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SELECTED PROPERTIES OF BIOCOMPOSITES ON THE BASIS OF PHBV WITH CELLULOSE FILLERS

The paper presents selected properties of the developed biocomposites based on PHBV poly (3-hydroxybutyric co-3-hydroxyvaleric acid) biopolymer. The PHBV biopolymer is obtained by the copolymerization of 3-hydroxybutyric acid and 3-hydroxyvaleric acid. The biopolymer used for the tests contained 8% of poly (3-hydroxyvaleric acid). For the preparation of the composite, three types of fillers: wood flour, hemp fiber and flax fiber were used in search for the best possible mechanical properties of composite. During the selection of filler types, the availability and price in the geographical area of Poland as well as mechanical properties were taken into account. Fillers were alkalized and fiber modification parameters were determined. The following mass percentages of fillers in the tests: 15%, 30%, 45%, 50% and various fiber lengths were used. To produce the biocomposites the single- and twin screw extruders made by Zamak Company were used. The initial processing parameters were determined using DSC thermogram analyses. The technological parameters depended on the type of filler and its percentage content. The best mechanical properties, compared to generally available polymers like PP, PE, PVC or PS were obtained for the composite with hemp fiber. The developed composite is completely biodegradable. Better mechanical properties of produced composite in relation to e.g. PE or PP allow using it for the production of parts that are used in various branches of the economy.

Keywords: PHBV, natural fibers, composites, biopolymers, injection moulding

1. Introduction

Management of plastic waste is a significant problem that is increasing year by year. Considering these problems and biodegradability of polymers, and also the source of its production, polymers can be classified as follows [1]:

- non-biodegradable and manufactured from petrochemical raw materials,
- biodegradable and produced from petrochemical raw materials,
- non-biodegradable and produced from renewable raw materials,

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- biodegradable and produced from renewable raw materials (so-called „double green”).

Apart from the first group, the other three can be called „bioplastics” because they are materials that are biodegradable or they are of natural origin. Today, bioplastics comprise only 1% of the total annual production of plastics, but the group of these materials is constantly growing and the demand for such materials is increasing. The data developed by the European Bioplastics in cooperation with the Nova-Institute research institute shows that global bioplastic production capacities are supposed to increase from approx. 2.05 million tonnes in 2017 to approx. 2.44 million tonnes in 2022 [2]. The greatest hope is seen in the development of the group of double green bioplastics, which are of natural origin and are fully biodegradable. The main reason for slow development and commercialization of this type of polymers are quite high production costs.

An interesting group of double green polymers are polyhydroxyalkanoates (PHAs), which are produced by microorganisms as a backup material. Microorganisms are able to synthesize various types of PHA depending on the availability of carbon sources and biochemical reactions in cells. The production of PHA takes place in the cytoplasm of a bacterial cell, while the process of producing this biopolymer takes place in two stages. In the first stage, the bacterial inoculum is introduced into a sterile solution of nutrients, a carbon source and traces of metals. In the second stage, essential nutrients like N_2, C and O_2 are deliberately limited, which results in accumulation of PHA as a backup material [3]. One of the polymers belonging to the PHA group is poly (3-hydroxybutyric acid) (PHB). Despite similar physical properties to polypropylene, it is characterized by fairly high brittleness [4], which results from formation of large crystalline domains in the form of spherulites and can be associated with the exceptional purity of the obtained biopolymer. The above feature makes PHB microbiologically an ideal system for spherulites investigation [5], but it is also a serious disadvantage of the commercial use of this homopolymer [6, 7]. The possibility of improving mechanical properties of PHB is insertion of a second monomer, i.e. poly (3-hydroxyvaleric acid) (HV or PHV) to the PHB chain, which allows to obtain poly (3-hydroxybutyric acid-3-hydroxyvaleric acid) (PHBV). Copolymerization leads to reducing the crystallinity [8-10]. In comparison to PHB, PHBV is characterized by reduced stiffness and brittleness, higher elongation at fracture and increased tensile strength. Depending on the amount of HV in the polymer chain, a significant drop in the melting point can be obtained, increasing the difference between the melting point and the onset of the thermal decomposition, thus expanding the processing window [11]. Wider commercial use of this biopolymer is still difficult due to the high production costs as well as small difference between the melting temperature and the degradation temperature of this polymer, as well as low flexibility and fairly high brittleness [12-15]. For this reason, further plans in the research of scientists are to improve the mechanical properties and processing windows of this biopolymer, as well as the possibility of producing composites with a PHBV matrix [16, 17].

