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THERMOPLASTIC STARCH AS PACKAGING MATERIAL

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Abstract. Attempts to reduce net CO_2 emission and to increase the use of sustainable materials pose great challenges at the interface of chemical engineering and agricultural engineering. One of the products involved is thermoplastic starch that can partly substitute synthetic plastics, amongst others in packaging. In a first step a semi product is produced by mixing starch and a polyol in a cooking-extrusion process. The material obtained can than be used in other polymer processes, like extrusion, film blowing and injection moulding. Films with thicknesses of 200 µm can be achieved if gelatinisation is good and moisture content constant. In injection moulding shape stability can be retained by a judicious combination of moisture content and process temperature. The final objects can reach a strength comparable to commercial packaging plastics, like polystyrene.
A problem that still exist is the sensitivity of the material to ambient moisture, both at short terms during production as at long times during usage. These problems increase with increasing surface to volume ratio of the final product like, for instance, films. Technologies where the material is coated or where the lubricant is immobilized have to be investigated to expand the use. From economical point of view it can be expected that the costs of the extra extrusion step during manufacturing of the semi-product can easily be covered by the price difference between starch and synthetic packaging plastics, like polyethylene, polypropylene or polystyrene.

Key words: thermoplastic starch, extrusion, film blowing, injection moulding

INTRODUCTION

In chemical engineering clear trends are emerging to substitute, where possible, petrochemistry based products by agriculture based products. Examples of this substitution are the development of starch based packaging material, synthesis of bio-diesel and the use of modified starches and proteins as basis chemicals [Leszczyński 2001]. The ad-

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vantages concerning sustainability are clear, starch is a renewable resource, the CO_2 cycle closes, and, if wanted, biodegradability can be build into the final products. However, the most important consideration for the public acceptance of this type of sustainable products will be the comparison of properties and price with traditional products.

Thermoplastic starches, consisting of starch and polyoles can be used for disposable products and they form an interesting and economically attractive alternative for traditional packaging plastics. Because of the economic viability the production of these thermoplastic starches should preferably be restricted to of-the-shelf chemicals, which is especially the case if the products are used for single use packaging. From production point of view the properties should be such that standard unit operations can be used without the necessity to develop new equipment and new production processes [Leszczyński 1999].

From thermoplastic starch different products can be formed by classical polymer processes. Researches have been taken in this field by both: University of Groningen (NL) and Lublin Agricultural University (PL). Extrusion in a twin screw extruder provided good profiles, a film blowing process is used for producing flexible films, and 3D objects with or without biodegradable fibres as reinforcement can be made by injection moulding [de Graff at all 2003, Janssen at all 2003, Mitrus at all 2003, Mitrus 2004].

THE PRODUCT AND PROCESS

Starch consists of poly-α-glucan as a linear (amylosis) or a branched (amylopectine) polymer. The advantages of the polymer, apart from its natural origin and biodegradability, are that it has flexible chains with strong intramolecular bonds; the disadvantages are its brittleness and a relatively fast retrogradation. These disadvantages can be overcome by substituting part of the water in the starch by a highly viscous lubricant with low volatility. Addition of such a lubricant decreases the friction between the molecules and therefore lowers the glass transition temperature, which marks the transition between brittle and ductile. From the two most promising polyoles, sorbitol and glycerol, the last one appeared to give by far the best results [Burgt at all 1996]. As starch, potato starch was chosen. If desired the starch can be modified to add particular properties to the final product. Styrenisation, for instance, increases the hydrophobicity and leads to a material with improved miscibility with a-polar synthetic plastics [Janssen at all 1997].

Application of thermoplastic starch is possible in a large number of products like protection 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 100^0C 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 cooled surroundings and it should be bio-degradable with a controlled hydrophobicity. Finally it has to be competing with traditional plastics in mechanical properties, processability and price.

