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Abstract. Nowadays as a result of the increasing environmental friendly consciousness and the decreasing oil reserves, natural origin based materials are developed. These materials are not only based on renewable, natural resources, but capable of biodegradation in compost. These biodegradable polymers (biopolymers) can be inserted into the nature's recycling process. One of the most important biopolymers is starch. Starch can be processed like a thermoplastic material by adding plasticizers, creating the so called thermoplastic starch. However the price of starch is rather low, it has certain drawbacks retarding its wide industrial usage. It is sensitive to moisture, disrupts in pure water, has low mechanical properties, and in time it ages. This ageing or time-dependent behavior was analyzed with injection molded tensile specimens. The shrinkage and mechanical properties of the specimens were determined as a function of ageing time. The fracture surface was analyzed by scanning electron microscope. The results of the measurements were compared with previous examinations.

Introduction

In developing countries, environmental pollution by synthetic polymers has assumed dangerous proportions [1]. Therefore, and because of the decreasing oil reserves, the demand on renewable resources has grown in recent years. Many attempts have been made to solve these problems through the everyday use of biodegradable polymers. These materials can degrade in biological environment by different microorganisms. Under appropriate conditions it is a relatively rapid process, and the degradation by-products do not have toxic or environmentally harmful residue.

Biodegradable polymers can be divided into three main groups. The first family contains agro-polymers, obtained from biomass by fractionation (e.g. polysaccharides, proteins, lipids). The second group includes polymers, obtained by fermentation from biomass (e.g. polyhydroxyalkanoate, polyhydroxybutyrate) or by synthesis of monomers obtained from biomass (e.g. polylactide). The third family "members" are totally synthesised by petrochemical process (e.g. polycaprolactone, polyglycolide, polyanhydride, polyesteramide) [2].

Biopolymers are polymers produced in nature during the growth cycles of organisms. Their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes [1]. Starch is a polysaccharide which occurs in different plants like wheat, maize, potato, rice, etc. This material is in abundance all over the world. Starch has a granular structure, which vary in size and in composition from plant to plant. It is a physical combination of a linear and a branched polymer (namely: amylose and amylopectin), but contains only a single type of carbohydrate, glucose. Amylopectin can form crystalline structure, while amylose is an amorphous material.

Starch can be processed into thermoplastic starch (TPS) under the action of both temperature and shearing stress [3]. Plasticizers, like glycerol, urea, polyethylene glycol, etc. or water have to be used while processing, because of the low decomposition temperature of the starch. Processing usually takes place in an extruder, where the granules are disintegrated. With this, biodegradable

products can be prepared by the well-known thermoplastic polymer processing techniques like injection molding, extrusion or compression molding. The products made from starch can be used as waste bags, disposable products or even as technical products or can have medical applications. Although starch has many advantages, like rapid biodegradation or cheapness, it has some drawbacks which retard its widespread usage as material for biodegradable products. These are the low mechanical properties, the high rates of hydrophilicity, swelling and shrinkage or the so-called ageing or retrogradiation. Many authors reported these behaviors of starch. While ageing, the crystallinity of starch increases, which results in higher stress at elongation and tensile modulus and in lower strain values [4, 5]. In contract with water, pure starch products easily swell and then simply dissolve. To overcome these disadvantages, a vast number of experiments were taken. Many authors reported the behavior of natural fiber reinforced starch materials [2, 6-8]. With the reinforcement, the mechanical properties of starch were improved significantly, while the ageing and the shrinkage values decreased. Many authors also reported the behavior of starch-based blends [9-12]. In these cases starch was associated with an other degradable polymer, usually with a linear aliphatic polyester, like poly(lactic-acid) or poly(ε-caprolactone). The blending also decreased the hydrophilic behavior and shrinkage, but it had no effect on the ageing properties. In recent years, the researchers concentrated on the cross-linking of starch [13-15]. With cross-linking, the ageing rates, and strong hydrophilic character of thermoplastic starch can be reduced, but thus the material gets more expensive.

This paper focuses on the long time retrogradiation (ageing) of a previously developed thermoplastic starch material [16]. The shrinkage, tensile, bending and impact strength properties of the injection molded specimens were measured as a function of the ageing time. SEM images were taken to analyze the changes in the material.

Experimental

Maize starch was used for thermoplastic starch production. According to the manufacturer, the amylopectin/amylose ratio was 75/25. The processing steps are as follows: The maize starch, glycerol and water were mixed in a mixing chamber. The weight ratio of the starch/glycerol/water was 70/16/14. 20 g glycerol-monostearate was added as a sliding agent for each kilogram of mixture to get a material suitable for injection molding. Prior extrusion and injection molding, the screw of the machines were cleaned with a special silicone based screw cleaner material (provided by Szilor Ltd., Hungary), insuring that no other thermoplastics remained in the barrel. This cleaning procedure has special importance because of the low processing temperature of TPS (see later).

