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APPLICATION POSSIBILITIES AND PROPERTIES OF PLASTIC MIXTURES BASED ON BIODEGRADABLE POLYMERS

MOŻLIWOŚCI STOSOWANIA ORAZ WŁAŚCIWOŚCI MIESZANIN TWORZYWOWYCH NA BAZIE POLIMERÓW BIODEGRADOWALNYCH

***Summary**: in this study, an attempt was made to develop generalized conclusions based on previous publications regarding research on the processing possibilities and analysis of the mechanical properties of PLA and TPS polymer mixtures and the possibility of modifying TPS with calcium carbonate. An in-depth analysis of the obtained results turned out to be quite interesting. Further research is necessary to explain the phenomena occurring when mixing two biodegradable polymers, where a certain synergism and the impact of the filler on the polymer matrix are observed.*

***Keywords**: biodegradable polymers, polylactide, thermoplastic starch, mechanical properties*

***Streszczenie**: w niniejszym opracowaniu podjęto próbę opracowania uogólnionych wniosków na podstawie wcześniejszych publikacji dotyczących badań nad możliwością przetwórstwa oraz analizy właściwości mechanicznych mieszanin polimerowych PLA i TPS oraz możliwości modyfikacji TPS węglanem wapnia. Pogłębiona analiza uzyskanych wyników okazała się dosyć intersująca. Konieczne są dalsze badania polegające na wyjaśnieniu zjawisk zachodzących podczas mieszania dwóch polimerów biodegradowalnych, gdzie zaobserwowane pewien synergizm oraz odziaływania napełniacza na osnowę polimerową.*

***Słowa kluczowe**: polimery biodegradowalne, polilaktyd, skrobia termoplastyczna, właściwości mechaniczne*

Introduction

Polymeric materials have become synonymous with progress and modernity. They dominate almost every area of life and economy, and it is difficult to imagine today's world without these materials. Apart from the benefits brought by the development of polymer chemistry and technology of their processing, they also pose a certain problem related to their accumulation in landfills. Degradation of the discussed materials in the natural environment takes an unimaginably long time and poses a significant threat to living organisms [1–5].

An alternative to traditional polymer materials is the development of the so-called biodegradable polymers, which constitute a kind of revolution both in processing and in application. The discussed materials, unlike traditional plastics, can undergo the so-called biological degradation in natural environmental conditions [6–8]. This means that they do not create a lasting burden on the environment, provided that they are also produced from renewable raw materials. This is important when considering the problem of so-called global pollution and its negative impact on water, soil and marine ecosystems [9–10]. The packaging industry undoubtedly has great expectations for these materials, where there is a particular need to use ecological materials that can be easily disposed of and do not leave any lasting waste. Biodegradable packaging can be produced from materials such as PLA (polylactic acid, also known as polylactide) or less durable thermoplastic modified starch (TPS) [11–15]. Biodegradable petrochemical plastics may also be an alternative, but in this case we cannot talk about the so-called "green chemistry" [16–20].

The idea behind the development of biodegradable polymer materials included mainly their applications, but also processing processes, which should be the same or similar to those used in the case of traditional plastics [21–24]. It facilitates the adaptation of existing machines without costly modifications, but only by appropriate selection of technological process parameters. Most biodegradable plastics are compatible with existing production infrastructure [25–28]. This advantage facilitates the introduction of these materials to the market [29–32]. With the growing interest in the so-called ecological substitutes for traditional plastics, investments in research on new or existing biodegradable materials are attractive to many research centres, which leads to the creation of new innovative solutions and technologies in the field of application, modification and improvement of the properties of these materials while maintaining their biodegradable nature [33–36]. There is a certain contradiction here – on the one hand, durable and resistant products are expected that meet different standards depending on the field of economy. On the other hand, it is expected that after a period of use, the product will degrade in the natural environment without affecting it [37–40].

Biodegradable polymer materials are a revolution in the plastics industry, providing ecological alternatives to traditional plastics. As technology continues to advance, they can be expected to play an increasingly important role in various sectors of the economy.

Main biodegradable polymers

The main representatives of biodegradable polymer materials that arouse the greatest interest due to their origin, properties and possibilities of use are polylactide (PLA) and thermoplastic starch (TPS).

Both of these materials are sometimes called "double green", which means that they are produced from renewable raw materials (corn, other cereals), and that they biodegrade in the natural environment after a period of use [41–43]. It can be stated that currently the achievements of chemical synthesis in the production of these materials are ahead of detailed knowledge of their properties, both processing and operational [44–45]. In other words, processors and mechanical engineers are "out of step" with the chemical industry. Therefore, it is advisable to investigate the possibilities of processing and using these materials in order to, on the one hand, optimize the production process and, on the other hand, strive for waste-free operation.