THE SEMI-PRODUCT

The production of objects from thermoplastic starches can be achieved in a two step process. In the first step a semi-product is made. Starch and glycerol have to be premixed and, if necessary, the moisture content must be adjusted. Extra water improves the extrudability and decreases degradation of the molecules during extrusion, to much water decreases the viscosity and prevents complete gelatinisation. In this first processing step the starch is gelatinised and thoroughly mixed with glycerol in an extruder after which the material can be pelletized to form thermoplastic starch pellets as semi-product. These pellets are fed to the second step, being extrusion, film blowing or injection moulding.

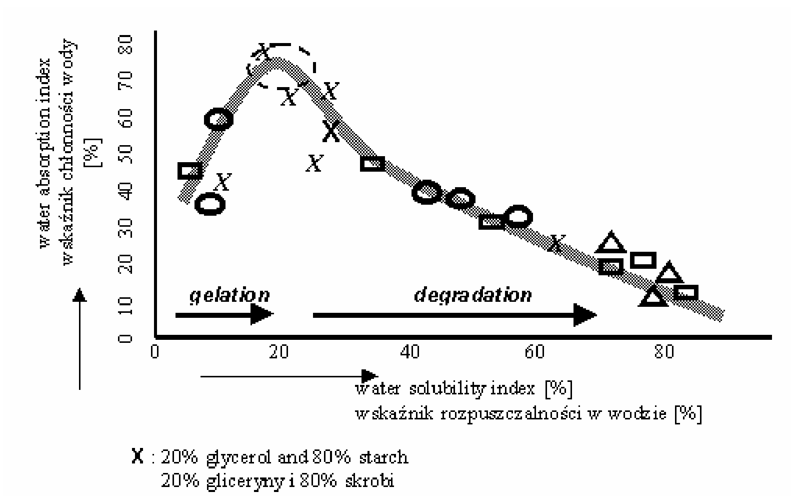

Fig. 1. Water absorption index versus water solubility index after the first process step for different glycerol content and different extruder settings
Rys. 1. Zmiany wskaźnika chłonności wody oraz wskaźnika rozpuszczalności w wodzie po pierwszym przetworzeniu dla różnych udziałów gliceryny i parametrów procesu ekstruzji

The quality of the semi-product can easily be judged from the water absorption and the water solubility coefficient. The water solubility signifies the amount of starch that really dissolves in water and it is a measure for the degradation of the starch molecules. The water absorption coefficient is a measure for the water retention and it is related to the gelatinisation and (to a lesser extend) to the degradation of the starch. In general terms it can be stated that an optimal thermoplastic starch product can be achieved if the water solubility index is low and the water absorption index is high. In figure 1 these two indices are plotted for a large number of different experiments with different glycerol content and water content. Several experiments with a starch to glycerol ratio of 80/20 and 6% water added clearly fulfil the requirement of high water absorption and low water solubility. This composition was selected as standard recipe and during further testing after the second production step samples made from the semi-product with the standard recipe gave the best mechanical properties.

FILMS

For the production of thermoplastic starch films a classical single screw film blowing line with a modified screw design was used. In this line an annulus is extruded and before solidification this annulus is blown up to a bubble with desired dimensions. If the same configuration is used as in film blowing of synthetic plastics the bubble stability can be poor due to regions with poorly gelatinised or ungelatinised starch. Both poor gelatinisation and temperature differences introduce viscosity differences in the bubble and the resulting irregular stretching induces bubble breaking. The use of a mixing head at the end of the screw improves the process considerably. It ensures better gelatinisation and good macro-mixing, therefore stabilizing the film bubble and making it possible to achieve thinner films. It is expected that further improvement of the homogeneity will make it possible to achieve smaller film thicknesses resulting in material savings. A second problem that is not encountered in synthetic film production is the sensitivity to moisture. The surface to volume ratio of the film during blowing is very large. The influence of changes in ambient moisture content can be estimated from the Fourier number for mass transfer. At measured film thicknesses (d) of 200 μm and an estimated diffusion coefficient of water in the plastic starch matrix (D) of 10^{-10} m^2s^{-1} the reaction time equals:

$$Fo = \frac{Dt}{d^2} = 0{,}1 \qquad \rightarrow \qquad t \approx 40\,s \tag{1}$$

This means that at solidification times of longer than roughly 40 seconds the moisture content of the surrounding air is important for the stability of the process. Especially if smaller film thicknesses are achieved moisture stabilization will be necessary.

