Effect of Amylose Content on Expansion of Extruded Rice Pellet

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ABSTRACT

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Rice pellets were prepared by single-screw extrusion cooking with an in-barrel water content of 50 wt%. Three different types of rice, indica glutinous, japonica, and indica, were used as raw materials. Reconstituted rice flour was made to study the effect of amylose content on pellet expansion. The glass transition (T_g) and expansion (T_e) temperatures of extruded pellet were determined by differential scanning calorimetry (DSC) and noncontact infrared thermometer, respectively. The amylose content was not significantly affected by extrusion cooking. The reduction in intrinsic viscosity indicated that amylopectin experienced some degradation. The T_g and T_e were not functions of amylose content, which affected the expansion ratio of the pellets. The Gordon-Taylor equation was applied to estimate the T_g of the rice pellets.

Third-generation snack foods are made from farinaceous materials using extrusion cooking technology. After drying, the extrudate becomes a pellet or half-product and is shelf-stable in a glassy state. The pellet can be further expanded by various heating methods such as frying, hot-air oven, and microwave. The puffed product made by hot-air oven or microwave could meet demand for low or zero oil content. Appropriate expansion is desirable for successful product development, thus it would be beneficial if relationships between expansion performance and the variety of raw materials were understood.

Expansion of starch material affects the texture and structure of finished products. Expansion by extrusion cooking has been widely investigated. In general, temperature and feeding moisture content affect the expansion as a function of amylose content. Mercier and Feillet (1975) pointed out that expansion ratio decreased as the amylose content increased when the barrel temperature was 135°C. When the barrel temperature was raised to 225°C, more expansion was associated with higher amylose content. Nevertheless, Della Valle et al (1997) reported that the expansion increased with amylose content at any temperature and moisture content. Higher amylopectin content provided a light, elastic, and homogeneous texture with a smooth, sticky external surface. High-amylose blends were harder and less expanded. Matz (1984) recommended a 5–20% amylose level in starch to give acceptable texture with adequate crispness. An understanding of the expansion of extruded pellets is important for designing product properties or selecting puffing conditions. However, the studies on the effect of amylose content on pellet expansion are limited and the mechanism of expansion still remains unclear.

Pellets appear to expand after being softened by heating durng vaporization of water. Softening of the pellet indicates the transition from glassy pellet to rubbery material. In other words, the expansion temperature (T_e) would be above the glass transition temperature (T_g). However, the experimental evidence on this phenomenon is limited. Molecular weight, structure, and plasticizer govern the T_g, which is relevant to food processing (e.g., freezing, drying, and extrusion) and correlates well with quality attributes (e.g., texture, stability, and flavor release in low-moisture systems) (Levine and Slade 1988; Noel et al 1990). T_g has been proposed as a criterion to adjust extruder operating conditions for optimal textural properties, as well as to select optimum storage conditions for improving stability of extruded products (Kaletunc and Breslauer 1993). Measuring or estimating T_g would be helpful for understanding the role of glass transition in pellet expansion. Several empirical and theoretical equations relating mechanical properties of polymers, their composition, and molecular weight to the T_g have been reported (Fox and Flory 1950; Gordon and Taylor 1952; Tant and Wilkes 1981). Orford et al (1990) and Roos and Karel (1991) discussed methods to predict T_g of amorphous food components as a function of composition and molecular weight. The Couchman-Karasz equation was used to predict T_g of amylopectin-water (Kalichevsky et al 1993):

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{1}$$

where w_i is the weight fraction of component i, and ΔC_{pi} is the difference in heat capacity between the liquid and glass state at T_g. Both T_{gi} and ΔC_{pi} are required to apply Equation 1.

The Gordon-Taylor equation is frequently used for plasticization with water:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{2}$$

Comparing both equations mathematically, k in Equation 2 is equivalent to $\Delta C_{p2}/\Delta C_{p1}$ in Equation 1. The Gordon-Taylor equation fits well with the data of amorphous carbohydrates and water system (Roos and Karel 1991). Due to the complexity of the system, both Couchman-Karasz and Gordon-Taylor equations underestimated T_g for extruded corn meal melt (Brent et al 1997).

The objectives of this study were to investigate the effect of amylose content on pellet expansion and to evaluate the relationship between T_g and T_e.

