5

Starch Protective Loose-Fill Foams

Marcin Mitrus
University of Life Sciences in Lublin
Poland

1. Introduction

Shredded newsprint and cardboard, popcorn, flour, starch and expanded polystyrene (EPS) are the most common materials used to protective packing products. Their function is to provide cushioning, protection, and stabilization of articles packaged for transport. EPS-based loose-fill foam products have enjoyed a steady growth in this application over the last decades, but became targeted recently in the solid waste disposal debate. Huge quantities of plastic is used for refuse and retail bags, egg cartons, packaging film, and loose fillers.

Fig. 1. Extruded starch foams.

As an alternative to very popular polymer foams such as expanded polystyrene (EPS), loose-fill (foamed chips for filling space around goods within a packing box) extruded from starch (fig. 1) 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 et al., 1998a, 1998b; Bellotti et al., 2000; Xu & Doane, 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, 1995; Tatarka & Cunningham, 1998).

Extruded starch foams are generally water soluble, and their properties are sensitive to moisture content. Greatest expansion and lowest densities are generally achieved through the use of modified high amylase starches. Various synthetic polymers, like poly(vinyl alcohol) or polycaprolactone, have been blended with unmodified starches to produce foams with lower densities and increased water resistance.

2. Thermoplastic starch

Starch biodegrades to carbon dioxide and water in a relatively short time compared with most synthetic polymers. Considering some drawbacks of the existing technologies of biodegradable materials manufacture, in the recent years there have been started large-scale researches to increase amount of starch in starch-plastic composites to the highest possible level. The final objective of these investigations is to obtain commercial items for one-time use, produced from pure starch and to exclude synthetic polymers from the formulation. Thermoplastic starch (TPS) seems to be a perfect solution because it can be processed with conventional technologies used in synthetic plastic manufacture (extrusion, injection moulding) (Shogren et al., 1993; Wiedmann & Strobel, 1991).

To obtain thermoplastic starch, thermal and mechanical processing should disrupt semi crystalline starch granules. As the melting temperature of pure starch is substantially higher than its decomposition temperature there is a necessity to use plasticizers, for example water. Under the influence of temperature and shear forces, disruption of the natural crystalline structure of starch granules and polysaccharides form a continuous polymer phase is reported (Avérous et al., 2001; Nashed et al., 2003; Shogren et al., 1993; Van Soest et al., 1996).

TPS produced from starch plastified only with water becomes very brittle at room temperature. To increase material flexibility and improve processing other plasticizers are also used, e.g. glycerol, propylene glycol, glucose, sorbitol and others (Nashed et al., 2003; Van Soest et al., 1996).

To improve the mechanical properties of TPS based materials also other additives can be applied, like emulsifiers, cellulose, plant fibres, bark, kaolin, pectin and others (Avérous et al., 2001; Ge et al., 2000).

Thermoplastic starch can be obtained by the proper treatment with temperature and pressure in the presence of a plasticizer, like water, glycerol or sorbitol. The plasticizer penetrates into the starch granules and disrupts the initial crystallographic structure. Due to temperature and shear forces the material undergoes a melting process and forms a continuous amorphous mass that does not exhibit diffraction anymore. If the total thermal and mechanical energy provided to the starch is insufficient the product will show

unmolten starch granules of clear crystallographic structure. Similarly, an insufficient amount of plasticizer may result in incomplete destruction of the crystallographic structure of starch (Souza & Andrade, 2002; Van Soest & Knooren, 1997).

One of the major drawbacks connected with starchy materials is their brittleness. This is related to a relatively high glass transition temperature T_g. This temperature marks the transition from a highly flexible state to a glassy one. T_g is considered the most important parameter for determining the mechanical properties of amorphous polymers and for the control of their crystallisation process (De Graaf et al., 2003).

The effect of starch plastification with water was repeatedly studied and various techniques for glass transition temperature were compared. The method of differential scanning calorimetry DSC is used most commonly, but the glass transition temperature found by DSC can be 10 – 30°C higher than the T_g value obtained by NMR (nuclear magnetic resonance) or DMTA (dynamic mechanical thermal analysis). The analysis of the influence of water on the T_g of amylose and amylopectin showed that the very branched amylopectin had a slightly lower glass transition temperature than the amylose. On the grounds of published researches and practical observation it can be stated that starchy material containing water is generally in the glassy state and therefore brittle under natural conditions (De Graaf et al., 2003; Moates et al., 2001; Myllarinen et al., 2002).

However, the results of measurements published by various authors are inconsistent to a high degree due to complex changes that occur in starch due to high temperatures and different measurement conditions.

Zeleznak & Hoseney (1997) found that the glass transition temperature of wheat starch with 13 - 18,7% moisture varies between 30 and 90°C and that T_g is likely to be lower than room temperature if the starch humidity increases above 20%. Van Soest et al. (1996) detected a T_g of 5°C for extruded potato starch with 14% moisture content, while at higher moisture T_g could not be determined. Shogren showed that the glass transition temperature for starch with 7 - 18% moisture ranged from 140 – 150°C (Shogren, 1993).

Myllarinen et al. (2002) indicated that T_g of amylose and amylopectin may equal the room temperature when the water content in a blend is 21%, however, at the same glycerol content it goes up to 93°C. This leads to the conclusion that glycerol is a less effective plasticizer than water. Moreover, on the basis of calculations they found out that a glycerol content as high as 35% is required to let T_g drop to the room temperature.

