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## AN EVALUATION OF THE CHANGES TO THE MECHANICAL PROPERTIES OF POLYMER BIOCOMPOSITES RESULTING FROM THEIR LONG-TERM STORAGE AT LOW TEMPERATURES

### OCENA ZMIAN WŁAŚCIWOŚCI MECHANICZNYCH BIOKOMPOZYTÓW POLIMEROWYCH W PROCESIE DŁUGOLETNIEGO SKŁADOWANIA W NISKICH TEMPERATURACH

#### Abstract

This paper presents an analysis of the properties of biocomposites that were stored for four years in the refrigerator at 6°C and were investigated for detailed information of mechanical properties like tensile strength and bending. The study was based on test results obtained in 2011. Comparison of changes in the structure of composite materials was carried out an analysis of SEM image. Matrix filling materials were made of wood fibres and tuff.

*Keywords: biodegradable composites, strength properties, stores in low temperature*

#### Streszczenie

W artykule przedstawiono analizę właściwości materiałów kompozytowych, które przechowywano przez cztery lata w lodówce w temperaturze 6°C. Wykonano badania wytrzymałościowe w tym, m.in. testy wytrzymałości na rozciąganie i zginanie. Przeprowadzono również porównania zmian struktury materiałów kompozytowych na podstawie wykonanych zdjęć SEM. W próbkach, jako napełniacz zastosowano mączkę drzewną i tuf wulkaniczny.

*Słowa kluczowe: kompozyty biodegradowalne, właściwości wytrzymałościowe, przechowywanie w niskich temperaturach*

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### 1. Introduction

Given the state of the environment and the widespread concern for its protection, industry strives to develop methods for the preparation of biocomposites using plastics and natural energy sources. Thus, the development of new plastic products has occurred as a result of desire to protect the environment. These materials have low impact on the environment. Cellulose fibres, starch and wood fibres may be used in production of the natural raw material. The substance with the greatest potential for use is starch because of its low price and wide availability. An additional advantage of starch is that it is highly renewable [7].

Biocomposites form a group of materials where at least one component is biodegradable or a bio-derivative. Frequently, a component has these two features at the same time. To a group of composites we may include polymers of petrochemical origin and polymers with additives natural or synthetic fibers. Fibres are obtained from plants. They may also be, for example, the shells of crustaceans or chitosan, fungi or bacteria. The most interesting group of composites is one considered to be those based on starch and polylactide. These biocomposites are well established on the Polish market and are already produced on a massive scale [3, 8].

The biocomposites includes thermosetting materials (during the manufacture have a plastic properties and can be easily formed) and thermoplastic materials (repeatedly formed in high temperature). In Fig1 the devision of distribution biocomposites are shown [2, 4].

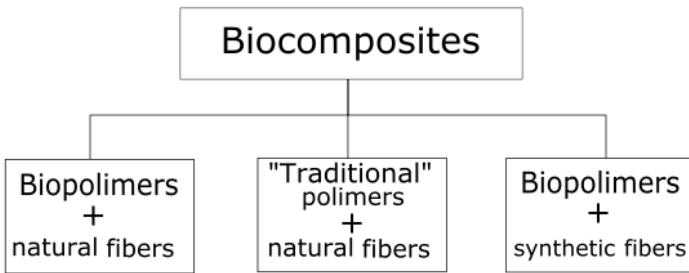


Fig. 1. General division biocomposites [1]

Composites are increasingly used in industry, they are used as decorative elements and components of household appliances. Examples include gears, garden hosepipes and sewer pipes. Composites also started to be incorporated into machines. Research is ongoing and its aim is to expand the use of biocomposites as elements of pressure devices, e.g. tubesheets.

### 2. Fillers (additives) used in investigated biocomposites

In these tests, the filler was made up of wood fibres and tuff. Below show the short characteristics:

- **Wood fibres** – the natural organic filler. These form part of a group of additives being used for the first time in the world. They are most commonly used as an additive for plastics which are of plant origin.
- **Tuff** – this is a natural, inorganic filler obtained from volcanic rock. It was created as a result of the deposition process, as well as the consolidation of products formed during volcanic eruptions.

In the investigation carried out for the 4 types of warps. The types of warp in the industry are identified as BioCérès® BC-LBI01, BioCérès® BC-LBI08, Bio-Flex® F6510 and Biograde® C9555. The information about the particular composition of the warp are kept secret by global companies. For each type of the warp created three types of samples: without additives, with 25% mas wood fibres and with 25% mas tuff. A total were carried out analysis of 12 types of samples which were shown in Tab 1.