The starch-glycerol-water mixture was weighted and introduced to a double screw extruder type Brabender Plasticorder PL 2100, equipped with a diameter 25 mm screw (Length/Diameter=20). Table 1. contains the main parameters for extrusion.

Table 1. Extrusion parameters

Extrusion parameter	Value
Rotational speed	8 [1/min]
Temperature of the 1. heated 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	90 [°C]

The 4. heated zone of the extruder represents the nozzle. After extrusion the TPS extrudate was pelletized, and stored at 50% relative humidity for 2 weeks. After the storage process, the pellets were injection molded with an Arburg 320C 600-250 injection molding machine equipped with a diameter 35 mm screw. Table 2. contains the main injection molding parameters.

Table 2. Injection molding parameters

Injection molding parameter	Value
Volume	44 [cm^3]
Injection rate	50 [cm^3/s]
Injection pressure	1500 [bar]
Switch-over point	12 [cm^3]
Holding pressure	800 [bar]
Holding time	20 [s]
Cooling time	15 [s]
Screw rotational speed	15 [m/min]
Decompression volume	5 [cm^3]
Decompression rate	5 [cm^3/s]
Temperature of the 1. heated zone	110 [°C]
Temperature of the 2. heated zone	115 [°C]
Temperature of the 3. heated zone	120 [°C]
Temperature of the 4. heated zone	125 [°C]
Temperature of the 5. heated zone	130 [°C]
Mold temperature	20 [°C]

The 5. heated zone of the injection molding machine represents the nozzle. Dumbbell test specimens were injection molded. The specimens were stored at 50% relative humidity and at 25 °C before testing. According to EN ISO standards, tensile (EN ISO 527-5), bending (EN ISO 178), Charpy impact tests (EN ISO 179-2), and shrinkage measurements (EN ISO 294-4) were performed at 24-72-168(1 week)-336(2 weeks)-504(3 weeks) hours after injection molding in order to determine the time-dependent behavior of the obtained TPS. A crosshead speed of 50 mm/min was used to determine the tensile properties, and a crosshead speed of 5 mm/min was used to determine the flexural properties. A 15 J pendulum was used for the impact test, but the impact angle was set to 90° to create an impact energy of 8,04 J. 8 samples were tested for each measurement.

Results and discussion

During the injection molding of TPS, a special phenomenon took place. Due to the high shear stress required to plasticize the TPS, the material was overheated, and its water content was volatilized, which prevented injection molding. This phenomenon was ceased by using the appropriate sliding agent content, and by controlling the water content of TPS granules. The processability of the TPS will be further researched in upcoming papers.

The effect of ageing on tensile stress and tensile modulus (Young's modulus) is plotted on Figure 1.
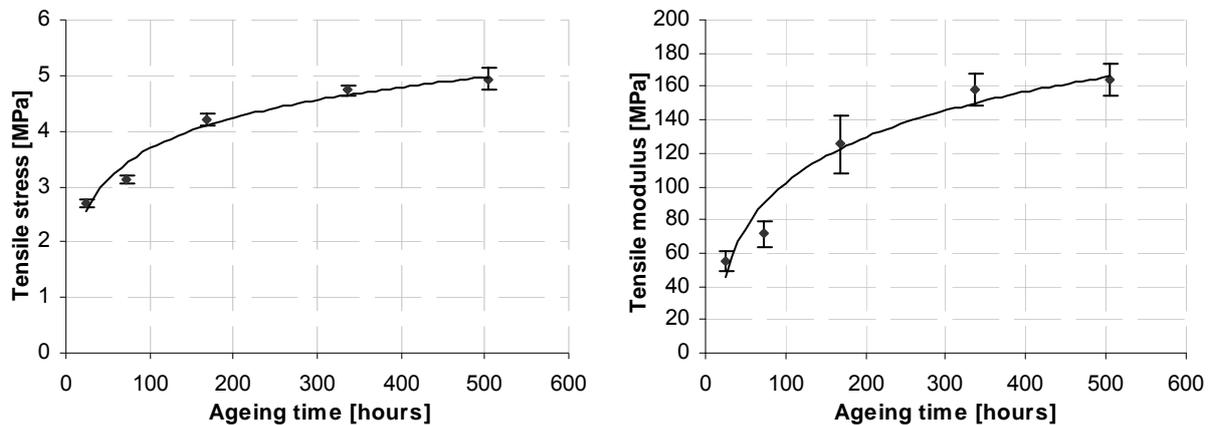
Figure 1. The effect of ageing time on the tensile stress (left) and tensile modulus (right)