Also for other plasticizers, like sorbitol the T_g of TPS decreases at increasing concentrations. Yu et al. (1998) hold that TP maize starch with 10% moisture and 25-35% glycerol shows a T_g running from 83 – 71°C. Van Soest & Knooren (1997) proved that potato TPS with 11% moisture and 26% glycerol had a T_g = 40 °C, whereas for the materials of higher moisture and glycerol content it fell below 20°C. Lourdin et al. (1997) reported that potato starch of 13% moisture with 15% glycerol content had the T_g around 25°C, while at 25% glycerol the T_g dropped to around 0°C.

The TPS mechanical properties depend on the temperature of starch production, water content as well as quantity and type of added plasticizers and aid materials. The most considerable influence on the changes in mechanical properties proved to be the amount of plasticizer and aid materials.

The most common plasticizers like, glycerol, glycol or sorbitol possess the same hydroxyl groups as those appearing in starch, thus being compatible with starch macrogranules.

Increase of the plasticizer content brings about a decrease in tensile strength of thermoplastic starch, whereas the elongation at break increases. Starch is a natural polymer containing numerous hydrogen bonds between the hydroxyl radicals in its molecules, therefore it manifests substantial tensile strength values. Glycerol, sorbitol or glycol behave like diluents and decrease the interaction between molecules and consequently, they diminish tensile strength. At the same time they act as placticizers that improves macromolecular mobility and leads to a rise in elongation at break (Yu et al., 1998).

The increase of elongation at break at increasing plasticizer content occurs at some ranges of glycerol only. If this content surpasses 35%, a decrease of the elongation at break is noted. This effect is caused by too high percentage of glycerol, and therefore the molecular interactions are so weak that some interactions between starch molecules are replaced by the interactions between glycerol and starch molecules (Liu et al., 2001; Shogren, 1993; Yu et al., 1998).

An increase of water content in the blend induces an decrease of the tensile strength of the TPS and increase of the elongation at break. Yet, if water content exceeds 35% there is detected drop in the elongation at break of the TPS (Shogren, 1993).

Additon of filler materials like cellulose fibres, flax, kaolin or pectin increase the tensile strength but decrease the elongation at break. In turn, urea or boric acid addition improve the elongation at break but decreases the tensile strength (Fishman et al., 2000; You et al., 2003; Yu et al., 1998).

During storage of TPS some recrystallisation of amylose and amylopectin occurs. Together with a longer storage period, and consequently TPS crystallinity, tensile strength increases and elongation at break decreases. The increase of moisture content of the starchy materials storage conditions brings about intensification of their mechanical properties changes (Van Soest & Knooren, 1997).

On the basis of investigations made by Mitrus (2009) it was found out that with glycerol content increase in material mixture, a decrease of maximal stress formed at granulate compression was detected. Besides, blend moisture was also noted to affect on maximum stress generated in a compressed granulate. Along with mixture moisture growth the formed stresses are greater, however a faster drop of stress values was recorded together with glycerol increase. In the case of granulate produced from mixtures with glycerol content over 27% the stresses generated in granulate from more humid blends are lower than those are for more dry ones. The results emphasise that glycerol percentage growth is accompanied by lower tensile strength of thermoplastic starch. Although, water content increase may improve the strength of the obtained material, still it is most probable that some boundary value of total plasticizer content exists and when it has been surpassed the material becomes soften.

The excessive expansion and pore presence abates TPS tensile strength. Investigating of granulate from corn and wheat starch with 20% of glycerol content there were detected very low values of stress. The presence of pores had a significant impact on tensile strength weakening the obtained extrudate. In case of trials with 25% of glycerol the highest tensile strength values were recorded for the materials from corn starch, while the lowest for those containing wheat starch.

The investigations on water absorption by starch without a plasticizer revealed that amylopectin absorbs less water than amylose. The influence of a glycerol addition on water absorption is similar for both starch components (Myllarinen et al., 2002).

At low relative ambient moisture, i.e. below 50%, water content for both, amylopectin and amylose turned out to be lower in the blends with/without glycerol addition. This effect is probably connected with the replacement of strongly structurally immobilised water by glycerol. Similar behaviour was detected for starch plastifyied with sorbitol.

At the relative ambient moisture higher than 50% the mixtures with highest glycerol concentration showed the highest water content. When ambient moisture exceeded 70%, water content in the starch plastifyied by glycerol proved higher than in starch without glycerol.

Although both starch components behave alike at water absorption, in case of high ambient moisture amylose absorbs greater amount of water compared to amylopectin because the crystallisation reduces water absorption of hydrophilic polymers (Nashed et al., 2003, Myllarinen et al., 2002).

3. Methods of production

Starch offers a structural platform to manufacture sustainable, biodegradable foam packaging. As a basic material can be mixed with other polymers or with plasticizers and other additives. This blends can be produced with conventional technologies used in synthetic plastic manufacture.

Starch-based loose-fill can be manufactured, in a one-step process, via an extrusion cooking process. Granular starch and water are fed into an extruder, usually a twin screw, where heat and shear causes the starch to gelatinize. Water, released as steam at the die of the extruder, is the primary blowing agent. Complete expansion or density reduction takes place immediately after the product exits the extruder (Tatarka & Cunningham, 1998).

