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Structure and properties of starch-based foams prepared by microwave heating from extruded pellets

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Abstract

The physical properties of microwave-foamed starch-based pellets, including density, porosity, cell structure, water absorption characteristics and mechanical properties were characterized. It was found that the physical properties of these starch-based foams produced by microwave heating are highly dependent on the raw materials and additives. Foam density decreased significantly after addition of 5.5–10.5% w/w salts, while foams containing nucleation agent (talc) were denser than the control with reduced cell size. A proprietary blowing agent did not affect the foam density markedly. Addition of salts also increased the water sorption of foams and plasticized cell walls. Mechanical behaviour of foamed pellets can be adjusted effectively by controlling the cell structure through using different additives. Mechanical properties of the foamed pellets in the elastic region as well as under large deformation (up to 40% strain) all follow a power–law relationship with foam density.

Keywords: Foam; Foaming; Wheat flour; Starch; Pellets; Extrusion and Microwave heating

1. Introduction

In recent years, many biodegradable polymers have been developed for packaging applications. These materials are designed to be compostable so as to facilitate waste management by composting and reduce landfill.

Starch has been used widely as a common raw material in these biodegradable polymers. They can used in the forms of a biodegradable filler (Kim & Lee, 2002), a thermoplastic starch (Baumberger, Lapierre, Monties, Lourdin, & Colonna, 1997), a compound with synthetic polymers (Petersen, Nielsen, & Olsen, 2001; Ratto, Stenhouse, Auerbach, Mitchell, & Farrell, 1999) or a raw material to produce a synthetic polymer such as polylactic acid through bio-processing (Vink, 2001).

Polymer foams, among polymers in films, sheet and moulded forms, have been widely used for packaging. This generates a large quantity of household waste (Klingbeil, 2000) and raised concerns over their impact on the environment (Wasteline, 2002) and tightening of legislation (Packaging and Packaging Waste Directive 94/62/EEC and UK Packaging Regulations, 1998). Various starch-based foams have been developed to provide biodegradable alternatives.

As an alternative to polymer foams such as expanded polystyrene (EPS), loose-fill (foamed chips for filling space around goods within a packing box) extruded from thermoplastic starch is probably the most successful application of starch-based material in cushion packaging. Several patents on the extruded foams based on starch and blends of starch with various additives have been filed (Bastioli, Bellotti, Del Giudice, Lombi, & Rallis, 1994; Bastioli, Bellotti, Del Tredici, Montino, & Ponti, 1998a; Bastioli, Bellotti, Del Tredici, & Rallis, 1998b; Bellotti, Bastioli, Rallis, & Del Tredici, 1995; 2000; Lacourse & Altieri, 1989; 1991; Xu & Doane, 1997; 1998) and the material is commercially available. Considerable effort has been made to study the influence of extrusion conditions, moisture content and composition on the physical properties of starch-based foams (Bhatnagar & Hanna, 1995a,b; Cha, Chung, Seib, Flores, & Hanna, 2001; Fang & Hanna, 2001a,b; Tatarka & Cunningham, 1998; Willett & Shogren, 2002).

Moulded foam trays have been developed based on baking technology (Shogren, Lawton, & Tiefenbacher, 2002) and are commercially available. Batter is foamed up and dried within heated moulds to foam thin-shelled containers similar to the process for making ice cream cones. The foam structure is featured by a highly porous centre sandwiched by much denser

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skin layers. The technology is somewhat limited by the slow processing rate necessary to dry off the moisture in the batter, which in turn restricts the maximum wall thickness of the foams.

Technologies for producing bulk starch forms have also been developed. Corrugated foam planks (Lye, Lee, & Chew, 1998) made by extrusion foaming of modified cornstarch have been shown to have good cushion performance. The high foam density and cost of the materials, however, have somewhat restricted their widespread applications in packaging. Block foams have been made by combination of extrusion foaming and adhesion technology (Wang, Song & Kang 2001, 2002). The foams are of lower density and made from low cost wheat flours. When combined with other materials to form light-weight sandwich composites, mechanical properties and resistance to water attack can be drastically enhanced (Song, 2005).

Among the physical properties of starch-based foams, mechanical properties have an important impact on their practical applications. For protective or cushion packaging, it is desirable that foams are able to absorb impact energy by compression and recover to their original dimensions after impact. Therefore, uniaxial compression tests should be carried out to assess the mechanical properties relevant to cushioning applications, such as compressive modulus of elasticity, compressive strength and deformation energy. Since, the mechanical properties of starch-based foams are dependent on the structure (related to density or expansion ratio during processing) and cell wall material which are in turn determined by processing conditions and compositions, it is necessary to study the relationship between composition, structure, and mechanical properties, which could provide a route to improve mechanical properties of starch-based foams through adjusting their formulation and structure.

Moulded starch block foams are highly desirable in order to provide biodegradable counterparts to moulded polymeric foams. Recently, a microwave foaming process has been described for making moulded starch foams from extruded pellets (Zhou, 2004). This involves converting starch-based raw materials into pellets by extrusion processing and foaming the extruded pellets by microwave heating. The effects of various additives, including blowing agent, nucleation agent and microwave energy absorbent, on the microwave foam-ability of the extruded pellets were also investigated. The microwaveable starch pellets are compact for transportation and storage and can be expanded using microwave when needed. They may be formulated to produce microwaveable snacks in food industry. In non-food applications, free-flowing foamed balls may be produced for loosefill packaging. When the pallets are foamed in a mould, lightweight mouldings can be produced in forms of containers, end caps, edge or corner cushion pads for protective packaging, which are difficult to produce with extrusion foaming technology. In this paper, physical properties of microwave-foamed extruded pellets made from different raw materials and various additives were characterized in order to better understand how the raw materials and additives influence foam structure and properties.

2. Experimental details

2.1. Raw materials and additives

Two types of wheat flour were used (referred hereafter as Temple and Superfine flours). These raw materials were supplied by Heygates Limited (Northampton, UK). Based on the information from the supplier, the Temple flour contains 9–10% protein and about 11–14% moisture, while the Superfine flour contains 7.5–8.5% protein and about 11–14% moisture. A purified wheat starch, Meritena 200, produced by Amylum Europe NV, Belgium, supplied via Heygates Ltd, was also used as a raw material.

Calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were supplied by Sigma. Hydrocerol® BIH (Clariant), a blowing agent which decomposes at temperatures above 160 °C was supplied by Alfa Chemicals (UK). A talc powder (FINNTALC M50) with an average particle size of 22 μm was supplied by Omya UK Limited (Surrey, England).

