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Influence of amylose content on starch films and foams

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After extraction of smooth pea starch and waxy maize starch from pure amylose and amylopectin fractions, films with various amylose contents were prepared by casting in the presence of water or water with glycerol. For unplasticized films, a continuous increase in tensile strength (40–70 MPa) and elongation (4–6%) was observed as amylose increased from 0 to 100%. Discrepancies with values obtained for native starches with variable amylose content and different botanical origins were attributable to variations in the molecular weights of components. Taking cell wall properties into account, the values obtained in the laboratory were used to improve the relation between the flexural behavior of extruded foams and the model of cellular solids with open cavities.

The properties of plasticized films were not improved by the presence of glycerol and remained constant when amylose content was higher than 40%. Results are interpreted on the basis of topological differences between amylose and amylopectin.

INTRODUCTION

Unlike synthetic polymers, starch is renewable and biodegradable. It can also be processed by a classical industrial technique previously developed for polyolefins and involving mainly extrusion and injection (Stepto, 1987; Wiedmann & Strobel, 1991). Several publications have reported advances in the production of starch-based biodegradable materials (Doane, 1994; Savary *et al.*, 1993; Shogren *et al.*, 1993).

The idea of using starch inside synthetic polymer matrix emerged in the 1970s (Griffin, 1977). The first studies were based on introducing starch into the synthetic matrix at amounts lower than 10% while keeping the granular structure intact. In this case starch is only a filler susceptible to enzymatical degradation but unable to affect the mechanical properties of the final material (20–30 MPa tensile strength and 700–900% elongation at break point for a 90:10 polyethylene:starch blend).

A second approach was to use polymer blends. To obtain this morphology, the granular structure of starch had to be modified (generally by extrusion) to allow thorough mixing of α-glucan and synthetic polymer. The notion of 'starch destructuration' attributable to Tomka (1988), refers to the loss of native granular structure and is achieved by melting under shearing and low hydration. These forms of processing, which differ completely from classical pasting obtained in high moisture conditions (Zobel, 1984), had already been described in reviews concerning extrusion (Colonna *et al.*, 1989). Starch destructuration is rather well understood and controlled at the present time. However, the main difficulties encountered in the addition of starch to synthetic polymer are due to the chemical incompatibility of these two types of polymers. Two studies (Otey *et al.*, 1974, 1980; Westhoff *et al.*, 1979) have shown that hydrophilic synthetic polymers such as poly(ethylene-*co*-acrylic acid) or poly(vinyl alcohol) give final blends with acceptable compatibility. Several patents have been issued recently for materials produced by blending starch with one or several synthetic polymers (Bastioli, 1991; Fleche, 1992; Sachetto, 1989; Wittwer & Tomka, 1987). More sophisticated solutions based on the grafting of synthetic fragments have also been reported (Narayan *et al.*, 1988).

The mechanical properties of these materials, which are dependent on the quantity of starch, diminish rapidly when starch level increases (tensile strength ranges from 22 to 28 MPa and maximum elongation from 260 to 60% when starch level increases from 10 to 60% in a starch-poly(ethylene-*co*-acrylic acid) blend) (Otey *et al.*, 1980). Despite their poor mechanical properties, these materials have been recommended because

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of their biodegradability, and several commercial applications have been proposed (e.g. pharmaceutical bottles, container closures, cutlery and cotton swabs).

Several studies concerning the enzymatic degradation of these materials indicate that the biodegradability concept has been overemphasized and that a biofragmentability concept is also needed (Allenza *et al.*, 1989; Austin, 1989; Klemchuk, 1990). Biodegradation of the starchy fraction leads to loss of mechanical properties throughout the material, and the synthetic fraction from the oil source does not show better susceptibility to biodegradation.

The most recent research has focused on pure starch-based materials (Arvanitoyannis *et al.*, 1994; Bader & Göritz, 1994; Shogren, 1992) or other biopolymers such as proteins (Zasypkin, 1992) involving the addition of a plasticizer but with no addition of synthetic polymer. Poor mechanical properties constitute one of the major unresolved problems. Even if tensile strength is rather high (30–60 MPa), and in the same range as for polyethylene (around 30 MPa), these materials remain fragile and their elongation properties are poor (6% maximum elongation). Several studies concerning the mechanical properties of starch of defined botanical origin have shown that the choice of raw material is critical (Jane *et al.*, 1993; Swinkels, 1985). These differences are generally related to the content of amylose and amylopectin, the two main components of starch, and the amylose–amylopectin ratio is dependent on botanical origin. Unfortunately, studies of this type fail to take account of the effect of molecular weight or the influence of lipids (0.05–0.09%) or proteins (0.01–1.2%) still present in starches from cereals.

An understanding of the impact of amylose content on the solid properties of starch is particularly important since amylose may also be a major component of some cellular materials such as solid food foams. When amylaceous raw materials are used, the texture of these foams may be obtained by expansion of a homogeneous molten phase at the die outlet of an extruder (see for instance Colonna *et al.*, 1989). By analogy with the concept of bubble growth in a viscous fluid (Kokini *et al.*, 1992), this phenomenon could be modeled to allow prediction of the bulk density of extrudates in the near future (Fan *et al.*, 1994). As in the case of solid foams, the bulk density of extrudates could be related to their mechanical properties as measured by impact (Hayter *et al.*, 1986) or by compression, flexion and tension (Hutchinson *et al.*, 1987), according to a power law:

$$\sigma_e \sim \rho_e^{\,n} \tag{1}$$

where σ_e is the mechanical property (modulus, stress) of the extrudate and ρ_e its density. However, the value of power law indices is not always in good agreement with the theoretical values of solid foams, which may partly be explained by our lack of knowledge of the properties of cell wall materials. The role of this factor may be twofold: first, a difference in macromolecular structure due to a dissimilar thermomechanical history relating to botanical origin may give rise to different mechanical properties; and, secondly, a possible difference in glass transition temperature T_g may induce a different mechanical behavior. Warburton *et al.* (1990) found different T_g values for extrudates produced under various thermomechanical conditions. Therefore, mechanical properties of extrudates may be correlated with both factors (bulk density and the T_g of cell wall material), whereas the mechanical properties of cell wall material show no significant variations. However, it seems unlikely that the T_g of cell wall material directly influenced the mechanical properties of dry extrudates (moisture content < 10%) since T_g values for these low moisture levels were much higher than ambient temperature, which is in agreement with results obtained by Zeleznak and Hoseney (1987) and Kalichevsky *et al.* (1992). This hypothesis is confirmed by the results of Aynie-Davidou (1994) who used DMTA to show that extruded flat breads have a brittle solid behavior as long as their moisture content is lower than 14%. Moreover, Warburton *et al.* (1993) showed that, for the same raw material, the role of the mechanical properties of cell wall material is due to the heterogeneities created during the stage of film manufacturing, whether by extrusion or casting, which enhances the role of thermomechanical history.

The main purpose of the present study was to determine the specific influence of amylose on film and solid foam properties. To overcome the influence of any other component, films were prepared from blends of these two macromolecules which had been previously extracted, purified and well characterized. As extrusion-cooking, which is still the only way to prepare solid foams, requires higher amounts of materials, solid foams were prepared from blends of waxy maize and high-amylose maize starches.

MATERIALS AND METHODS

Starches

Maize and potato starches were purchased from Roquette (F-62 Lestrem, France) and pea starch from Grinsted; wheat starch was a gift from Amylum Aquitaine (F-33 Bordeaux, France). For the production of solid foams, blends with intermediate amylose contents were obtained from high-amylose maize and waxy maize starches in the following ratios 67/33 (blend 1) and 33/67 (blend 2). The resulting amylose content is indicated in Table 1.

Amylopectin

Pure amylopectin was purified starting from waxy maize starch. Starch was solubilized in DMSO (95%),

Table 1. Values chosen for the mechanical properties of extrudate cell walls

	Amylose (%)	σ_w (MPa)	E_w (MPa)
High amylose maize starch	70	60	24.7
Blend 1	47	53	21
Blend 2	23	46	23.1
Waxy maize starch	0	38	16.5

and the solution was kept at room temperature under magnetic stirring for 48 h. Amylopectin was then precipitated by the addition of ethanol (95%) and dried by solvent exchange.

Amylose

Amylose was obtained by leaching smooth pea starch which has an amylose content of approximately 34%. A 2% aqueous starch suspension was kept at 70°C under nitrogen bubbling for 30 min. The suspension was then centrifuged (20°C, 20 min, 2×10^4 g) and filtered on paper (Whatman 113V, Maidstone, England). Filtered amylose was immediately complexed with n-butanol (8% v/v) (Ring, 1985).

Plasticizer

The glycerol used as a plasticizer was obtained commercially (Merck, Darmstadt, Germany) and had a purity above 99.5%.

Film preparation

Without plasticizer

All films were obtained by casting. An amylose solution was prepared by solubilization of the amylose–butanol complex in water at 95°C under nitrogen bubbling. When *n*-butanol disappeared (leached by water evaporation), a precisely determined quantity of amylopectin was introduced into the solution which was maintained under vigorous stirring for a further 30 min at 90°C. The final α-glucan concentration of the solution was approximately 1.5%. The solution was then poured over a plate at 70°C. The Teflon coating on the plate allowed the film to be easily removed when dry. Before mechanical testing, all films were stored for 48 h in a controlled atmosphere: water activity 0.57, temperature 23°C.

Native granular starches from botanical origins were solubilized at 135°C for 20 min, and films were obtained as described above.

With plasticizer

The α-glucan solution was prepared starting from freeze-dried amylose and amylopectin. Freeze-drying was carried out after removal of all *n*-butanol, as previously described. Solubilization of freeze-dried amylose in the water–plasticizer system was done in an autoclave with stirring for 5 min at 160°C under a nitrogen atmosphere. For amylose–amylopectin blends, amylopectin was added after the autoclave was opened at 90°C. To obtain thorough mixing, the autoclave was closed again and kept at 130°C for 20 min with stirring. After cooling at 90°C, the films were prepared as described above.

Foam production

Starch blends were fed into a Clextral BC 45 twin-screw extruder (barrel length 1 m) provided with a standard screw arrangement, including a reverse screw element just before the die. The die was a slit rheometer with a balanced feed rate (Rheopac), the principle of which was to create various local flow conditions (shear rate and viscosity) without modifying the thermomechanical history in the extruder, i.e. maintaining the same molecular modifications (Vergnes *et al.*, 1993). Various extrudate densities could then be obtained by modifying only the on-line viscosity of molten starch (Patria *et al.*, 1993).The extruder was operated according to the following conditions: feed rate (25 kg/h), barrel temperature just before the die (130°C) and in the die (150°C). Screw speed was adjusted between 160 and 240 rpm in order to perform similar thermomechanical treatments, as reflected by the value of specific mechanical energy (SME). The rate of added water was set at two levels so that the total moisture content (MC) of the matter in the extruder was MC = 20% or MC = 24%. For each shear rate value, expanded ribbons were taken directly at the die outlet, without stretching. One part was immediately ground for intrinsic viscosity measurement, whereas the other was oven-dried (2 h, 60°C) and stored in sealed plastic bags.

Size exclusion chromatography and intrinsic viscosity

Size exclusion profiles were determined by chromatography on FRACTOGEL TSK HW-75 eluted by 0.1 N KOH at a flow rate of 18 ml/h. The carbohydrate content of the collected fraction was measured by the sulphuric acid orcinol procedure (Planchot *et al.*, 1995). The intrinsic viscosity of amylopectin dissolved in 0.2 N KOH was measured using an Ubelhode capillary viscosimeter.