Application of extrusion-cooking technique to process starch-plasticizer mixtures is one of the most economical and efficient way to produce TPS loose-fill foams. The process conditions are to be very stable and strictly determined according to the expected quality of the extrudates. Also raw materials used (starchy components mixed with the plasticizers) have to be fitted properly. All together need many trials and detailed measurements to find optimal process conditions which can guarantee the best quality of the product. One of the most interesting question connected with extrusion-cooking is energy consumption. Specific Mechanical Energy (SME) consumption is defined as the amount of energy that is consumed per kilogram product. Knowledge of SME is not only important for design purposes, but it is also an indication of the mechanical forces on the material and consequently of degradation an viscous heating during the process. The specific mechanical energy for extrusion cooking of thermoplastic starch are in the order of $2,52 \cdot 10^5$ J/kg, which is equivalent to 0,07 kWh/kg. This rather low SME value depends on material composition of the mixtures, temperature and rotation speed (Mitrus & Moscicki, 2009).

Harper (1981) gave a detailed description on the mechanics of starch extrusion. The phenomenon of starch foaming involves the physicochemical properties of starch, which are

modified during extrusion (Moscicki, 2011). The rheological properties of the starch plastic are in turn reliant on these physicochemical properties (Mercier et al.,1998), which affect the quality attributes of the foamed product. Extrusion process parameters, such temperature, screw speed, feed rate and moisture have direct influence on density, expansion ratio and other physical properties of extruded foams. Extrusion temperature depends on processed blend composition and ranged from 100°C to 180°C (Bhatnagar & Hanna, 1995; Cha et al., 2001; Shogren et al., 2002).

Moulded foam trays have been developed based on baking technology (Shogren et al., 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 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 et al., 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 et al., 2001). The foams are of lower density and made from low cost wheat flours. When combined with other materials to form lightweight sandwich composites, mechanical properties and resistance to water attack can be drastically enhanced (Song, 2005).

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 et al., 2006). This involves converting starch-based raw materials into pellets by extrusion processing and foaming the extruded pellets by microwave heating. 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 loose-fill 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.

4. Properties of the loose-fill foams

Properties of the loose-fill foams highly depend on raw materials and process parameters used in production. Addition of synthetic polymers, plasticisers or other additives, different temperatures of processing are causing changes in products properties.

4.1 Cell structure

Open cells in foams occur if at least part of one wall is missing, creating an opening onto adjacent cells. Tatarka and Cunningham (1998) compared properties of two expanded polystyrene (EPS) based foams (PELASPAN PAC and FLO-PAK S) and six commercially

available starch-based foams (CLEAN GREEN, ENVIROFIL, ECO-FOAM, FLO-PACK BIO 8, RENATURE and STAR-KORE), manufactured in extrusion cooking process. They reported that all starch-based foams have higher open-cell content than either EPS-based foam. Considering the manufacturing process used, it is not surprising that starch-based foams have more open cells. The expansion is attributable to the escape of water as steam during the extrusion process, resulting between 96 and 99% open cells. Steam can easily rupture the cell walls because thermoplastic starches have poor melt strength. After exposure to high humidities and temperatures, most foams exhibited a statistically significant, but trivial increase, about 1,0%, in open-cell content. Commercial starch-based foams have an open cellular structure. This differs from patents that claim hydroxypropylated high amylose foams as having a closed-cell structure, but the method used to make this assessment was not disclosed.

Bhatnagar and Hanna (1995) tested commercial polystyrene (PS) loose-fills, commercial starch-based loose-fills and starch-based plastic loose-fills with addition of polystyrene and poly(methyl methacrylate) (PMMA). Tests showed that the PS loose-fills and the starch-based loose-fills had uniform cell size. The commercial starch foams and starch-based PS foams had cells larger than the commercial PS foams. The commercial starch foams also had fewer large-diameter cavities. These cavities can help to reduce the density, but also affect other functional characteristics of the foams.

Willet and Shogren (2002) reported that surface of starch-based foams have many small holes, suggesting that the starch outer wall burst during extrusion foaming. This reflects the low melt strength and elasticity of starch melts and is consistent with previous studies indicating that starch foams have open cells (Tatarka & Cunningham, 1998). Surface of starch foams containing poly(lactic acid) (PLA) or poly(hydroxyester ether) (PHEE) had fewer or no holes. This suggests that these foams have greater melt strength and resistance to bubble rupture. The average cell size is much larger for foams containing addition of polymer, reflecting the higher volume expansion of these foams than the starch-based foams.

According with Zhang and Sung (2007a) foams of PLA/starch were successfully prepared by using water as a blowing agent in the presence of talc, which acted as an effective nucleation agent. Water concentration, foaming temperature, nucleation agent concentration, screw speed, and die nozzle diameter were factors influencing foam forming, cell size, and cell distribution. Water was a good blowing agent for the PLA/starch system. The foam structure was dramatically affected by solid inorganic fillers that acted as nucleation agents. With 0,5% talc the expansion ratio of the foam was dramatically reduced by almost 50%. The expansion ratio was further reduced with talc concentration. At 3% talc, the foam expansion was 11,2, <25% of the expansion ratio of the foam without talc. In contrast, the bulk density remained the same and increased slightly at a talc concentration of 3%. With a reduction in the expansion ratio by talc, the foam cellular structure was also changed dramatically. Compared with foams without talc, the texture of the foam with talc became uniform and fine. Cell size distribution became narrower as talc content increased from 0,5 to 2,0%. Majority cell size (MCS) was also reduced. For example, the MCS was between 0,6 and 1,2 mm for the foam with 0,5% talc, whereas the MCS was about 0,4 mm with 2% talc. At 3% talc, the cell size becomes larger and distribution becomes broader again.

