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Microstructure of thermoplastic starch polymers**

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A b s t r a c t. Environmental problems with conventional packaging materials developed the need of searching for new alternatives. Thermoplastic starch polymer (TPS) has been found to be a good source of raw materials for new packaging materials. In the paper changes of microstructure of TPS produced from different type of starch with glycerol content have been discussed. In general it can be stated that an increase of glycerol content in the mixture improves material structure quality.

K e y w o r d s: thermoplastic starch, microstructure, extrusion-cooking

INTRODUCTION

Environmental pollution is the most vital problem all over the world. A comprehensive strategy concerning the rational production, use and neutralization of plastics should also include elaboration of safe and fast degradation process of synthetics discarded in landfills. The solution, however, should be the development of safer and more effective recycling technologies as well as generation of new materials, mainly biodegradable, easy to be reused or recycled.

Thermoplastic starch (TPS) seems to be a perfect solution as it can be processed with conventional technologies for synthetic plastics (extrusion, injection moulding). Having been used up, these products can be recycled in a simple way, *eg* in the composting process.

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, at the processing there is a necessity of plasticizer addition, for example water. Under the influence of temperature and shearing forces there is reported disruption of natural crystalline structure of starch granules and polysaccharides form a continuous polymer phase (Aichholzer and Fritz, 1998; Avérous, 2001; De Carvalho *et al*., 2001; Hulleman *et al*., 1998; Lörcks, 1998; Nashed *et al*., 2003; Shogren *et al*., 1993; Stepto, 1997; Van Soest, 1996; Van Soest *et al*., 1996a and b; Van Soest and Vliegenthart, 1997).

TPS produced from the starch plastified only with water becomes very brittle at room temperature. To improve processing and the mechanical properties of TPS based materials, other plasticizers are also used, *eg* glycerol or sorbitol and some additions, *eg* cellulose, pectin and others (Avérous, 2001; De Carvalho *et al*., 2001; Funke *et al*., 1988; Ge, 2000; Lörcks, 1998; Mundigler *et al*., 1995, Nashed *et al*., 2003; Van Soest, 1996; Yu *et al*., 1999).

MATERIALS AND METHODS

Materials

The basic material for investigations was made by potato starch Superior type produced by the Food Industry Plant 'PEPEES' S.A. in Łomża, Poland. To make comparative studies there were used: wheat starch type Excelsior MB manufactured by AVEBE b.a. in the Netherlands and corn starch type Cargill 2000 produced by Hanseland B.V. in the Netherlands. Among the numerous useful materials mentioned in the professional literature, applied as plasticizers or additions improving the quality of the materials obtained, the most popular proved to be glycerol of 99% purity and it was used in the tests, being added in the amount of 15-30% of starch dry mass.

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Blend preparation

All the starch types were blended in a standard bakery kneading pan and made 20 kg of sample material; while mixing, the glycerol was added. The obtained mixture was stored for 24 h in air tight polyethylene bags at room temperature to make the whole sample material homogeneous, to facilitate penetration of additions into starch granules, and to prevent moisture absorption.

Extrusion cooking

A modified version of single screw extrusion-cooker type TS-45 (Z.M.Ch. Metalchem, Gliwice, Poland) was used to produce thermoplastic starch. The extruder was fitted with a new plastifying system (barrel and screw) of L/D = 16/1 as well as with an additional cooling system of the final barrel part (Fig. 1) (Wójtowicz, 2003). The extruder head was also modified as it was fitted out with a brass die with 3 openings of 1.5 mm diameter and 20 mm depth. The extruder was equipped with a high-speed cutter for chopping the product to granulate of fixed, small dimensions (Mitrus, 2005).

Fig. 1. Modified single screw extruder TS-45.

Scanning electron microscopy

Granulate microstructure was analysed in the scanning electron microscope type JEOL JSM 5200 with accelerating voltage of 10 kV. Microstructure of the cross-section and the surface of the granulate was examined at magnification ratios from 300 to 1500 times.