MATERIALS AND METHODS

Three rice cultivars were selected based on amylose content: Taichung Sen Glutinous 1 (TSG-1), an indica glutinous type; Taigern 9 (TG-9), a japonica type; and Taichung Sen 10 (TS-10), an indica type. All rice was purchased from Fen-Yuan Agriculture Association in Central Taiwan. Polished rice was ground using a stamp mill to pass an 80-mesh (ASTM) screen. Proximate composition was analyzed using official methods (AOAC 1984). TSG-1 and TS-10 were mixed at ratios of 4:1, 3:2, 2:3, and 1:4 to obtain reconstituted rice flour with different amylose contents. Amylose content was analyzed according to the method of Juliano et al (1981). Rice flour or reconstituted flour was put in a silent cutter and sprayed with distilled water. The silent cutter not only provided the mixing for uniform moisture distribution but also prevented the flour from caking. The admixture had a moisture content of 40% (wb). The preconditioned admixture was stored at 4°C before use.

Preparation of Pellets

Extrusion cooking with a single-screw extruder (Yeh and Jaw 1998) was used to prepare pellets. The bore of the profiled barrel had a diameter of 8.5 cm with an L/D of 5.1. A diaphragm-type pressure

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transducer and a thermocouple were inserted into the die for measuring die pressure and temperature. A torque transducer (TP-10KMCB, Kyowa Co., Tokyo, Japan) was fitted between the motor and gearbox to measure the torque. The energy losses in bearings and the drive train were assumed to be negligible as they did not affect the reproducibility of the control system. The screw profile was built up by segmented forwarding elements, except that a 2-cm nonflight element was used near the tip of the screw. The forwarding elements had a flight height of 1 cm. The nonflight element was cylindrical with a diameter of 6.3 cm. There were two barrel sections, one jacketed and the other nonjacketed. Water flowed inside the jacket for cooling. A heating tape around the nonjacketed barrel was used for heating. A thermocouple was attached to the surface of the nonjacketed barrel to measure barrel temperature. The heating tape and water flow were on/off controlled to keep the nonjacketed barrel at 88 ± 2°C. A slit die 85 mm wide by 3 mm high was used to form sheet-type extrudate.

From preliminary tests, a screw speed of 82.5 rpm and a feed rate of 8 ± 0.3 kg/hr were selected. The extruder was run at starved-fed conditions in this study. Preconditioned admixture was fed into the extruder through a twin-screw feeder which was calibrated before each experiment. During experimentation, the admixture in the feeder hopper was manually controlled at a given level (≈5 cm above the screw). Thus, the feed rate was kept consistent at ±0.3 kg/hr. Additional water was pumped into the extruder to maintain the in-barrel water content at 50 ± 0.3%, except for TSG-1 at 45 ± 0.3%. The extrusion conditions yielded pellet with <95% gelatinization as analyzed by an enzymatic method. After stable operations were established, judged by constant torque readings and consistent product output, extrudates were collected, molded to 3 cm in diameter, and dried in an air-oven at 40°C to prepare dry pellets with a moisture content of ≈12%. Each extrusion condition was conducted in triplicate to evaluate the pellet properties.

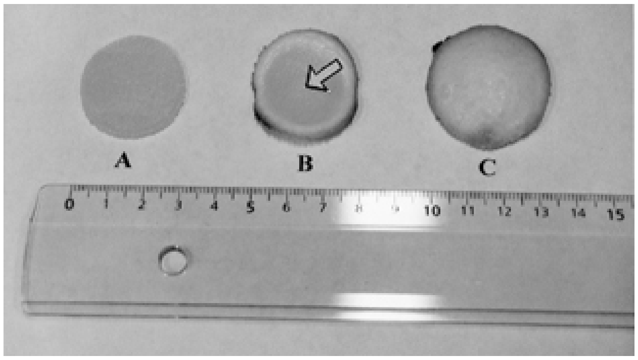

Fig. 1. Initial pellet appearance (A), expansion at the peripheral region as it becomes white (B), and finished product (C). Arrow indicates center of the pellet where surface temperature was measured.

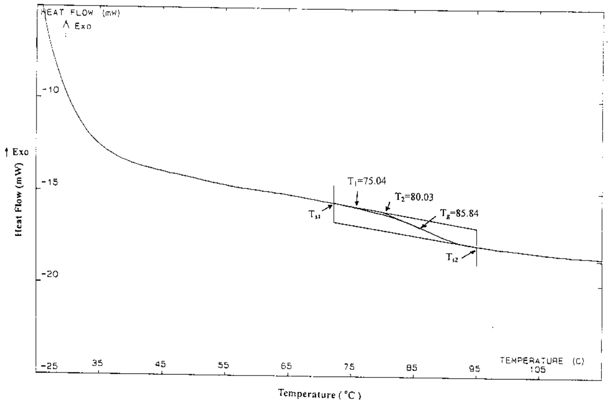

Fig. 2. Differential scanning calorimetry thermogram for determining glass transition temperature.