2.2. Extrusion and microwave foaming

A Betol BTS40 twin-screw co-rotating extruder with 40 mm diameter, 870 mm long screws and a single 4 mm diameter die was used for the extrusion. The screws consisted of: 545 mm 24-mm pitch screws; 120 mm 16-mm pitch screws; 45 mm mixing element; 160 mm 16-mm pitch screws. The barrel consisted of five sections, each with independent temperature control. To prepare unexpanded pellets, barrel sections 1–5 were maintained at 60, 80, 120, 80 and 70 °C, respectively. A screw speed of 100 rpm was used. Flour and water were fed independently to give an overall feed rate of 145 g/min and an overall water content of 22.8% w/w (wet weight basis). Once stable extruder operation was achieved, as judged from constant torque and product output, extrudates were collected. Once cooled these were manually cut into cylindrical pellets about 4 mm long. These were further dried in the laboratory atmosphere (about 23 °C, 40–50% RH) to moisture contents of 12–13% w/w.

The addition rates of the additives were: Hydrocerol BIH, 1.5% w/w (following the manufacturer's recommendation); talc (two addition rates), 0.8% w/w and 2.2% w/w; and NaCl and $CaCl_2$, 5.5% w/w and 10.5% w/w, respectively (Zhou, 2004).

Microwave foaming tests were carried out in a combined microwave oven (Sharp R-8720M, 1000W), which allowed both convection hot air and microwave heating. Ten pellets were placed in a Pyrex Petri dish, preheated to 165 °C as measured by a non-contact infrared thermometer (Raytek® Raynger® ST6™, Santa Cruz, USA), and located at the centre of the rotating plate in the microwave oven, then heated by microwaves at full power. About 50–65 s was required to foam the pellets, depending upon their composition. Excessive heating, which lead to burning of the pellets, was avoided.

2.3. Determination of density

The density of the pellets before and after foaming were measured by placing ten pellets in a graduated cylinder, then a known volume of 60-mesh solid glass beads, V_{gb}, (BDH Chemicals Ltd, Poole, England) was poured into the cylinder. The total volume of glass beads and pellets, V_t, were recorded after tapping the graduated cylinder for 1 min. The volume of pellets, V_p, was calculated by subtracting V_{gb} from V_t. The density of the pellets was calculated from the mass of pellets divided by V_p. Microscopic examination showed that the foamed pellets were not uniformly dense and had a denser skin layer on their surface. The density of the core material without this skin was obtained by using callipers to measure flat-surfaced rectangular prism-shaped samples of the core material cut from foamed pellets (the glass bead displacement method being inapplicable to these samples as the beads are able to penetrate into the voids). Ten replicates for each formulation were measured.

2.4. Scanning electron microscopy

Foamed pellet samples for scanning electron microscope (SEM) observations were sectioned with a single-edged razor blade. Samples were then mounted on aluminium stubs with a graphite-filled double-sided adhesive tape, and coated with gold in a SEM sputter coating unit, then examined with a Cambridge Stereoscan scanning electron microscope (250 MK2 Cambridge, England).

2.5. Measurement of moisture sorption isotherms

For the measurement of moisture sorption isotherms of foamed pellets, the samples were placed in the desiccators containing saturated salt solutions in distilled water (LiCl, $MgCl_2$, NaCl and $BaCl_2$), and weighed daily until the weight became constant (in about 8 days). These samples were then dried in a vacuum oven under full vacuum at 85 °C for 8 h, cooled to room temperature and held for another 16 h with the vacuum pump on. The equilibrium moisture contents (EMC) of foamed pellets at different relative humidities were calculated based on Eq. (1) using the equilibrium wet weight, W_w, and the dry weight, W_d:

$$\mathrm{EMC} = \frac{W_w - W_d}{W_w} \quad (1)$$

2.6. Characterization of mechanical properties of the foams

For compression tests, a single-edged razor blade was used to cut rectangular prism-shaped samples from the foamed pellets, using a slicing motion to avoid crushing the foam cells. In addition to producing a regular shape this removed the dense skin of the foamed pellets. The height of sample was 10 mm, the cross sectional areas of the samples were dependent on the available size of the foamed pellets. It ranged from 45 to 65 mm^2 for Temple/talc pellets, which have the smallest expansion ratio, and 110–160 mm^2 for Superfine flour pellets, which have the largest expansion ratio. All the specimens were placed in a controlled environment (20–22 °C and 50% relative humidity) for 10 days prior to testing.

A Hounsfield universal testing machine (Model H10KT, Hounsfield Test Equipment Ltd, Surrey, England) with a 100 N load cell and a 25 mm diameter cylindrical plate were used to compress the samples to achieve a deformation of 50% of their original dimension at a 10 mm/min deformation rate. According to British Standard BS ISO 844:2001 (E), *compressive modulus* of elasticity of samples was calculated based on the slope of initial linear portion of load-displacement curves. *Compressive strength* was determined by dividing the peak force reached within 10% deformation by the corresponding cross-sectional area of the sample. For samples without a peak stress under 10% deformation, the compressive stress at 10% deformation was taken as the compressive strength, as suggested in the British Standard. The absorbed energy during elastic deformation (‘*elastic deformation energy*’) was obtained from integration of the area under load-displacement curve to the load peak and then normalised by the initial sample volume. For specimens without a load peak in the studied strain range, 10% was selected as the corresponding point for the calculation. The *compressive stress* at 40% strain was recorded as a measure of load-bearing capacity of the foam during plastic deformation and *deformation energy*, which represents the energy absorption during the dominating plastic deformation was obtained in the similar way as elastic deformation energy using the integration of the area under load-displacement curve up to 40% strain.

Some commercial protective packaging materials, EPS cushion block and starch-based loose-fill prepared by extrusion foaming, were also tested for the purpose of comparison. The EPS block samples with density of 0.0195 g/cm^3 were rectangular prisms, 10 mm high and about 60 mm^2 cross sectional area. The wheat flour loose-fill samples with density of 0.0127 g/cm^3 (Green Light Products Ltd, UK) were cylinders 10 mm high and about 15 mm in diameter.