In recent years there has been a significant increase in the use of natural fibres as fillers in the polymer matrix in order to create new types of environmentally friendly composites. These fibres are characterized by low density while maintaining high strength, renewability and full biodegradability, with production requiring low energy. It should be noted, however, that these materials have lower durability than synthetic fibres, are characterized by quite high variability of properties and have a tendency for quite high water absorption [18-21]. The tensile strength as well as the Young's modulus of natural fibres are usually lower than for glass fibres used in composites production. However, the density of glass fibre is significantly higher (about 2500 kg/m^3) than natural plant-derived fibres (about 1500 kg/m^3), which is especially important for the weight of components made of composites, where the mass must be significantly reduced [22, 23]. Higher mechanical properties are noticeable for fibres with a high content of cellulose and cellulose microfiber arranged in the direction of reinforcement - this situation is often found in bast fibres, which have higher structural requirements to ensure adequate scaffolding for the stem of the plant. The properties of natural fibres are significantly diversified – this is due to growing conditions, harvesting time, processing and storage [24-26].

The possibility of commercialization of double green polymers (PHBV in particular) may be the use of natural fibre fillers in a biopolymer matrix. This may enable to improve mechanical properties of the manufactured biocomposites while maintaining full biodegradability at reduced production costs in relation to the pure biopolymer. The aim of the work is to present selected properties of PHBV-cellulosic fibre biocomposites.

2. Manufacture of biocomposites

The composites were produced using a twin screw extruder RES-2P12A made by Zamak company using adjustable temperature values in heating zones, in the range from 145°C to 160°C (Tab. 1). The fibres at this stage of the research were not surface modified. The extruded composite was granulated on a stand equipped with a water cooling bath and a granulator. Extrusion was carried out at the screw speed of 50 rpm. In the case of higher velocity, the process was unstable, i.e. the fibres were accumulated in the area before the extruder head. Moreover, the extrudate was characterized by very low viscosity when leaving the extrusion head. In turn, lowering the rotational speed of the screw below 50 rpm caused degradation of the biocomposite in the plastification unit due to too long heating time. These phenomena were particularly visible for composites with flax fibre. This was the cause of significant pressure fluctuations on the screw's forehead, which made it difficult to maintain the stability of the technological process. The obtained granulate was used for the production of test specimens by means of the injection moulding process. The stages of composite production are shown in Fig. 1. The configurations of produced PHBV biocomposites are presented in Tab. 2. SEM investigations were performed for each batch of composites produced. Selected images of composite areas fractures are shown in Fig. 2.

Table 1. The temperature of extruder heating zones

Head	Adapter	Zone 6	Zone 5	Zone 4	Zone 3	Zone 2	Zone 1	Feed hopper zone
160ºC	160ºC	160ºC	160ºC	160ºC	160ºC	155ºC	145ºC	50ºC

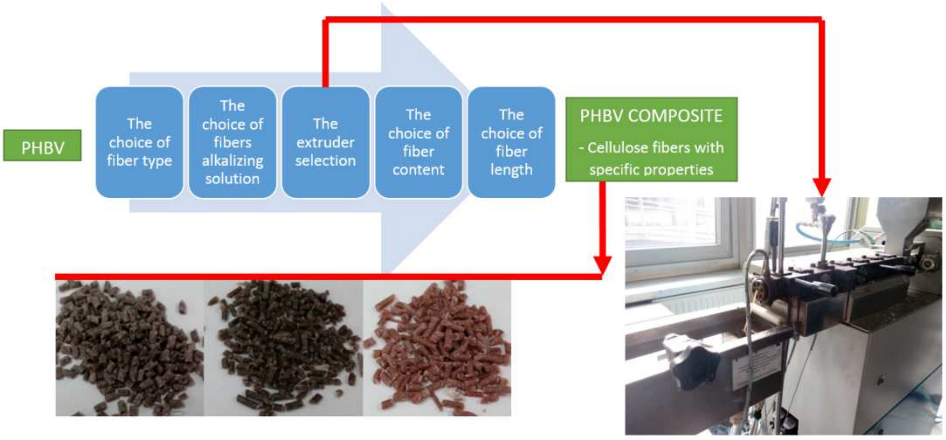

Fig. 1. The production stages of PHBV biocomposites.