Glass Transition Temperature

Dry pellets were ground in a rotary speed mill (Pulverisette 14, Fritsch, Germany) to pass a 20-mesh screen. Powder was equilibrated with saturated salt solutions of LiCl, CH_3COOK, $MgCl_2 \bullet 6\,H_2O$, KNO_2, $Mg(NO_3)_2{\bullet}6H_2O$, $NaNO_2$, NaCl, KBr, and $Na_2CO_3{\bullet}10H_2O$ in a desiccator at 25°C for seven days. Before equilibration, the desiccator pressure was reduced to 60 mmHg by an aspirator (A-3S, Tokyo Rikakikai Co., Tokyo, Japan). The equilibrium moisture content was double-checked using official methods (AOAC 1984) with five replicates. Once the moisture content was confirmed, the sample (≈80 mg) was put in a crucible for thermal analysis using differential scanning calorimetry (DSC 121, Setaram Co., France) equipped with a liquid nitrogen cooling system. The crucible was hermetically sealed using an aluminum O-ring with an empty crucible as reference. The scan rate was 5°C/min and the temperature range was –40 to 100 or 200°C, depending on occurrence of the glass transition phenomenon. The T_g was determined using software provided by Setaram according to the method of Sperling (1993). The determination of T_g was conducted for five replicates, and the average value was recorded. The T_g at nine different equilibrium moisture contents was determined for a pellet prepared at one set of extrusion conditions.

Expansion Temperature

Dry pellets were also equilibrated with saturated salt solutions to different equilibrium moisture contents using the above procedures. The equilibrium moisture content of the pellet was double-checked using official methods (AOAC 1984) before the expansion experiment. A home-made laboratory-scale oven with temperature controller was used for the expansion of equilibrated pellets at an oven temperature of 350°C. A noncontact infrared thermometer (Ray PM30L3U, Raytek Co., Santa Cruz, CA) with data acquisition and analysis software (DataTemp 2) measured the surface temperature at the center when the expansion occurred in the peripheral region of the pellet. The emissivity of the thermometer was set at 1.0.

The appearance of the pellet and the expansion at the peripheral region as it becomes white are shown in Fig. 1. The preliminary tests showed that ≈50% of water loss occurred at this stage. Thus, the surface temperature at the center was considered as the T_e. The

TABLE I
Amylose Content (%) of Rice Flour and Extruded Pellet

Raw Material[a]	Flour	Extruded Pellet
TSG-1	9.52 ± 0.11	9.03 ± 0.12
TG-9	17.15 ± 0.09	16.70 ± 0.15
TS-10	23.02 ± 0.15	22.50 ± 0.19
Reconstituted flour ratios		
4:1	12.22 ± 0.12	11.32 ± 0.08
3:2	14.92 ± 0.13	13.84 ± 0.12
2:3	17.62 ± 0.13	17.25 ± 0.13
1:4	20.32 ± 0.14	19.25 ± 0.16

[a] TSG-1: Taichung Sen Glutinous 1; TG-9: Taigern 9; TS-10: Taichung Sen 10. Amylose content of reconstituted flour calculated as ratio of TSG-1 to TS-10.

TABLE II
Moisture Content (%) of Powder and Pellet After Equilibration with Saturated Salt Solutions

Solution	a_W[a]	Powder	Pellet
LiCl	0.12	6.13 ± 0.05	5.95 ± 0.11
CH_3COOK	0.20	9.32 ± 0.09	9.16 ± 0.11
$MgCl_2{\bullet}6H_2O$	0.33	10.29 ± 0.09	10.18 ± 0.13
KNO_2	0.45	10.84 ± 0.07	10.72 ± 0.09
$Mg(NO_3)_2{\bullet}6H_2O$	0.52	11.49 ± 0.06	11.35 ± 0.17
$NaNO_2$	0.66	12.67 ± 0.09	12.56 ± 0.11
NaCl	0.76	13.77 ± 0.12	13.57 ± 0.09
KBr	0.84	15.35 ± 0.08	14.99 ± 0.14
$Na_2CO_3{\bullet}10H_2O$	0.92	26.43 ± 0.16	25.74 ± 0.18

[a] Water activity data from Labuza et al (1976).

finished product is shown in Fig. 1C. Five replicates were conducted to obtain the average T_e.