THREE DIMENSIONAL OBJECTS

Three dimensional objects are produced by injection moulding. The thermoplastic starch is continuously molten in an extruder and collected in a reservoir after which it is batch wise injected under high pressure into a cooled mould. Due to the flow into the mould the molecules will stretch and orient. During the solidification the molecules partly relax and the frozen in stresses can cause deformation of the objects after release from the mould.

Figure 2 shows an example of test strips, all coming from the same mould. If the material is injected under high temperatures the time for relaxation is sufficiently long and it is clearly visible that this results in good shape stability. The test strips produced are used to determine the mechanical properties. Figure 3 shows the tensile strength of the thermoplastic starch at changing starch to glycerol ratios and changing injection temperatures. Strengths up to 20 MPa can be reached which is comparable with commercially available polystyrene. This figure also illustrates the importance of a good recipe but surprisingly, the injection temperature in the second step has hardly any influence on the strength of the final product. An increase of the glycerol content from 20 to 22% leads to a five fold decrease of the tensile strength from 20 to 4%.

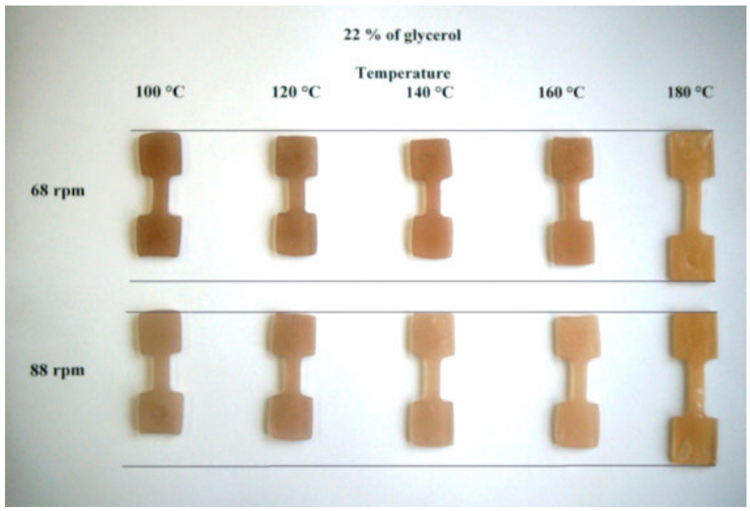

Fig. 2. Shrinkage after injection moulding at different operating conditions
Rys. 2. Skurcz próbek po wtrysku wysokociśnieniowym dla różnych warunków procesu

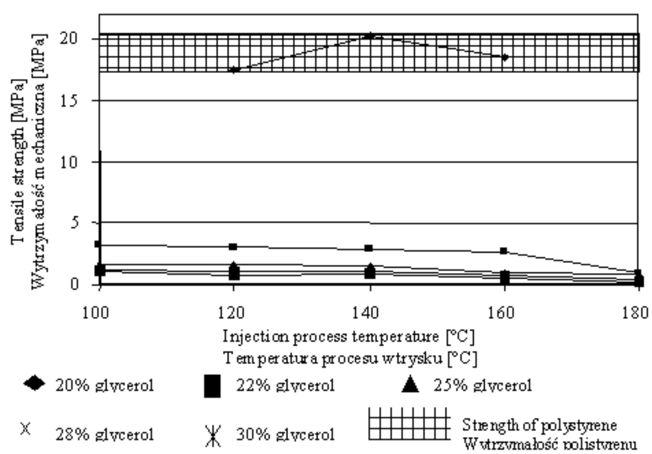

Fig. 3. Strength of injection moulded test samples from thermoplastic starch with different glycerol contents, produced at different injection temperatures
Rys. 3. Wytrzymałość próbek ze skrobi termoplastycznej z różnym udziale gliceryny uzyskanych metodą wtrysku wysokociśnieniowego przy zmiennych temperaturach wtrysku