Table 2. Configurations of manufactured biocomposites based on PHBV matrix

Composite designation	Type of fibre	Extrusion method	Mass filler content	Length of fibre	Mercerization of fibres
K15mas0rr1mmDwu	hemp	concurrent	15%	1 mm	no
L15mas0rr1mmDwu	flax	concurrent	15%	1 mm	no
D15mas0rr1mmDwu	wood	concurrent	15%	1 mm	no

In order to determine the processing window, among others, DSC analysis using TA Instruments Q2000 microcalorimeter was made. The recorded thermograms (Fig. 3) indicate that composites with a high degree of fibre adhesion to the matrix were produced – this is evidenced by high peaks on the thermograms. Glass transition and melting temperature of PHBV and its composites was observed, which shows semicrystalline materials. In addition, in the case of PHBV, the so-called „cold crystallization" was observed. Based on the obtained results, it was estimated that the glass transition temperature (T_g) of unfilled

PHBV is 6.4°C, and the change in specific heat (ΔC_p) is equal to 0.094 J/g°C. The onset temperature (T_m) of the polymer is 164.95°C. Estimated parameters for the composites produced are listed in Tab. 3. No significant changes in melting temperature were observed in relation to PHBV.

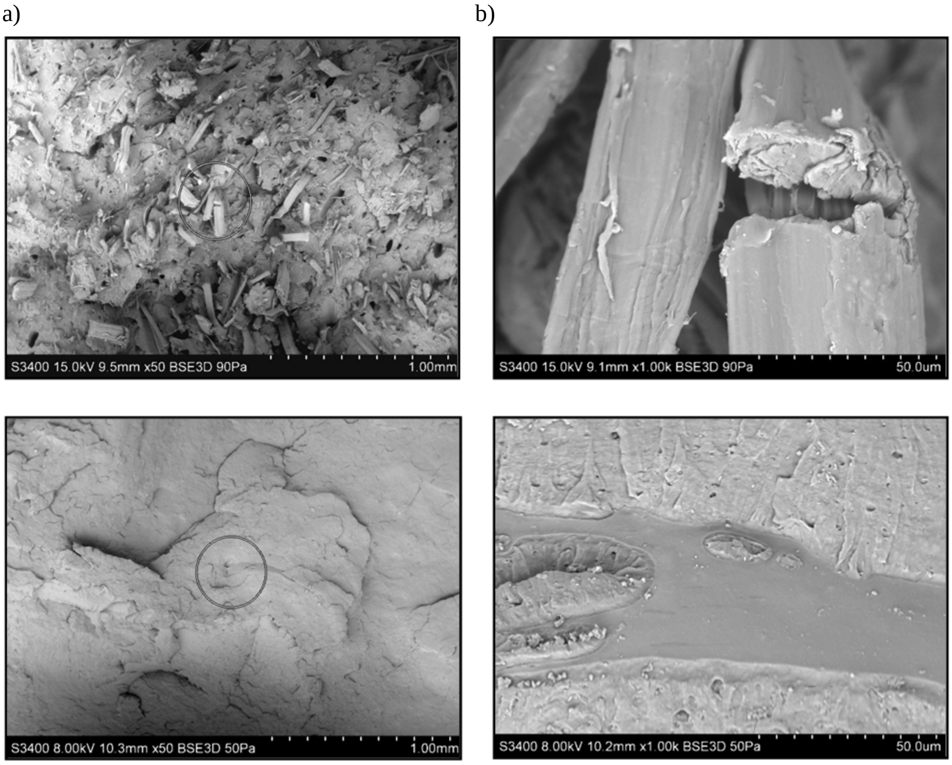

Fig. 2. Examples of SEM images of fracture areas for: a) composites filled with hemp fibres, b) pure PHBV biopolymer

Table 3. Comparison of thermal parameters of biocomposites for a variable type of filler and for a pure biopolymer

Type of material	ΔCp, J·g-1·°C-1	T_g, °C	T_m, °C	T_c, °C
L15mas0rr1mmDwu	0.077	6.40	164.30	101.10
K15mas0rr1mmDwu	0.067	3.60	164.20	106.60
D15mas0rr1mmDwu	0.080	5.58	163.20	101.70
PHBV	0.094	6.40	164.95	75.05