To avoid destruction of samples by the electron beam, the samples of 2-3 mm size were stuck to metal disks with silver paste and then gold sputtered in the vacuum sublimator type JEOL JEE 400.

RESULTS

The surface structure of TPS granulate directly after processing depended to a great extent on a starch type used. In the case of potato starch application there is reported a gradual smoothing of granulate surface together with glycerol content growth (Fig. 2a, b, and c). Owing to great viscosity caused by glycerol migration, granulate surface containing 30% of this plasticizer got defects due to granule stickiness. The material obtained from potato starch exhibited a relatively smooth structure with visible creases of irregular size and broadened contours of gelatinised swollen starch clusters (Mitrus, 2004).

In the case of corn starch with 20% glycerol content there was observed a smoother surface with smaller creases, without clear starch fractions marked (Fig. 2d). For granulate manufactured from wheat starch (Fig. 2e), the surface of most uniform structure was noted. In the case of this material there was visible a parallel configuration of long polymer chains that attributed to grooved character of the surface (Mitrus, 2004). A similar fibrous structure was reported by Soral-Śmietana *et al*. (1998) analysing a wheat starch structure heated at the temperature of 121°C in the presence of water.

Analysing the photos of cross-section of the potato TPS granulate (Fig. 3), similar conclusions can be made as in the case of surface, *ie* with glycerol percentage growth in material blend, the homogeneity of material internal structure rises. In granulate containing 20% of glycerol there are visible clusters of starch grains with free volume implying non-uniformity of material. Having increased glycerol content up to 25% there is recorded further flowing of starchy structures inducing smoothing and uniformity of the whole mass. There are also noticed irregular shapes of gelatinised starch granules. Further increase of plasticizer amount up to 30% resulted in the development of compact, gelatinised inner structure of granulates where few single starch granules appeared. In Fig. 3c some free volumes are the residues of steam bubbles formed during the extrusion cooking process (Mitrus, 2004).

TPS material obtained from corn and wheat starch demonstrated a spongy structure with numerous pores along

