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INVESTIGATION AND DEVELOPMENT OF THE PROCESSABILITY OF BIODEGRADABLE POLYMER

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Abstract: *Due to the environmental friendly consciousness, the ever higher amount of waste and the shrinking oil reserves, there is a growing demand for using biodegradable materials in certain (short-life) applications. Starch is a promising biodegradable polymer; it is in abundance on Earth. It can be converted into thermoplastic starch (TPS) by extrusion. TPS can be processed further into products by ordinary thermoplastic processing methods like injection moulding or compression moulding. The natural moisture content of native starch and the processing aid additives have significant effects on the convertibility of native starch into TPS and on the properties of TPS. In our study the effect of moisture content of maize starch, and that of added sliding agent content on the convertibility of starch into TPS was investigated.*

Keywords: *biodegradable material, thermoplastic starch, moisture content, granule disruption level*

1. INTRODUCTION

Shrinking oil reserves and ecological concerns such as litter problem has created an urgent need to develop new biodegradable materials that could replace commodity, non-biodegradable plastics [1]. Many different biopolymers exist already that can be obtained from either renewable, agricultural, or non-renewable, petroleum-based resources, but most of them are quite costly [2]. Starch is a particularly interesting material because it is inexpensive and can be transformed into a thermoplastic material named thermoplastic starch (TPS) by destructuring and plasticization of native starch granules, and therefore can be processed further by common technologies such as extrusion or injection moulding.

Starch is a polysaccharide which occurs in abundance in different plants like wheat, maize, potato, rice, etc. It has a granular structure which can vary in size and in composition depending on its source. Starch granules are built-up of two different polymers, the linear amylose and the branched amylopectin, both of which contain only a single type of carbohydrate, glucose. Amylopectin can form crystalline structure, while amylose is an amorphous material.

Thermoplastic starch (TPS) can be obtained by processing native, granular starch at high temperatures under shear with the aid of plasticizers such as water, glycerol or urea. During processing the semicrystalline structure, as present in the granule, is lost and the molecules are partially depolymerised [3]. Processing usually takes place in an extruder, where the granules are disintegrated. Thermoplastic starch can be processed like synthetic plastics by extrusion and injection moulding. Some products made from starch are already established on the market, such as composting bags, agricultural foils and other disposable products. It can also have even technical (engineering) or medical applications. Fig.1. represents the life-cycle of a biopolymer product made from starch.

Fig.1. Life-cycle of starch based biopolymer

Though TPS is a relatively cheap material, and its great advantage is its rapid biodegradation, it has some serious drawbacks as well. To begin with, TPS products have very low mechanical properties and high shrinkage values (when injection moulded) as compared to their synthetic counterparts. Another major disadvantage is the material's hidrophilicity, which prevents its widespread use. While in contact with water strach products swell rapidly and start to dissolve. Finally, even if stored at constant humidity and temperature, the mechanical properties of TPS products change with time. This is the so-called ageing or retrogradiation. While ageing, the crystallinity of starch increases, which results in higher stress at elongation, higher tensile modulus and lower strain values [4, 5]. Many authors have reported these characteristics. As any marketable material must have comparable properties with today's common polymeric materials at an equivalent cost, in recent years many attempts have been taken to overcome these problems. Several authors have investigated the behaviour of natural fibre (flax, cellulose, jute, ramie) reinforced, starch-based composites [2, 6-8]. Reinforcement made the material better in all of the above mentioned aspects. It reduced hidrophilicity, the ageing-effect and shrinkage values, while improved mechanical properties. Many authors have reported their results on TPS associated with other biodegradable polymers, usually with poly(lactic-acid) or aliphatic polyesthers such as poly(ε-caprolactone) [9-12]. These starch-based blends also performed better then pure TPS regarding hidrophilicity or shrinkage, but there was no effect on the time-dependent behaviour. Most recently, researchers are trying to improve the properties of starch-based materials with the help of cross-linking [13-15]. Though this way the ageing rates and the hydrophilic character of TPS can be reduced, the material gets much more expensive.