Piece Density

A densimeter (MD-200S, Mirage Co., Osaka, Japan) was used to determine the piece density of pellets and expanded products by applying the Archimedes principle. Silicone oil was used as the solvent to avoid the dissolution of samples. Five replicates were made to obtain the average piece density. The expansion ratio was calculated as the ratio of the piece density of pellet to that of expanded product.

Intrinsic Viscosity

Dry pellets were ground by a rotary speed mill (Pulverisette 14, Fritsch, Germany) to pass an 80-mesh screen, according to Greenwood (1964) and Mahanta and Bhattacharya (1989). The samples were refluxed with 85% methanol for 24 hr, then dried in an air-oven at 40°C. The dried sample (≈0.15 g) was mixed with 25 mL of 0.5*N* KOH and heated in boiling water while purging with nitrogen gas. The heated sample was cooled first and then centrifuged (9,000 × *g*) for 10 min. The supernatant was prefiltered through a glass fiber filter (G4). The total polysaccharide in the filtrate was determined by the phenol-sulfuric method (Dubois et al 1956). The intrinsic viscosity was determined at 25 ± 0.1°C using a Cannon-Fenske viscometer with 0.5*N* KOH as the solvent. Intrinsic viscosity was determined in triplicate and the average value was recorded.

Transparency

The pellet transparency was measured with a color meter (TC-1, Tokyo Denshoku Co., Japan) using the Hunter *L,a,b* color scale. The instrument was set at transmission mode and calibrated using a standard tiles (L = 99.99, a = 0.06, b = –0.08). The value of L was recorded as the transparency. The determination of transparency was conducted in triplicate, and the average value was recorded.

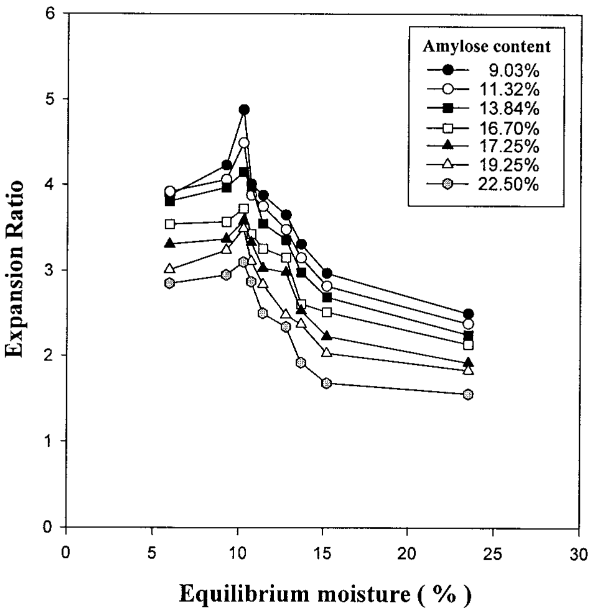

Fig. 3. Expansion ratio as function of equilibrium moisture and amylose content.

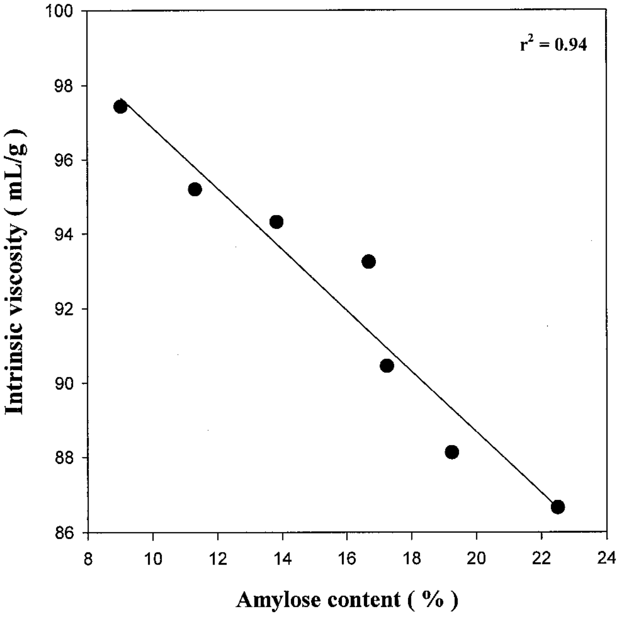

Fig. 4. Intrinsic viscosity of pellets decreased as amylose content increased.

