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Glass transition temperature of thermoplastic starches

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Abstract. Thermoplastic starch was produced by mixing potato starch and glycerol in a single screw extruder. The glass transition temperatures of the materials obtained were measured by differential scanning calorimetry (DSC). Both the influence of extruder parameters and material parameters, such as moisture and glycerol content and amyloses/amylopectine ratio were investigated. Repeated extrusion cycles affect the glass transition temperature only to a very small extent.

Keywords: thermoplastic starch, glass transition temperature, differential scanning calorimetry, extrusion

INTRODUCTION

Over the last decade the increasing amount of refuse and the reduced space for landfill have given rise to an interest in new easily biodegradable materials. Several scientific centers performed research on a special group of natural materials – starch thermoplastics (De Graaf *et al*., 2003; Myllärinen *et al*., 2002; Shamekh *et al*., 2002). To obtain these plastics, starch should be perfectly mixed with a proper quantity of plasticizer to make the material flow at temperatures below the decomposition temperature. In this way it is possible to obtain a product in which the polysaccharides form a continuous, polymeric entangled phase. This form of starch is called thermoplastic starch (TPS) (Van Soest, 1996).

Using the polymer technology designed for synthetic polymers, the starch plastics can be manufactured as a supplement to the existing synthetic products. However, thermoplastic starch is not widely used as a commercial product because of some drawbacks. One of the major problems connected with starchy material is its brittleness. This results from a relatively high glass transition temperature (T_g) (De Graaf *et al*., 2003). The T_g is a very important parameter for determining the mechanical properties.

For dry starch the T_g reaches 227°C, whereas with 13% water content a T_g decrease to 56°C is recorded. The glass transition temperature of gelatinized wheat starch with 22% moisture approximates the ambient temperature (Myllärinen *et al*., 2002).

The effect of starch plasticized with water addition has been studied frequently just like the comparison of various techniques for glass transition temperature measurement. The method of differential scanning calorimetry (DSC), which is most often used, showed a T_g that is 10 to 30°C higher than that measured by the nuclear magnetic resonance (NMR) (Myllärinen *et al*., 2002). The analysis of water influence on the T_g of amylose and amylopectin proved that branched amylopectin had a slightly lower glass transition temperature than linear amylose.

On the basis of the researches published and of practical observations it can concluded that starch plastics containing water are brittle under the condition of natural surroundings (Bizot *et al*., 1997).

The three component systems obtained when starch is plasticized with water and glycerol behave in a more complex way. In research on the influence of glycerol and other plasticizers on the T_g of potato starch it was found that glycerol plasticizes starch in conformity with Couchman`s model that is valid for polymer-solvent combinations (Lourdin *et al*., 1997). Studies on barley starch plasticized with water and glycerol showed that phase separation is possible and two calorimetric glass transition temperatures can be obtained (Forssell *et al*., 1997). Moreover, basing on the dielectric-mechanical analysis, the researches where amylose and maltose were plasticized with glycerol showed an increase of the phase separation process together with a decrease of glycerol content below 25%. Only recently, in a study on the behaviour of such two-component systems as

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amylose-glycerol, it was found that these systems are composed of phases rich in amylose and phases abounding with glycerol (Moates *et al.*, 2001).

Determination of the glass transition temperature of thermoplastic starch using DSC showed so called ‘higher’ and ‘lower’ T_g values or both simultaneously. The higher and lower T_g’s are generally found in mixtures containing less than 30% glycerol. This behaviour is likely to be connected with the formation of an area rich in starch and an area rich in glycerol that causes partial phase separation. The higher and lower transitions seem to be characteristics for starch plasticized with glycerol and are independent of the processing method (Forssell *et al.*, 1997).

The tests show that both amylose and amylopectin had a higher T_g`s in the absence of glycerol. The estimates demonstrated that the T_g of dry amylose and amylopectin is 227°C, while Bizot *et al.* (1997) assessed the dry starch T_g as 332°C. What is more, to lower the T_g of potato starch closer to the ambient temperature, 0.21 g of water should be used for 1g of starch (Bizot *et al.*, 1997; Myllärinen *et al.*, 2002).

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.

MATERIALS AND METHODS

Materials

Potato starch (Superior Standard) was purchased at the producer, *ie* Food Industry Company ‘PEPEES’Stock Company in Łomża (Poland), Potato Company ‘Iława S.A.’ in Iława (Poland) and AVEBE Company (the Netherlands).

Glycerol (98.5% purity) originated from the Chemical Plant ‘Odczynniki’ Ltd in Lublin.