A vast amount of experiments were made to get to know the possibilities residing in thermoplastic starch better, but most of these researches focused only on the composition of the material itself, not taking into account the processing parameters that could affect its properties. Substantial parameters are the moisture content of starch and the disintegration level of starch granules in TPS. This paper focuses on the monitoring of moisture content of starch through major processing steps, and the effect of the magnesium-stearate as a sliding agent on the disintegration level of starch granules.

2. EXPERIMENTAL

The processing of starch usually begins with its drying to decrease its moisture content and make it even in every segment of the material. Maize starch (which was used in the experiments) naturally contains about 13,3 wt% moisture which is dependent on its source and the relative humidity the starch was stored at. After the drying process, certain amount of plasticizer like glycerol or water is added so it can be extruded. Even when the starch is dried, water is often added as a plasticizer, because it is one of the most effective plasticizers of starch. In this case the drying process is used to make the moisture content of starch uniform. In an extruder, as a result of plasticizers, shearing, and temperature, the starch granules disintegrate and form a homogenous melt, the so-called thermoplastic starch (TPS). After extrusion it is recommended to equilibrate the moisture content of TPS by conditioning it under certain relative humidity. After equilibration, TPS can be processed further by common thermoplastic processing technologies.

In the first part of our experiments, the natural moisture content of maize starch was investigated while drying. A type Heraeus UT 6 dryer was used in the experiment. The starch was kept in the dryer at 85°C in various layer thicknesses (30-60-90 mm), and the weight loss was measured for determining the moisture content. The effect of the different drying temperatures (85-120-130 °C) was also analysed.

Secondly, the previously dried starch was used to convert it into TPS using a Brabender Plasti-Corder PL 2100 double screw extruder (diameter of the screw is 25 mm, L/D=20). Table.1. contains main extrusion parameters.

Extrusion parameter	Value
Revolutions per minute (rpm)	8 [1/min]
Temperature of the 1. heated zone (feed zone)	90 [°C]
Temperature of the 2. heated zone	130 [°C]
Temperature of the 3. heated zone	120 [°C]
Temperature of the 4. heated zone (die)	90 [°C]

Table.1. Main extrusion parameters

The starch-glycerol-water ratio was 70-16-14 wt%. Different amounts (1-2-3 wt%) of sliding agent (Magnesium-stearate) was used, and the native starch granule disruption was analysed by a scanning electron microscope as a function of the added sliding agent content.

Thirdly, TPS made beforehand was conditioned at different relative humidities to examine the change in water content of TPS before further processing (injection moulding). The influence of different magnesium-stearate content on the moisture content of TPS while conditioning was also investigated. The conditioning chamber used in this experiment was a Memmert HCP 153. The relative humidity was 25% and 50%, and the temperature was 40 °C.

3. RESULTS

According to the literature, maize starch contains 13,3 wt% moisture. 20g starch samples were kept in the dryer at 85-120-130 °C to study the desorption character. The final weight loss of dried starch represents the moisture content of the original (undried) starch (Fig.2.).

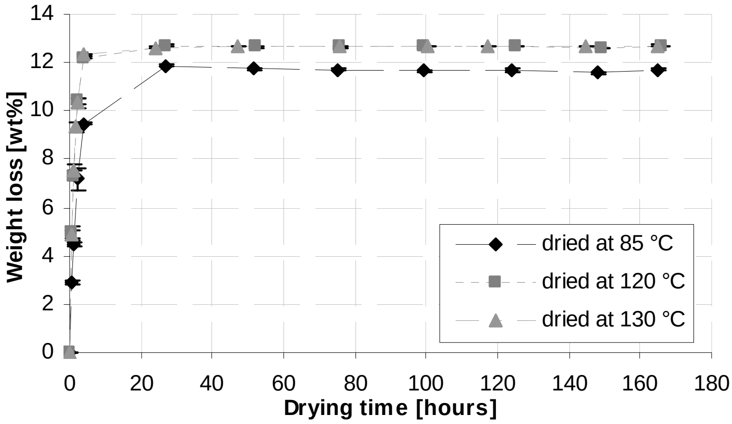

Fig.2. Starch desorption character at different temperatures

It can be observed that the higher the drying temperature was, the more moisture vaporized, and the quicker it vaporized from the samples. One can see that a certain final weight loss belongs to each drying temperature. This final weight loss cannot be increased by increasing the drying time, but only the drying temperature. These results are only valid for the 20g starch samples.