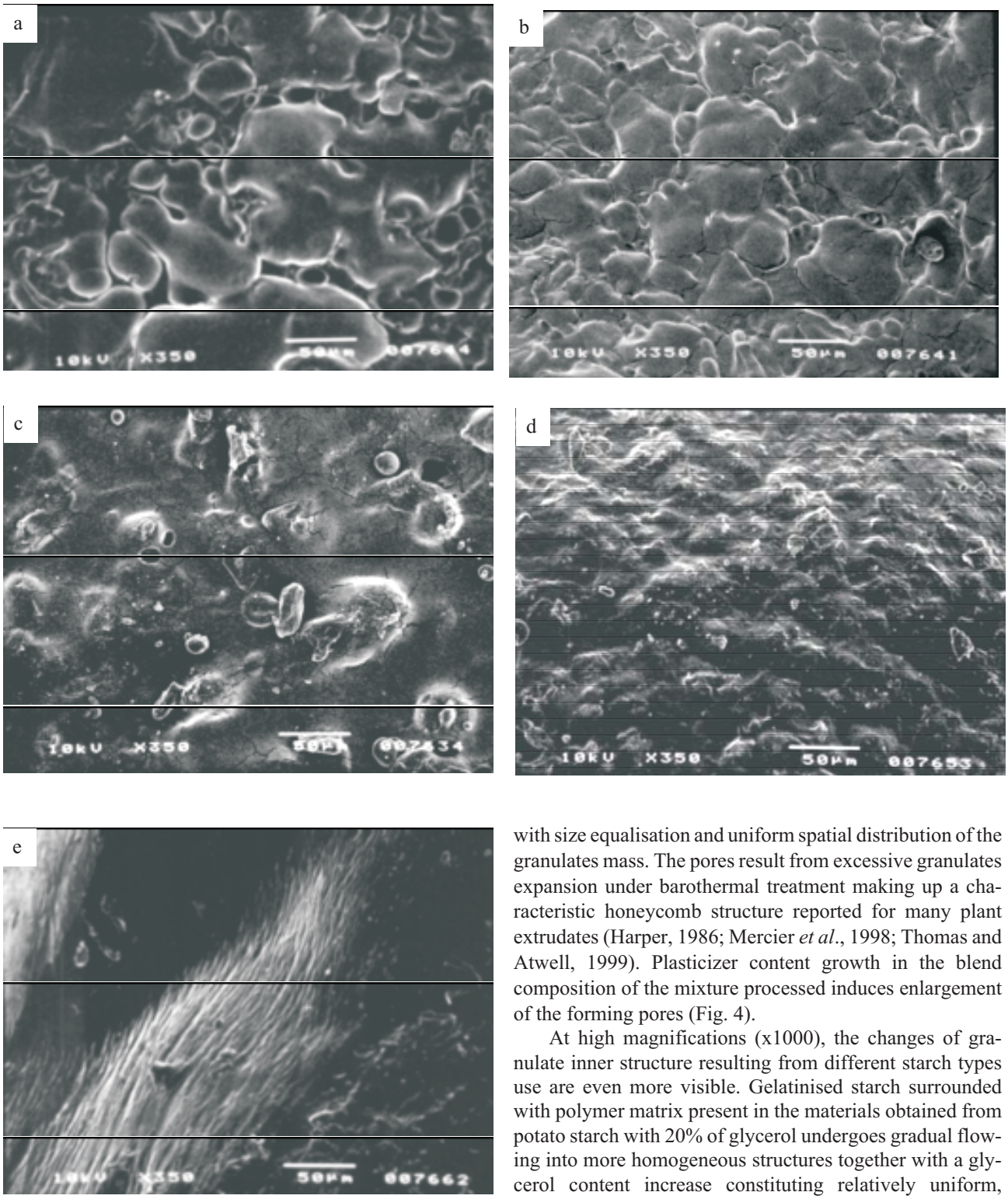
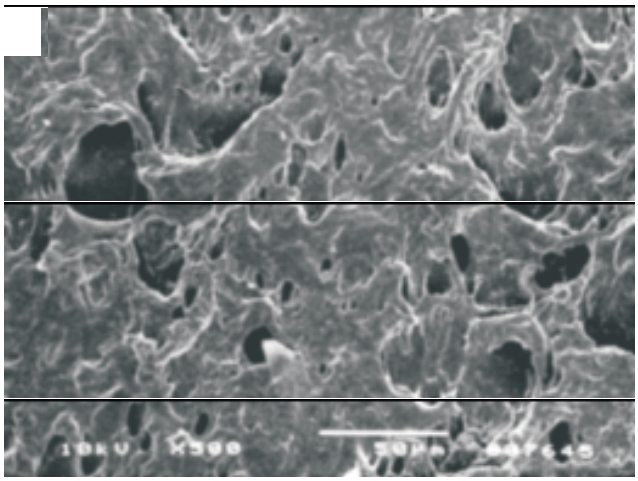


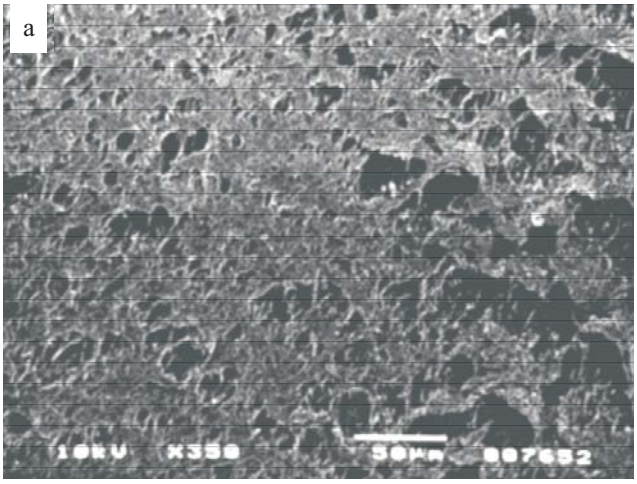
Fig. 2. Surface of TPS granulate produced with differing glycerol content, magnification x350: a) potato starch with 20% of glycerol, b) potato starch, 25% of glycerol, c) potato starch, 30% of glycerol, d) corn starch, 20% of glycerol, e) wheat starch, 20% of glycerol.