3. Results and discussion

3.1. Density of foamed pellets

Fig. 1 shows the dependence of the densities of foamed pellets made from five different formulations on the pellet moisture content prior to microwave foaming. The data indicate that the lowest density foams for all the individual formulations are achieved when foaming is carried out at about 10% w/w moisture content. The lowest densities of microwave-foamed extruded pellets, ranged between 0.114 g/cm^3 (Superfine flour) and 0.145 g/cm^3 (Temple flour), are significantly denser than commercial extruded starch-based loose-fills with densities typically between 0.0167 and 0.0226 g/cm^3 (Tatarka et al., 1998). This disparity is attributable to the difference in expansion ratio during the foaming process and the existence of a denser skin layer in the microwave-foamed pellets (see Fig. 2). The formation of this denser skin layer is

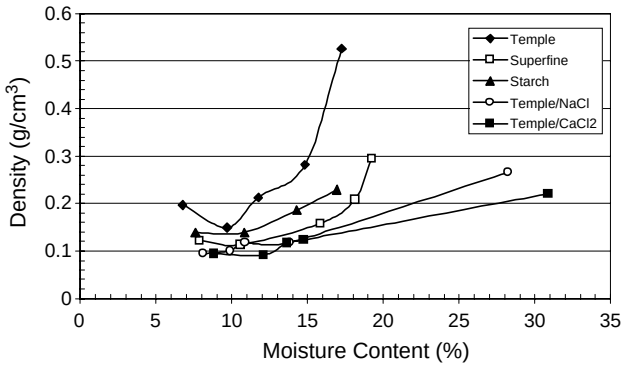

Fig. 1. The densities of pellets microwave-foamed at different moisture contents.

likely to have resulted from moisture loss from the surface of a pellet during heating and hence a reduced driving force for foaming in this region.

The data in Fig. 1 indicate that addition of 5.5% w/w NaCl or 10.5% w/w $CaCl_2$ has significantly reduced the density of the foamed Temple flour pellets, from 0.145 to 0.095 and 0.092 g/cm^3, respectively. Since no attempts were made to optimize the formulation variables, there should be a scope for further reduction in density.

Fig. 3 presents the means and standard deviations of the densities of microwave-foamed pellets (maximum expansion) from various formulations with the denser skin layer removed and conditioned at 50% relative humidity. The data in Fig. 3 and Table 1 indicate that after removing the denser skin layer, the densities of some of microwave-foamed pellets, such as those made from the Superfine flour, purified wheat starch and Temple/$CaCl_2$, are very close to the upper range of density of some extruded starch foams (Willett & Shogren, 2002). These results clearly demonstrate the significant contribution of the denser skin layers to the overall high density of the microwave-foamed pellets. Thickness of the skin layer relative to the radius of a spherical foamed pellet can be estimated assuming that a foamed core is enclosed by a solid skin layer with a density,

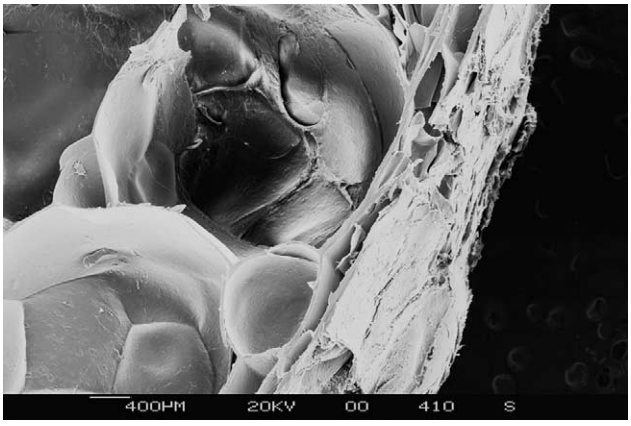

Fig. 2. Scanning electron micrograph of the denser skin layer of microwave-foamed Superfine flour extruded pellet.

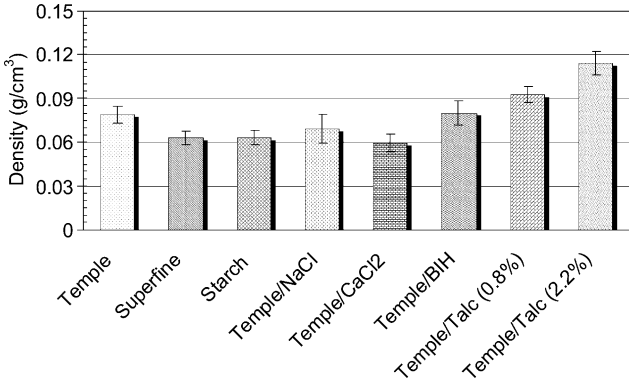

Fig. 3. Densities of microwave-foamed pellets once the denser skin layer is removed.

ρ_s of 1300 kg/m^3 using Eq. (2):

$$\frac{t}{r} = 1 - \left(\frac{\rho_s - \rho_t}{\rho_s - \rho_c}\right)^{1/3}, \quad (2)$$

where t is the thickness of skin layer; r is the radius of a spherical foamed pellet; ρ_t is overall density of the foamed pellet and ρ_c is the density of the foamed core with skin removed. The results are also presented in Table 1. It is interesting to note that low relative skin layer thickness is achieved for those pellets with high expansion ratio (or low density).

3.2. Cell structures of foamed pellets

SEM micrographs of cross-sections of foamed pellets with three different raw materials at maximum expansion are shown in Fig. 4. The cell structures and cell section sizes of these three foams are quite different. The sectioned cell section sizes are estimated about 0.2–2, 0.5–3 and 1–4 mm in diameter for Temple flour, Superfine flour and purified wheat starch foams, respectively. Moreover, the percentage of large sized cells in Superfine flour and purified wheat starch foams is much higher than that in the Temple flour foam. The finer cell structure in Temple flour foam is probably due to the presence of bran in

Table 1
Effect of formulation on density at maximum expansion for the microwave-foamed pellets at optimal moisture content

Foam	Density of foamed pellets, ρ_t (g/cm^3)	Density with skin removed, ρ_c (g/cm^3)	Skin thickness/radius of foamed pellet, t/r (%)
Temple	0.150	0.079	2.0
Superfine	0.114	0.063	1.4
Starch	0.139	0.063	2.1
Temple/NaCl	0.095	0.069	0.7
Temple/$CaCl_2$	0.092	0.060	0.9
Temple/BIH	0.144	0.080	1.8
Temple/talc (0.8%)	0.165	0.093	2.0
Temple/talc (2.2%)	0.188	0.113	2.1
Loose-fill	0.0167–0.0226[a]	–	–

[a] After Tatarka & Cunningham, 1998.