When a bigger amount of starch is dried at the same temperature (85 °C), the weight loss is dependent on the thickness of the starch layer (Fig.3.).

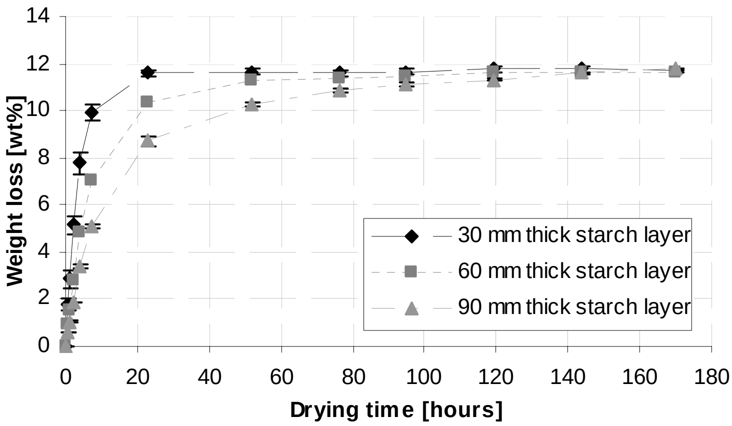

Fig.3. Starch desorption character at different starch layer thicknesses (at 85 °C)

As it can be seen, the thickness of the starch layer had only effect on the speed of moisture vaporization, but not on the final weight loss. After that native starch was dried at

85 °C for a certain time to get uniform moisture content, TPS was made using 70 wt% starch, 16 wt% glycerol, 14 wt% water, and different amounts of magnesium-stearate. This mixture was extrudated and pelletized. The pellets were investigated by scanning electron microscope (Fig.4.-6.).

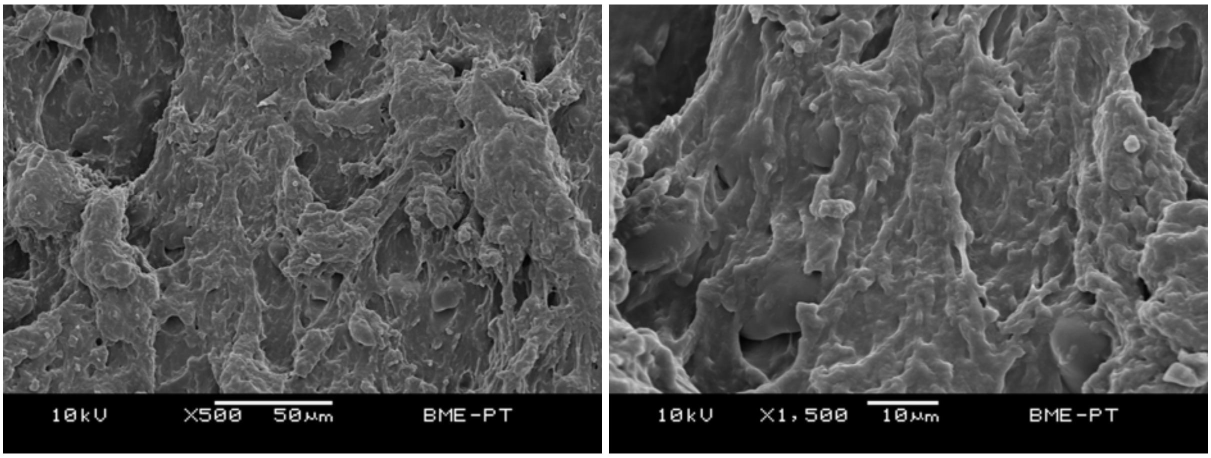

Fig.4. TPS with 1wt% magnesium-stearate content

A homogeneous thermoplastic starch material can be observed on the images taken of the 1 wt% magnesium-stearate content TPS (Fig.4.). The number of the residual starch granules is low.