Table 1

**The compositions and marking tested polymer composites**

Lp.	Marking samples	Type of warp	Wood fibres [% mas]	Tuff [% mas]
1	<b>L1</b>	BioCérès® BC-LBI01 (wheat starch)	-	-
2	<b>L1M</b>		25	-
3	<b>L1T</b>		-	25
4	<b>L8</b>	BioCérès® BC-LBI08 (wheat starch)	-	-
5	<b>L8M</b>		25	-
6	<b>L8T</b>		-	25
7	<b>FF</b>	Bio-Flex® F 6510 (polylactide + polyester)	-	-
8	<b>FFM</b>		25	-
9	<b>FFT</b>		-	25
10	<b>BC</b>	Biograde® C 9555 (polycellulose)	-	-
11	<b>BCM</b>		25	-
12	<b>BCT</b>		-	25

### 3. Test results

The tests were carried out on samples that were stored for 4 years in a refrigerator at 6°C. They were intended to demonstrate the effect of storage conditions on the mechanical properties of the polymer biocomposites during periods of long-term storage.

The mechanical properties of the composites were tested on a MTS 030 Criterion extensometer testing machine. The mechanical properties were determined on the basis of PN-EN ISO 527-1 using a sample in the shape of a dumb-bell – the cross-sectional dimensions were 10×4 mm. The statistic tensile test was performed at room temperature. The investigation carried out of basic mechanical properties: tensile strength  $\sigma_m$ ,

$E$  modulus, elongation at break  $\varepsilon_r$ . Used in research polymer matrix belong to three groups of polymers. The first two (BioCérès® BC-LBI01 and BioCérès® BC-LBI08 are based on wheat starch. The difference between these two webs is primarily the varying content of plasticizers. Two further groups of biopolymers (Bio-Flex® F6510 and Biograde® C9555) are manufactured by the German company, FKUR. The same group of biopolymers (Bio-Flex®) consists of a mixture of polylactide and polyesters in different ratios, depending on the variety. Genre Bio-Flex® F6510 can be formed during of ejaculation and process of blowing up. Biograde® C9555 biopolymer is selected from cellulose-based matrices [5, 6].

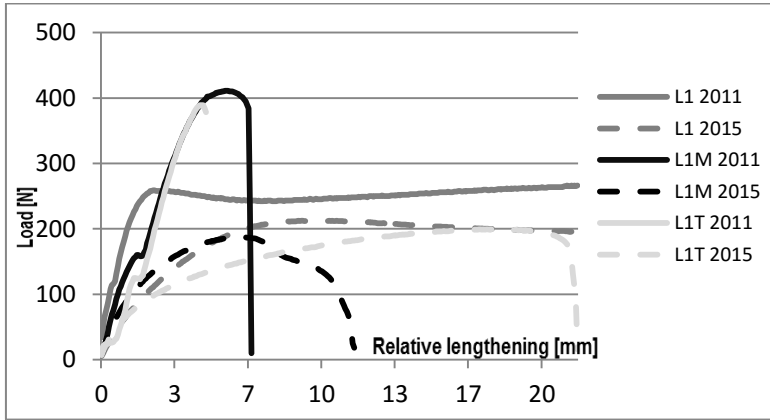


Fig. 2. Stress- strain curve L1 before (2011) and after (2015) storage in low temperature

For each type of samples decrease of the yield strength and tensile strength were noted. The samples with additives change the shape of the graph were observed, lower values of maximum force and increase in value of relative lengthening. The samples without additives were observed large decrease in the value of tensile strength. The graphs shape of the samples before storage is similar.