4.2 Foam unit density and bulk density

Foam unit density describes the density of an individual expanded loose-fill foam specimen. Bulk density is more complex than specific density. Bulk density takes into account not only material and foam densities, but also packing efficiency, which depends on size, shape, and uniformity of the loose fill. Packing efficiency describes how well the loose fill fills the voids among adjacent foam specimens and can be measured by the ratio of bulk density to foam density. If this ratio is equal to one, the efficiency is very high because no voids exits among adjacent foam specimens. A low packing ratio can be achieved from irregular shaped foams. A loose-fill product with low packing is most desirable because the end-user reduces material consumption and saves transport costs.

The foam density of starch-based products was much higher than EPS-based ones (Tatarka & Cunningham, 1998). These values ranged between 16,7 and 22,6 kg/m^3. These products are approximately two to three times more dense than EPS-based foams. This difference is attributable to the large difference in density between polystyrene and starch and a lower expansion factor. Dry, unmodified granular starch has a nominal density of 1500 kg/m^3. During the extrusion process, the starch density has been reduced by factors ranging between 60 and 90. Open cells created during expansion will prevent the foam from continuing the expansion.

All commercial starch-based foams have a significantly higher bulk density by a factor of two to three than EPS-based foams or commercial PS loose-fills (Bhatnagar & Hanna, 1995; Tatarka & Cunningham, 1998). Starch-based foams have bulk densities between 8,8 and 11,3 kg/m^3. Foam density of starch-based foams correlated well with bulk density. The correlation coefficient for this relationship is 0,97. The packing ratio of the starch-based foams is between 0,435 and 0,538. Irregular cylindrical shapes impart products with lower packing ratios than does uniform cylindrical or dual cylindrical shapes with two similar dimensions (Tatarka & Cunningham, 1998).

Generally, the bulk density of starch-based foams decreased as extrusion temperature increased, whereas it was not significantly changed as moisture content increased. This might be reasonably explained by changes in cell wall thickness and viscosity caused by extrusion temperature and the changes in the volume and weight of cells after absorbing sufficient water (Cha et al., 2001).

The microwave-foamed extruded pellets have lower densities, ranged between 114 kg/m^3 and 145 kg/m^3 and are significantly denser than commercial extruded starch-based loose-fills. 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 (Zhou et al., 2006). The formation of this denser skin layer is 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.

Investigations made by Willet and Shogren (2002) indicated that density of foam prepared from normal corn starch had average density 61,4 kg/m^3, from wheat starch 58,6 kg/m^3 and from potato starch 40,6 kg/m^3. Foam densities for commercial starch foams are approximately 20 kg/m^3. Addition of PLA or PHEE to starch yields foam densities comparable to commercial starch products.

Fang and Hanna (2001) investigated the effect of blending Z class Mater-Bi® (MBI) resin with corn starches on the properties of the starch-based foam materials. They demonstrated that waxy starch had better foaming capabilities than regular starch mainly due to their differences in amylopectin content. Foams made from the waxy starch had slightly lower unit density (83,4 kg/m³) and lower bulk density (49,2 kg/m³) than the foams made from regular starch (83,7 and 56,6 kg/m³ respectively). However, the bulk densities were still much higher than the 8,9 kg/m³ of commercial EPS foams. The unit density increased as MBI and moisture content increased, indicating less expansion of the extrudates at higher MBI and moisture content. The bulk density data also showed a similar trend as the unit density. The relationship between the unit and bulk densities and the MBI and moisture contents were relatively linear.

Bhatnagar and Hanna (1996) extruded five types of starch (normal corn, wheat, potato, rice and tapioca) with polystyrene (starch to polystyrene ratio 70:30) and addition of three additives: azodicarbonamide, magnesium silicate and polycarbonate. Unit density was dependent on source of starch and type of additive. Foams made from tapioca and corn starches had the unit densities ranging from 36 to 39 kg/m³ and from 30 to 86 kg/m³ respectively. Results indicate that corn starch performed better than the wheat starch. The autors reported unit density of 23 to 59 kg/m³ for commercial starch or starch-based plastic foams, which compares favorably with tapioca and corn starch-based foams in their study. The unit densities of all the foams including commercial starch foams were much higher than commercial polystyrene foams (8,9 kg/m³)

4.3 Compressive stress

Compressive stress is the maximum force required to compress the foam by 3 mm. High compressive stress implies foams resist compression. Tatarka and Cunningham (1998) reported that the compressive stress of commercial starch-based foams does not significantly differ from EPS-based foams. As-received FLO-PAK BIO-8, STAR-KORE, ECO-FOAM and ENVIROFIL have lower values between 0,0565 and 0,0853 MPa, whereas CLEAN GREEN and RENATURE have higher values of 0,0927 and 0,1051 MPa. Compressive stress of starch-based foams was generally insensitive to changes in relative humidity. At 20% relative humidity (r.h.) and 23°C, only the chemically modified starch-based foams, ECO- FOAM and STAR-KORE, significantly increased compressive stress by 17 and 28%, respectively. At 80% r.h., 23°C, FLO-PAK BIO-8, RENATURE, and CLEAN GREEN significantly decreased compression stress by 22 to 32%. The higher moisture content in these products was sufficient to lower their resistance to compression. Although the chemically modified STAR-KORE and ECO-FOAM and the unmodified ENVIROFIL absorbed 13 to 16 % water at this condition, compressive stress did not significantly change. Chemically modified starches produced foams with good resistance to compression over a broad humidity range (Tatarka & Cunningham, 1998).