Amylose content

The amylose content of the films and foams was determined by iodizing binding capacity (IBC) (Larson, 1953). Purified smooth pea amylose presented an IBC of 18 mg/100 mg.

Water content

Water content was determined by the weight loss of the sample after 2 h at 130°C. When glycerol was present, the quantity of glycerol lost during heating was determined by high-performance liquid chromatography (HPLC). The sample (approximately 15 mg) after heating was washed in pure water (100 ml) under vigorous stirring to achieve complete diffusion of the glycerol in the solution. Glycerol was then determined by HPLC (ACIDEX H^+ column, at room temperature, elution by water at 0.6 ml/min, differential refractometer at a sensitivity of 2×).

Mechanical testing

Maximum stress, strain rupture and elastic modulus were measured on an Instron 1122 universal testing machine. After conditioning, six–eight samples were cut off each film according to the standard ASTM D 412 method. Their thickness, measured by a micrometer, ranged from 30 to 60 μm; stretching speed was set to 2 mm/min. Prior to mechanical testing, bulk density for extruded foams was calculated first by weighing a quantity M_e and then by measuring its volume through the displacement of glass beads (bulk density ρ_b, ϕ 3 mm). M_b indicates the mass of beads excluded when extruded ribbons were introduced; the bulk density of extrudates was:

$$\rho_e = \frac{M_e}{M_b} \times \rho_b. \qquad (2)$$

Each measurement was performed eight times.

A three-point flexural test was then performed on samples (length $L = 10$ cm) whose thickness h and width l were measured with a vernier calliper. The sample was placed on the bend rig, and crosshead speed was set to 5 mm/min, according to the procedure used by Hutchinson *et al.* (1987). The classical relations of material resistance were then used to compute rupture stress σ and elastic modulus E:

$$\sigma = 6\frac{Fr\,L}{(4h\,l^2)} \quad \text{and} \quad E = \frac{(\Delta F/\Delta t)\,L^3}{(4Vh\,l^3)} \qquad (3)$$

where Fr is the maximum flexural force and $\Delta F/\Delta t$ the slope of the $F(t)$ curve in its linear part. Each measurement was performed six times.

RESULTS AND DISCUSSION

Characterization of molecular distribution

Table 2. Amylose content and intrinsic viscosity of different substrates

	Amylose (%)	[η] (ml/g) KOH 0.2 M 25°C
Amylopectin	0	121
Waxy maize	< 1	121
Potato	19	270
Wheat	26	210
Pea	33	250
Amylose	100	161

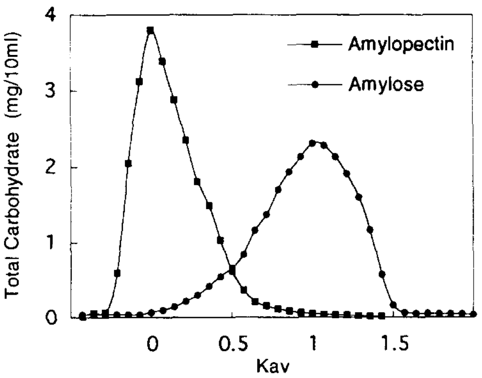


Fig. 1. Elution profiles on HW 75 of amylopectin (■) and amylose (●).

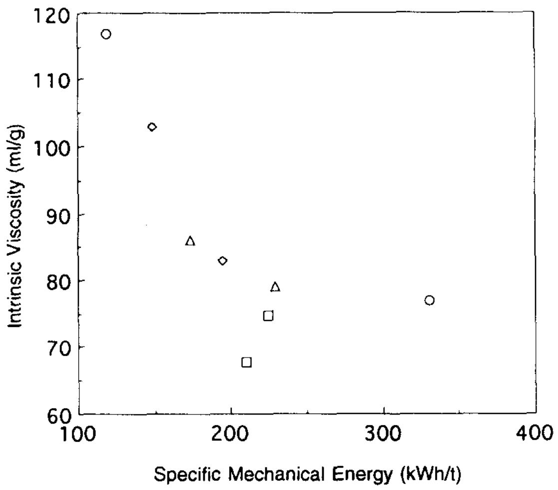


Fig. 2. Variations of intrinsic viscosity of extruded starches of various amylose contents (□, 70%; △, 47%; ◇, 23%; ○, 0%) against specific mechanical energy (SME) during extrusion.

The results for intrinsic viscosity measurements performed on extracted amylose and purified amylopectin are reported in Table 2. Amylose and amylopectin chromatograms obtained by low-pressure size exclusion chromatography are shown in Fig. 1. Amylopectin was eluted at a much lower elution time than amylose due to its high molecular weight ($M_v = 11.43 \times 10^6$ g/mol) compared to pea amylose ($M_v = 393.4 \times 10^3$ g/mol). This result allowed us to check the accuracy of substrate extraction and purification procedures.

Compared to native starches, intrinsic viscosities of extruded starches were much lower, which is in agreement with the expected effect of molecular degradation. In Fig. 2, intrinsic viscosity values are plotted against SME measured during extrusion. The trend of a decrease of $[\eta]$ with SME shows the importance of shear forces on macromolecular chain-splitting, which was previously demonstrated by Vergnes *et al.* (1987), Della Valle *et al.* (1989), Parker *et al.* (1990) and Orford *et al.* (1993) for standard maize and waxy maize starches. These variations were greater for lower amylose contents, confirming the higher sensitivity of amylopectin-rich starches during thermomechanical treatment as well as the difficulty of processing starches with high-amylose content (Harper & Tribelhorn, 1992).

