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Biocomposites based on PHB filled with wood or kenaf fibers

Summary — In this paper, possibilities of processing biocomposites based on polyhydroxybutyrate (PHB) filled with 25 and 40 wt. % of wood flour or kenaf fibers are presented. Mechanical properties (tensile strength, modulus of elasticity) under three testing temperatures, a water absorption and its influence on properties, the process of biodegradation in the garden compost as well as SEM images of fractured composites are discussed. Modulus of elasticity and tensile strength increased with rising content of wood flour and kenaf fibres. The results show that PHB filled with kenaf fibers has higher mechanical properties, even despite higher ability to absorb water. Tested biocomposites absorb water and their mechanical properties decrease after exposure to water. It is caused by beginning of biodegradation process and resolving a biodegradable biopolymer in water. This property can be interesting for packaging especially for fresh produce like fruit or vegetables and for industrial products with short-time life cycles.
Keywords: biocomposites, kenaf fiber, wood flour, mechanical properties.

KOMPOZYTY NA OSNOWIE PHB NAPEŁNIANE WŁÓKNAMI NATURALNYMI
Streszczenie — Wytworzono biokompozyty na podstawie polihydroksymaślanu (PHB) napełniane dodatkiem 25 lub 40 % mączki drzewnej bądź włókien kenafu. Zbadano ich właściwości mechaniczne w statycznej próbie rozciągania (tabela 1), chłonność wody (rys. 2), oceniono także wpływ temperatury (rys. 3—6) oraz kompostowania na właściwości otrzymanych kompozytów (tabela 2). Zaobserwowano 5-krotny wzrost modułu sprężystości oraz 1,5-krotny wzrost wytrzymałości na rozciąganie kompozytów PHB z dodatkiem 40 % włókien kenafu. Kompozyty PHB napełniane włóknami kenafu, pomimo większej zdolności do wchłaniania wody, charakteryzują się lepszymi właściwościami mechanicznymi niż napełniane mączką drzewną. Obrazy SEM przedstawiają pęknięte, prostopadle do płaszczyzny rozciągania, włókna kenafu (rys. 7) oraz bardziej wzdłuż przekroju popękane włókna mączki drzewnej (rys. 8). Biodegradacja wytworzonych kompozytów przebiega stosunkowo wolno i po 40 dniach inkubacji w kompoście zmiany właściwości mechanicznych są niewielkie (nie przekraczają 10 % ich początkowych wartości). Predysponuje to takie biokompozyty do zastosowań na opakowania owoców i jarzyn (łubianki, koszyki, skrzynki *etc.*) lub na elementy ogrodowe bądź rolnicze (słupki, wsporniki).
Słowa kluczowe: biokompozyty, włókna kenafu, mączka drzewna, właściwości mechaniczne.

Biopolymers are attracting more and more attention being seen as environmentally friendly (biopolymers are produced from renewable resources with lower energy consumption and can be designed to be biodegradable). Yet the biopolymers market is still relatively small compared to traditional petroleum polymers. Biopolymers can be mainly classified as agro-polymers (starch, cellulose) and biodegradable polyesters [polyhydroxyalkanoates — obtained by microbiological production, poly(lactic acid) — chemically synthesized using monomers obtained from agro-resources, *etc.*] [1]. Polyhydroxybutyrate (PHB) is an isotactic, linear homopolyester built of 3-hydroxy butyric acid behaving as a conventional thermoplastic material [2]. It is a biopolymer which is present in all living organisms (many bacteria produce PHB in large quantities as a storage material). It can be processed into pellets that can be handled on plastics machines in the same way as traditional plastics produced from oil. PHB has attracted much attention as biodegradable thermoplastic polyester and has high potential as an environmentally degradable plastic as it can degrade through various types of bacteria and fungi application into carbon dioxide and water through secreting enzymes [3, 4]. PHB serves as nutrient and provides conditions which are present in compost (when phosphates, nitrogen, salts, humidity, and heat allow the microorganisms to grow). Therefore articles made of PHB stay unharmed for years [5]. It can also be degraded through

nonenzymatic hydrolysis. The advantageous properties of PHB and its copolymers are biodegradability and biocompatibility (meaning it is a metabolite normally present in blood [1]) with the present drawbacks of poor thermostability and relatively low impact resistance. Brittleness and slow crystallization of PHB reduce its processability [6].

Despite high prices, there are many places where PHB is used. The US Navy opted to use PHB cups, which can be easily thrown overboard after use and degrade in the sea. In Japan, PHB is being used for manufacture of women's disposable razors. Over the longer term, PHB producers believe the material will be suitable for food packaging such as yoghurt cups and beverage bottles. However, a big obstacle is obtaining food contact approvals. Due to the many substances present in the residual biomass, food-approval testing is prohibitively expensive. Suppliers such as Biomer are putting food-approval effort on hold until it can secure a commitment from a large food processor [1].