Fang and Hanna (2001) found that compressibility of the waxy starch samples were significantly lower than those of the regular starch samples, indicating that the regular starch foams were more rigid than the waxy starch foams. Foam compressibility increased with increases in the MBI content, but compressibility increased more rapidly as the moisture content increased. High moisture content in the processed materials resulted in more rigid products, which was due to low expansion.

Lin et al. (1995) show direct influence of water activity index on a compressive strength of extruded starch foams. A maximum compressive strength occurred at water activity of 0,53 which is close to normal ambient conditions. Further increase in water activity levels result in a decrease in compressive strength. Water acts as a plasticizer, which lubricates the starch chains. As the water activity increased, the starch chain mobility is also increased. This chain softening results in lower resistance to compression and lowers compressive strength values. It was observed that the foams become more flexible at higher water activity levels, probably due to the plasticization of foam walls by water. At lower water activity levels the starch chain mobility is decreased. This chain stiffening might result in higher resistance to compression and cause a higher compressive strength values. Examination of the samples showed that samples contain tiny fissures or fractures and, with the lower water activity came the more fissures. The effect of fissure or fracture formation in compressive strength of extruded foams at lover water activity levels is more important than the effect of the chain mobility of starch in compressive strength. In other words, fissure or fracture formations controls the compressive strength. The maximum compressive strength at water activity level of 0,53. It seems to be caused by the combination effect of starch chain mobility and fissure or fracture formation.

During measurements a power-law relationship was observed between compressive strength and foam density (Lin et al., 1995, Willett & Shogren, 2002; Zhou et al., 2006). Denser foams tend to have thicker cell walls and hence resist deformation better than lower density foams with thinner cell walls. A strong correlation exists between foam density and compressive strength, regardless of the type of polymer blended with the corn starch.

According to Zhou et al. (2006), 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. The 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.

Greater compressibility values correspond to a sample which is more difficult to compress, while easily compressible samples have lower values of compressibility. Researches of Bhatnagar and Hanna (1995) indicated, that the starch-based PMMA foam had the lowest value of compressibility, which was consistent with its low resiliency. This was expected because this product also had the largest cell size. The starch-based PS loose-fill had more compressibility than the commercial PS foam. They found that compressibility was significantly affected both by the type of starch and type of additive (Bhatnagar & Hanna, 1996). For foams made from corn and tapioca starches compressibility values were quite comparable to that of commercial polystyrene foams. Compressibility values of potato starch extrudates were dependent on type of additive, with magnesium silicate and polycarbonate giving comparatively better products.

4.4 Resiliency

Resiliency describes the ability of the foam to recover to its original form after deformation. Resiliency less than 100% implies that the polymer was strained beyond its elastic limit, for example, by cell wall rupture, which prevents the foam from recovering to its original state.

The resiliency of comercial starch-based foams with values between 69,5 and 71,2% are, as a group, about 10% lower on a relative basis than EPS-based foams (Tatarka & Cunningham, 1998). After conditioning, the resiliency of all starch-based foams were significantly lower, with values between 60 and 70%. Although starch-based foams absorbed 13 to 16% moisture after conditioning at 80% r.h. and 23°C, the 62 to 67% resiliency retained is sufficient for the product to function.

Fang and Hanna (2001) showed that the resiliency value of the regular starch samples was 89,5% compared to 86,6% for the waxy starch foams. The resiliency increased with increases in MBI and moisture content. The addition of Mater-Bi® resin improved the mechanical properties of the starch foams. However, moisture content had a more significant positive effect than the MBI content on resiliency. The achieved results ranged between 80 and 95% which indicated a good deformation resiliency.

According to Lin et al. (1995) extruded starch foams at water activity levels below 0,23 are brittle and easily crushed, disintegrating upon compression. It was evident that, in these conditions, they are not suitable for packaging use. The resiliency of foams increased with increasing water activity levels (0,33 – 0,53). This was probably due to the increase in starch chain mobility of extruded foams at the higher water content. Further increases in water activity (0,53 – 0,75) caused the foams to soften and thus decreased the resiliency.

Bhatnagar and Hanna (1995) reported that the resiliency of starch-based PS loose-fill is not different from the resiliency of PS loose-fill or starch loose-fill. The ideal elastic body will have a resiliency of 100%, whereas the foams had resiliency of the order of 80 to 90%. The resiliency of starch-based PMMA foam was significantly lower than the PS loose-fill. They found resiliency values of 97% and 96% for commercial polystyrene and commercial starch foams, respectively. They found that, resiliency was significantly affected by the type of starch but not by the type of additive (Bhatnagar & Hanna, 1996). For corn and tapioca starches, the resiliency was quite comparable to that of commercial polystyrene loose-fill. Potato starch extrudates had good resiliency with all the additives.

Nabar et al. (2006) investigated influence of polymer addition into starch on foam resiliency. The control starch foams provided a resiliency of 69,7%. The addition of poly(butylene adipate-co-terephthalate) (PBAT) improved the resiliency considerably, from 69,7% to 85,9% at a PBAT content of 7% of the starch used. Polycaprolactone and cellulose acetate helped increase the spring index up to ~78%, while poly(vinyl alcohol) and methylated pectin barely increased the resiliency to ~71–72%. When glyoxal was added as a crosslinker, it increased the rigidity of the starch foams and, thus, the resiliency of the foams decreased by ~3%.