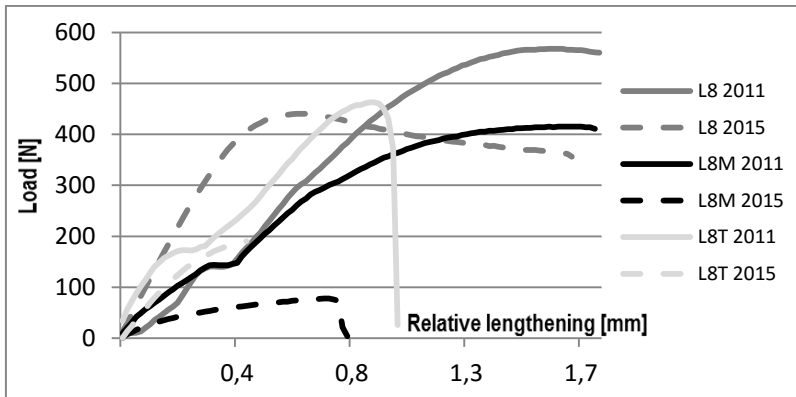


Fig. 3. Stress- strain curve L8 before (2011) and after (2015) storage in low temperature

After four years storage change of the shape of the graph for the type of samples without additives were observed. In this type of samples we observed increase the yield strength and tensile strength. The structure was strengthened. The samples with additives were observed reduction value of relative lengthening.

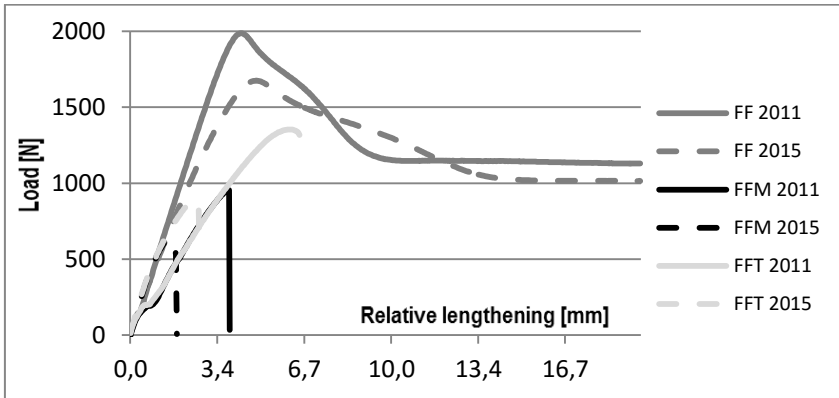


Fig. 4. Stress- strain curve FF before (2011) and after (2015) storage in low temperature

After four years of storage decreases of tensile strength and yield strength and tensile strength were observed. For samples with additives were observed lower relative lengthening. The general conclusion is that the polymers based on cellulose practically no damping a natural and mineral (inorganic) additives. Therefore, the cellulose-based the warp is not used in the biocomposites.

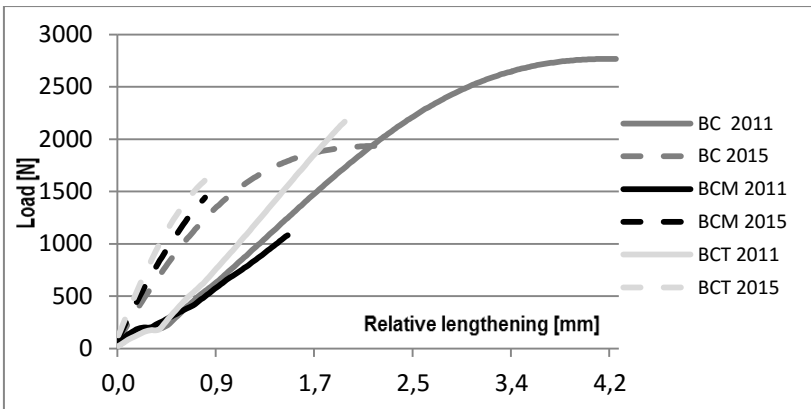


Fig. 5. Stress- strain curve BC before (2011) and after (2015) storage in low temperature

Again, note the decline in the value of tensile strength and yield strength of the samples without additives after the storage period. It is also noted that there was a significant reduction of the elongation of samples after storage. An interesting phenomenon is the tensile strength of the samples in polymers composite with wood fibres after storage.

#### 4. SEM analysis

SEM images were made at the site of samples after fracture. Images were carried out of after static tensile test. The images were made by scanning electron microscope JOEL JSN5510LV and used of different magnifications (x100; x200; x500).

In Fig 5 are shown SEM images of one of the tested composites (L1M) taken before and after storage – the images were taken at different levels of magnification. Changes in the structure that have occurred over the years can be observed in these images; these changes in structure have an obvious negative impact on the strength of the samples.

