Biodegradation of TPS mouldings enriched with natural fillers

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Summary. The aim of the present study was to investigate the biodegradation of thermoplastic starch (TPS) mouldings in the soil. Samples, produced from mixtures of potato starch, glycerin and added fillers (natural fibers) were obtained in two steps: TPS granules by extrusion-cooking, than the extrudates were processed by injecting moulding technique to get mouldings. The varied weight loss of mouldings was observed during storage, depending the time of storage and raw materials composition. Those collected after 12 weeks of storage in the soil had the highest weight loss. It was noticed that the increased addition of glycerol in the mouldings had an effect on the higher degradation rate. To the contrary, the addition of fillers to the mouldings' composition, especially flax fibers, slowed down the process.

Key words: thermoplastic starch, extrusion-cooking, biodegradation, natural fibers

INTRODUCTION

Extrusion-cooking, popular in food processing, causes the destruction of starch and leads to its thermoplastic nature. Mixing and processing of starch with other components allows to form new materials – thermoplastic starch (TPS) used in packaging sector [6, 8, 17, 19, 20, 21].

TPS can be used as stand-alone packaging material or as an additive that improves the degradation of plastics. Its application is possible due to the relatively short time of degradation to CO_2 and water. Biocomposites that are enriched with starch are mainly used in making films, containers, and in the production of foams used for filling of empty space contained in the packs [10, 14].

Packaging materials made from thermoplastic starch can be produced by two methods: single- and two-stage. A single-stage method involves prior formation of the components mixture and its application to the devices producing the packaging material. An example of such a device is an extruder, the universal machine widely used in plastic film production. A single-stage method is also used in the production of the mentioned before foams and fillers [5, 12, 13, 15].

In the case of two-stage method of production, the first step consists the production of TPS pellets – half-products processed by extrusion-cooking [11, 16]. The second stage is the production of packaging material, which can be performed with conventional equipment used in plastic processing, including film-blowing extruders and injection moulding machines.

MATERIALS AND METHODS

MATERIALS

The basic raw material was potato starch type Superior produced by AVEBE b.v. (NL), mixed with a technical glycerol of 99% purity produced by Odczynniki Chemiczne-Lublin (PL) – the plasticizer, and cellulose fibers vivapur type 102 (JRS GmbH, D) and flax fibers (Polish rural producers) – as the fillers.

PREPARATION OF MIXTURES

All ingredients were mixed using a laboratory ribbon mixer. The effective mixing time of 20 minutes was set after repeated attempts. The share of glycerol was 20%, 22% and 25% by the weight in the mixture, whereas the contribution of fibers in the prepared mixtures was 5% and 10%. After mixing, samples were left in sealed plastic bags for 24 hours in order to maintain the homogenous mixture. Immediately before the extrusion the blends were mixed once again for 10 minutes, which guaranteed getting looser structure of the mixture.

EXTRUSION-COOKING

TPS granules enriched with natural fibers were produced using a modified single screw extrusion-cooker type TS-45 (ZMCh Metalchem, PL) with L/D = 18/1, equipped with an additional cooling section of the barrel and a forming die with a hole diameter of 3 mm. Extrusion-cooking process temperature was set at the range from 60°C to 110°C and maintained appropriately adjusting the intensity of the flow of cooling liquid [1, 2, 3, 4].

HIGH-PRESSURE INJECTION MOULDING

The high-pressure injection moulding machine ARBURG 220H90-350 type, L/D=20.5 was used. The injection speed was maintained at (70-90) mm/s, the injection time: 5 sec., the process temperature ranged from 100° C to 180°C. Since the injection-moulded samples were used in the production, it gave the basic matrix in the form of 'shoulders', useful in the subsequent run-time tests of mechanical properties of moulded samples and their biodegradability. For biodegradability tests mouldings processed at 160°C were selected.

ASSESSMENT OF BIODEGRADABILITY TEST

The mouldings prepared with a moisture content of about 4% were placed in special baskets and stored in plastic boxes covered with 15 cm layer of garden soil with a moisture content of 70% and pH 6.5 for 2, 4, 8 and 12 weeks [18]. In order to ensure constant initial soil moisture, the content of soil and the process of water loss were determined twice a week (Fig. 1, 2).

The boxes with samples were kept in autumn in an unheated room at constant humidity at 15°C. Afterwards, mouldings were cleaned, weighed and dried to a moisture content of 4%. The determination of mass loss was carried out in the final stage of storage intervals [7, 9].