Film and foam composition

Amylose and amylopectin content, as well as the water content of all studied films, are indicated in Table 3. The water content for films without and with glycerol was approximately 15.7% (weight/total weight) and 15.2% (weight/total weight), respectively. Under the same conditions of hygrometry, cast films showed water affinity in the same range as that of native wheat (15.5% weight/total weight) and maize starches (16.2% weight/total weight). The hydration level measured on the films was similar to that observed for extruded starches (considered generally as being totally amorphous) and rather independent of the amylose–amylopectin ratio, which suggests that the mechanical property could be studied as a function of amylose content, without any correction for water content. For extruded foams, water content was approximately 9% (weight/total weight) after 5 day storage of water activity at 0.57.

Crystallinity

No crystalline structures (A, B or V) were detected on films by X-ray diffraction after 24 h storage of water activity at 0.57, or in foams after drying. Unpublished results from our laboratory have shown that the detection threshold for crystallinity is 15% when pure amorphous and crystalline materials are mixed. Nonetheless, films can be considered amorphous.

Hulleman *et al.* (1994) observed V-type crystalline structures in starch films plasticized with glycerol. Glycerol purity varies according to grade, ranging from 95% (technical grade) to 99.9% (analytical grade). The main impurities are fatty acids and triglycerides, which can be complexed by amylose.

Table 3. Compositions of different cast films with amylose content

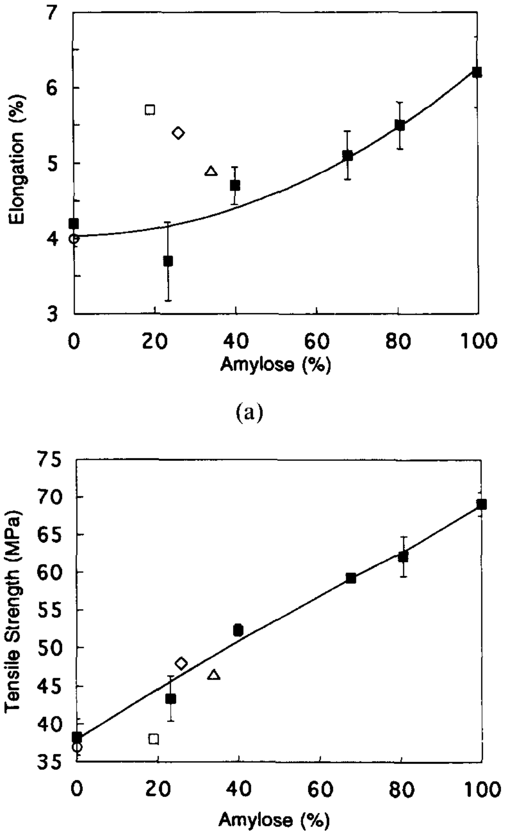
Without plasticizer		With plasticizer	
Dry matter (amy/amp)	Film (dry st/water)	Dry matter (amy/amp)	Film (dry st/water/gly)
0.0/100.0	84.8/15.2	0.0/100.0	70.5/15.4/14.1
23.3/76/7	84.3/15/7	10.0/90.0	70.1/15.9/14.0
39.9/60.1	83.5/16.5	30.0/70.0	71.4/14.3/14.3
67.6/32.3	84.6/15.4	45.1/54.9	70.6/15.3/14.1
80.7/19.3	84.4/15.6	59.9/40.1	70.7/15.1/14.2
100.0/0.0	84.3/15.7	79.7/20.3	70.7/15.1/14.2
		100.0/0.0	70.4/15.6/14.0

Glycerol content corresponds to 20% dry basis.

Mechanical properties of unplasticized films

Except for the low value (3.7%) for elongation of films containing 23.3% of amylose, elongation at break point increased continuously with increasing amylose content (Fig. 3a), ranging from 4.2% to 0% amylose film up to 6.2% for pure amylose film (i.e. an increase of approximately 50%). Tensile strength increased linearly with the amount of amylose, from 38 MPa for pure amylopectin film up to 69 MPa for pure amylose film (i.e. an increase of more than 80% (Fig. 3b)). In these films, regardless of amylose content, stress–strain curves were characteristic of brittle materials.

With synthetic polymer, the influence of the branch-



(a)

(b)

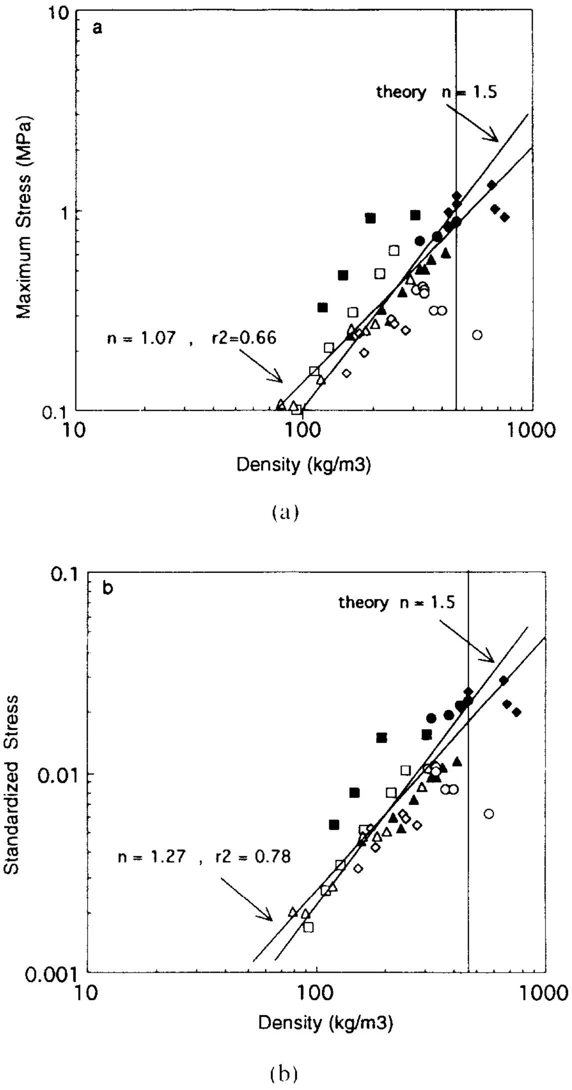
Fig. 3a and b. Variations of mechanical properties of different films with amylose content (■). Mechanical properties of starch from different botanical origins are reported (○, corn; □, potato; ◇, wheat; △, pea). On some plots, the standard deviation is hidden by the symbol.

ing level on mechanical properties has been mainly described for polyethylene, whose simple structure is generally used as a model (Woodward & Sauer, 1958). The plasticity of these materials decreases when the crystallinity level (inversely related to branching density) increases from 20 up to 80%. With starch films, the change in mechanical properties is not attributable to crystallinity which was lower than 15% in all cases.