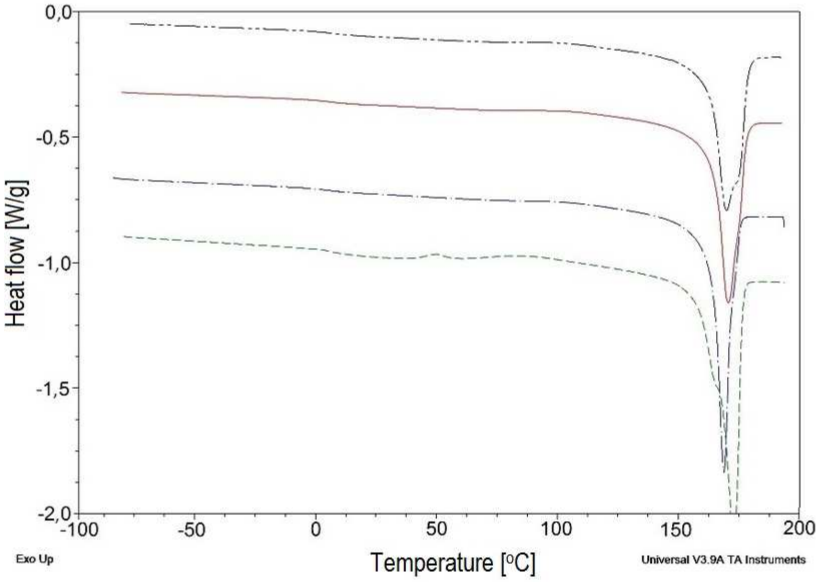

Fig. 3. Dependence of heat flow on temperature for unfilled PHBV (---) and its composites: with unmodified fillers: L15mas0rr1mmDwu (-), K15mas0rr1mmDwu (-·), D15mas0rr1mmDwu (-··)

3. Selected properties of produced biocomposites – preliminary tests

The Dr Boy 55E injection moulding machine was used to produce test pieces (Fig. 4). The tests of mechanical properties were carried out by means of the Zwick Roell Z030 testing machine and the Ceast 9050 impact hammer. The results of the performed tests are presented in Fig. 5-10.

Fig. 4. The moulded piece made of composite PHBV-hemp fibres (fibre content: 15% by weight)

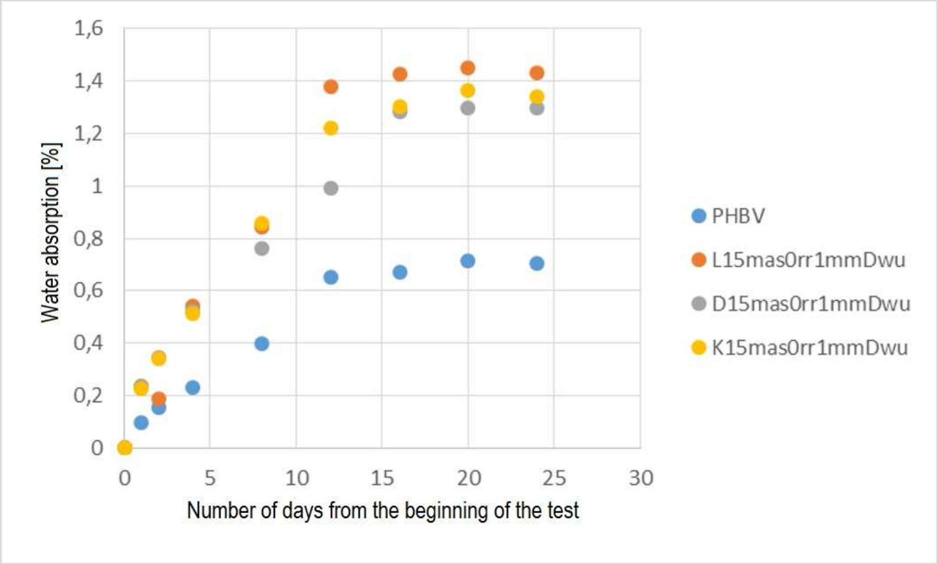

Fig. 5. Water absorption for a variable type of filler and for pure PHBV biopolymer