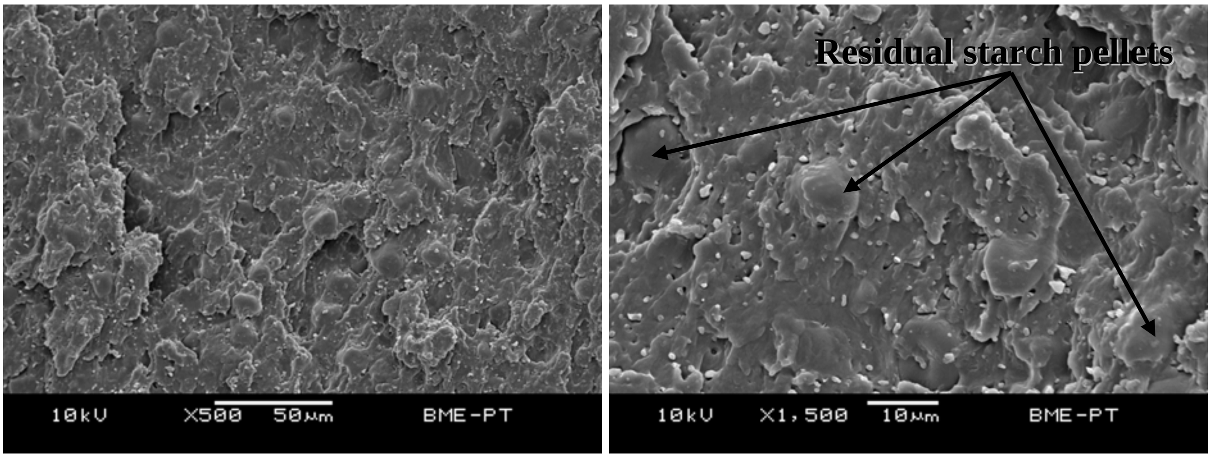

Fig.5. TPS with 2wt% magnesium-stearate content

In the images taken from the 2 wt% magnesium-stearate content TPS, not only the magnesium-stearate granules (white pellets, 1-3 µm) can be found, but because of the high sliding agent content, residual starch granules (2-100 µm) also appear (Fig.5.).

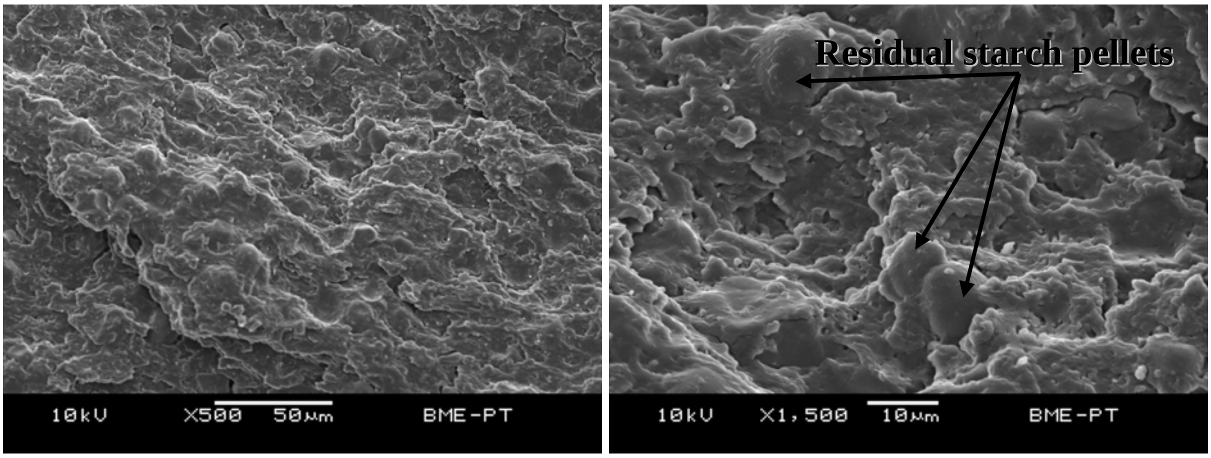

Fig.6. TPS with 3wt% magnesium-stearate content

In the TPS containing 3 wt% magnesium-stearate, the amount of residual starch granules and sliding agent granules can be found was the highest (Fig.6.). The higher the added sliding agent content was, the more residual starch granules can be found in the TPS, because no high shearing rates were present in the extruder that would disrupt the starch granules. In our experiments, the usage of 1 wt% of magnesium-stearate proved to be the optimum regarding the low residual starch granule content and also the further processing. After TPS was made, it was conditioned for 1 week at 25% (Fig.7.) and 50% (Fig.8.) relative humidity (at 40 °C), and the weight loss of the TPS pellets was registered.