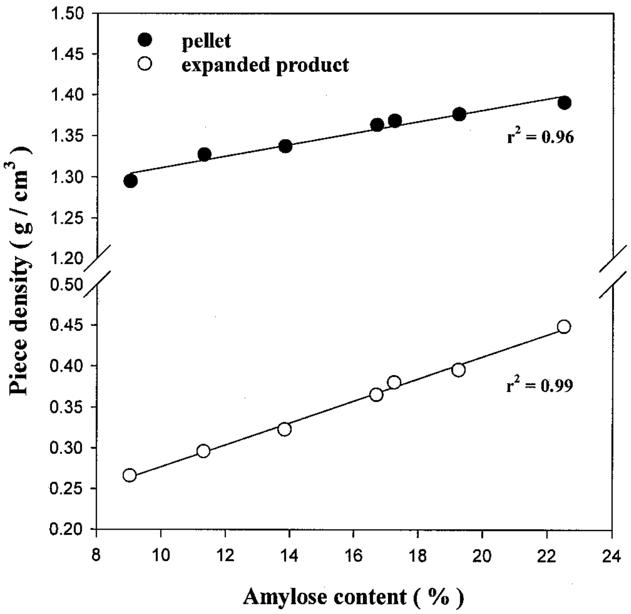

Fig. 5. Amylose content affected piece density of pellets and expanded product.

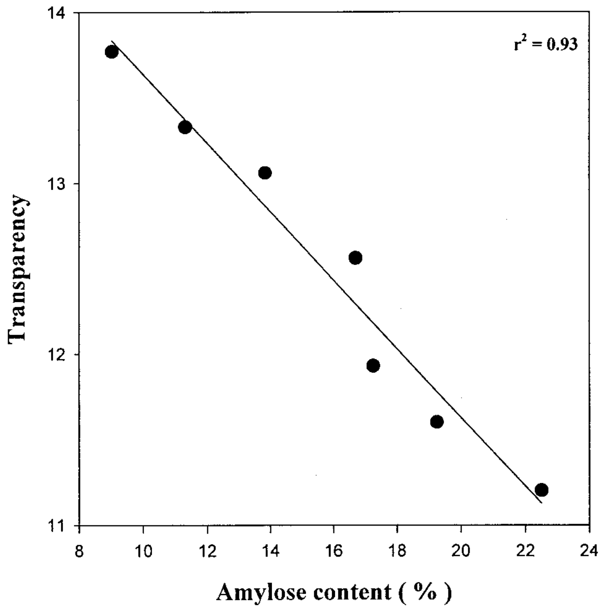

Fig. 6. Transparency of pellets decreased as amylose content increased.

Data were analyzed using Sigmaplot for Windows to obtain the regressed curves and correlation coefficients. Because the variations in data were <8%, the average values were reported without showing the error bars.

The software of nonlinear estimate in Statistica 5.1 (Statsoft Inc., Tulsa, OK) was used to fit the models for estimating T_g.

RESULTS AND DISCUSSION

The three rice cultivars had similar moisture, crude protein, fat, and ash contents. Crude protein content was 7.45–8.57%. Fat content was 0.57–0.71%. Ash content was 0.46–0.64%. It appeared that the major difference in composition was the amylose content as listed in Table I. TSG-1 had the lowest amylose content at 9.52%. The amylose content of TS-10 was the highest at 23.02%. TG-9 had an intermediate amylose content at 17.52%. The data were in agreement with literature (Huang 1987). Equilibrium moisture contents of powder and pellet are listed in Table II. The water activity of saturated salt solutions was 0.12–0.92 (Labuza et al 1976). The corresponding equilibrium moisture content was 6.1–26.4%. Powdered samples had slightly higher moisture content than pellets, possibly because of increased surface area. Pellets prepared from different raw materials yielded same equilibrium moisture content when subjected to one saturated salt solution. Powder exhibited similar behavior.

Figure 2 is one example of a thermogram obtained from DSC for determining T_g. The pellet made from TG-9 was ground and then equilibrated with saturated $MgCl_2{\bullet}6H_2O$ solution. The transition was observed as a shift of baseline, which indicated a change in heat capacity (Sperling 1993). As analyzed by the software, T_1 corresponded to 2% of transition and T_g corresponded to 50% of transition. T_2 was the intersect of the tangents between T_g and T_{s1}. The thermal analysis was repeated after storing pellets for six months, resulting in the same thermogram. Thus, aging was not a concern