In these low hydration conditions (10–20% water content), no tools are available for direct observation of the conformation and localization of amylose and amylopectin in an amorphous phase. Zobel (1988) and Young (1984) who investigated this topic used a molecular model previously demonstrated for gels. However, this model, which is very powerful for the semicrystalline structure of gels, is based on phase separation involving amylose and amylopectin. Thus, it could not be used here directly for the strictly amorphous and single-phase structure of films.

Values obtained for starches from different botanical origins showed significant differences to those for corresponding amylose–amylopectin mixtures (Fig. 3a,b). The maximum elongations for potato and wheat starch films (respectively 23 and 26% amylose content) were higher than the corresponding values for amylose–amylopectin blends. This behavior is attributable to the high molecular weight of amylose in potato (M_v 1680 × 10^3 g/mol) and wheat (M_v 965 × 10^3 g/mol) starches, which is three to four-fold heavier than pea amylose (M_v 393 × 10^3 g/mol). The mechanical properties of films obtained from pea starch are very similar to those for the films represented in Fig. 3a,b made with the same amylose–amylopectin mixture. This indicates that no residual structure or grain ghost was present after starch solubilization, so that the dispersion procedure can be considered satisfactory.

Mechanical properties of extruded foams



(a)

(b)

Fig. 4. Variations of breaking stress (a) and relative breaking stress (b) of extruded starch foams, with their apparent density for various amylose contents (□, 70%; △, 47%; ◇, 23%; ○, 0%). Open symbols: MC = 20%, closed symbols: MC = 24%. MC is the water content of starch during extrusion.

Starches were extruded under two hydration conditions. For the same thermomechanical treatment, Rheopac allowed the preparation of extrudates with various densities in a range of 1 to 4, only by modifying the local flow rate in the slit die (3–30 kg/h) in order to vary the shear rate (20–200 s^{-1}). Expansion is favored by a decrease in melt viscosity (Kokini *et al.*, 1992; Patria *et al.*, 1993). The flexural bending test always produced brittle solid behavior, so that maximum stress σ_e could easily be calculated regardless of extrudate shape. The relative error of 15% was related to the standard deviation of geometrical measurements (h and l) and of the bending test itself. For bulk density ρ_e, ranging from 80 to 500 kg/m^3, maximum stress values increased from 0.1 to 1.5 MPa, which is lower than the values published by Hutchinson *et al.* (1987): $0.2 < \sigma_e < 4$ MPa for lower bulk density ($50 < \rho_e < 250$ kg/m^3). A general increasing trend was obtained when maximum stress σ_e was represented as a function of bulk density ρ_e in logarithmic coordinates (Fig. 4a). Such behavior of extruded foams can be compared to that of cellular solids or solid foams:

$$\sigma_e \sim \rho_e^{\,n} \tag{4}$$

with $1.5 < n < 2$ in the case of the three-point flexural bending test.

An analogy with solid foams is feasible when bulk density is lower than 30% of the density of cell wall material ρ_w:

$$\rho_e/\rho_w < 30\%. \tag{5}$$

In our case, ρ_w was the density of starch, for which a value of 1500 kg/m^3 was chosen, according to Colonna et al. (1989) and Millauer et al. (1992). An upper limit at $\rho_e = 450$ kg/m^3 was then drawn on every plot, resulting in the discarding of four extreme density values obtained for starches with low amylose content (23 and 0%) extruded under higher hydration conditions.

Apart from the experimental points obtained with waxy maize starch extruder at lower hydration conditions, all σ_e values showed a similar behaviour. Linear regression performed on the data for which $\sigma_e < 450$ kg/m^3 gave:

$$\sigma_e = 1.1 \times 10^{-3}\,\rho_e^{\,1.07} \quad (r^2 = 0.66). \qquad (6)$$

Data scattering led to a low value for r^2, and the power law index was lower than the theoretical value for open cell foams ($n = 1.5$). Data scattering may have been due either to a difference in moisture content during extrusion or to the specific role of cell wall properties. The first factor may have produced various cellular structures during expansion at the die outlet, e.g. because of anisotropy of cellular structure related to the axial component of expansion. This factor seems particularly influential in the case of pure starches (70 or 0% amylose) (Fig. 4a). The influence of the second factor, cell wall properties, may be reflected by the difference in behavior of the extruded foams according to their amylose content.

Theoretically, the solid foam model is given more precisely by:

$$\frac{\sigma_e}{\sigma_w} \sim \left(\frac{\rho_e}{\rho_w}\right)n, \qquad (7)$$

where index w indicates the property of cell wall material, and ρ_w is the same regardless of amylose content.