Zhang and Sung (2007b) tested the properties of PLA/starch foams. The foam samples dried at 135°C for 2 h, then immediately undergoing mechanical compression testing, showed no recovery at all, and all inside structure fractured into pieces, regardless of starch/PLA ratios.

The foam samples conditioned at 50% relative humidity for one week at room temperature and then tested yielded up to 73% recovery after 1 h of force removal. The recovery was reduced with the reduction in starch content. Water can be a good plasticizer for starch, and PLA could reduce water diffusion into the starch phase. After immersing the foams in distilled water at room temperature for one week, however, foams with PLA showed instant recovery to their original shape after one minute of force removal regardless of PLA/starch ratio.

The addition of poly(hydroxyamino ether) (PHAE) to starch improved the foam resiliency considerably from 69,7% (only starch) to 93,5% at a PHAE content of 7% of the starch used (Nabar & Narayan, 2006).

4.5 Friability

Friability is a measure of the fragmentation of foam during handling. Fragmentation of loose-fill during handling and use is an important product quality concern among end-users. Tests made by Tatarka and Cunningham (1998) indicated that the friability of commercial starch-based foams ranged between 0,003 and 2,3%. Although these values are lower than EPS-based foams, they are not significantly different. After conditioning, the friability of these starch-based foams increased significantly when exposed to 80% r.h. and 23°C 50% r.h. and 35°C. Quantitatively, starch- and EPS-based foams fragmented similarly at 2 to 6 % of the total weight, but starch-based foams broke down into a fine dust, whereas virgin EPS-based foams broke into large fragments.

Willet and Shogren (2002) founded that friability of starch/polymer foams is high for all tested formulations and starches at 10% r.h. Of the control starch foams, only the high amylose starch has friabilityof less than 95%. Under these conditions, the starch matrix is well below its glass transition temperature and its brittle. As the relative humidity increases to 50%, the equilibrium moisture content of the starch rises, and the foams are consequently less brittle. The friability decreases significantly, but only the high amylose starch foam displays negligible friability (0,4%). The addition of polymer generally reduces friability at 50% r.h. Corn starch loss-fills with the greatest density also exhibited greater friability, while corn starch foams with low densities had insignificant levels of friability. Friability decreases as polymer surface concentration increases. The presence of a ductile polymer on the foam surface may retard the formation of cracks and fragments under impact by the wooden blocks. One cannot, however, rule out indirect effects of the polymer on foam structure, i.e. lower foam density and thinne cell walls as contributing to the greater flexibility of the foam structure.

5. Conclusions

Although the use of starch in loose-fill products gives advantages in the form of biodegradability and environmental protection, these products have been criticized for their imperfection compared with EPS loose-fill products. EPS- and starch-based foams have differences, but the differences do not compromise performance.

These products differ with respect to composition and method of manufacture. Foam and bulk densities, which are higher by a factor of two to three times than either EPS-based foams, are attributable to the density of starch, which is 50% higher than polystyrene

homopolymer and to the direct water-to-steam expansion process, which creates a predominately open cellular structure that stops foam expansion. Starch-based foam loose-fill is very hygroscopic. Foam density of starch-based products is significantly increasing between 10 and 30% after conditioning at high humidity.

The compressive stress of most starch-based foams does not differ significantly from EPS products. Chemically modified starches gives foams with good retention of compressive stress over a broad humidity range.

The resiliency of starch-based foams with values between 69,5 and 71,2% are, as a group, about 10% lower on a relative basis than EPS foams. Although starch-based foams absorbs 13 to 16 wt % moisture after conditioning at 80% r.h. and 23°C, these products are retaining between 62 and a 67% resiliency.

Both starch- and EPS-based foam fragmentation amounts to 2 to 6 wt %, but starch-based breaks down into a fine dust, whereas EPS-based foams breaks into large fragments.

All starch-based foams have a significantly higher foam and bulk density and open cell and moisture content than EPS-based foam. Both product types have similar compressive stress, resiliency, and friability. Starch-based foams are more sensitive to changes in relative humidity and temperature than EPS-based foam, but the higher amount of absorbed moisture does not compromise its mechanical integrity.

Generally, extrusion technique can be successfully employed for starch-based foams production. The physical properties of loose-fills, such as density, porosity, cell structure, water absorption characteristics and mechanical properties are highly dependent on the raw materials and additives. Mechanical behaviour of foamed pellets can be adjusted effectively by controlling the cell structure through using different additives. At room temperature and 50% relative humidity, some mechanical properties, such as compressive strength or compressive modulus of elasticity are comparable to commercial EPS foams.

Starch-based foams can be prepared from different starch sources replacing 70% polystyrene with biopolymer starch. Functional starch-based plastic foams can be prepared from different starch sources depending on their availability.

Starch-based foams with polymer addition (for example: PS, PMMA, PHEE) exerts improved properties in comparison with 100% starch foams. The addition of polymers significantly increases radial expansion and gives low density foams. Compressive strength is depending primarily on foam density, and not on starch type or polymer structure. Friability is reduced when polymer is present in the foam.