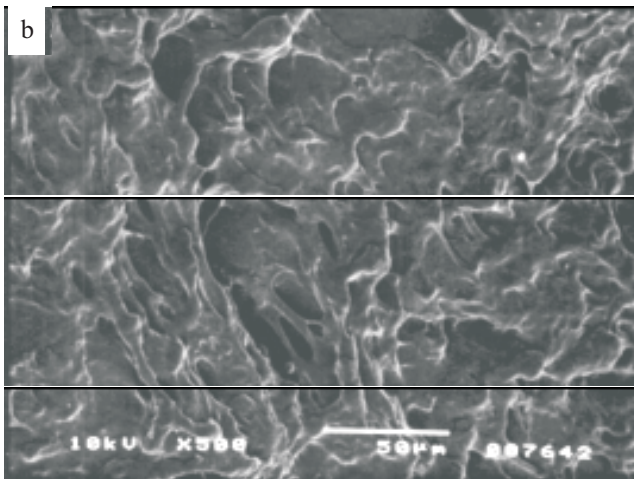
with size equalisation and uniform spatial distribution of the granulates mass. The pores result from excessive granulates expansion under barothermal treatment making up a characteristic honeycomb structure reported for many plant extrudates (Harper, 1986; Mercier *et al*., 1998; Thomas and Atwell, 1999). Plasticizer content growth in the blend composition of the mixture processed induces enlargement of the forming pores (Fig. 4).

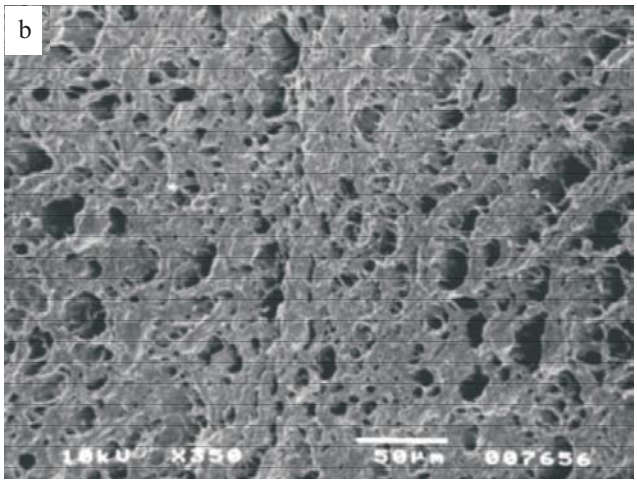
At high magnifications (x1000), the changes of granulate inner structure resulting from different starch types use are even more visible. Gelatinised starch surrounded with polymer matrix present in the materials obtained from potato starch with 20% of glycerol undergoes gradual flowing into more homogeneous structures together with a glycerol content increase constituting relatively uniform, compact mass at 30% plasticizer presence (Mitrus, 2004).

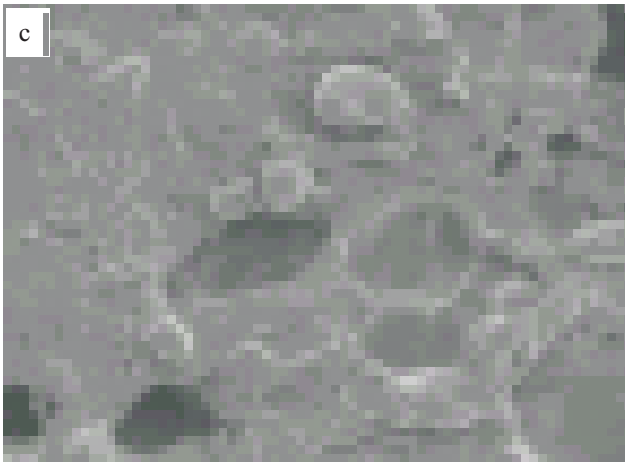
In case of materials obtained from corn and wheat starch there is clearly marked formation of greater pores following glycerol content growth from 20 to 25%. The relatively dense material structure reminds of the honeycomb structure to a greater extent (Mitrus, 2004).