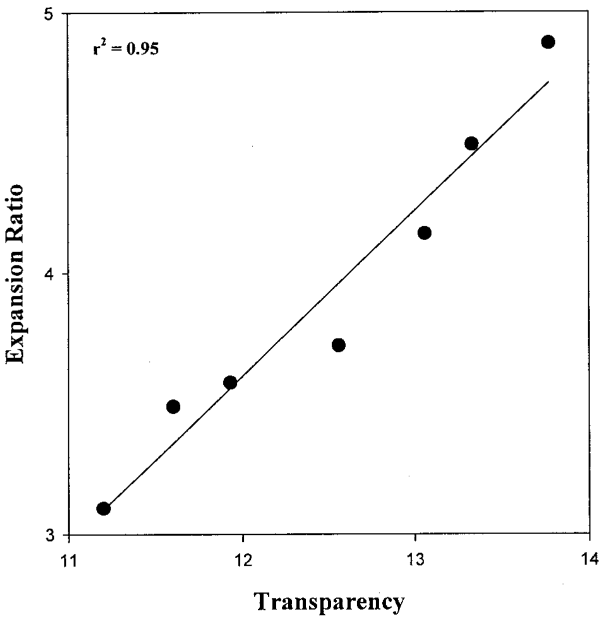

Fig. 7. Expansion ratio increased with pellet transparency.

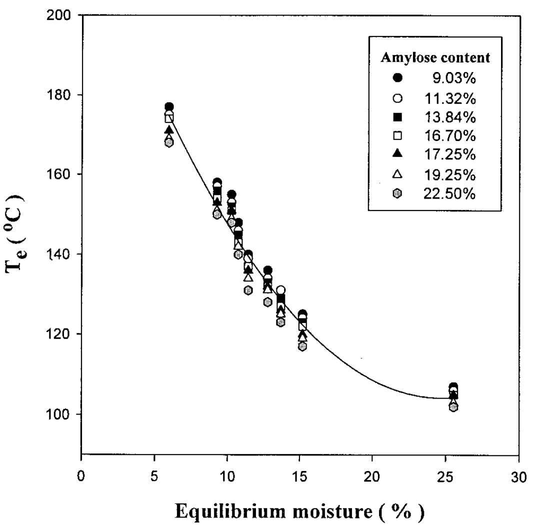

Fig. 8. Dependence of expansion temperature (T_e) on equilibrium moisture and amylose content.

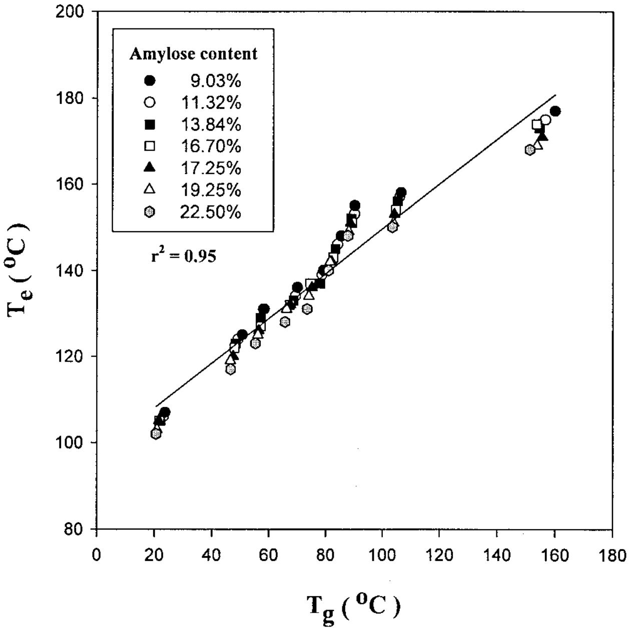

Fig. 9. Expansion temperature (T_e) increased linearly with glass transition temperature (T_g).

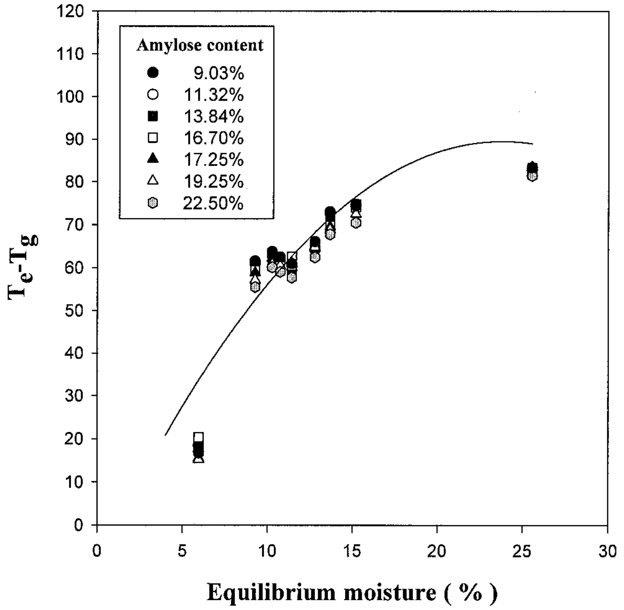

Fig. 10. Value of ($T_e - T_g$) as a function of equilibrium moisture content.