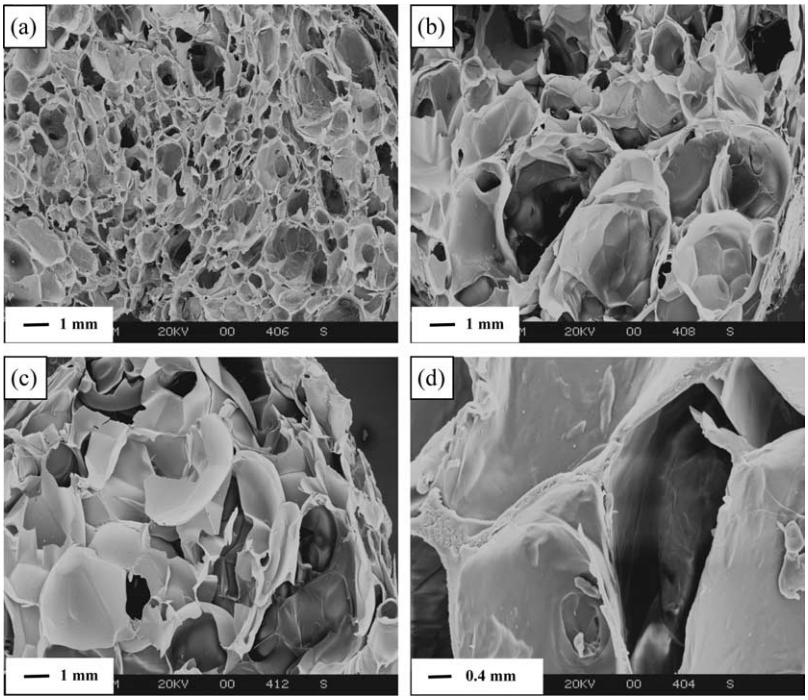

Fig. 4. Scanning electron micrographs of cross-sections of foamed pellets with different raw materials: (a) Temple flour, (b) Superfine flour, (c) purified wheat starch, (d) cell wall in temple foam shown in (a) at higher magnification.

the Temple flour, which could act as nucleation agent. The cell wall thickness for Temple flour, Superfine flour and the purified wheat starch foams were all around 10–40 μm.

Fig. 5 shows the SEM micrographs of foamed Temple pellets with different additives. There is no marked change in the foam structure when the blowing agent BIH is used (see Fig. 5(a) and (b)). BIH is added as a blowing agent in addition to the main blowing agent (moisture) intended to provide additional driving force for foaming. Although it is stated by the manufacture that BIH decomposes at about 160 °C, no information on the kinetic characteristic of the decomposition is available. It is possible that decomposition did not take place to a significant level to build up internal gas pressure to assist the foaming process during the short period when the pellets are between the nominal decomposition temperature, 160 °C and the foaming temperature. The maximum foaming temperature for the pellets is estimated to be 195 °C based on measurements of glass transition temperature of the pellets, which range from 65 to 95 °C (Zhou, 2004) and the observations that foaming temperature of starch materials is up to 100 °C above their glass transition temperature (Chen & Yeh, 2000). However, the addition of talc powder has significantly reduced the size of the foam cells, and the average cell section sizes decrease with increasing talc powder concentration (see Fig. 5(a), (c) and (d)). For the foam with 0.8% w/w talc powder, the cell section diameters are in the range of 0.2–0.8 mm in diameter. While for the foam with 2.2% w/w talc powder, the cell section diameters are in the range of 50 μm to 0.5 mm.

The addition of NaCl and $CaCl_2$ gives rise to a marked increases in expansion ratio as stated earlier and in cell sizes of the Temple flour foams (see Fig. 5(a), (e) and (f)). Since the cell cavities are deep and some cells are interconnected, it is difficult to estimate the cell size range in Temple/NaCl and Temple/$CaCl_2$ foams. The large cell sizes in the foams with the salt additives are thought to result from the more effective microwave energy absorption arisen from the addition of salts (Metaxas & Meredith, 1983) and hence more rapid heating and low moisture loss by diffusion. It was observed that it took about 30 s for the pellets with the salts to foam compared with 45–60 s for those without the salt additives. This may have given rise to higher water vapour pressure in the foam cells causing them to grow to larger sizes.

3.3. Water sorption characteristics of foamed pellets

Fig. 6 shows the water sorption isotherm measured at room temperature for foamed pellets made from Temple flour, Superfine flour, purified wheat starch, Temple/NaCl and Temple/$CaCl_2$. The water sorption isotherms are almost the same for the wheat flours (Temple and Superfine) and purified wheat starch. The EMC of foamed wheat flours and purified wheat starch ranged from about 5% at 11% RH to about 21% at 93% RH. The foamed wheat flours and wheat starch can absorb more than twice the moisture at 93% RH than that at an average environment humidity (50% RH). It is interesting to note that the EMC increases almost linearly below 78% RH and then sharply at RH greater than 78%.

Comparing with foamed pellets without salts, the addition of salts raised the capacity of water absorption. Although 5.5% w/w addition of sodium chloride did not change significantly the EMC of the Temple/NaCl foam at lower humidity levels, at

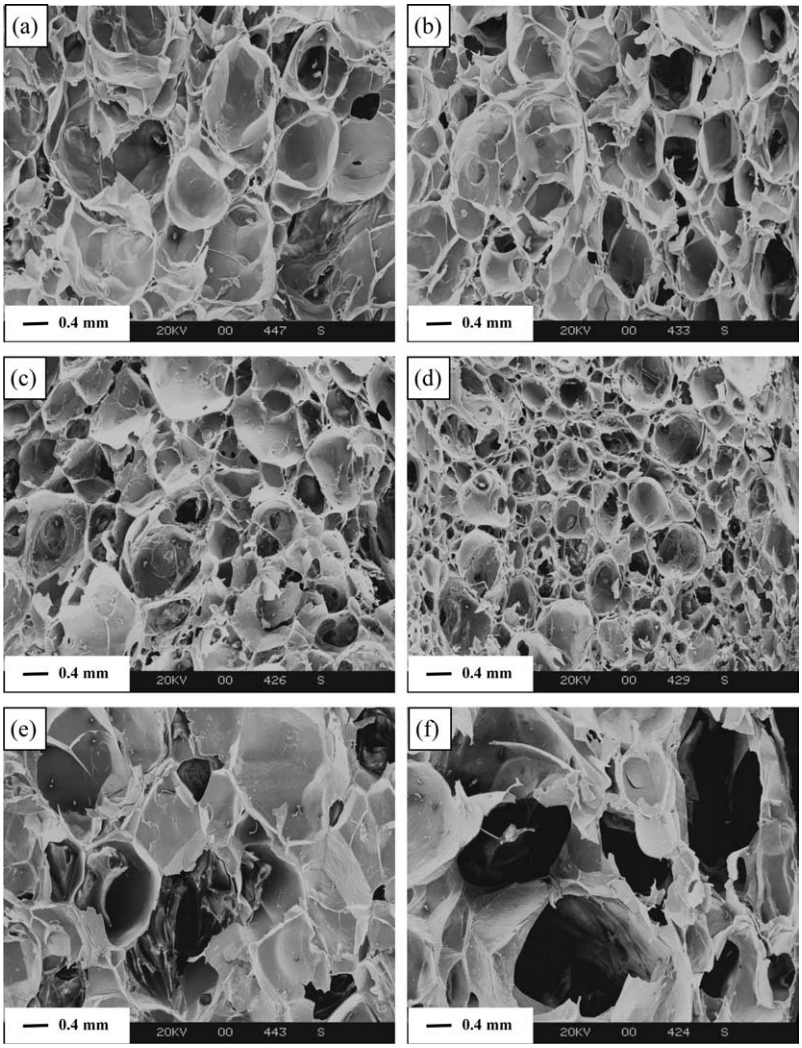

Fig. 5. Scanning electron micrographs of foamed temple pellets with various additives: (a) Temple; (b) Temple/BIH (1.5% w/w); (c) Temple/talc (0.8% w/w); (d) Temple/talc (2.2% w/w); (e) Temple/NaCl (5.5% w/w); (f) Temple/$CaCl_2$ (10.5% w/w).

higher humidity levels, however, this addition did increase the EMC markedly. The addition of 10.5% w/w calcium chloride has significantly increased (over 50%) the EMC of the Temple/$CaCl_2$ foam at various levels of humidity by comparing with the Temple flour foam. This, as will be discussed in Section 3.4, has a marked influence on the flexibility of the foam equilibrated at typical environmental humidities.