For certain applications, biopolyesters cannot be fully competitive against conventional thermoplastics since some of their properties are too weak. Therefore, into order extend their applications, these biopolymers have been filled with natural fillers such as wood flour, kenaf, flax, jute, hemp, sisal and kapok, which could bring an improvement of some properties such as stiffness or thermal stability. Natural fibers are biodegradable and renewable resource-based bioplastics can be designed to be either biodegradable or not, according to the specific demands of a given application. Biocomposites can supplement and eventually replace petroleum-based composite materials in several applications such as packaging, automotive industry, construction materials, furniture and consumer goods.

Kenaf fiber composites are increasingly used for making automotive interior trim parts because of their excellent strength and renewability. An illustrative example is the use of kenaf fiber instead of glass fiber in making automotive headliner. With blast fibers, such as kenaf, the fiber needs to be removed from the plant core (decortication) and extracted from the natural plant polymer (retting) before it can be used for composite manufacture. Pretreatment with some chemicals will increase the penetration and bonding efficiencies of the polymer matrix [7].

The aim of our was processing and estimation of properties of new biocomposites based on PHB, thermoplastic and biodegradable polymer of natural origin filled with commonly used wood flour and kenaf fiber.

EXPERIMENTAL

Materials

The research has been done for biocomposites based on polyhydroxybutyrate (PHB) filled with two types of natural fibers (wood and kenaf).

— As a matrix, polyhydroxybutyrate Biomer P226 was used, biodegradable polyester produced by German company Biomer.

— Wood flour CB 120 produced by J. Rettenmaier & Söhne and kenaf fiber produced by Kenaf Eco Fibers Italy were used as a filler. The wood flour CB 120 is produced from pine, has fibrous structure and the length of particles is about 70—150 μm. Lignocel is a natural fiber which is "ready-to-use" for direct processing at extrusion facilities and injection-molding machinery [8—11].

The kenaf fiber derived from processing the bark of the kenaf plant is pale yellow in color and is the most highly valued natural product. It has a degree of purity from wood debris and pectins equal to 99 % and is highly appreciated in the construction of mats with thermoset for the automotive industry and technical applications. The fibers after grinding in our laboratory on Retsch ZM 200 mill machine have approximately the length about 200—300 μm and the diameter about 40—50 μm.

Sample preparation

Standard dumbbell specimens were produced by injection molding in the laboratory of University of Technology and Life Sciences in Bydgoszcz (Poland), using an injection molding machine Wh80 Ap with double cavity mould. The injection process was done under following conditions: temperatures — 120 °C, 180 °C and 185 °C, a speed of screw rotation — 100 min^{-1}, an injection time — 3 s, a holding pressure time — 7 s, a cooling time — 20 s. Additionally, for preparing and better homogenization of PHB granulates with the fillers, rolling and extrusion processes were carried out. The roll stand machine (the roll length — 380 mm and the diameter — 200 mm) was used. Composites were rolled under the following conditions: a temperature — 180 °C, a rotational speed — 20 and 25 min^{-1}, a slot between the rollers — 1,5 mm. The weight of the charge (300 g) was readjusted to provide continuous flow of polymer at the length of the slot. Then the sheet was granulated and extruded using an extruder W32 (L/D = 25). The extruder barrel temperature zones were: 130 °C, 160 °C, 175 °C and 180 °C, a speed of screw rotation — 30 min^{-1}.

The weight content of fibers in composites was 25 and 40 % of wood flour and kenaf fibers (specimens indicated 25W, 40W and 25K, 40K).

Methods of testing

— The injection-molded specimens were tested at 21 °C and 65 % RH on an universal testing machine (Instron type 4465) according to the PN-EN ISO 527 standard. The test was carried out with the constant crosshead speed of 5 mm/min. Five specimens were tested for each composite and the mean value and the range of the specific modulus of elasticity, specific ultimate tensile strength and strain at break was measured. The tensile

test in higher temperatures (40 and 60 °C) was carried out by putting specimens in the temperature chamber (Instron) mounted between the jaws of tensile machine. The specimens were conditioned in the temperature of test for 30 minutes before the tensile test. Three-point bending test was done according to PN-EN ISO 178:2006 standard using bending machine BPG 50/2, Charpy impact test was done on Zwick pendulum machine HIT5.5P according to PN-EN ISO 179 standard.

— The water absorption of composites was measured after immersion in distilled water in 23 °C for 7 and 90 days according to PN-EN ISO 62:2000 standard. The specimens were dried and weighted with accuracy of 0,0001 g. The density was measured using immersion method according to PN-92/C-89035 (ISO 1183) on the WAS 220X.

— The images of structure were taken from samples after tensile test using scanning electron microscope SEM (JEOL 5510LV low vacuum) with an accelerating voltage of 10 kV at the Institute of Material Engineering, Cracow University of Technology.

— To estimate the influence of biodegradation process on the properties of tested materials, the specimens were placed in the garden compost for 40 days and then tested on the tensile machine.