in this study. DSC analysis of powder with excess water (80% water) showed no heat absorption due to residual crystallinity. Although the extrusion condition was not very drastic, apparently single-screw extrusion cooking resulted in a homogenous extrudate and the pellet was amorphous (Lee and Kim 1997; Van Soest and Knooren 1997).

Both equilibrium moisture and amylose content affected pellet expansion (Fig. 3). There was a maximum expansion at a moisture content of 10%. The expansion ratio decreased dramatically when the moisture was raised from 10 to 15%. The pellets were weak and soft with low elongation as the equilibrium moisture increased (Van Soest et al 1996). In other words, the pellets were not completely elastic but acted more like stiff gel-like materials. It was difficult to expand, which resulted in low expansion ratio. The expansion ratio did not drop too much when the equilibrium moisture was further increased from 15 to 25%. Air bubbles were not uniform size at high equilibrium moisture. On the other hand, the pellets became brittle and hard to expand as the equilibrium moisture was reduced from 10 to 5%. Therefore, the pellet yielded a low expansion ratio. It appeared that the expansion ratio was related to mechanical properties of materials at a rubbery state. The increase in amylose content resulted in less expansion. The result is similar to the direct expansion of cereal products extruded at 135°C (Mercier and Feillet 1975), but opposite to the finding of Della Valle et al (1997). The differences may be caused by the variation in extrusion cooking and puffing conditions. The change in amylose content did not alter the water dependence of the expansion ratio.

TSG-1 had the highest intrinsic viscosity of 135.65 mL/g. TS-10 had the lowest intrinsic viscosity of 129.08 mL/g. TG-9 had an intermediate intrinsic viscosity of 131.07 mL/g. There was no significant difference in intrinsic viscosity among three rice cultivars. The average value of 131.93 mL/g was used to address the change of molecular weight due to extrusion cooking. The intrinsic viscosity of pellets was <98 mL/g and decreased linearly ($r^2 = 0.94$) with the increase of amylose content (Fig. 4). As reported by Yeh et al (1999), the reduction of intrinsic viscosity indicated degradation of starch during single-screw extrusion cooking. Examining the amylose contents of raw materials and pellets (Table I) showed that the decrease in amylose content was <7.5% due to extrusion cooking. Using the Mark-Houwink equation (Young 1984), there was a ≈30–40% reduction in molecular weight estimated from intrinsic viscosity. It appeared that the degradation mostly occurred with amylopectin. Rice amylopectin has higher viscosity than amylose (Juliano 1984). Usually higher viscosity leads to more degradation in the extruder when the water content is low. When the water content was high enough to have a cooling effect on the screw, the high viscosity reduced the heat transferred by convection as well as the degradation at the cooking zone of the extruder. Amylose reduced the viscosity and enhanced the degradation. Thus, the higher the amylose content, the more degradation occurred.

The nonbranched structure of amylose resulted in an increase in piece density of the pellet (Fig. 5). Starches with high amylopectin content tend to give a product of lower density (Matz 1984). This indicated that amylose reduced the swelling at the exit of the extruder. The linear relationships between piece density and amylose content for pellet and expanded product were almost parallel, which implied that piece density could be a quality index of the pellet. Another possible quality index would be transparency, which decreased linearly ($r^2 = 0.93$) as amylose content increased (Fig. 6). More studies are needed to understand why amylose content affected transparency, which was also related to expansion. The pellet with 10.18% equilibrium moisture expanded linearly ($r^2 = 0.95$) with transparency (Fig. 7). Transparency can be easily measured on-site and could be used as a quality index to monitor pellet quality.

Although amylose content affected pellet expansion, it did not significantly alter the T_e, which decreased as the equilibrium moisture content increased (Fig. 8). The increase in moisture from 5.95 to 25.74% resulted in a decrease in T_e from 175 to 105°C. The decrease in T_e could save a lot of energy for puffing. However, the product quality (such as expansion ratio) needs to be considered in order to select optimum puffing conditions. The data demonstrated the importance of adjusting the moisture content of pellet, which played a key role in the expansion phenomenon. The T_e increased linearly ($r^2 = 0.95$) with the T_g (Fig. 9). The regressed equation is $T_e = 0.52\ T_g + 97.57$. The relationship confirmed that T_g was a good reference point for pellet expansion.

