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Note

Physical properties of thermoplastic starches

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A b s t r a c t. Results of thermoplastic starch (TPS) physical properties investigations are presented. The research showed significant influence of the addition of glycerol on changes in the value of TPS glass transition temperature as well as on its mechanical properties. Higher content of glycerol content in the processed blends caused a decrease of Young modulus measured in TPS granulates. The highest storage modulus value was obtained for the blend of potato starch and 25% of glycerol, while the lowest for maize starch material mixed with the same quantity of glycerol.

K e y w o r d s: thermoplastic starch, extrusion-cooking, glass transition temperature, physical properties

INTRODUCTION

The environmental impact of persistent plastic wastes is raising a general global concern, and disposal methods are limited. Incineration may generate toxic air pollution, satisfactory landfill sites are limited, and recycling methods of commingled wastes are expensive and often energy intensive. Also, the petroleum resources are finite and are becoming limited. It will be important to find durable plastic substitutes, especially in short-term packaging and disposable applications. The continuously growing concern of the public for the problem has stimulated research interest in biodegradable polymers as alternatives to conventional non-degradable polymers such as polyethylene and polystyrene *etc*. In recent years, many biodegradable materials have been developed for packaging applications (Baillie, 2004; Smith, 2005). One of these materials is a thermoplastic starch (TPS). Starch, after mixing with a plasticizer which lowers its glass transition temperature, under the influence of shearing forces and high temperature creates a continuous polymer phase. In this way, TPS can be processed with conventional technologies for synthetic plastics (Avérous *et al*., 2001; Mościcki *et al*., 2007; Shamekh *et al*., 2002; Soest, 1996; Tábi and Kovács, 2007).

Application of thermoplastic starch is possible in a large number of products like protective foam, compostable garbage bags, agricultural film, plant pots for seedlings, controlled release agents, seed protection, and in single-use packaging, as films, containers or bag closures. From the point of view of product technology the products should have certain properties. The material should form an amorphous and (preferably) transparent thermoplastic mass with a melting temperature below 100°C to avoid evaporation of traces of water during shaping, it should have a low glass transition temperature to avoid brittleness at low temperatures because of application in refrigerated environments, and it should be biodegradable with a controlled hydrophobicity. Finally, it has to be competing with traditional plastics in terms of mechanical properties, processability and price. Unfortunately, thermoplastic starch is generally water soluble, and its properties are sensitive to moisture content. Various synthetic polymers, like poly(vinyl alcohol) or polycaprolactone, have been blended with unmodified starches to produce products with increased water resistance (Baillie, 2004; Ge *et al*., 2000; Smith, 2005).

Impact of glycerol content on glass transition temperature and mechanical properties of TPS produced from 3 different type of starch was the main target of this research.

MATERIALS AND METHODS

The basic material for the investigations was potato starch type Superior (24% amylose), produced by the Food Industry Plant 'PEPEES' S.A. in Łomża (Poland). Materials used for comparative studies were wheat starch type Excelsior MB (24% amylose, according to producer), manufactured by AVEBE B.V. in the Netherlands, and corn starch type Cargill (26% amylose, according to producer)

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produced by Hanseland B.V., the Netherlands. The moisture content of the potato starch was 15.5, 14.2% for wheat starch and 14.4% for corn starch. The protein content in the starchy raw material was approximately 0.3% (according to producer). Glycerol (98.5% purity), originated from the Chemical Plant 'ODCZYNNIKI' Ltd in Lublin (Poland), was used as a plasticizer, being added at the amount of 15-30% of starch dry mass.

All the starch types were blended in a standard bakery kneading pan and made 20 kg of sample material, with the glycerol being added while mixing. 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.