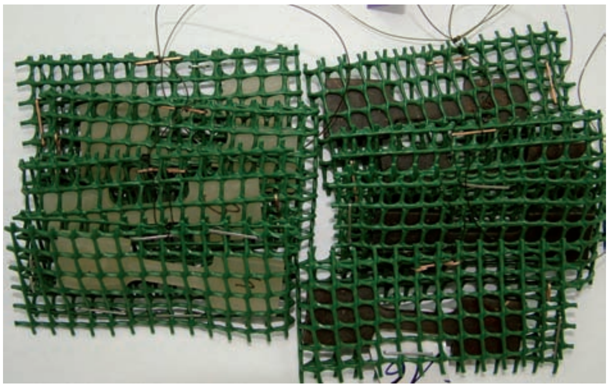

Fig. 1. The mouldings placed in the boxes with soil

Fig. 2. The distribution of samples in the boxes to the ground

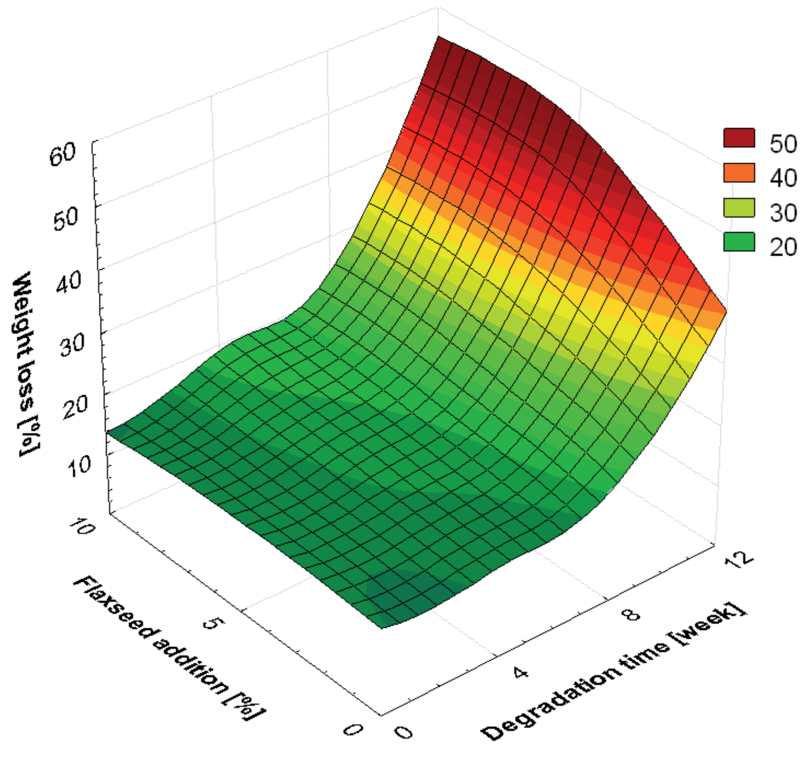

Fig. 3. The influence of storage time and the amount of flax fibers on the weight loss of the mouldings containing 20% of glycerol

RESULTS

The highest weight loss was observed after 12 weeks storage period for the whole range of the investigated samples. The results of the weight loss in mouldings containing 20% of glycerol and the addition of flax fibers are shown in Figure 3.

For all the samples after the first two weeks of storage, the recorded weight loss ranged from about 13% (for the samples containing 20% of glycerol) to approximately 23% (for the samples containing 25% of glycerol).

In the case of starchy samples without natural fibers, stored for 12 weeks, a greater weight loss at a higher content of glycerol in the formulation of granulates was observed. Moreover, the moulding's surface underwent decomposition faster in contact with moist soil than in its inner layer (the moulding's core).

Fig. 4. Samples with flax fibers after 12 weeks of storage

The addition of flax fibers influenced the degree of biodegradation. It was observed with the increase of the flax fibers content in the blend an increase in the weight loss of tested mouldings.

The highest weight loss, which reached about 56%, was observed in samples containing 10% of flax fibers after 12 weeks of storage. The samples processed without the addition of flax fibers characterized smaller weight loss, which was about 40% after 12 weeks (Fig. 4).The increase in the amount of plasticizer in the samples (22% and 25% of glycerol) increased the rate of biodegradation during the first 8 weeks of the experiment (Fig. 5, 6).