The problem is to determine the value of σ_w. It can be assumed that the role of amylose content in the behavior of the material was the same, whether tested by flexion or tension, even though the mechanical test was not identical. For this reason, due to the difficulty of producing non-expanded extrudates, σ_w values were derived by interpolation of the graph in Fig. 3a for targeted amylose content values (Table 3). These values were lower than those calculated by Warburton et al. (1993) ($2 < \sigma_w < 2.4$ MPa), which may have been due to the different type of mechanical testing (flexion instead of tension). It was then possible to compute the relative values of maximum stress (σ_e/σ_w) and plot them against density. This treatment reduced data scattering, leading to an improved adjustment after linear regression (Fig. 4b):

$$\frac{\sigma_e}{\sigma_w} = 7.37 \times 10^{-6}\,\rho_e^{\,1.27} \quad (r^2 = 0.78). \qquad (8)$$

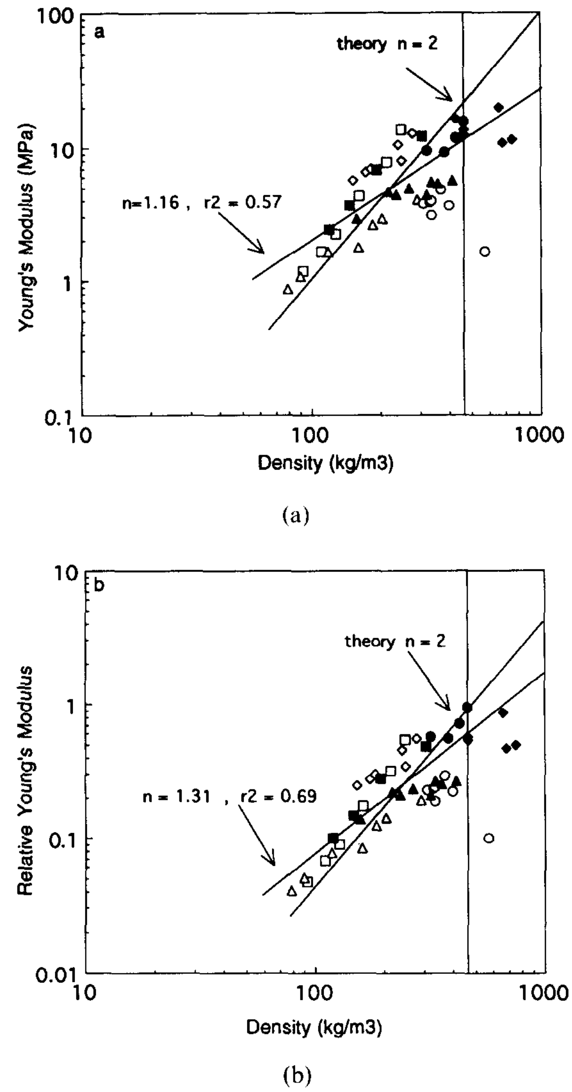
Moreover, the value of the power law index was closer to the theoretical value for open cells foams.

In the same way, it was possible to study the variation in Young's modulus E as a function of bulk density ρ_e (Fig. 5a). E values were lower (1–20 MPa) than those found by Hutchinson et al. (1987) and Warburton et al. (1993) ($4 < E < 280$ MPa) for densities of the same order of magnitude. It would thus seem possible to discard the effect of water addition, at least for starches containing amylose, although the lack of fit on a power law is greater than for σ_e:

$$E = 9.1 \times 10^{-3}\,\rho_e^{\,1.16} \quad (r^2 = 0.575) \qquad (9)$$

The greater data scattering can be explained by the fact that extrudate width (l) had an exponent of 3 in the expression of E, whereas the exponent was 2 in the case of σ, thereby increasing the error made in calculating E.

The values of Young's elastic modulus for cell wall material, derived from the results of tensile testing, are reported in Table 1. The relative Young's modulus



(a)

(b)

Fig. 5. Variations of Young's modulus (a) and relative Young's modulus (b) for extruded starch foams with apparent density for various amylose contents (□, 70%; △, 47%; ◇, 23%; ○, 0%). Open symbols: MC = 20%; closed symbols: MC = 24%. MC is the water content of starch during extrusion.

E_c/E_w was calculated, and its values are represented against ρ_e (Fig. 5b). Data were less scattered, giving the following equation by linear regression:

$$\frac{E_c}{E_w} = 1.91 \times 10^{-4} \rho_e^{1.31} \quad (r^2 = 0.69) \qquad (10)$$

The quality of fit was improved and the exponent of the power law higher than when cell wall properties were not taken into account, though still far from the theoretical value ($n = 2$).

These different results show that the mechanical properties of cell wall material play an important role in the behavior of solid foams, as already noted by Warburton *et al.* (1990) for maize grit extrudates. In our case, this role was particularly important since it allowed the difference between starches with various amylose amylopectin ratios to be taken into account. However, this factor was not sufficient to account for the variations in mechanical properties as a function of bulk density. In the case of extrudate foams, the possibility of obtaining a given cellular structure is governed by the expansion phenomenon at the die outlet. This phenomenon is reduced and stopped when extrudate temperature decreases below T_g during cooling after extrusion. The temperature of glassy transition, T_g, appears to determine extrudate texture partly by influencing the cell wall distribution. This latter parameter can only be measured by image analysis. Unfortunately, studies using image analysis have not been performed on samples with similar density (Moore *et al.*, 1990; Barrett & Peleg, 1992). The variations in mechanical properties observed in these works are in fact attributable to differences in density as much as to those in size and number of cavities. The specific role of cell distribution still needs to be determined.

Mechanical properties of films containing glycerol

Theoretically, the addition of a plasticizer should decrease the T_g of material below room temperature in order to increase the width of the plastic deformation zone (mainly the elongation). One unavoidable consequence of plasticization is a decrease in the tensile strength of the material.