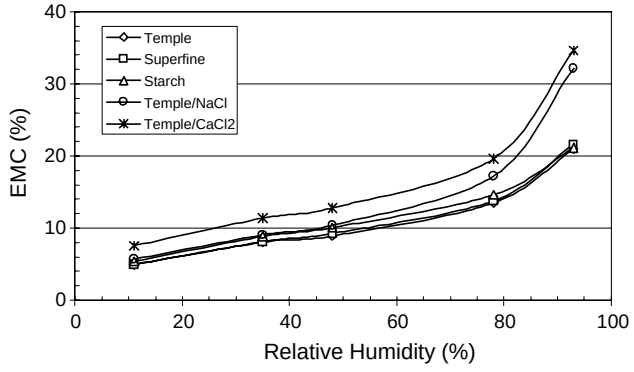

Fig. 6. Water sorption isotherms for the microwave-foamed pellets with different compositions at room temperature.

In addition to significant effects on the EMC of the foamed pellets, relative humidity affects the cell structures of the foams. It was noticed that the size of foamed pellets reduced and became denser when treated at 93% RH during the moisture equilibrium tests, especially for Temple/NaCl and Temple/$CaCl_2$ which absorbed more moisture. While at 11–78% relative humidities the foamed pellets without salts have hardly any change in size, the foamed pellets with salts, however, have a noticeable shrinkage at 78% RH. This shrinkage in the foam volume at the higher moisture content is clearly caused by the plasticizing effect of the absorbed moisture, which enabled the relaxation of tension within cell walls originated during the foaming process and possibly collapsing of some cells.

3.4. Mechanical properties

Fig. 7 shows the typical compressive stress–strain curves for the microwave-foamed pellets produced from different raw

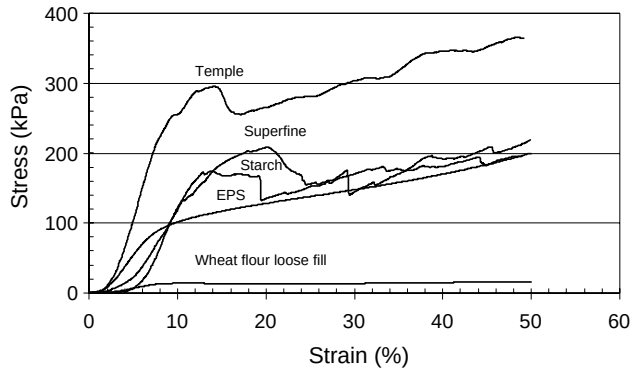

Fig. 7. Comparison of typical compressive stress–strain curves (22 °C, 50% RH) for the microwave-foamed pellets made from different raw materials with commercial protective packaging materials.

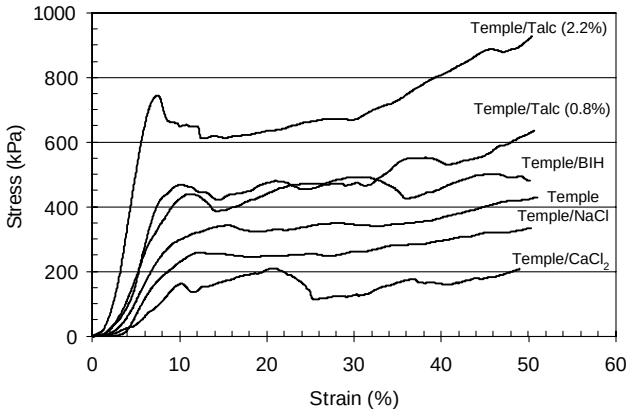

Fig. 8. Typical compressive stress–strain curves (22 °C, 50% RH) for the microwave-foamed pellets made from Temple flour and different additives.

materials. Generally, the stress increases linearly with the strain initially typical for elastic deformation. With further compression, the stress increases non-linearly and reaches a peak value during which, buckling of cells can be observed. The compressive stress then decreases slightly as the result of the cell wall collapsing across the specimen at the peak stress. This is followed by a steady increase of the stress as the cells collapse progressively throughout the specimen giving rise to an increase in foam density. During this process, for all the samples made from the purified wheat starch and some samples of the Superfine flour, there are some abrupt changes in stress accompanied by the noise of cell collapse. These foams had coarser cell structures than the Temple flour foams. Collapse of any individual large cell therefore has a marked effect on the stress.

For comparison, the compressive stress–strain curves of some commercial foams for protective packaging, samples from expanded polystyrene (EPS) cushion block and a wheat flour loose-fill, are also presented in Fig. 7. The most marked difference in the stress–strain behaviour between the microwave foamed pellets and the commercial products is that there is no stress peak under 50% strain for the EPS block and the wheat flour loose-fill. The reason is probably that the cell walls of these two commercial products are much thinner (those of the loose-fill foam are typically below 10 μm compared with 10–45 μm for the microwave-foamed pellets) and more flexible than that of the microwave-foamed pellets, and hence cell collapse took place in a more progressive manner.

Fig. 8 presents the typical stress–strain curves for the foamed pellets from Temple flour alone and Temple flour with various additives. As can be seen, mechanical behaviour of the foams can be adjusted effectively by controlling the foam cell structure through using different additives.

Table 2 summarizes the mechanical properties (mean values and standard deviations) obtained from the compression tests for all the foam specimens investigated in this study. While the *compressive modulus of elasticity* characterises the elastic behaviour under small strain; the *compressive strength* and *strain* describe the load and deformation of the foam as the cell structure starts to collapse; the *elastic deformation energy* is a measure of the elastic strain energy stored in the foam; the *compressive stress* and *deformation energy* at 40% strain represent the large strain behaviour of the samples, reflecting the capabilities of load-bearing and energy absorption during compression of the foams.