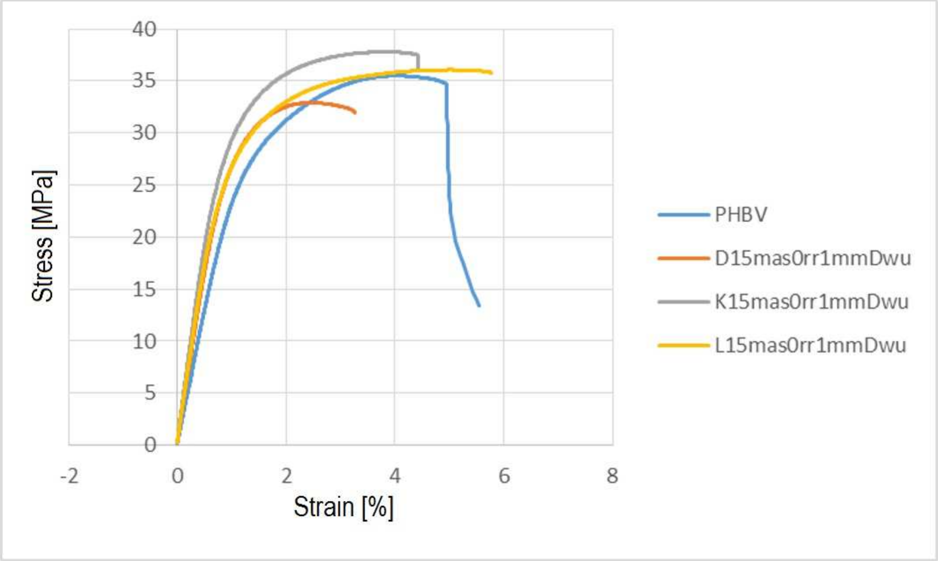

Fig. 6. The stress – strain characteristics for a variable type of filler and pure PHBV biopolymer

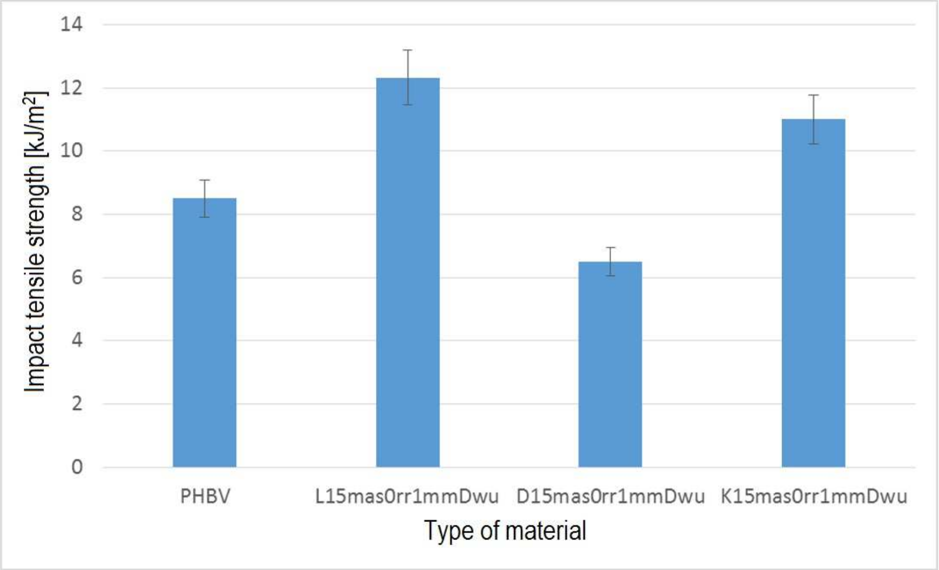

Fig. 7. The impact tensile strength results for composites with variable type of filler and for pure PHBV biopolymer