In our previous work [16], the ageing effect was examined for 1 week with the same storage method (50% relative humidity, 25 °C). In that paper, a linear correlation was found between the ageing time and the tensile properties (both stress and modulus) during the first week of ageing. The analysis of this phenomenon was extended in order to support a reliable data. In case of higher ageing times, a logarithmic correlation was observed between the ageing time and tensile properties for the 24-504 hour time period. One explanation can be for this behavior that the tensile properties only raise for a certain value, after reaching this value, micro cracks appear in the material, causes the mechanical properties to drop instantly. After the appearance of cracks, the test specimens fall apart. This behavior represents the life-cycle of the TPS material. Our experiments clearly indicate that the time-dependent material behavior is not only affected by the storage method (ambient conditions, controlled conditions, storing in vacuum, etc.), but by the processing parameters as well. The strain of the TPS had a similar, logarithmic behavior in time as the tensile properties (Figure 2.).
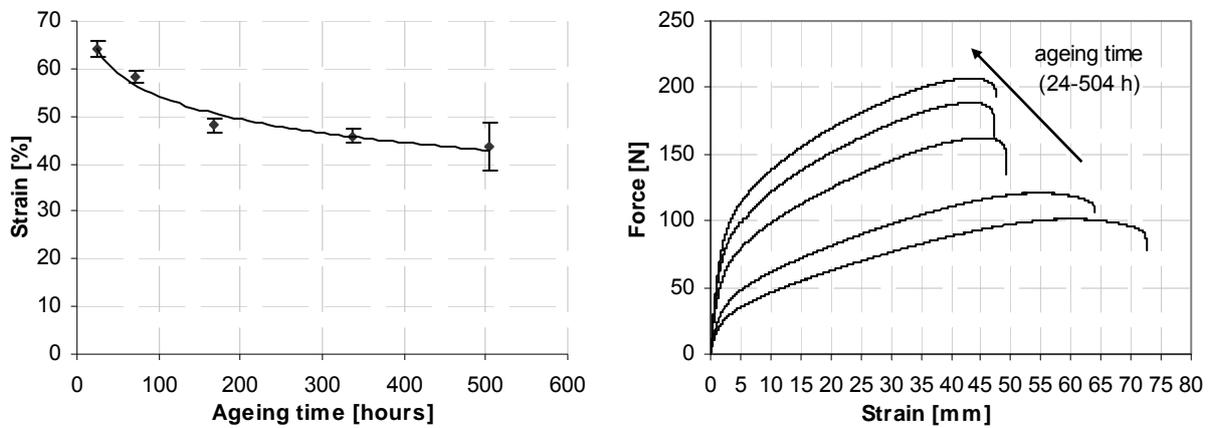
Figure 2. The effect of ageing time on the strain (left) and the changes in the tensile test diagrams (right)

The strain was found to also have a logarithmic correlation with ageing time, but in this case it decreases as ageing time increases for the 24-504 hour time period. The phenomenon of ageing can be observed also in the change of tensile test diagrams. As ageing occurs, the tensile stress and modulus increases while the strain decreases (Figure 2.). The results of the bending test can be inspected on Figure 3.
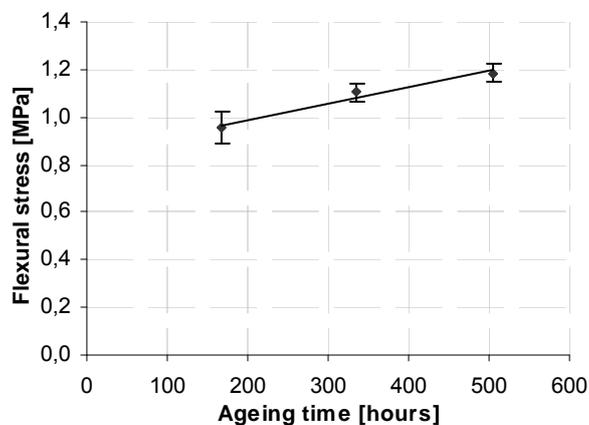
Figure 3. The effect of ageing time on the flexural stress

The flexural properties also increased in time. Due to the low mechanical properties of the specimens, the 24 and 72 hour measurements could not be evaluated. The specimens were so

flexible, that the required minimum load of the test machine was not reached, so thus the measurement could not be evaluated. Figure 4. reveals the impact properties and the shrinkage of TPS in time.
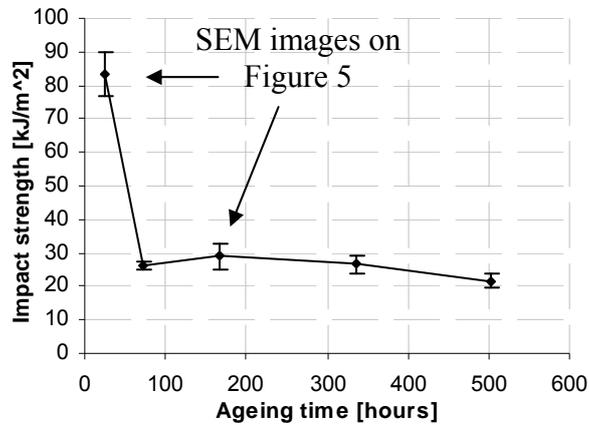
Figure 4. The effect of ageing time on the impact strength