Weight losses of samples were greater than in the mouldings made from granulates containing 20% of glycerol. Mouldings with 22% of glycerol and 5% of flax fibers indicated the smallest weight losses during

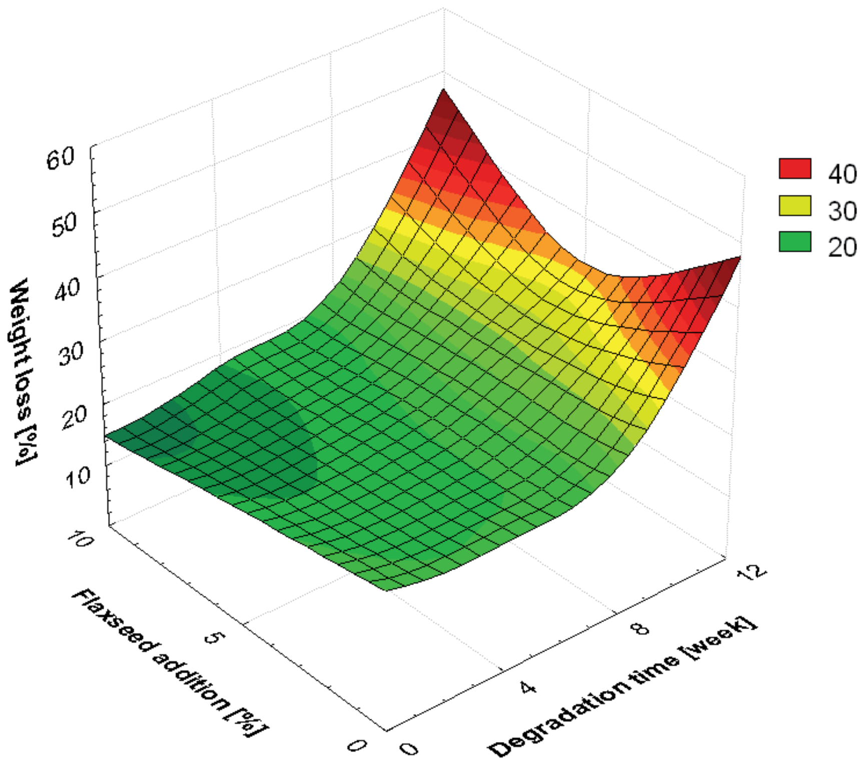

Fig. 5. The influence of storage time and the amount of flax fibers on the weight loss of the mouldings containing 22% of glycerol

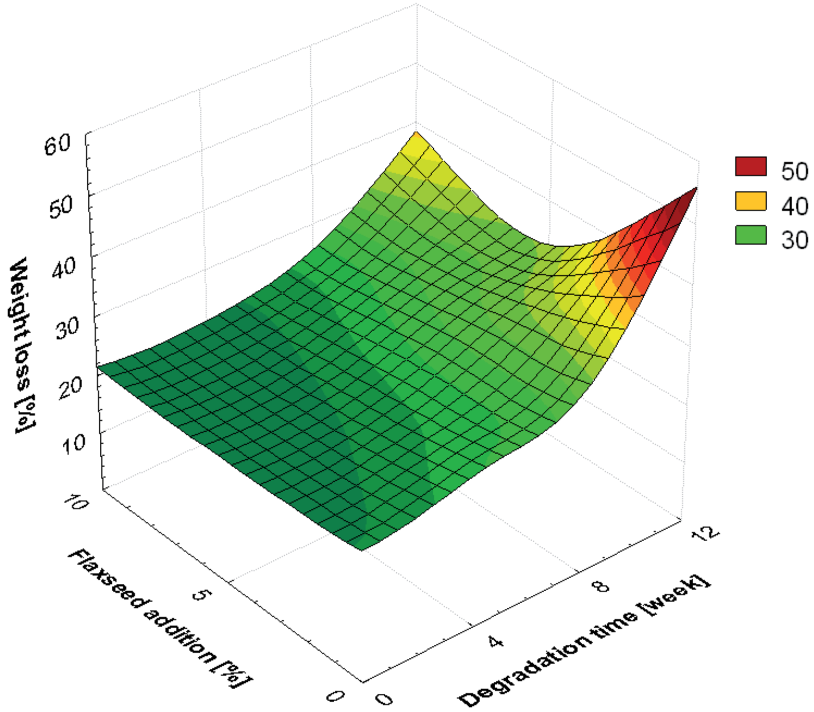

Fig. 6. The influence of storage time and the amount of flax fibers on the weight loss of the moulding 25% of glycerol

storage, reaching about 32% after 12 weeks (Fig. 5). The increase in the content of fibers from 5% to 10% in samples caused the increase in the weight loss by approximately 16%.