The decrease of strength at increasing glycerol content has an important product technological implication. Although products with 20% glycerol are strong and flexible at room temperature they become brittle at lower temperatures, which restricts their use in applications in freezers. Increasing the glycerol content gives lower glass transition temperatures, resulting in non-brittleness at low temperatures, but also in a decreased strength. Addition of reinforcements in the form of cellulose or flax fibres increases the strength and can lead to an interesting extension of the use of thermoplastic starches but this needs further investigation.

CONCLUDING REMARKS

Starch is a natural polymer that has the potential to compete with various synthetic polymers. Disadvantages of using pure starch for packaging purposes are both the brittleness and the fast retrogradation. This can be avoided by using a high viscosity internal lubricant that increase the mobility and therefore facilitate the movement of the chain molecules. This lubricant should be hydrophilic and also possess a low vapour pressure to increase the shelf life of the starch plastic. If starches and polyoles are mixed and cooked a thermoplastic mass results that has properties alike synthetic plastics and, moreover, classic polymer processes like extrusion, film blowing and injection moulding can be used for shaping. The strength of this thermoplastic starch can be similar to the strength of polystyrene. A problem that still exist is the sensitivity of the material to ambient moisture, both at short terms during production as at long times during usage. These problems increase with increasing surface to volume ratio of the final product like, for instance, films. Technologies where the material is coated or where the lubricant is immobilized have to be investigated to expand the use. From economical point of view it can be expected that the costs of the extra extrusion step during manufacturing of the semi-product can easily be covered by the price difference between starch and synthetic packaging plastics, like polyethylene, polypropylene or polystyrene.

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SKROBIA TERMOPLASTYCZNA JAKO MATERIAŁ OPAKOWANIOWY

Streszczenie. Próby ograniczenia emisji CO_2 i zwiększenia zastosowania nowych materiałów stwarza okazję dla współzależności pomiędzy inżynierią chemiczną a inżynierią rolniczą. Jednym z efektów jej współdziałania jest skrobia termoplastyczna, która może częściowo zastąpić tworzywa syntetyczne, m.in. w opakowalnictwie. Na początku z mieszanki skrobi i plastyfikatora produkowany jest półprodukt techniką ekstruzji. Tak uzyskany materiał może być zastosowany w innych procesach polimerowych, jak wytłaczanie folii czy wtrysk wysokociśnieniowy. Przy zachowaniu odpowiedniego stopnia skleikowania skrobi i wilgotności można wyprodukować folię o grubości ok. 200 µm. W procesie wtrysku wysokociśnieniowego stabilność kształtu produktu można uzyskać przy zachowaniu odpowiednich temperatur procesu oraz wilgotności. Uzyskane produkty mogą osiągnąć wytrzymałość porównywalną z komercyjnymi opakowaniami plastikowymi, np. z polistyrenu.
Nadal istotnym problemem jest wrażliwość materiału na wilgotność powietrza, zarówno krótkookresowa podczas produkcji, jak i długookresowa podczas stosowania. Problem ten rośnie wraz ze wzrostem stosunku powierzchni do objętości gotowego wyrobu, jak na przykład folii. Technologie powlekania materiału lub dodawania środków natłuszczających musi być jeszcze zbadana przed wprowadzeniem do użytku. Z ekonomicznego punktu widzenia oczekiwać można, że koszt dodatkowego procesu ekstruzji podczas wytwarzania półproduktu (granulatu) może być z łatwością zminimalizowany przez różnicę pomiędzy ceną skrobi a opakowaniowym tworzywem sztucznym, jak polietylen, polipropylen lub polistyren.

Słowa kluczowe: skrobia termoplastyczna, ekstruzja, wytłaczanie, wtrysk wysokociśnieniowy

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