T_e was ≈10–90°C higher than T_g as illustrated in Fig. 10. This was similar to $T_e - T_g \doteqdot 10 \sim 70$°C during frying (Della Valle et al 1997). For synthetic polymer, melting temperature (T_m) is ≈100°C higher than T_g (Slade and Levine 1988). T_e appears to be in a rubbery region. Increasing equilibrium moisture resulted in an increase in ($T_e - T_g$). The value of ($T_e - T_g$) increased rapidly as the moisture content increased from 5 to 15%. The increase in ($T_e - T_g$) was slowed when the moisture content exceeded 20%. At high moisture content, water-plasticized material should expand easier. Nevertheless, the expansion was delayed due to the increased energy needed to vaporize moisture. The value of ($T_e - T_g$) never exceeded 100°C, implying that pellet expansion occurred in the rubbery state.

As discussed above, T_g was used as a reference temperature for the pellet expansion. It is worth developing a model to estimate T_g of extruded rice pellets. Amylose content did not significantly affect T_g because of weak influence of the branched structure (Orford et al 1990). And, although the molecular weight of amylopectin is much higher than that of amylose, it does not cause any difference in T_g due to an entanglement effect. As reported by Orford et al (1989), amylose and amylopectin had similar T_g values. Thus, the pellet was considered as a binary mixture of starch and water. The Gordon-Taylor equation was used to estimate T_g as illustrated in Fig. 11. The T_g obtained was slightly higher than that for amylopectin (Kalichevsky et al 1993) but showed similar moisture dependence. The difference in T_g may be due to composition and preparation method. The moisture acted as plasticizer and lowered both T_g and T_e. It appeared that T_g was underestimated at low (5%) and high (25%) moisture content. Overall, the fitting was pretty good ($r^2 = 0.87$). The regressed value of k was 0.241, which was almost exactly equal to the ratio (0.242) of ΔCp_{starch} (0.47 J/g.k) to ΔCp_{H_2O} (1.94 J/g.k) from literature (Kalichevsky et al 1993). Gordon-Taylor equation was reported to underestimate T_g of extruded corn meal (Brent et al 1997). The results demonstrated that Gordon-Taylor equation could be used to predict T_g of the extruded rice pellet.

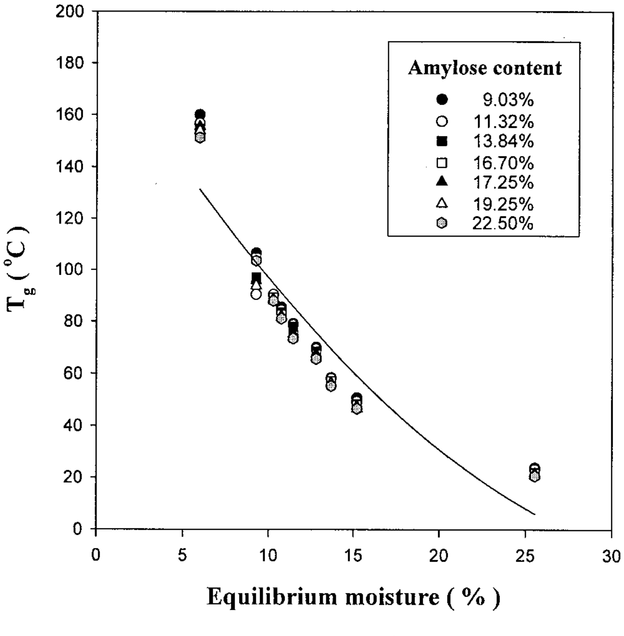

Fig. 11. Fitting the Gordon-Taylor equation for glass transition temperature (T_g) of extruded rice pellet.

CONCLUSIONS

The expansion ratio of rice pellets decreased as the amylose content increased. Maximum expansion occurred at 10% equilibrium moisture due to the transition of the pellet from brittle to ductile. Pellet transparency correlated well with expansion ratio and appeared to be a good quality index. The amylose content did not significantly affect T_e and T_g, both of which were dependent on the equilibrium moisture content. T_e increased linearly with T_g, which appeared to be a good reference temperature for studying pellet expansion. The data showed that T_e was 10–90°C higher than T_g and the expansion occurred at the rubbery region. The Gordon-Taylor equation was fitted well with the experimental data.

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