Polylactide (PLA)

Polylactide (PLA) is a thermoplastic linear polyester, completely biodegradable under industrial composting conditions, which is a process of biological transformation of organic materials, including biodegradable plastic packaging, into simple substances that do not pose a threat to the natural environment. This process takes place under controlled conditions, usually on a large scale, in specially designed industrial installations. In this process, appropriate conditions must be met, such as temperature, humidity, ventilation, mixing and pH. The mentioned parameters are monitored and controlled to create an optimal environment for the microorganisms responsible for decomposition. PLA is practically non-biodegradable under home composting conditions. This is, in a way, an advantage that gives quite a lot of possibilities of its use, but also a disadvantage [46–48].

Generally, PLA can be processed using typical processing technologies such as injection, thermoforming, extrusion and extrusion blow molding [49–52]. This material is obtained by condensation polymerization of lactic acid or cyclic lactides. Lactic acid, as a preliminary product, is obtained by bacterial fermentation of starch, most often from corn or milk processing [52–55]. Its main application is in the packaging industry, medicine and agriculture. Due to its processing parameters and the lack of release of harmful substances during this process, it is widely used in 3D printing technologies. PLA currently constitutes almost 40% of all currently known and used biodegradable polymers [56–58]. Its properties are similar to polystyrene. It is a stiff, brittle material. Its brittleness temperature is approximately 57°C and its flow temperature ranges between 170–180°C. It has a good transparency and gloss. It has good strength properties and low elongation at break (approx. 3–4%). Its disadvantage, but also its advantage, is easy water sorption, which affects the biodegradation process, but drying before processing is necessary [60–63].

Its disadvantage also includes low impact strength, which disqualifies it from many applications. In order to improve it, various fillers are introduced into pure PLA, both of natural origin such as plant fibers, wood flour, various nut shells and mineral fillers such as magnesium and aluminium hydroxides, calcium carbonate or phosphogypsum. Extensive research is also carried out on mixing PLA with other materials [64–66]. The research used PLA with the trade name Ingeo Biopolymer 3100HP from NatureWorks (USA).

Thermoplastic starch (TPS)

Thermoplastic starch (TPS) is a polymer material that is fully biodegradable both in home and industrial conditions. The material is mainly obtained from potatoes or corn [67–69]. Like PLA, it is called "double green". TPS is characterized by a high degree of homogeneity and favourable mechanical properties. Products made of it have good shape stability. TPS is commercially available in the form of granules ready for processing using traditional methods such as injection or extrusion. Thermoplastic starch is intended for the production of packaging, foil, garbage bags and disposable products such as cutlery and plates [70–72]. Thermoplastic starch is obtained by breaking the layered structure of native starch and transforming the partially crystalline structure into an almost completely amorphous and homogeneous material.

The crystalline structure of starch can be destroyed by the combined action of mechanical and thermal factors, which occurs during processing. This material has many advantages, first of all, it is fully biodegradable in all conditions; it does not leave any toxic substances during decomposition. Its properties and application depend on the plasticizer used and its botanical origin. The disadvantages include low resistance to moisture and average or even poor mechanical properties [73–76]. The research used TPS with the trade name Envifill MB173 manufactured by Grupa Azoty (Poland).

Description of conducted research work

In the papers [77–80] the subject of research on processing and properties, mainly mechanical, of two types of mixtures was discussed. Mixtures of the two biodegradable plastics mentioned at the beginning, PLA and TPS, and a mixture of

TPS and the inorganic filler $CaCO_3$. The presented research focused mainly on the mechanical parameters of the obtained mixtures. Strength, deformability and Young's modulus were tested for various mixture proportions as a result of static tensile tests. Hardness, impact strength and water absorption were also measured. Detailed results and their analysis can be found in [77–80]. This study presents some generalizing conclusions indicating the possibilities and directions of research on these biodegradable plastics, their mixtures and other modifications.

Therefore, attempts were made to investigate the properties of PLA mixtures with another, fully biodegradable material – thermoplastic starch (TPS). The experimental results prove that TPS as a component of the TPS/PLA mixture has a very positive effect on all the tested properties. The brittleness of pure PLA (which was its main drawback) has been removed, resulting in the resulting material being much less susceptible to cracking than pure PLA. The impact strength of pure PLA and pure TPS is approximately 10 kJ/m^2, while the 50/50 mixture has impact strength of 30 kJ/m^2, which is an amazing result and proves strong synergistic phenomena. Such strengthening of the obtained material was a bit of a surprise, because even the professional literature is very limited in this area.