Foams of PLA/starch can be successfully prepares by using water as a blowing agent in the presence of talc, which acts as an effective nucleation agent. Water is a good blowing agent for the PLA/starch system. Talc at 2% gives the PLA/starch foam fine foam cell size and uniform cell size distribution.

The addition of Mater-Bi® is affecting the foam expansion characteristic. High levels of MBI are resulting in low radial expansions and high densities. The resiliency is improving as the levels of MBI and moisture contents are increasing. The MBI-starch foams have the potential to be used as an environmentally friendly loose-fill packaging material.

6. References

Avérous, L.; Fringant, C. & Moro, L. (2001). Starch – based biodegradable materials suitable for thermoforming packaging. *Starch*, Vol.53, No.8, (August 2001), pp.368-371, ISSN 1521-379X

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

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. (1995). Properties of extruded starch-based plastic foam. *Industrial Crops and Products*, Vol.4, No.2, (February 1995), pp. 71–77, ISSN 0926-6690

Bhatnagar, S. & Hanna, M. A. (1996). Starch-Based Plastic Foams From Various Starch Sources. *Cereal Chemistry*, Vol.73, No.5, (May 1996), pp. 601-604, ISSN 0009-0352

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*, Vol.14, No.1, (October 2000), pp. 23–30, ISSN 0926-6690

De Graaf, R.A.; Karman, A.P. & Janssen, L.P.B.M. (2003). Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing. *Starch*, Vol.55, No.2, (December 2002), pp. 80-86, ISSN 1521-379X

Fang, Q. & Hanna, M.A. (2001). Characteristics of biodegradable Mater-Bi®-starch based foams as affected by ingredient formulations. *Industrial Crops and Products*, Vol.13, No.3, (August 2000), pp. 219-227, ISSN 0926-6690

Fishman, M.L.; Coffin, D.R.; Konstance, R.P. & Onwulata C.I. (2000). Extrusion of pectin/starch blends plasticized with glycerol. *Carbohydrate Polymers*, Vol.41, No.4, (July 1999), pp. 317-325, ISSN 0144-8617

Ge, J.; Zhong, W.; Guo, Z.; Li, W. & Sakai, K. (2000). Biodegradable polyurethane materials from bark and starch. I. Highly resilient foams. *Journal of Applied Polymer Science*, Vol.77, No.12, (June 2000), pp. 2575-2580, ISSN 1097-4628

Harper, J. M. (1981). *Extrusion of foods*, CRC Press Inc., ISBN 0849352037, Boca Ration, FL., USA

Lin, Y.; Huff, H.E.; Parsons, M.H.; Iannotti, E. & Hsieh, F. (1995). Mechanical properties of extruded high amylase starch for loose-fill packaging material. *Lebensmittel-Wissenschaft und-Technologie*, Vol.28, No.2, (September 1994), pp. 163-168, ISSN 0023-6438

Liu, Z.Q.; Yi, X.S. & Feng, Y. (2001). Effects of glycerin and glycerol monostearate on performance of thermoplastic starch. *Journal of Materials Science*, Vol.36, No.7, (July 2000), pp. 1809-1815, ISSN 0022-2461

Lourdin, D.; Bizot, H. & Colonna, P. (1997). "Antiplasticization" in starch – glycerol films?. *Journal of Applied Polymer Science*, Vol.63, No.8, (April 1996), pp. 1047-1053, ISSN 1097-4628

Lye, S. W.; Lee, S. G. & Chew, B. H. (1999). Characterisation of biodegradable materials for protective packaging. *Plastics Rubber and Composites Processing and Applications*, Vol.27, No.8., (May 1999), pp. 336–383, ISSN 09598111

Mercier, C.; Linko, P. & Harper, J. M. (1998). *Extrusion Cooking* (2nd edition). AACCH Inc., ISBN 0-913250-67-8, St. Paul, Minnesota, USA

Mitrus, M. (2009). TPS and Its Nature. In: *Thermoplastic Starch. A Green Material for Various Industries*, Janssen L.P.B.M., Moscicki L. (Eds.), 77-104, Wiley-VCH Verlag GmbH&Co. KGaA, ISBN 978-3-527-32528-3, Weinheim, Germany

Mitrus, M. & Moscicki, L. (2009). Extrusion-Cooking of TPS. In: *Thermoplastic Starch. A Green Material for Various Industries*, Janssen L.P.B.M., Moscicki L. (Eds.), 77-104, Wiley-VCH Verlag GmbH&Co. KGaA, ISBN 978-3-527-32528-3, Weinheim, Germany

Moscicki, L. (2011). *Extrusion-Cooking Techniques. Applications, Theory and Sustainability*. Wiley-VCH Verlag GmbH&Co. KGaA, ISBN 978-3-527-32888-8, Weinheim, Germany

Myllärinen, P.; Partanen, R.; Seppälä, J. & Forssell P. (2002). Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymers*, Vol.50, No.4, (February 2002), pp. 355-361, ISSN 0144-8617

Nabar, Y.; Narayan, R. & Schindler, M. (2006). Twin-Screw Extrusion Production and Characterization of Starch Foam Products for Use in Cushioning and Insulation Applications. *Polymer Engineering and Science*, Vol.46, No.4, (February 2006), pp. 438–451, ISSN 1548-2634

Nabar, Y.U.; Draybuck, D. & Narayan, R. (2006). Physicomechanical and Hydrophobic Properties of Starch Foams Extruded with Different Biodegradable Polymers. *Journal of Applied Polymer Science*, Vol.102, No.1, (July 2006), pp. 58–68, ISSN 1097-4628