Samples made of granulate containing cellulose fibers of 5% and 10%, as well as those with the addition of 20% of glycerol, indicated similar properties to the samples containing flax fibers (Fig. 7).

The addition of cellulose fibers influenced their biodegradation process. As it was observed, the increase of cellulose fibers in the blend resulted in the increase in the weight loss. The highest weight loss, which ranged from about 51%

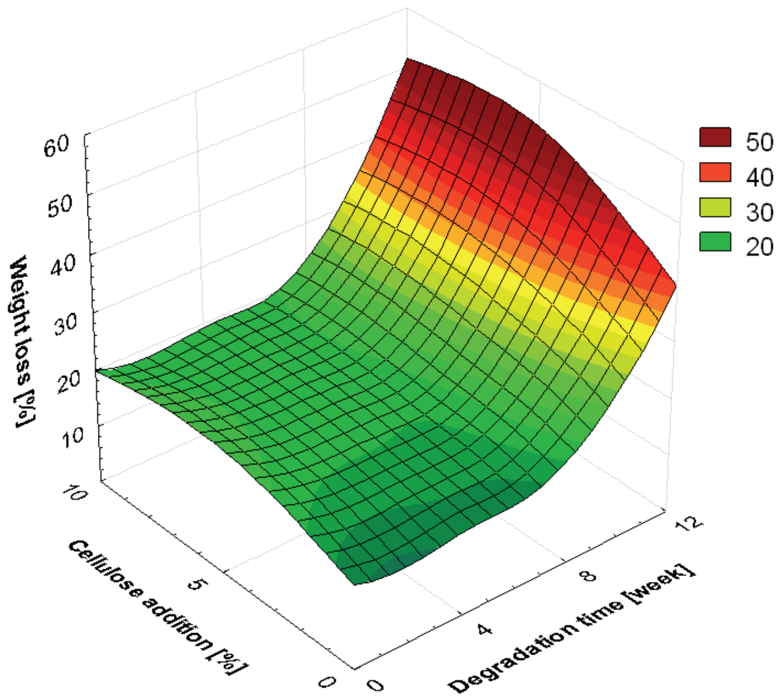

Fig. 7. The influence of storage time and the amount of cellulose fibers on the weight loss of the mouldings containing 20% of glycerol

- 53%, was observed for the mouldings containing 5% and 10% of cellulose fibers after 12 weeks of storage (Fig. 8).

Fig. 8. Samples with cellulose fibers after 12 weeks of storage

Figure 9 presents a similar tendency, where the weight loss for tested samples produced from granulates containing cellulose fibers is similar to the weight loss for those containing flax fibers.

Within the course of the experiment it was proved that the mouldings containing cellulose fibers displayed the same quality as those with flax fibers. Numerous cracks and groves which occurred on the surface of compacts as the result of consecutive biodegradation were observed (Fig. 10).

Figure 11 presents the influence of storage time and amount of cellulose fibers on the weight loss of the mouldings.

The highest weight loss was observed for the samples made of granulate containing 25% of plasticizer without the addition of fibers. After 12 weeks the weight loss was about 57%. The addition of cellulose fibers resulted in the decrease of weight loss in comparison to the samples produced without fibers.

Samples prepared without the addition of fibers and those containing cellulose were fragile and prone to cracking during storage according to the weight loss. Samples containing flax fibers displayed good resistance to the damage.

CONCLUSIONS

It was indicated that the weight losses were higher with the increase of glycerol content in the mouldings.