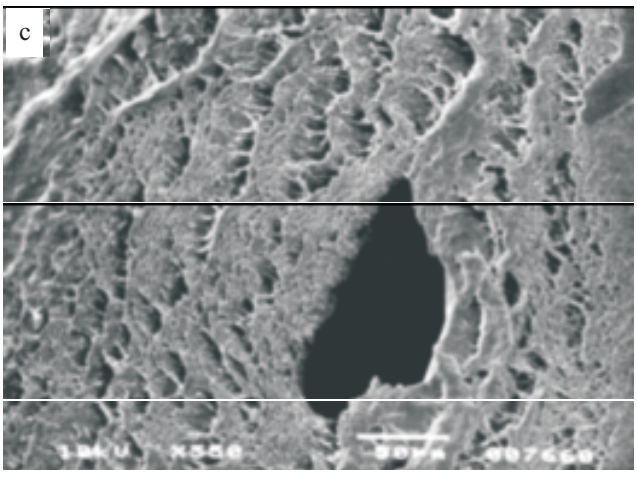


Fig. 3. Cross-section of potato TPS granulate developed with varied levels of glycerol content, magnification x500: a) 20% of glycerol, b) 25% of glycerol, c) 30% of glycerol.

Fig. 4. Inner structure of granulates from corn and wheat starch with varied levels of glycerol content, magnification x350: a) corn starch, 20% of glycerol, b) corn starch, 25% of glycerol, c) wheat starch, 20% of glycerol.

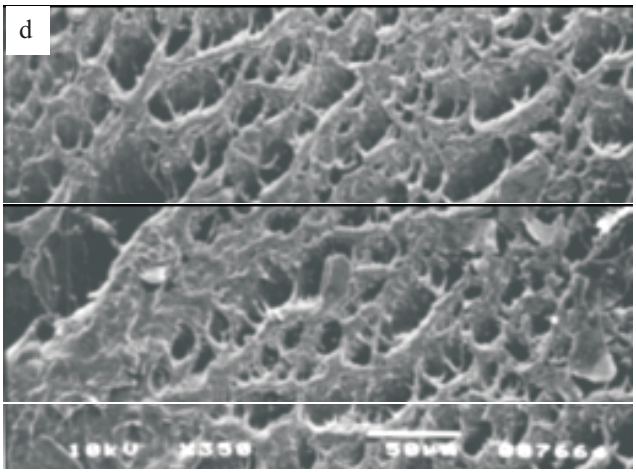


Fig. 4. Continuation. Inner structure of granulates from corn and wheat starch with varied levels of glycerol content, magnification x350: d) wheat starch, 25% of glycerol.

CONCLUSIONS

1. The studies on extrudate microstructure with scanning electron microscope confirmed the differentiated structure of TPS subject to material composition of the processed mixtures.

2. The materials produced from potato starch had uniform and compact structure and their structure quality improved with increasing glycerol percentage.

3. The materials from corn and wheat starch showed structure similar to honeycomb, rather unfavourable in this case.

4. Honeycomb structure of this materials causes higher water absorption and changes in glass transition temperature and in the mechanical properties.

5. The structure of those materials indicates a necessity of observing the technological procedure very strictly at the biopolymer extrusion cooking, and of maintaining appropriate parameters of barothermal treatment for particular material.

6. Testing of structural changes occurred during extrusion can be helpful in evaluation of functional behaviour of TPS processed.

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