A modified version of a single screw extrusion-cooker type TS-45 (ZMCh 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 an additional cooling system of the final barrel part. The extruder head was also modified, as it was fitted 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. The extruder was operated according to the following conditions: barrel temperature 85-100°C, screw speed 80 r.p.m. Measurements of the glass transition temperatures were performed using a Perkin Elmer DSC 7 apparatus. The thermoplastic starch specimens of 7-10 mg mass were heated from 25 to 180°C at a rate of 10°C min^{-1} and then cooled at the same rate to 25°C to be finally reheated to 180°C. The measurements were carried out in 3 replications. The results of measurements of some samples were inconclusive. In order to confirm and to clarify the obtained results the tests were repeated in a DSC 2920 modulated DSC TA Instruments. The samples were heated from 0°C up to 150°C at the rate 1°C min^{-1} and then cooled at the same rate to 0°C. The measurements were carried out in 3 replications. That technique is often used in such cases (Graaf, 1996; Soest, 1996). The study of mechanical properties of thermoplastic starch was carried out on the Instron 4200 model in the compression test. The device was fitted with a 5 kN head. The head moved at a speed of 50 mm min^{-1}. The maximum compression strength was measured during granules compression in the way of 2 mm. From the obtained results, deformation, stress and Young modulus were calculated. The measurements were carried out in 10 replications. The statistical evaluation of the observed differences was carried out with the variance analysis test (statistical software SAS 9.1.3) at significance level of α=0.05, while means differentiates were performed by the Duncan range test.

The investigations of visco-elastic properties of thermoplastic starch were carried out with the Rheometrics RSA II Solids Analyzer. Granules of TPS were pressed at a temperature of 140°C under pressure of 3 MPa for 5 min in order to obtain samples with dimensions of 22x5.2x1.4 mm. These samples were subjected to the action of sinusoidal strain with amplitude of 0.02% and a frequency of 1 Hz. During the study, samples ware heated at a rate of 2°C min^{-1} in the range of 25 to 135°C. The strength with which the sample corresponds to the applied stress was measured. The results were converted by a computer program to storage modulus E', loss modulus E'' and tan δ=E''/E'.

RESULTS AND DISCUSSION

One of the major problems connected with starchy material is its brittleness. This results from a relatively high glass transition temperature (T_g) (Graff *et al.*, 2003). The T_g is a very important parameter for determining the mechanical properties. The type of plasticizer used in the production of TPS has a significant impact on the value of glass transition temperature. Myllärinen *et al.* (2002) confirmed that the T_g of amylose and amylopectin can be equal to the ambient temperature when the water content is 21%, however at the same glycerol level the T_g can be still as high as 93°C. It can be concluded that glycerol is a less effective plasticizer than water. On the basis of computations they claim that in order to lower the T_g value to the ambient temperature 35% glycerol should be applied.

Our researches have shown a significant influence of the addition of glycerol on changes in the value of glass transition temperature of thermoplastic starch. In the case of TPS obtained from potato starch it was observed that with an increase in the glycerol content the glass transition temperature decreased. The highest T_g was 132°C for 15% glycerol, and it decreased almost linearly to 18°C at a glycerol level of 30% (Mitrus, 2005).

Graff *et al.* (2003) found that starch from different sources, like waxy maize, wheat, potato and pea starch, behave differently when extruded with glycerol. When the amylose/amylopectin ratio increased, a decrease in T_g was found. For pea, wheat, potato and waxy maize starch (without plasticiser) the T_g are 75, 143, 152 and 158°C, respectively. This leads to the contention that products with higher percentages of amylose are more flexible.

Our investigations proved that irrespective of the starch type applied, the T_g of TPS produced decreased with an increase of glycerol content in material mixture (Fig. 1). In the case of mixtures with 20% of glycerol, the lowest T_g was recorded for the materials obtained from potato starch, while the highest for those from wheat starch. For the materials containing 25% of glycerol the lowest T_g was noted for potato starch and the highest for corn starch. According to Yuryev *et al.* (1995) and Graff *et al.* (2003), products containing a higher amount of amylose have lower T_g's than materials with less amylose. The lower molar mass of amylose and its lack of branches results in a greater free volume of starch so that (parts of) the chains can move more easily.