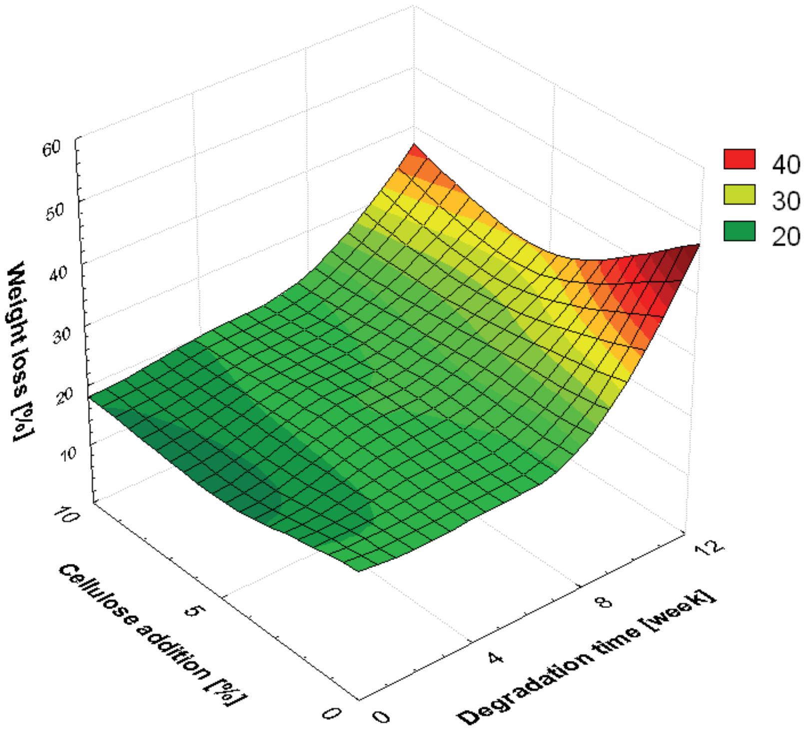

Fig. 9. The influence of storage time and the amount of cellulose fibers on the weight loss of the mouldings containing 22% of glycerol

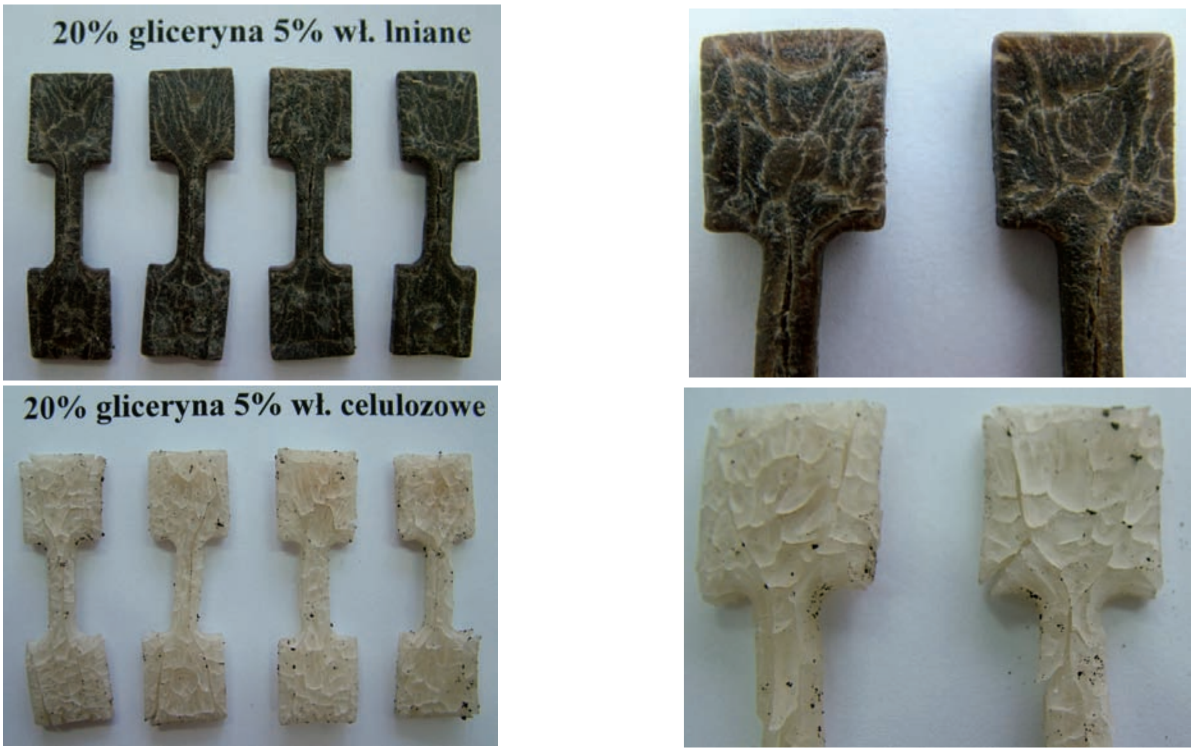

Fig. 10. The mouldings containing flax (a) and cellulose (b) fibers after 2 weeks storage time

The highest weight loss (ca. 57%) was observed in the samples with 25% of glycerol.