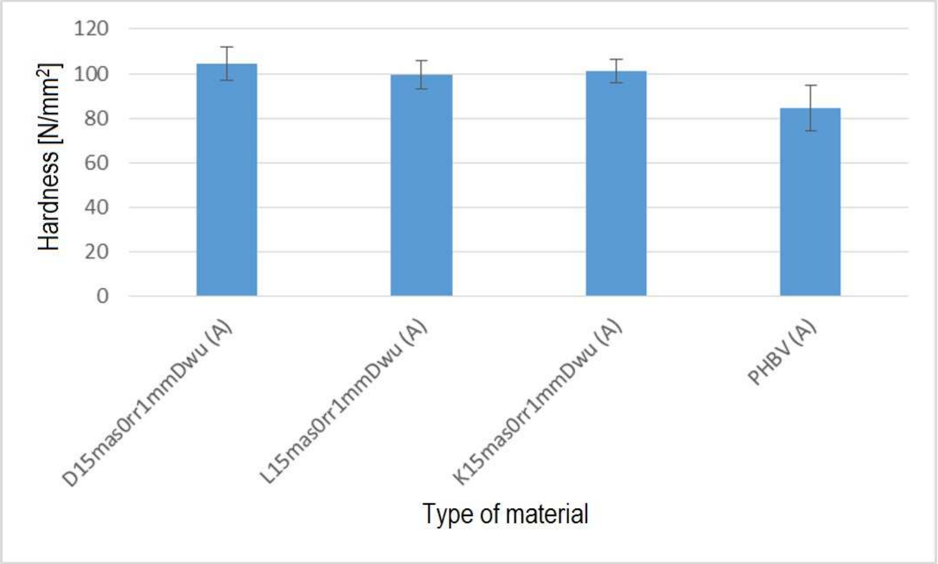

Fig. 8. The hardness test results for a variable type of filler and for the pure PHBV biopolymer

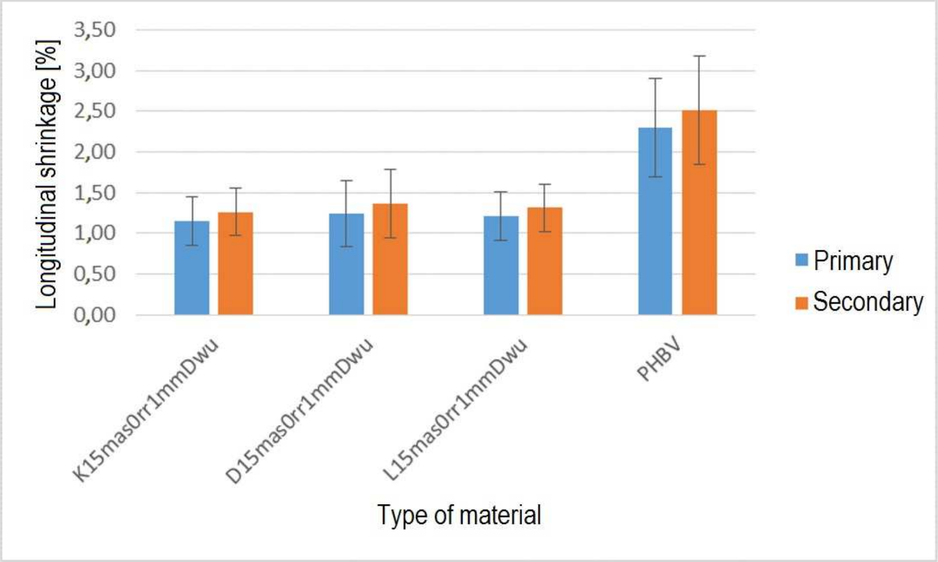

Fig. 9. Primary and secondary shrinkage of the moulded piece measured in the longitudinal direction for a variable type of filler and for a pure PHBV biopolymer