The data in Table 2 indicate that, for the foamed pellets made from three different raw materials without additives, the Temple foams are more rigid, as they have the higher compressive modulus of elasticity and compressive strength. While the foamed pellets made from the Superfine flour and purified wheat starch have comparable compressive modulus of elasticity and compressive strength. These are true reflections of their cell structures as the Temple foams have higher density and finer cells than the other two, as presented previously.

Theoretical modelling on elastic mechanical behaviour of cellular solids (Gibson & Ashby, 1997) showed that mechanical properties (e.g. compressive modulus and strength) of foams are related to that of the solid but more sensitive to the foam density. The starch solid materials have similar composition and thus are not expected to make significant impact on properties of the solids. However, as shown in Table 2, composition of the pellets has significant effect on the foam densities and thus the mechanical behaviour of foams as shown in Figs. 7 and 8. Denser foams tend to have thicker cell walls or higher solid fraction and hence are able to resist deformation better than lower density foams with thinner cell walls or lower solid fraction. Addition of nucleation agent (e.g. talc powder) gave rise to high foam densities and significantly increased the compressive strength, elastic modulus and elastic deformation energy. Hence, nucleation agents are suitable to refine the foam cell structures to produce more rigid foams with high load bearing capacity and yet able to deform at higher stress levels to absorb impact energy and hence suitable for protecting heavy goods. The addition of salts, on the other hand, decreased all these values markedly except the compressive strain. Due to the low density and larger cells the foams are less rigid and able to be compressed at relatively low stress to absorb impact energy and thus suitable for protect more fragile or light goods. In this case, the higher moisture

Table 2
Mechanical properties of microwave foamed pellets and commercial protective packaging materials at 22 °C and 50% RH

Sample	Density (mg/cm^3)	Compressive modulus (kPa)	Compressive strength (kPa)	Compressive strain (%)	Elastic deformation energy (kJ/m^3)	Compressive stress at 40% strain (kPa)	Deformation energy at 40% strain (kJ/m^3)
Temple	78.7	55±22	314±47	7.9±2.0	15.4±3.3	377±30	129±22
Superfine	62.8	24±6	180±36[a]	–	11.3±2.5[b]	212±37	69±10
Starch	63.1	22±4	161±27	8.3±1.9	7.8±2.5	241±36	68±6
Temple/BIH	80.2	53±19	334±69	7.9±1.6	16.9±6.2	439±68	136±19
Temple/NaCl	69.0	36±16	250±97	8.1±1.2	12.2±4.6	265±60	88±25
Temple/$CaCl_2$	59.6	31±10	174±42	6.3±1.8	6.9±2.9	175±20	63±11
Temple/talc	92.8	102±17	489±87	5.9±1.1	18.4±5.5	555±70	193±21
Temple/talc	113.4	142±48	737±187	6.2±1.4	27.4±7.8	789±127	267±50
EPS block	19.5	16±4	107±8[a]	–	7.0±0.9[b]	175±8	49±3
Loose fill	12.7	2.5±0.2	15±1.2[a]	–	1.1±0.1[b]	15±1	5.4±0.4

[a] Compressive stress at 10% strain.
[b] Deformation energy at 10% strain.

absorption described previously may also have contributed some plasticizing effect of the cell walls.

Comparing with the EPS block, some of the mechanical properties such as compressive modulus of elasticity, compressive stress and deformation energy at 40% strain of foamed pellets made from the Superfine flour and purified wheat starch were close to that of EPS block. This suggests that by further optimizing the cell structure and flexibility of cell wall material, it is possible to produce foam by a microwave process so that its mechanical properties match that of EPS block. It should be mentioned that starch loose-fill produced by extrusion foaming have very low density, and thus they are suitable for cavity filling in packaging for light weight goods under low compressive stress. While the microwave processed starch foams have relatively high density, they are more suitable for packaging under high compressive stress levels or for heavy goods.

Fig. 9 shows the compressive strength as function of density for all the microwave-foamed samples in this work. As can be seen that there is a strong correlation between the compressive strength and foam density, regardless of the types of raw materials and additives. A similar correlation has also been observed between the elastic modulus and the foam density, which is shown in Fig. 10. These suggest that the stiffness of microwave-foamed pellets is dominated by the foam density.

The data in Figs. 9 and 10 were fit to a simple power–law relationship between elastic mechanical properties, σ, and foam density ρ for solid foams (Warburton, Donald, & Smith, 1992)

$$\sigma \infty \rho^n \tag{3}$$

The results yield an exponent of 2.3 with a correlation coefficient of 0.90 for the compressive strength, and an exponent of 2.7 with a correlation coefficient of 0.79 for the compressive modulus. It was noted that the modulus data (Fig. 10) deviated more from the model than the strength data (Fig. 9), which is consistent with the report of Hube & Gibson (1988) that the shape anisotropy has a greater effect on stiffness than strength. Considering the non-uniform nature of the starch foams (e.g. Figs. 4 and 5) and in comparison with the regular model structure of foams (Gibson et al., 1997), the agreement is good.

It is known that the properties of foams are related to the cell structure (density as well as architecture of the cells) and the properties of the material from which the cell walls are formed (Gibson et al., 1997). Theory predicts the relationship between structure and mechanical properties (Gibson et al., 1997; Smith, 1992) with the exponent of the power–law relationships depending upon whether the foams are open or closed cells. In the case of linear elasticity, the exponent is 2 for open cells

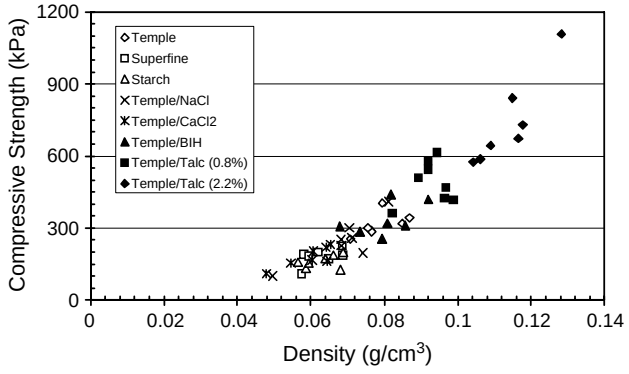

Fig. 9. Scatter plot of compressive strength and density of microwave-foamed pellets with various compositions (22 °C, 50% RH).