The results presented in Fig. 6 show that for plasticized films the positive influence of amylose was completely masked by the presence of glycerol. In plasticized materials, the efficiency of plasticization with the same amount of plasticizer was dependent on the amylose/amylopectin ratio. For pure amylopectin materials, the effect of plasticization was rather great since maximum elongation reached 25% and tensile strength 5 MPa. Conversely, the effect of the plasticizer decreased continuously in the 0–40% amylose range. From 40 to 100% amylose, no plasticization of the material was apparent since maximum elongation and tensile strength were, respectively, 5% and 25 MPa, regardless of amylose content. Figure 7 shows the elongation curve of plasticized films composed of pure amylopectin and pure amylose (respectively noted 1 and 2). Curve 1 is clearly characteristic of a ductile material, whereas curve 2 is typical of brittle behavior. This behavioral difference could have been due to the different locations of the T_g of these different films in room temperature conditions. In the case of amylopectin, a T_g

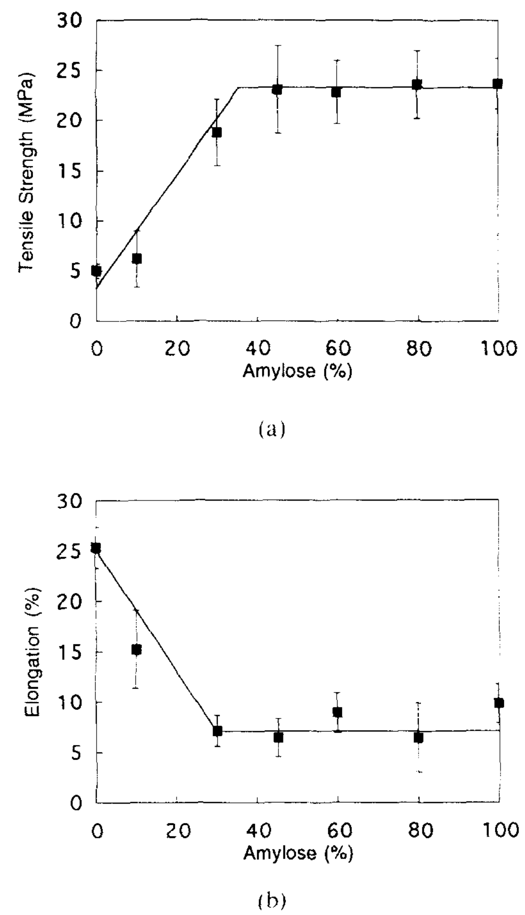


Fig. 6a and b. Variations in mechanical properties of different plasticized films (20% glycerol dry basis) with amylose content (■).

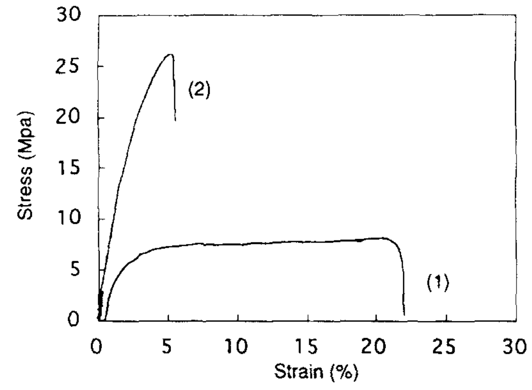


Fig. 7. Typical stress–strain behavior of pure amylopectin (curve 1) and pure amylose films (curve 2).

slightly lower than room temperature would have produced a plastic material, whereas above 40% amylose a T_g slightly above room temperature would not have provided good maximum elongation, thereby producing a fragile material. This hypothesis is contrary to the recent results for the T_g of amylose and amylopectin obtained by Yuryev (1995). These observations suggest that amylopectin is more sensitive than amylose to glycerol plasticization.

The function of a plasticizer in a solid foam cannot be studied directly. When a plasticizer is present, molten flow expands directly at the die first, so that the extrudate remains in rubbery phase. Subsequently, the three-dimensional structure collapses, producing a dense and flexible material in which dimensional features cannot be treated as previously described in this study for foams.

CONCLUSION

Amylose appears to be an important parameter for mechanical properties in unplasticized starch films. When end-properties do not require the addition of a plasticizer, amylose-rich starches such as wrinkled pea starch are most convenient. A similar trend has been noted for extruded foams of various densities. Their behavior is closer to that of solid foams or cellular solids, provided that film properties such as the cell wall properties of the foams are taken into account. However, better accuracy is required in the description of the morphological features of these foams in order to distinguish between the influence of cell size distribution and connectivity, on the one hand, and that of cell wall properties on the other. A study of amylose influence on melting properties above T_m is also in progress in our laboratory.

The addition of 20% glycerol (dry basis) as plasticizer changed the mechanical behavior by extending the plasticity zone, though this influence was only apparent for amylose contents between 0 and 40%. Amylopectin was more sensitive than amylose to the action of this plasticizer, and the mechanical properties of films containing glycerol remained constant between 40 and 100% amylose. The interactions between the plasticizer and α-glucanes need to be investigated using a molecular approach and taking chemical structures into account. Our results are in agreement with the customary interpretation given for the plasticization of amylose and amylopectin in concentrated medium. A study of the specific role of molecular weight is now being carried out to clarify certain points.

REFERENCES

Allenza, P., Schollmeyer, J. & Rohrbach, R.P. (1989). In *Degradable Materials: Perspectives, Issues and Opportunities*. CRC Press, Cleveland, USA, p. 357.

Arvanitoyannis, I., Kalichevsky, M. & Blanshard, J.M.V. (1994). *Carbohydr. Polym.*, **24**, 1–15.

Austin, R.G. (1989). In *Degradable Materials: Perspectives, Issues and Opportunities*. CRC Press, Cleveland, USA, p. 209.

Aynie-Davidou, S. (1994). Doctoral dissertation, Univ. de Bourgogne, France.

Bader, H.G. & Göritz, D. (1994). *Starch*, **46**, 229–232.

Barrett, A.H. & Peleg, M. (1992). *J. Food Sci.*, **57**, 1253–1257.

Bastioli, C. (1991). Butterfly s.r.l., Patent No. 91/02024.

Colonna, P., Tayeb, J. & Mercier, C. (1989). In *Extrusion Cooking*, eds C. Mercier, P. Linko & J.M. Harper ACCC, St. Paul, Minnesota, USA, pp. 247–320.