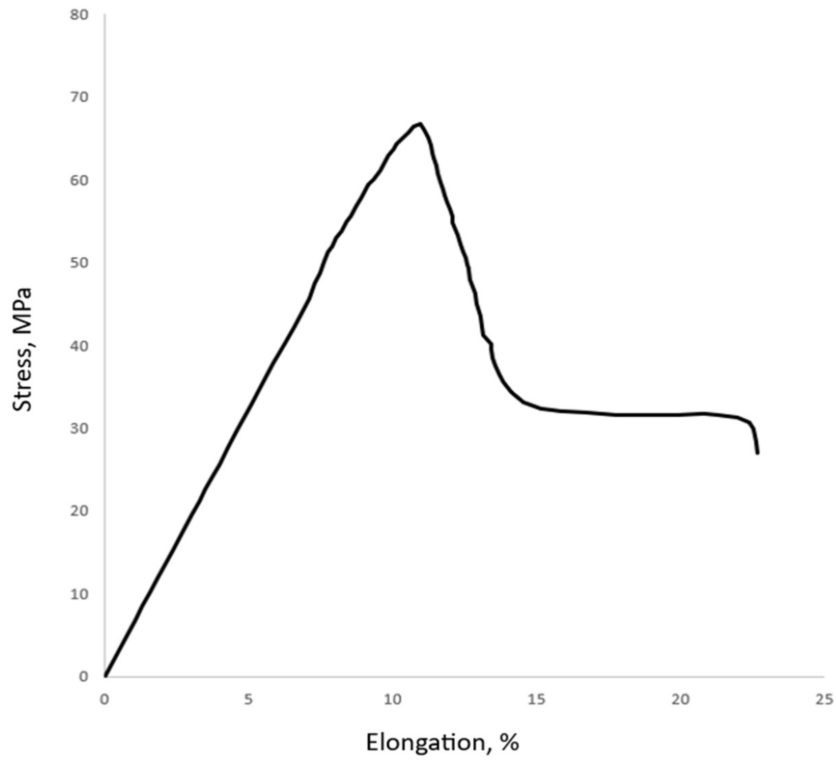

Fig. 1. Static tensile curve for a mixture of 50% wt. TPS + 50% wt. PLA

This is undoubtedly one of the further directions of more detailed research explaining the mechanism of mixing PLA and TPS and the phenomena occurring during this process. These studies require more advanced measurement equipment.

In the case of hardness, the differences are not too big. The hardness of pure TPS is lower than that of pure PLA. Therefore, the hardness of mixtures with a higher PLA content is approximately 62 degrees on the Shore "D" scale, while the hardness of TPS itself is approximately 55 degrees on the Shore "D" scale. Here, it would also be worth conducting further microscopic tests to possibly confirm when the matrix is PLA and when TPS, how both materials interact with each other and what phases they create.

Regarding water absorption, the following aspects should be taken into account: on the one hand, high water absorption is a disadvantage because it causes a change in the shape of the product and, therefore, dimensional instability. On the other hand, high water absorption is an advantage because it contributes to a high tendency to biodegradability. In the case of the tested materials, higher water absorption is characteristic of mixtures with a higher TPS content. Since the tested materials are mainly used as packaging, where easy biodegradability is a priority, the final conclusion is that TPS as a component in a mixture with PLA improves the quality of the material compared to pure PLA. TPS reduces brittleness and improves biodegradability.

The results of strength tests on a tensile testing machine confirm the above conclusions. Both PLA and TPS are characterized by a similar nature of stretching curves. Figure 1 shows an example tensile curve for a 50/50% mixture wt.

After an almost straight line course, after reaching the maximum, preparation and then breaking take place. The results show that TPS slightly reduces strength (63 MPa for PLA, 57 MPa for TPS) and quite significantly reduces Young's modulus (1100 MPa for PLA, 666 MPa for TPS). However, these decreases can be accepted due to the above-mentioned significant improvement in impact strength and biodegradability.

An alternative solution to modifying biodegradable polymers by mixing them may be the use of appropriate fillers. In this case, filling the TPS starch with powdered calcium carbonate $CaCO_3$ was used. Although it is not a biodegradable material, it is environmentally neutral. It is the main component of, for example, limestone rocks (Kraków-Częstochowa Upland, Poland).

Calcium carbonate (CaCO3) Omyalene 102-M-OM from OMYA (Switzerland) was used as the filler. It is in the form of a concentrate (granulate) containing 85% wt. natural calcium carbonate and approximately 10% wt. polypropylene and 2–5% wt. polyethylene.