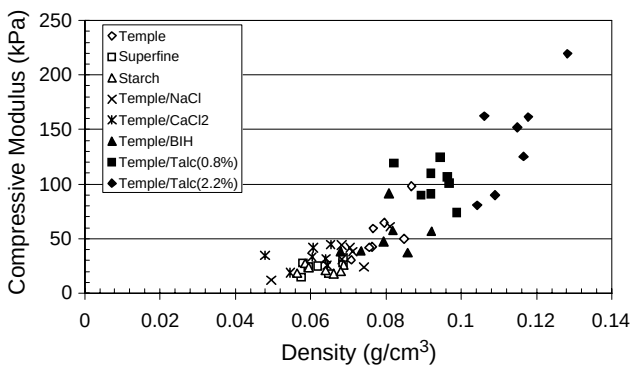

Fig. 10. Scatter plot of compressive modulus of elasticity against density of microwave-foamed pellets with various compositions (22 °C, 50% RH).

and 3 for closed cells in the equations describing both stiffness and strength of foams. The obtained values of the exponents between 2 and 3 by regression suggest that the foam cells are mixture of open cells and closed cells. In fact, the SEM observations indicated that the ratios of open cells to closed cells in the foams with different formulations are different. For instance, the foams of Temple/talc are dominated by closed cells, while in the foams of purified wheat starch and Superfine flour, the numbers of open cells are much greater than in the others. However, techniques, such as Air Comparison Pycnometer (Tatarka et al., 1998), to quantify the ratios of open to closed cells was not available and thus no further attempt was made to study this further.

Mechanical properties during large deformation are relevant to absorption of energy and resistance to further compression of foams in cushion packaging. Fig. 11 shows the elastic deformation energy and deformation energy at 40% strain. It is interesting to see that both are related to foam density and the power–law applies. The results yield an exponent of 2.4 with a correlation coefficient of 0.98 for deformation energy at 40% strain and an exponent of 2 with a correlation coefficient of 0.89 was found for the elastic deformation energy. This is consistent with the facts that foam density has a dominant affect on compressive strength of foams (Fig. 9) and that foams generally harden with deformation beyond compression strength (Figs. 7 and 8). The dependence of compressive stress level on form density at large deformation is shown in Fig. 12, which also obeys the power–law with an exponent of 2.3 and correlation coefficient of 0.97.

It is clear from Fig. 11 that elastic deformation energy only makes a small contribution compared with the total energy absorbed, which is dominated by that to collapse the foam cells.

According to the above discussion, two approaches could be taken to produce softer foams (i.e. to reduce the elastic modulus and compressive strength of foams): either change the foam structure to lower densities or soften the properties of cell wall material. The former has been clearly demonstrated in the results shown in Table 2, Figs. 9 and 10. While the latter is more challenging, it has been demonstrated that addition of

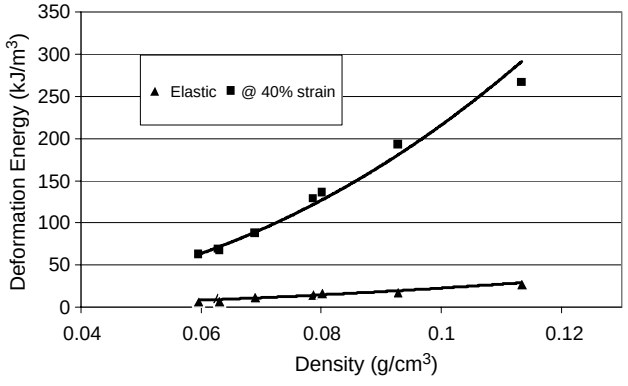

Fig. 11. Scatter plot of deformation energy at 40% strain and elastic deformation energy against density of microwave-foamed pellets with various compositions (22 °C, 50% RH).

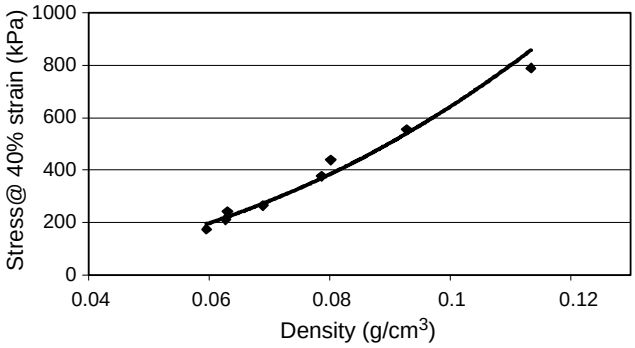

Fig. 12. Scatter plot of compressive stress at 40% strain against density of microwave-foamed pellets with various compositions (22 °C, 50% RH).

glycerol to plasticize the solid material may introduce complications in achieving the desired foamed structure (Zhou, 2004).

A good example is the Temple/NaCl and Temple/$CaCl_2$ foams. In comparison with the Temple flour foam, Temple/NaCl and Temple/$CaCl_2$ foams are softer. This may be partially attributable to the decrease in density because addition of salt increased the expansion ratio of these pellets. On the other hand, the addition of salts also increased the equilibrium moisture content in the foamed pellets (as shown in Fig. 6), which could have softened the cell wall material by plasticization (Ollett, Parker, & Smith, 1991; Orford, Parker, Ring, & Smith, 1989), and hence contributed to the overall softness of the foams. Further, as described in Section 3.3, water sorption can be used for adjusting the foam density or refining the foam cell structure by treating microwave-processed foam in a high humidity chamber to obtain foams with high density and fine cell structures for applications such as high impact cushioning.

From the viewpoint of foam structure engineering, either decreasing the foam density or increasing the number of open cells (i.e. reducing the value of the exponent in Eq. (3)) can produce less rigid foams. Thus, the further exploration of microwave-foamed pellets should be focused on decreasing the foam density (or to increase the expansion ratio) and/or increasing the number of open cells. In terms of formulation and processing control, selection of additives and foaming process conditions should aim to create higher heating rate, larger water vapour (and/or other gas) pressure, and low melt viscosity to allow extensive expansion and bubble burst to reduce density and increase fraction of open cells.

4. Conclusion

The physical properties of foamed pellets, such as density, porosity, cell structure, water absorption characteristics and mechanical properties are highly dependent on the raw materials and additives. Addition of salts reduces foam density and plasticizes cell walls, while addition of nucleation agent refines cell structure but increases foam density. Mechanical behaviour of foamed pellets can be adjusted effectively by controlling the cell structure through using different additives.

Compressive strength and compressive modulus of elasticity, energy absorption during elastic deformation and large deformation (40% strain) as well as stress at 40% strain are all closely related to foam density, the relationships can all be described by a power–law. At room temperature and 50% relative humidity, some mechanical properties, such as compressive strength, compressive modulus of elasticity and deformation energy at 40% strain are comparable to samples from a commercial EPS block.

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References

Bastioli, C., Bellotti, V., Del Giudice, L., Lombi, R., & Rallis, A. (1994). *Expanded articles of biodegradable plastic materials*. US Patent 5,360,830.

Bastioli, C., Bellotti, V., Del Tredici, G., Montino, A., & Ponti, R. (1998). *Biodegradable foamed plastic materials*. US Patent 5,736,586.