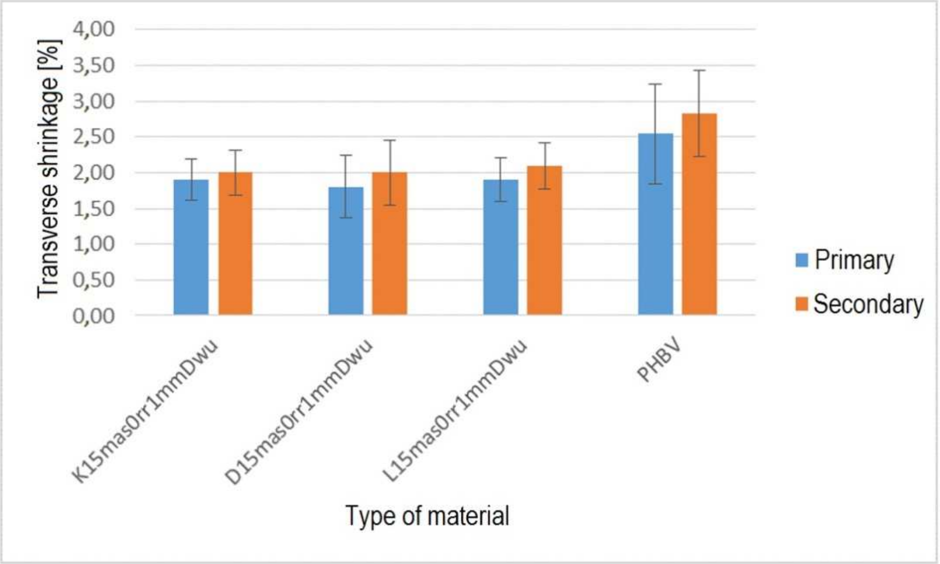

Fig. 10. Primary and secondary shrinkage of moulded piece measured in the transverse direction for a variable type of filler and for a pure PHBV biopolymer

4. Conclusion

1. As a part of the study double green composites with good mechanical properties, comparable to popular polyolefin's group of plastics and much better than pure PHBV biopolymer, were produced. The cost of producing the material based on fully biodegradable PHBV has been reduced thanks to the use of natural fibres.
2. When analysing the results of research, it should be noted that mechanical properties, as well as the quality of the PHBV biocomposites, improved when using flax and hemp fibres already by a small percentage of them (15% by mass).
3. In the case of wood fibres, despite correct chemical treatment applied by the manufacturer, poor results of mechanical properties were obtained, even in relation to the PHBV biopolymer.
4. For all the produced composites filled with cellulose fibres, greater adsorption of water, compared to pure PHBV is noticeable, which is evident due to the presence of polar OH groups in the structures of cellulose fibres.
5. The results obtained for PHBV composites filled with the flax and hemp fibre are the basis for further research. In the case of wood fibre – the subsequent stages of testing with the use of this filler will not be continued.
6. Higher mechanical properties of the produced composite in relation to, e.g. PE or PP, allow to use it for the production of more durable packaging, containers, and disposable transport pallets, elements of investment road infrastructure as well as for gardening, for example as covers of unique trees in parks and forests. Application in other areas of economy is conditioned by economic factors and the required durability of products.

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WYBRANE WŁAŚCIWOŚCI BIOKOMPOZYTÓW O OSNOWIE PHBV Z NAPEŁNIACZAMI CELULOZOWYMI

Streszczenie

W pracy przedstawiono wybrane właściwości wytworzonego biokompozytu w osnowie biopolimeru PHBV – poli(kwas 3-hydroksymasłowy-co-3-hydroksywalerianowy), który otrzymuje się przez kopolimeryzację poli(kwasu 3-hydroksymasłowego) i poli(kwasu 3-hydroksywa-lerianowego). Biopolimer stosowany w badaniach zawierał 8% poli(kwasu 3-hydroksywa-lerianowego). Do wytworzenia kompozytów użyto trzech rodzajów napełniaczy w formie włókien: drzewnych, lnianych i konopnych w celu otrzymania najlepszych właściwości mechanicznych kompozytu. Podczas doboru rodzajów napełniaczy uwzględniono dostępność i koszt w obszarze geograficznym Polski, a także właściwości mechaniczne. Napełniacze poddano zabiegowi merceryzacji oraz określono parametry modyfikacji włókien. W badaniach stosowano następujące zawartości masowe napełniaczy: 15%, 30%, 45%, 50% oraz różne długości włókien. Do produkcji biokompozytów wykorzystano wytłaczarkę jedno- i dwuślimakową firmy Zamak. Początkowe parametry przetwarzania zostały określone za pomocą analizy DSC. Parametry technologiczne dobrano w zależności od rodzaju napełniacza i jego zawartości procentowej. Najlepsze właściwości mechaniczne w porównaniu z ogólnie dostępnymi polimerami, takimi jak PP, PE, PVC lub PS, otrzymano dla kompozytu z włóknem konopnym. Opracowany kompozyt jest całkowicie biodegradowalny. Lepsze właściwości mechaniczne wytwarzanego kompozytu w stosunku do np. PE lub PP pozwalają na wykorzystanie go do produkcji wyrobów znajdujących zastosowanie w różnych obszarach gospodarki.

Słowa kluczowe: PHBV, włókna naturalne, kompozyty, biopolimery, formowanie wtryskowe

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