Determination of amylose in starch

Potentiometric titration with a Pt-electrode and a calomel reference electrode was used. A starch sample with a mass m = 200 mg was dissolved in 10 ml NaOH (5 M) . The solution was diluted with water to 100 ml exact. 25 ml of the solution was pipetted to an Erlenmeyer flask, 2 drops of methyl red indicator solution were added and neutralized with HCl (1 M) till it was just red. 1 ml HCl (1 M), 1 ml KI (1 M) and 28 ml NaCl (0.5 M) were added to this solution. The solution was titrated with KIO_3 (0.0050 M = t). 1 ml KIO_3 solution corresponds to 0.635 mg I_2. The potential drop, measured by the potentiometric system (volume V), determined the equivalence point and the amylose content can be calculated from (Bates *et al.*, 1943):

$$W\text{ (amylose)} = (V\,t\,127\times4\times5\times1000)\,m^{-1}\ (\text{mg g}^{-1}).$$

Blend preparation

Starch and glycerol blends were prepared with a ribbon blender type MPP-100, produced by FMR Rogóźno. The glycerol content varied between 15 and 30 wt %. First, the blends were damped up to the maximum moisture content of 20% based on dry mass. The mixtures were stored in plastic bags for 24 h to intensify glycerin penetration into starch granules. Immediately before the extrusion the blends were remixed (Mitrus, 2004; Mitrus, 2006).

Granulate extrusion

The extrusion process was conducted at the Department of Process Engineering at the University of Agriculture, Lublin, in a modified single-screw extruder with a screw diameter of 45 mm and a length to diameter ratio of 16/1 (TS-45 produced by ZMCh Metalchem in Gliwice) (Fig. 1). Two dies were used, *ie* one with a single opening of 3 mm diameter and one with a triple opening of 1.5 mm diameter. The extrudate was chopped to granulate of around 5 mm length with a high-speed cutter. From this material films were pressed for testing. The extrusion temperatures ranged from 75 to 140°C, and the screw rotations from 60 to 100 r.p.m. (Mitrus, 2006).

Fig. 1. Single screw extruder TS – 45.

Differential scanning calorimetry

The measurements of the glass transition temperatures were performed using a Perkin Elmer DSC 7 (Fig. 2) at the Department of Chemical Engineering at the Groningen University in the Netherlands. 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.

To confirm the obtained results the tests were repeated in a DSC 2920 modulated DSC TA Instruments (Fig. 3). The samples were heated from 0°C up to 150°C at the rate of 1°C min^{-1} and then cooled at the same rate to 0°C.

RESULTS

Figure 4 shows the influence of the blend moisture on the T_g of potato starch placticized with 20 and 25% of glycerol. The results show that, in the measured range, moisture of the mixture had only a minimal influence on the T_g of thermoplastic starch. At 20% glycerol content, a slight decrease of T_g was observed with an increase of moisture. This is consistent with the scientific reports published in literature. In the case of 25% glycerol level a reverse tendency was noticeable. Together with blend moisture growth, the T_g value went up as well. However, in those two cases, T_g value changes were very small and the blend moisture, in measured range, had no significant influence on T_g changes (Mitrus, 2004).

Fig. 2. Perkin Elmer DSC 7 apparatus.

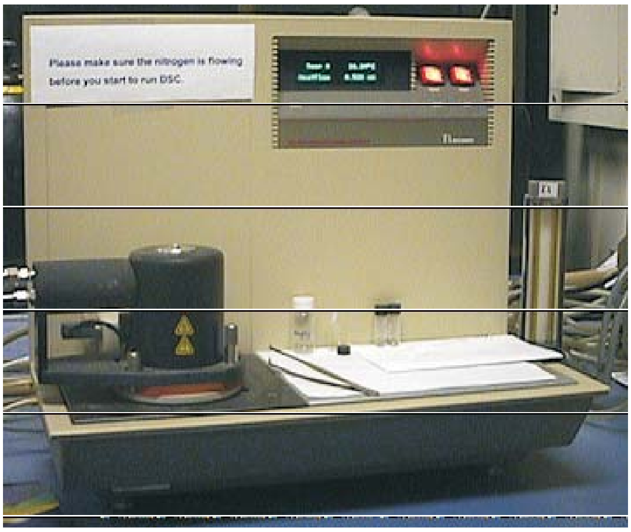

Fig. 3. Apparatus DSC 2920 modulated DSC TA Instruments.