The impact strength decreased rapidly as ageing advances; the basic behavior of TPS changes from a rubber-like soft material to a glass-like rigid material in time. On the SEM images (Figure 5.) the soft-to-rigid material transition can be observed by an image taken from the 24 hours aged TPS (soft) and from the 168 hours aged TPS (rigid).
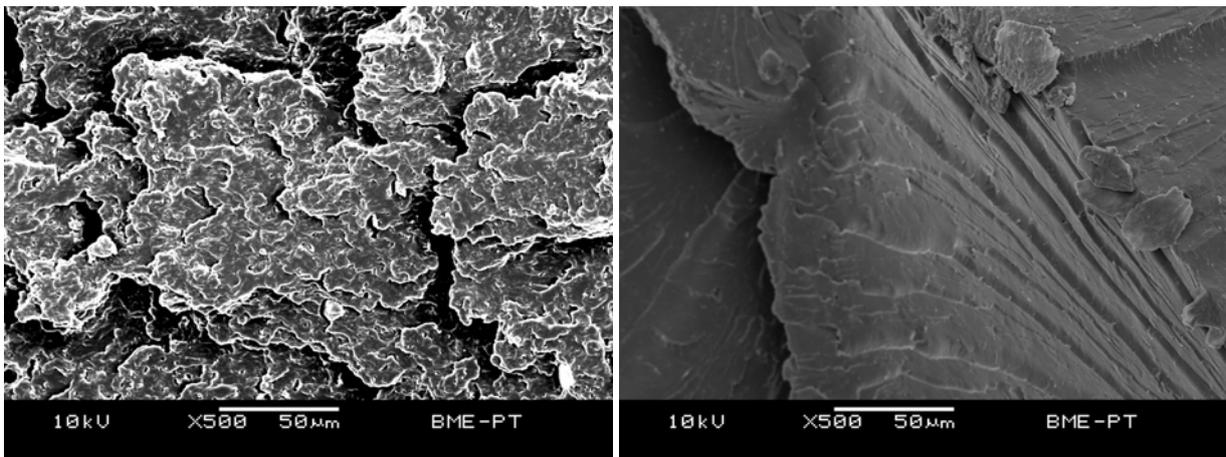
Figure 5. The fracture surface of the tensile specimens after 24 hours of ageing (left) and 168 hours of ageing (right)
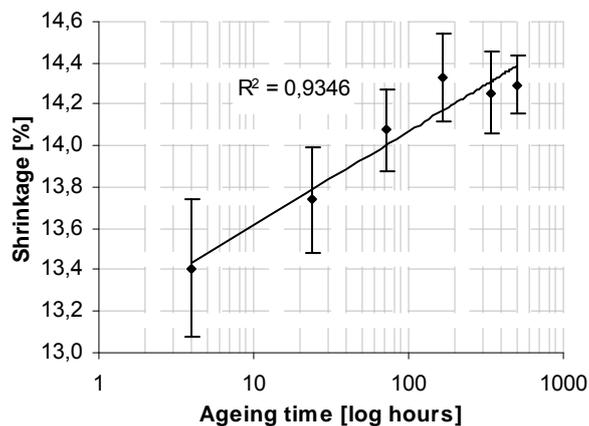
Figure 6. The effect of ageing time on the shrinkage

The shrinkage of the TPS increases logarithmically as ageing time increases. This behavior is similar to "ordinary" thermoplastics, except for the high values of shrinkage (Figure 6.).

Summary

The properties of starch based plastics change in time as the effect of biodegradation. While ageing, starch based plastics become more and more rigid until they fall apart. This behavior represents the life-cycle of a biopolymer based product.
In our work, the time-dependent behavior of injection molded starch was investigated. It was found that the tensile stress and the tensile modulus (Young's modulus) increased for a certain value while ageing. The same behavior is observed for the strain, but with a decreasing character. The impact strength of the TPS decreased rapidly while ageing. With the SEM images the soft-to-rigid transition was observed on the fracture surface of the tensile test specimens. The soft-to-rigid transition was found to be between 24 and 72 hours of ageing. The shrinkage character was similar to "ordinary" thermoplastic materials, namely it increased logarithmically in time.

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