Della Valle, G., Koszlowski, A., Colonna, P. & Tayeb, J. (1989). *Lebensm. Wiss. u.-Technol.*, **22**, 279–286.

Doane, W.M. (1994). *Cereal Foods World*, **39**, 556–563.

Fan, J., Mitchell, J.R. & Blanshard, J.M.V. (1994). *J. Food Engng*, **23**, 337–356.

Fleche, G. (1992). Roquette, Patent No. 0.497.706.

Griffin, G.J.L. (1977). U.S. Patent No. 4.021.388.

Harper, J.M. & Tribelhorn, R.E. (1992). In *Food Extrusion Science and Technology*, eds J.L. Kokini, C.T. Ho & M.V. Karwe. Marcel Dekker Inc., New York, USA, pp. 653–667.

Hayter, A.L., Smith, A.C. & Richmond, P. (1986). *J. Mater. Sci.*, **21**, 3729–3735.

Hulleman, S.H.D., Feil, H. & De Wit, D. (1994). *4th Int. Workshop on Oligo and Polysaccharides*, p. 127.

Hutchinson, R.J., Siodlak, G.D.E. & Smith, A.C. (1987). *J. Mater. Sci.*, **22**, 3956–3962.

Jane, J.-L., Lim, S.-T. & Paetau, I. (1993). In *Biodegradable Polymers and Packaging*. Technomic Publishing, pp. 63–73.

Kalichevsky, M.T., Jaroszliewicz, E.W. & Ablett, S. (1992). *Carbohydr. Polym.*, **18**, 77–88.

Klemchuk, P.P. (1990). *Polymer Degrad. Stabil.*, **27**, 183–202.

Kokini, J.L., Chang, C.N. & Lai, L.S. (1992). In *Food Extrusion Science and Technology*, eds J.L. Kokini, C.T. Ho & M.V. Karwe. Marcel Dekker Inc., New York, USA, pp. 631–652.

Larson, B.L. (1953). *Analyt. Chem.*, pp. 802–804.

Millauer, C., Rosa, G. & Schär, R. (1992). In *Plant Polymeric Carbohydrates*, eds F. Meuser, D.J. Manners & W. Siebel. Royal Soc. Chem, Cambridge, UK, pp. 86–104.

Moore, D., Sanei, A., Van Hecke, E. & Bouvier, J.M. (1990). *J. Food Sci.*, **55**, 1383–1387.

Narayan, R., Lu, Z.J., Chen, Z.X. & Stacy, N. (1988). *J. Polym. Prep.*, **29**, 106–107.

Orford, P.D., Parker, R. & Ring, S.G. (1993). *J. Cereal Sci.*, **18**, 277–286.

Otey, F.H., Mark, A.M., Mehltretter, C.L. & Russell, C.R. (1974). *Ind. Eng. Chem. Prod. Res. Dev.*, **13**, 3453–3455.

Otey, F.H., Westhoff, R.P. & Doane, W.M. (1980). *Ind. Eng. Chem., Prod. Res. Dev.*, **19**, 592–595.

Parker, R., Ollett, A.L. & Smith, A.C. (1990). In *Processing and Quality of Foods*, ed. P. Zeuthen. Elsevier, London, UK, pp. 1290–1295.

Patria, A., Colonna, P., Della Valle, G. & Vergnes, B. (1993). *Cereal Foods World*, **38**, 628.

Planchot, V., Colonna, P. & Saulnier, L. (1995). *Guide Pratique d'Analyse dans les Industries des Cereales*, in press.

Ring, S. (1985). *Starch*, **37**, 80–83.

Sachetto, J.P. (1989). Warner-Lambert Company, Patent No. 0.404.723.

Savary, C., Colonna, P. & Della Valle, G. (1993). *Industrie des Céréales*, **10**, 17–29.

Shogren, R.L. (1992). *Carbohydr. Polym.*, **19**, 83–90.

Shogren, R.L., Fanta, G.F. & Doane, W.M. (1993). *Starch*, **8**, 276–280.

Stepto, R.F.T. (1987). *Chimia*, **3,** 76–81.

Swinkels, J.J.M. (1985). *Starch*, **37,** 1–5.

Tomka, I. (1988). Warner-Lambert Company, Patent No. 0.282 451.

Vergnes, B., Delle Valle, G. & Tayeb, J. (1993). *Rheol. Acta*, **32,** 465–476.

Vergnes, B., Villemaire, J-P., Colonna, P. & Tayeb, J. (1987). *J. Cereal Sci.*, **5,** 189–202.

Warburton, S.C., Donald, A.M. & Smith, A.C. (1990). *J. Mater. Sci.*, **25,** 4001–4007.

Warburton, S.C., Donald, A.M. & Smith, A.C. (1993). *Carbohydr. Polym.*, **21,** 17–21.

Westhoff, R.P., Kwolek, W.F. & Otey, F.H. (1979). *Starch*, **31,** 163–165.

Wiedmann, W. & Strobel, E. (1991). *Starch*, **43,** 138–145.

Wittwer, F. & Tomka, I. (1987). Warner Lambert, Patent No. 4.673.438.

Woodward, A.E. & Sauer, J.A. (1958). *Fortschr. Hochpolymer Forsch.*, **1,** 136–145.

Young, A.H. (1984). In *Starch Chemistry and Technology*, 2nd edn. Academic Press, New York, USA, pp. 269–283.

Yuryev, V.P. (1995). *Carbohydr. Polym.*, **26,** 43–46.

Zasypkin, D.V. (1992). *Carbohydr. Polym.*, **19,** 107–114.

Zeleznak, K.J. & Hoseney, R.C. (1987). *Cereal Chem.*, **64,** 121–124.

Zobel, H.F. (1984). In *Starch Chemistry and Technology*, 2nd edn. Academic Press, New York, USA, pp. 285–309.

Zobel, H.F. (1988). *Starch*, **40,** 44–50.