In the images in Fig. 5, we can see:

- strong connection between the warp and additives after storage,
- the microstructures after storage in this type of samples were more developed surface,
- increase the area of the internal structure of the material,
- looser connections between the matrix and the reinforcement after storage.

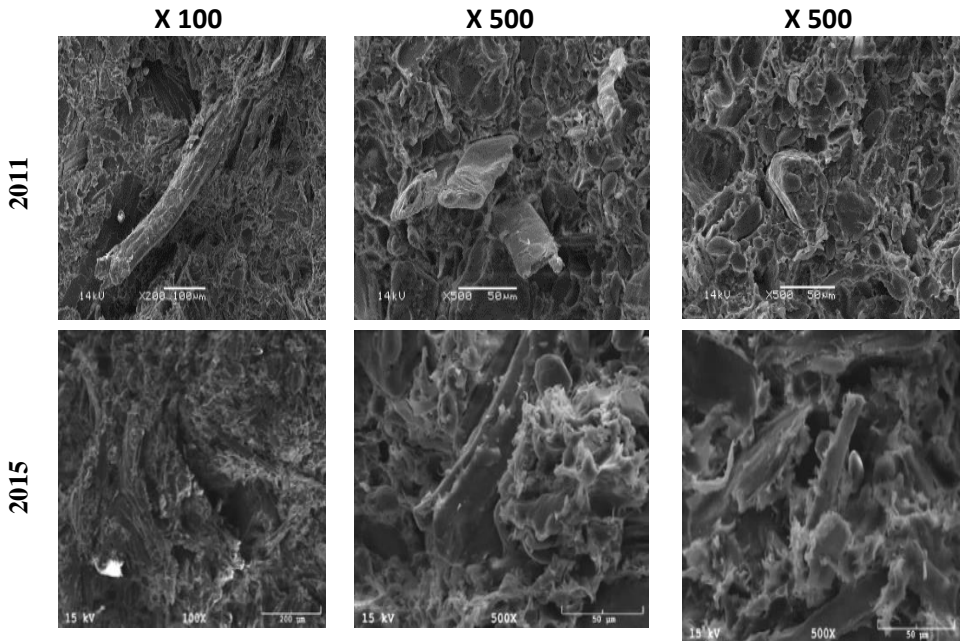


Fig. 6. Comparison of L1M samples before and after the four-year storage period

The following Tab 2 present all results of strength properties before and after storage.

Table 2

## The results of tests of selected strength properties before and after storage

Year	2011			2015		
Material	$\sigma_m$ [MPa]	$E$ [MPa]	$\varepsilon_r$ [%]	$\sigma_m$ [MPa]	$E$ [MPa]	$\varepsilon_r$ [%]
L1	8.02	808	51.7	4.88	487	70.1
L1M	9.22	1847	1.5	4.95	1341	1.1
L1T	10.64	2075	1.5	4.92	684	5.4
L8	14.72	2892	9.3	10.72	3114	1.1
L8M	10.68	2374	1.4	2.03	1303	0.5
L8T	9.68	4196	0.8	4.84	2184	0.45
FF	49.24	2916	127	34.35	2670	131.8
FFM	20.08	3550	1.6	19.91	3005	1.03
FFT	28.22	3609	1.4	23.30	3123	1.31
BC	67.34	6134	3.8	48.04	4601	2.13
BCM	22.36	6517	1.2	34.16	5488	0.76
BCT	44.74	9325	1.7	41.72	6836	0.86

where:

- $\sigma_m$  – is the tensile strength,
- $E$  – is the elastic modulus of material at design temperature,
- $\varepsilon_r$  – is the relative elongation.

## 5. Conclusion

Despite storage of samples at low temperatures and adverse conditions during the composting biodegradation was noted a decrease in the mechanical properties (tensile strength and yield strength). It confirmed the initial assumptions about the decrease in the value of the mechanical properties. However, there were exceptions described above where increases in the values for different types of thermoplastic polymer matrices and additives were noted.

The unplasticized thermoplastic starch (L8) is a low-biodegradable. The sample-based unplasticized thermoplastic starch (L8) with additives are more biodegradable. It does not depend on the type of supplement.

This is advantageous and resulted in a significant shortening of the life cycle of polymeric materials and the carbon cycle. The work pointed to the need for greater use of biodegradable materials in order to reduce waste and for improved utilisation of biological methods of recycling or composting. This is particularly important in the manufacture of disposable products and those which can easily penetrate the environment causing pollution.

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