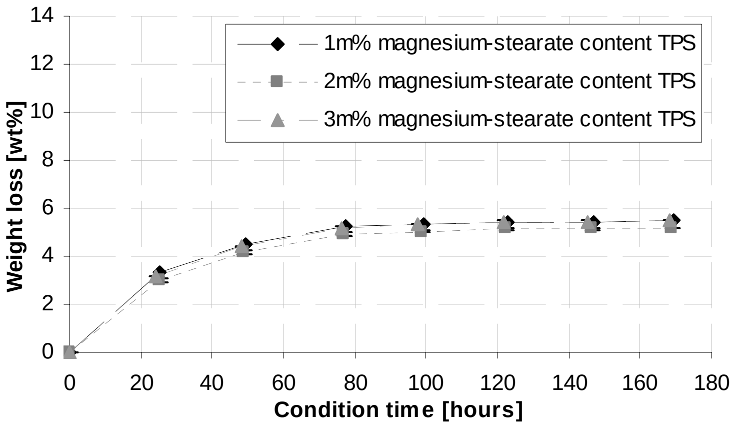

Fig.7. Conditioning of different magnesium-stearate content TPS at 50% relative humidity

It can be seen that the amount of magnesium-stearate had no effect on the desorption character of TPS. All of the studied materials lost about 5,5 wt% weight due to the vaporization. Consequently, the theoretical water content of the TPS is 8,5 wt%. The result is simply calculated from the added water content (14 wt%) and the weight loss (5,5 wt%). 80 hours was required for moisture equilibrium.

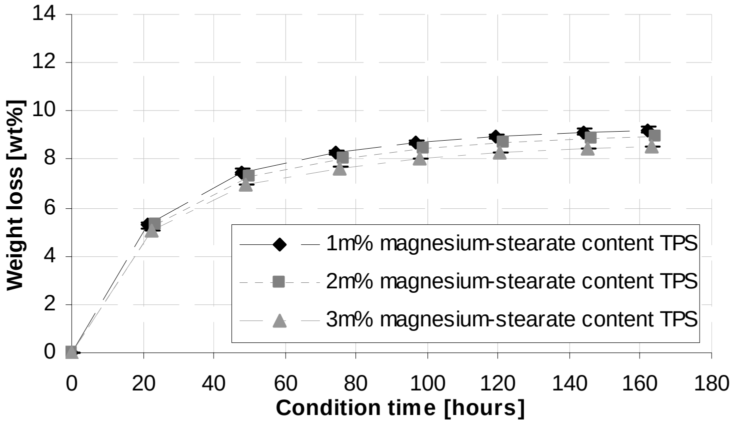

Fig.8. Conditioning of different magnesium-stearate content TPS at 25% relative humidity

The weight loss of the TPS conditioned at 25 % relative humidity was about 8,9 wt%, so the theoretical water content of the material is 5,1 wt%. In this case, the conditioning time required for moisture equilibrium was about 140 hours, and the magnesium-stearate had no significant effect on the vaporization character, similarly to the 50% relative humidity case.

The final moisture content of TPS is crucial regarding the further processing, especially when it is injection moulded. The moisture content acts as a plasticizer, so the quantity must be kept between certain values for successful processing. When the moisture content is too high the TPS begins to foam, but when it is too low, the screw cannot plasticize the material. For example, in our case, when a 70-16-14 starch-glycerol-water ratio TPS is made, the water content is to be kept between 4-8 wt%.

4. CONCLUSION

In our study the convertibility of starch into thermoplastic starch (TPS) was investigated in the aspect of the moisture content of maize starch and the added sliding agent (magnesium-stearate). The moisture content was trailed through the different processing steps (drying prior to extrusion, after extrusion while conditioning). The effects of different drying temperatures and different starch layer thicknesses were analysed on the vaporization character of starch prior to extrusion. The scanning electron microscope images revealed the changes in starch granule disruption levels in the TPS as the effect of different amount of magnesium-stearate. Finally, the effect of relative humidity on the moisture content of TPS was investigated. The moisture content of TPS and the starch granule disruption level has enormous influence on the further processing.

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