Bastioli, C., Bellotti, V., Del Tredici, G., & Rallis, A. (1998). *Biodegradable foamed articles and process for preparation thereof*. US Patent 5,801,207.

Baumberger, S., Lapierre, C., Monties, B., Lourdin, D., & Colonna, P. (1997). Preparation and properties of thermally moulded and cast lignosulfonates starch blends. *Industrial Crops and Products*, *6*, 253–258.

Bellotti, V., Bastioli, C., Rallis, A., & Del Tredici, G. (1995). *Expanded articles of biodegradable plastic material and a process for the preparation thereof*. Europe Patent, EP0667369.

Bellotti, V., Bastioli, C., Rallis, A., & Del Tredici, G. (2000). *Expanded articles of biodegradable plastic material and a process for the preparation thereof*. Europe Patent, EP0989158.

Bhatnagar, S., & Hanna, M. A. (1995a). Properties of extruded starch-based plastic foam. *Industrial Crops and Products*, *4*, 71–77.

Bhatnagar, S., & Hanna, M. A. (1995b). Physical, mechanical, and thermal properties of starch-based plastic foams. *Transactions of the ASAE*, *38*, 567–571.

British Standard (2001). *Cellular plastics—Compression test for rigid materials—specification* (BS ISO 844:2001 (E)).

Cha, J. Y., Chung, D. S., Seib, P. A., Flores, R. A., & Hanna, M. A. (2001). Physical properties of starch-based foams as affected by extrusion temperature and moisture content. *Industrial Crops and Products*, *14*, 23–30.

Chen, C.-M., & Yeh, A.-I. (2000). Expansion of rice pellets: Examination of glass transition and expansion temperature. *Journal of Cereal Science*, *32*, 137–145.

Fang, Q., & Hanna, M. A. (2001a). Characteristics of biodegradable Mater-Bi®-starch based foams as affected by ingredient formulations. *Industrial Crops and Products*, *13*, 219–227.

Fang, Q., & Hanna, M. A. (2001b). Preparation and characterisation of biodegradable copolyester-starch based foams. *Bioresource Technology*, *78*, 115–122.

Gibson, L. J., & Ashby, M. F. (1997). *Cellular solids: Structure and properties* (2nd ed.). UK: Cambridge University Press.

Hube, A. T., & Gibson, L. J. (1988). Anisotropy of foams. *Journal of Materials Science*, *23*, 3031–3040.

Kim, M., & Lee, S. (2002). Characteristics of crosslinked potato starch and starch-filled linear low-density polyethylene films. *Carbohydrate Polymers*, *50*, 331–337.

Klingbeil, M. (2000). *Working document of biodegradable waste management*. Brussels: European Commission.

Lacourse, N. L., & Altieri, P. A. (1989). *Biodegradable packaging material and the method of preparation thereof*. US Patent, 4,863,655.

Lacourse, N. L., & Altieri, P. A. (1991). *Biodegradable shaped products and the method of preparation thereof*. US Patent, 5,043,196.

Lye, S. W., Lee, S. G., & Chew, B. H. (1998). Characterisation of biodegradable materials for protective packaging. *Plastics Rubber and Composites Processing and Applications*, *27*, 336–383.

Metaxas, A. C., & Meredith, R. J. (1983). *Industrial microwave heating (p. 60)*. London: Peter Peregrinus.

Ollett, A. L., Parker, R., & Smith, A. C. (1991). Deformation and fracture behaviour of wheat starch plasticized with glucose and water. *Journal of Materials Science*, *26*, 1351–1356.

Orford, P. D., Parker, R., Ring, S. G., & Smith, A. C. (1989). Effect of water as a diluent on the glass transition behaviour of malto-oligosaccharides, amylose and amylopectin. *International Journal of Biological Macromolecules*, *11*, 91–96.

Packaging and packaging waste directive (94/62/EEC).

Petersen, K., Nielsen, P. V., & Olsen, M. B. (2001). Physical and mechanical properties of bio-based materials—Starch polylactate and polyhydroxybutyrate. *Starch/Stärke*, *53*, 356–361.

Ratto, J. A., Stenhouse, P. J., Auerbach, M., Mitchell, J., & Farrell, E. (1999). Processing, performance and biodegradability of a thermoplastic aliphatic polyester/starch system. *Polymer*, *40*, 6777–6788.

Shogren, R. L., Lawton, J. W., & Tiefenbacher, K. F. (2002). Baked starch foams, starch modifications and additives improve process parameters, structure and properties. *Industrial Crops and Products*, *16*, 69–79.

Smith, A. C. (1992). Studies on the physical structure of starch-based materials in the extrusion cooking process. In Jozef L. Kokini, Chi-Tang Hao, & Mukund V. Karwe (Eds.), *Food extrusion science and technology* (pp. 573–618). New York: Marcel Dekker.

Song, J. H. (2005). Lightweight sandwich panels based on starch foam. In *Proceedings of CIMNFC LINK seminar, Warwick University, 19th April, Warwick*.

Tatarka, P. D., & Cunningham, R. L. (1998). Properties of protective loose-fill foams. *Journal of Applied Polymer Science*, *67*, 1157–1176.

UK Packaging Regulations (1998). HMSO, UK. (SI 1998, no. 1165).

Vink, E. (2001). *ACTIN Proceeding—biopolymers, packaging—a new generation, University of Birmingham UK, March 2001*.

Wang, B., Song, J. H., & Kang, Y. (2002). On modelling of biodegradable foams for packaging applications. *Key Engineering Materials*, *227*, 253–260.

Wang, B., Song, J. H., & Kang, Y. G. (2001). Modelling of the mechanical behaviour of biodegradable foams—From physical fundamentals to applications. In L. C. Zhang (Ed.), *Engineering plasticity and impact dynamics* (Chap. 7) (pp. 117–134). Sinagpore: World Scientific.

Warburton, S. C., Donald, A. M., & Smith, A. C. (1992). Structure and mechanical properties of brittle starch foams. *Journal of Materials Science*, *27*, 1469–1474.

Wasteline (2002). *Information sheet on packaging*. Waste watch, UK.

Willett, J. L., & Shogren, R. L. (2002). Processing and properties of extruded starch/polymer foams. *Polymer*, *43*, 5935–5947.

Xu, W., & Doane, W. M. (1997). *Biodegradable polyester and natural polymer compositions and expanded articles therefrom*. US Patent 5,665,786.

Xu, W., & Doane, W. M. (1998). *Biodegradable polyester and natural polymer compositions and expanded articles therefrom*. US Patent 5,854,345.

Zhou, J. (2004). PhD thesis: *Microwave assisted moulding of starch-based foams*, Brunel University, UK.