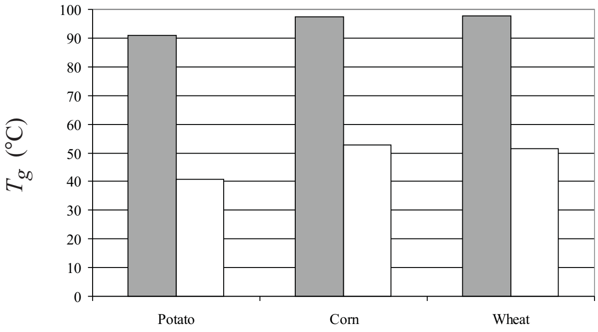

Fig. 1. Glass transition temperature (average) of TPS produced from different starch types (■ 20% glycerol, □ 25% glycerol).

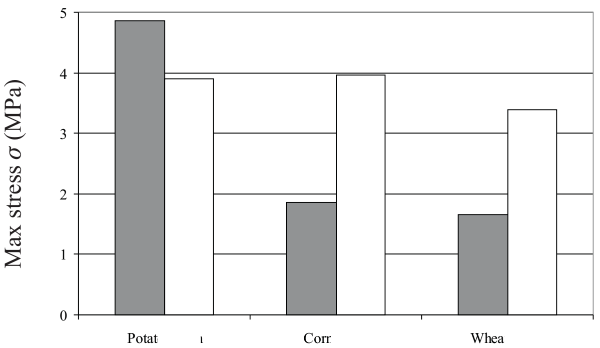

Fig. 2. Impact of glycerol percentage on maximum stress of granulates at compression for various starch types. Explanations as in Fig. 1.

This explains the lower T_g of amylose compared to the branched amylopectin, so materials with a higher amylose weight fraction will give a lower T_g. Our investigations shows that glass transition temperature value of thermoplastic starch depends on the botanical source of starch. It is clear that, for starches with almost the same amylose content, the T_g decreases in the order of corn > wheat > potato. This behaviour can be connected with the type of starch crystallinity (Bogracheva *et al.*, 2002, Zobel, 1988).

The heat capacity changes (Δc_p) were difficult to determine and the calculated values were small, varying from 0.012 to 0.047 $Jg^{-1}K^{-1}$. The value of Δc_p decreased with glycerol content in TPS. Similar dependences were obtained by Forssell *et al.* (1997) and Myllärinen *et al.* (2002).

On the basis of the research it was found that with the increase in the percentage of glycerol the maximal stress formed at TPS granulate compression decreases (Mitrus, 2007). The excessive expansion and pore presence abates TPS tensile strength. Investigating granulates from corn and wheat starch with 20% glycerol content, very low values of stress were detected. The presence of pores had a significant impact on tensile strength, weakening the obtained extrudate. In the case of trials with 25% of glycerol, the highest tensile strength values were recorded for the materials from potato starch, while the lowest for those containing wheat starch (Fig. 2). According to Lourdin *et al.* (1995), the mechanical properties of thermoplastic starch depends not only on amylose/amylopectin ratio but also on the botanical origin of starch. This behaviour is attributable to the molecular weight of amylose in starch.

Materials produced from wheat and corn starches behave like solid foams due to the presence of pores. In this case maximal stress increases with increase in the percentage of glycerol. This is related to the change in the bulk density of the foams. Materials with higher glycerol content had higher bulk density because of lower content of pores. Typically, a power-law relationship is observed between compressive strength, σ, and foam density, ρ ($\sigma \sim \rho^n$). Denser foams tend to have thicker cell walls and, hence, resist deformation better than lower density foams with thinner cell walls (Lourdin *et al.*, 1995, Yogaraj *et al.*, 2006).

