. The moisture contents of the equilibrated samples were determined by gravimetrically using an oven at 105 °C for at least 18 h of drying. The moisture sorption isotherms were modeled with Brunauer–Emme–Teller (BET) [31] and Guggenheim–Andersen–de Boer (GAB) [32]. BET equation is:

$$M_w = \frac{M_b B a_w}{(1-a_w)[1+(B-1)a_w]} \tag{1}$$

where M_b is the BET monolayer water content (g/100 g dry-solids), a_w is the water activity, and B is a constant related to the net heat of sorption. Moisture sorption isotherm data within water activity of 0.05 and 0.55 were also fitted to the theoretical BET model to determine the monolayer moisture content [29]. GAB equation is:

$$M_w = \frac{M_g C K a_w}{[(1-K a_w)(1-K a_w + C K a_w)]} \tag{2}$$

where M_g is GAB monolayer moisture content (g/100 g dry-solids), C is related to the heat of monolayer sorption, and K is related with the heat of multilayer sorption.

2.5. Thermal characteristics

2.5.1. DSC measurement for the samples containing unfreezable water

Thermal characteristics were measured by DSC (Q20) and modulated DSC (Q1000) (TA Instruments, New Castle, DE, USA) attached with mechanical refrigerated cooling system capable to cool down to −90 °C. The instrument was calibrated for heat flow and temperature using distilled water (melting point, mp = 0 °C; ΔH_m = 334 J/g) and indium (mp = 156.5 °C; ΔH_m = 28.5 J/g). Aluminum pans of 30 μL with lid were used in all experiments with an empty sealed pan as reference, and nitrogen at a flow rate of 50 mL/min was used as a carrier gas.

Table 1
Proximate analysis of artificial and commercial samples.

Content (g/100 g sample)	Artificial rice	Commercial rice
Moisture	10.82	13.21
Ash	0.52	0.56
Fat	0.59	3.41
Protein	6.34	11.66
Carbohydrate	81.75	71.16
Dietary fiber	6.66	0.13