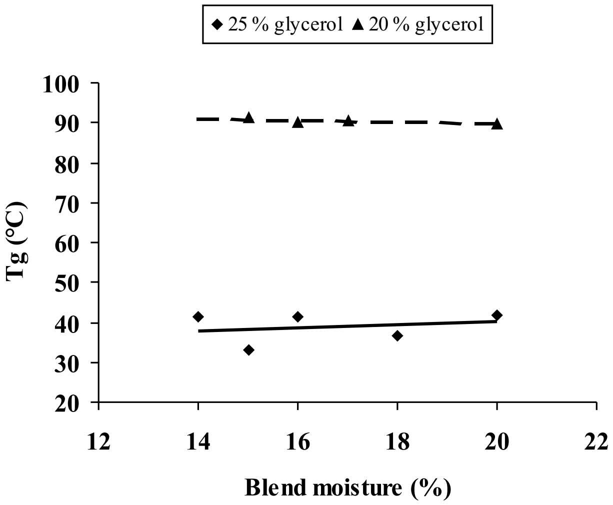

Fig. 4. Influence of blend moisture on the T_g of thermoplastic starch.

Figure 5 shows the changes of the glass transition temperature with changing glycerol content. The highest T_g was 132.7°C for 15% of glycerol, and it decreased almost linearly to 18.1°C at a glycerol level of 30%. The moisture content of all the mixtures was 15% (Mitrus, 2004).

Figure 6 illustrates the influence of repeated extrusion on the T_g of thermoplastic starch for the mixtures with 25% of glycerol. A slight drop of a T_g can be noted when reprocessing thermoplastic starch. The maximum decrease of the glass transition temperature did not exceed 0.15°C. However, it should be mentioned that to avoid thermal destructurization the repeated extrusion experiments were performed at slightly lower temperatures (by around 10°C) (Mitrus, 2004).

Figure 7 illustrates the influence of amylose content on the T_g of thermoplastic starch for the mixtures with 20 % of glycerol. A slight drop of T_g with amylose content increase was noticed. It is possible that the differences in amylose content in the investigated starches were too low to observe significant differences in T_g of thermoplastic starch (Mitrus, 2004).

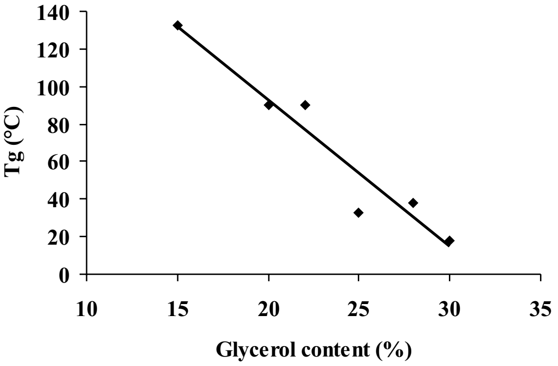

Fig. 5. Influence of the glycerol content on the T_g of thermoplastic starch.

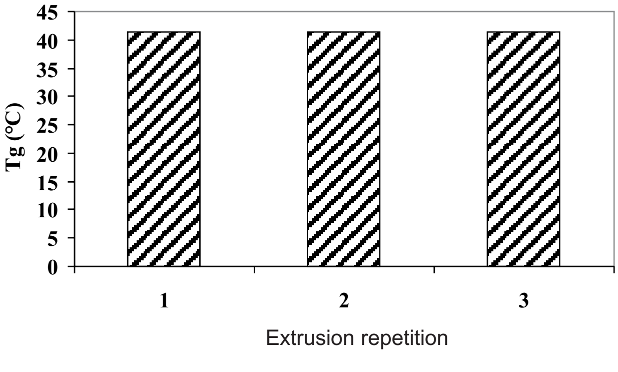

Fig. 6. Influence of multiple extrusions on the T_g of thermoplastic starch.

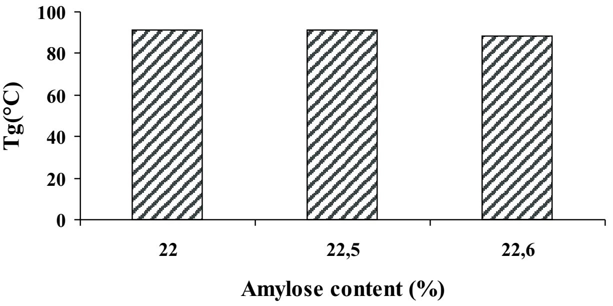

Fig. 7. Influence of amylose content on the T_g for samples with 20% of glycerol.

CONCLUSIONS

1. The changes in the glass transition temperature of thermoplastic starch were only minimally affected by the moisture content of the mixture. It was found that, in the measured range, the blend moisture had no significant influence on T_g changes.

2. When the glycerol content increased from 15 to 30%, the glass transition temperature decreased almost linearly from 132 to 18°C at moisture content of 15%.

3. Multiple extrusion affected the T_g of potato starch only to a very small degree. A slight downward trend of a T_g was recorded after multiple re-extrusion, but this did not exceed 0.15°C.

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