The studies on the mechanical properties of TPS granulate exhibited that with glycerol content increase in material blend there was a decrease of Young modulus, *E*, recorded. Glycerol percentage growth by 15% brings about a drop of Young modulus by over 50%. In the case of granulate from corn and wheat starch containing 20% of glycerol, the low values of Young modulus were obtained due to the presence of pores in the extrudate. It means that pores stiffened the material to a great extent and at the same time decreased its elasticity. Coming back to the samples with 25% of glycerol, the highest Young modulus values were recorded for potato TPS, while the lowest for wheat and corn thermoplastic starch. Analysis of variance of the mechanical properties using Duncan test confirmed significant differences (α=0.05) attributable to glycerol content when the maximal stress was measured in potato TPS. The results of the analysis of variance for corn and wheat TPS were distorted due to the excessive expansion of the extrudates.

The investigations on visco-elastic properties of thermoplastic starch granulates produced from different types of starch containing 20% of glycerol showed that at nearly the whole range of temperatures studied potato TPS demonstrated the highest values of E', whereas corn TPS the lowest. The research results of visco-elastic properties of TPS produced from different types of starch with 25% glycerol content indicated that the highest storage modulus values were obtained for potato starch, while the lowest for maize starch material (Fig. 3). Consequently, the highest internal friction tan values were recorded for maize starch, the lowest for potato starch. The highest elasticity difference of the produced materials occurred at temperatures approaching the room temperature and in the case of potato starch E' was five times as high as corn starch. With increasing temperature, the difference in the storage modulus values between the materials decreased, yet potato starch granulates still kept elasticity higher by at least 30% than those obtained from corn starch. The shape of curves illustrating the changes of storage modulus reported for all the TPS types with 25% glycerol content indicate the formation of cross-linking in

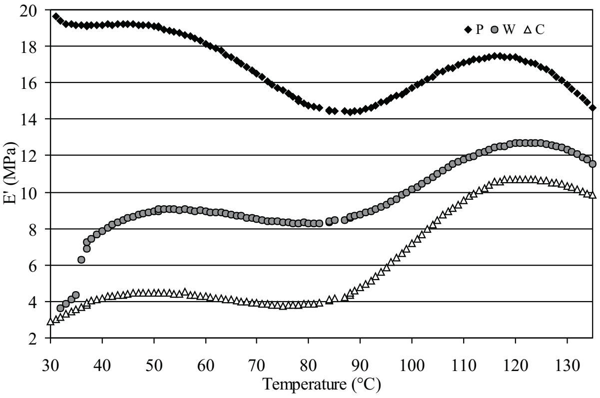

Fig. 3. Changes in storage modulus of TPS granulate obtained from different starch types with 25% glycerol content (P – potato starch, W – wheat starch, C – corn starch).

extrudate structure. The storage modulus for all materials displayed a plateau typical of semi-crystalline polymers. Similar changes in storage modulus were detected by Da Róz *et al.* (2006) for corn starch with addition of different plasticizers. As in the raw material composition there do not appear any factors inducing such behaviour, it is starch re-crystallization which is most likely to take place.

CONCLUSIONS

1. The applied range of thermal treatment of potato starch running from 85-100°C and extruder screw speed of 80 r.p.m. allowed getting a good quality product *ie* a product without any visible damage, cracks, pores or steam bubbles. Granulate produced from wheat and corn starch blends with glycerol addition at the same conditions did not meet the required quality parameters to the full due to excessive expansion. In this case, a more efficient cooling system or an extruder with greater L/D ratio should be used.

2. Analysing the measurements of TPS glass transition temperatures there was observed a direct influence of the plasticizer presence in a blend on its value. The lowest temperature, around 18°C, was recorded at 30% glycerol content in the mixture. Glass transition temperature value of thermoplastic starch depends on the botanical source of starch.

3. Glycerol content growth in mixture brought about a decrease of TPS tensile strength and Young modulus values. Materials produced from wheat and corn starches behave like solid foams due to the presence of pores. In this case maximal stress increases with increase of glycerol content, with resultant increase in foam density.

4. Out of the three basic extrudates, the best visco-elastic properties were shown for granulate from potato starch. It was found that a glycerol percentage increase in the mixture caused a drop of TPS elasticity. In the case of granulates produced from starchy mixtures with 25% glycerol content the possibility of cross-linking was supposed, which can be related with the starch re-crystallization process.

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