Nashed, G.; Rutgers, R.P.G. & Sopade, P.A. (2003). The plasticisation effect of glycerol and water on the gelatinisation of wheat starch. *Starch*, Vol.55, No.3-4, (March 2003), pp. 131-137, ISSN 1521-379X

Shogren, R.L. (1993). Effects of moisture and various plasticizers on the mechanical properties of extruded starch. In: *Biodegradable polymers and packaging*, Ching Ch., Kaplan D.L., Thomas E.L., (Eds.), 141-149, Technomic Publishing Company Inc., ISBN 1566760089, Lancaster-Basel, USA-Switzeland

Shogren, R.L.; Fanta, G.F. & Doane, W.M. (1993). Development of starch based plastics – a reexamination of selected polymer systems in historical perspective. *Starch*, Vol.45, No.8, (May 1993), pp. 276-280, ISSN 1521-379X

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*, Vol.16, No.1, (January 2002), pp. 69–79, ISSN 0926-6690

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

Souza, R.C.R. & Andrade, C.T. (2002). Investigation of the gelatinization and extrusion processes of corn starch. *Advances in Polymer Technology*, Vol.21, No.1, (October 2001), pp.17-24, ISSN 1098-2329

Tatarka, P. D. & Cunningham, R. L. (1998). Properties of Protective Loose-Fill Foams. *Journal of Applied Polymer Science*, Vol.67, No. 7, (February 1998), pp. 1157–1176, ISSN 1097-4628

Van Soest, J.J.G. Benes, K. & de Wit, D. (1996). The influence of starch molecular mass on the properties of extruded thermoplastic starch. *Polymer*, Vol.37, No.16, (December 1995), pp. 3543-3552, ISSN 0032-3861

Van Soest, J.J.G.; Bezemer, R.C.; de Wit, D. & Vliegenthart J.F.G. (1996). Influence of glycerol on melting of potato starch. *Industrial Crops and Products*, Vol.5, No.1, (September 1995), pp. 1-9, ISSN 0926-6690

Van Soest, J.J.G. & Knooren, N. (1997). Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging. *Journal of Applied Polymer Science*, Vol.64, No.7, (November 1996), pp. 1411-1422, ISSN 1097-4628

Wang, B.; Song, J. H. & Kang, Y. G. (2001). Modelling of the mechanical behaviour of biodegradable foams—From physical fundamentals to applications. In: *Engineering plasticity and impact dynamics*, L. C. Zhang, (Ed.), 117–134, World Scientific, ISBN 981-02-4803-2, Singapore

Wiedmann, W. & Strobel, E. (1991). Compounding of thermoplastic starch with twin-screw extruders. *Starch*, Vol.43, No.4, (February 1991), pp. 138-145, ISSN 1521-379X

Willett, J. L. & Shogren, R. L. (2002). Processing and properties of extruded starch/polymer foams. *Polymer*, Vol.43, No.22, (June 2002), pp. 5935–5947, ISSN 0032-3861

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

You, X.; Li, L.; Gao, J.; Yu, J. & Zhao, Z. (2003). Biodegradable extruded starch blends. *Journal of Applied Polymer Science*, Vol.88, No.3, (April 2002), pp. 627-635, ISSN 1097-4628

Yu, J.; Chen, S.; Gao, J.; Zheng, H.; Zhang, J. & Lin, T. (1998). A study on the properties of starch/glycerine blend. *Starch*, Vol.50, No.6, (December 1998), pp. 246-250, ISSN 1521-379X

Zeleznak, H.F. & Hoseney, R.C. (1987). The glass transition in starch, *Cereal Chemistry*, Vol.64, pp. 121-124, ISSN 0009-0352

Zhang, J.-F. & Sun, X. (2007a). Biodegradable Foams of Poly(lactic acid)/Starch. I. Extrusion Condition and Cellular Size Distribution, *Journal of Applied Polymer Science*, Vol.106, No.2, (June 2007), pp. 857–862, ISSN 1097-4628

Zhang, J.-F. & Sun, X. (2007b). Biodegradable Foams of Poly(lactic acid)/Starch. II. Cellular Structure and Water Resistance, *Journal of Applied Polymer Science*, Vol.106, No.5, (August 2007), pp. 3058-3062, ISSN 1097-4628

Zhou, J.; Song, J. & Parker, R. (2006). Structure and properties of starch-based foams prepared by microwave heating from extruded pellets. *Carbohydrate Polymers*, Vol.63, No.4, (November 2005), pp. 466–475, ISSN 0144-8617
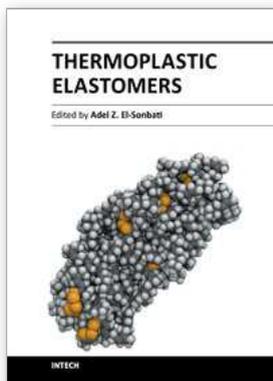
Thermoplastic Elastomers
Edited by Prof. Adel El-Sonbati

Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

Marcin Mitrus (2012). Starch Protective Loose-Fill Foams, Thermoplastic Elastomers, Prof. Adel El-Sonbati (Ed.), ISBN: 978-953-51-0346-2, InTech, Available from: http://www.intechopen.com/books/thermoplastic-elastomers/starch-protective-loose-fill-foams

INTECH
open science | open minds