The increase in the content of flax fibers slowed down the process of decomposition in the first two weeks of storage. Numerous changes visible on the surface of mouldings in the early stage of storage (cracks, grooves, etc.) are considered to be the result of the consecutive biodegradation process.

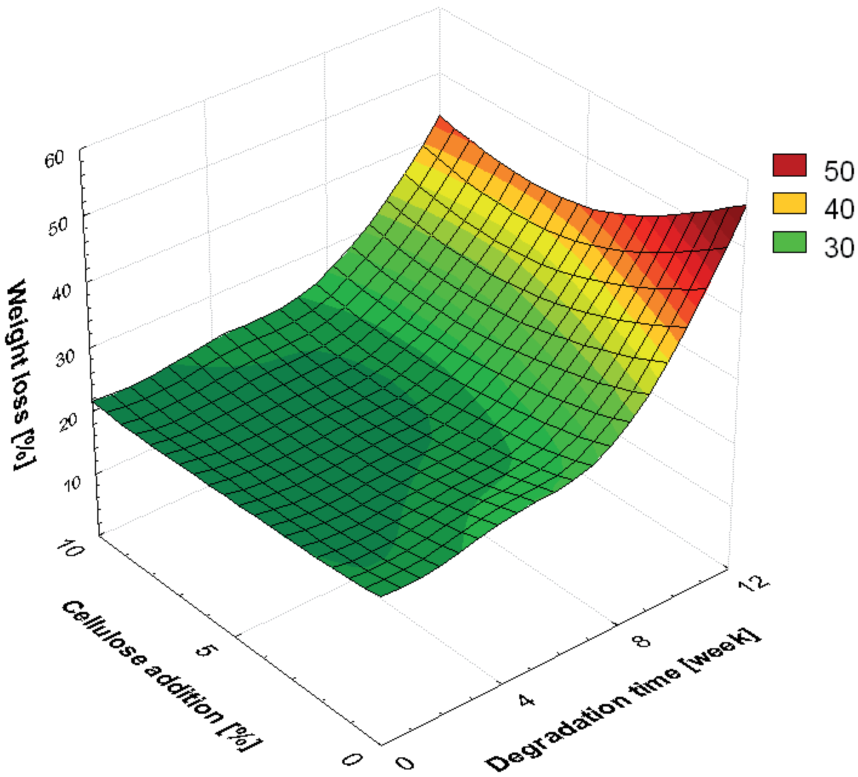

Fig. 11. The influence of storage time and the amount of cellulose fibers on the weight loss of mouldings containing 25% of glycerol

The addition of flax and cellulose fibers resulted in quicker biodegradation process in soil, which was observed in the final stage of storing (after 12 weeks).

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BIODEGRADACJA WYPRASEK SKROBI TERMOPLASTYCZNEJ WZBOGACONYCH NATURALNYMI WYPEŁNIACZAMI

Streszczenie. Badaniom poddano formy sztywne w postaci wyprasek wytworzonych ze skrobi termoplastycznej (TPS). Granulaty zostały wyprodukowane z mieszanek skrobi ziemniaczanej, gliceryny oraz dodatku wypełniaczy w postaci włókien naturalnych. Następnie formy sztywne w postaci wyprasek wytworzono metodą wtrysku wysokociśnieniowego z granulatów TPS charakteryzujących się zróżnicowaną zawartością gliceryny (plastyfikatora) i włókien (substancje wzmacniające). Podczas pomiarów zaobserwowano zróżnicowany ubytek masy wyprasek zależny od czasu ich przechowywania w glebie. Po 12 tygodniach przechowywania w glebie stwierdzono najwyższy ubytek masy próbek. Zwiększenie dodatku gliceryny w wyprasce wpływało na większe tępo biodegradacji natomiast dodatek wypełniaczy szczególnie włókien lnianych proces ten spowalniał.

Słowa kluczowe: skrobia termoplastyczna, ekstruzja, biodegradacja, włókna naturalne