Therefore, the influence of the content of this filler on the properties of the composition was examined. The proportions used were 10, 20, 30 and 40% wt. filler. First of all, the impact strength increased significantly, from 10 kJ/m^2 for pure TPS

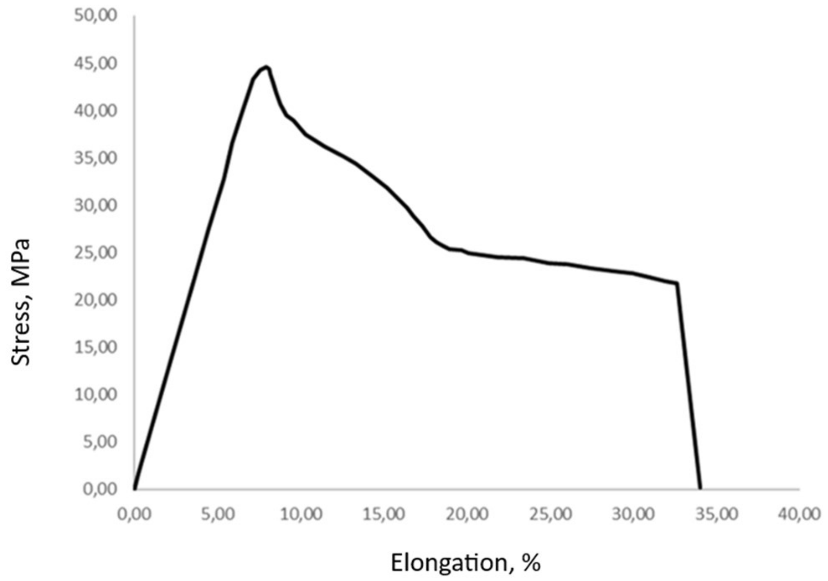

Fig. 2. Static stretching curve for a mixture of 80% wt. TPS and 20% wt. $CaCO_3$)

to about 35 kJ/m^2 for each of the fillings used (regardless of whether it was 10% wt. or 40% wt). This is a very interesting and unexpected result, requiring further research and phenomena occurring between the TPS matrix and the filler molecule.

The hardness was the highest for the content of 20% wt. $CaCO_3$ (over 57 degrees on the Shore scale "D"), while for 40% wt. it was only just over 53 on the Shore "D" scale.

However, water absorption increased dramatically – more than twice. Summarizing the results of static stretching, it can be stated that the nature of the stretching curves was similar for all compositions, as exemplified in the figure. 2

Young's modulus showed some correlation with hardness. Its maximum value was for a filler content of 10–20% weight. However, the strength decreased significantly from 57 MPa for pure TPS to 30 MPa for 40% TPS weight filler content. Ultimately, it can be assumed that the filler content is approximately 20% weight is optimal. It combines maximum impact strength, hardness and Young's modulus with a slight decrease in strength and good water absorption.

Conclusions

Biodegradable polymers are undoubtedly an alternative to traditional plastics. Extensive research on both the chemistry of these materials and their processing contributes significantly to their promotion. It is also worth emphasizing the changing legal regulations regarding the use of polymer materials. This also influences and even forces research into new materials and their modifications. It is also worth emphasizing that the production of these materials is also associated with environmental impact by modifying plants so that more substances can be obtained from them for the production of these polymers. This is not entirely a favourable phenomenon and requires detailed analysis. Also, using them for a short time and "throwing" them into the compost involves a financial loss. Therefore, it is definitely worth conducting research related to the processing, modifications and more rational use of these materials in which quite a large amount of energy was put into their production. These materials are too valuable not to seek new and broader applications for them.

The use of typical machines to prepare polymer mixtures and basic tests of mechanical properties provide the basis for further, in-depth research. Already at this stage we can observe certain phenomena and mechanisms related to the interaction of two biodegradable polymers in the mixture and the filler on the polymer matrix. The reinforcement in the TPS/PLA mixture is particularly interesting, where the phenomenon of synergy has been observed. This means that the final effect of the mixture is greater than the sum of the effects that would be expected based on the individual properties of each of these polymers. In the case of a TPS/PLA blend, the synergy phenomenon can have various manifestations and causes, but in general it means that the blend exhibits better properties than expected based on the properties of both components separately.

The phenomenon of synergy in mixing TPS/PLA may be the result of complex interactions between both components and appropriate processing conditions. Further research and analysis may help to better understand the mechanisms of this phenomenon and use them to design materials with even better properties. The reinforcement of the TPS/PLA mixture can be adapted to specific requirements, allowing you to obtain a material with the desired mechanical, aesthetic and functional properties.

In the case of TPS modification with a filler in the form of powdered calcium carbonate, research confirms that this type of mixtures can be successfully processed and calcium carbonate is a good filler. The analysis of stretching curves and other mechanical properties allows indirect identification of phenomena occurring between the filler and the TPS matrix. This provides the basis for further research work including microstructural analyses.

Summing up the analysis of the work carried out on the properties of biodegradable polymer mixtures, it can be concluded that there is a solid basis for the thesis that these materials will continue to develop dynamically in various directions to increase their effectiveness and application possibilities. Research on these materials is innovative and brings benefits related to a more rational use of not only traditional polymer materials, but also biodegradable ones.

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