RESULTS AND DISCUSSION

Mechanical properties

In Table 1, changes of basic mechanical properties after immersion in water (7 and 90 days) and in the garden compost (40 days) were presented. In case of unfilled biopolymer, mechanical properties change insignificantly under influence of water and the garden compost. Biopolymers filled with kenaf fibers show higher values of modulus of elasticity and tensile strength than wood flour composites. The effect of the matrix reinforcement is decreasing due to long time of incubation in water and in the garden compost, which is the effect of partial biodegradation of the material. For biocomposites the water is the agent which increases the degradation effect. Adding fibers caused reduction of the elongation at break, comparable for both types of the filler. For biocomposites Charpy impact strength stayed at the same level as for pure PHB (Fig. 1).

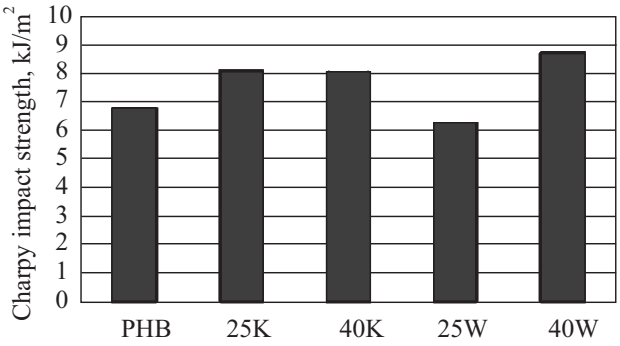

Fig. 1. Comparison of Charpy impact strength for PHB and biocomposites with wood flour or kenaf

T a b l e 2. Density and mechanical properties of the composites and PHB obtained in bending test for dry and incubated in the garden compost specimens*)

	Dry				Compost		
	density g/cm^3	σ_g MPa	E_g MPa	f mm	σ_g MPa	E_g MPa	f mm
PHB	1.23	13.0	598	6.5	13.0	589	6.6
25K	1.27	16.5	2481	2.0	13.8	1969	2.1
40K	1.30	19.6	4516	1.3	19.6	4198	1.4
25W	1.26	15.2	1819	2.5	13.2	1726	2.3
40W	1.30	15.7	2772	1.7	12.7	2004	1.9

*) σ_g — bending strength, E_g — bending modulus of elasticity, f — deflection at break.

Density of tested composites maximally increased by approx. 5 % in the case of 40 % weight content of the filler (Table 2). Biocomposites filled with kenaf fibers have higher values of bending modulus than wood flour composites. After placing in the garden compost (40 days), pure PHB measured properties didn't change, but adding natural fiber caused decrease of bending mechanical properties by approx. 10 %.

T a b l e 1. Mechanical properties of the composites and PHB after various time of immersion in water and incubation in the garden compost*)

Symbol of specimen	σ_z, MPa				E, MPa				ε_z, %			
	dry	7 days in water	90 days in water	40 days in compost	dry	7 days in water	90 days in water	40 days in compost	dry	7 days in water	90 days in water	40 days in compost
PHB	21.6	20.1	19.0	19.3	1750	1400	1440	1627	4.5	5.7	4.4	4.0
25W	23.7	19.6	14.9	22.3	3900	2850	2630	3434	1.0	1.2	1.9	1.5
25K	26.3	23.4	15.4	23.9	5600	5190	3540	5821	1.3	1.0	0.4	1.1
40W	22.0	19.4	10.8	21.5	6200	4560	3800	5022	0.5	1.1	0.5	1.0
40K	28.2	22.7	12.2	18.9	10 000	5910	3600	5739	0.7	0.5	0.8	0.6

*) σ_z — tensile strength, E — modulus of elasticity, ε_z — strain at break.

Water absorption

Composites absorb moisture in humid environments and undergo dilatational expansion. The presence of moisture and the stresses associated with moisture-induced expansion may cause lower damage tolerance and structural durability [12].

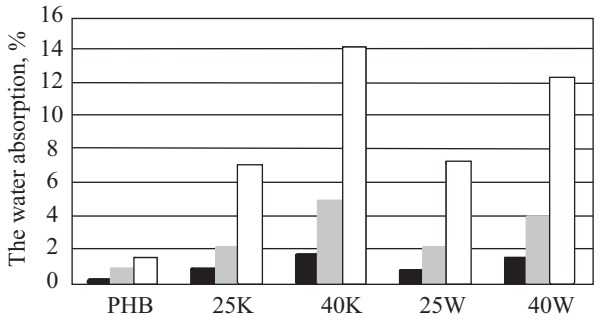

Fig. 2. Comparison of water absorption by PHB and biocomposites with wood flour or kenaf: ■ — samples soaked for 24 hours, ■ — samples soaked for 7 days, □ — samples soaked for 90 days

The level of absorbed water of tested composites was shown in Fig. 2. The weight of soaked specimens was measured after one day, one week and 90 days. We can observe that adding wood flour and kenaf fibers to PHB caused an increase of absorbed water by composites. As it can be seen, composites filled with 40 % of kenaf fibers have higher content of absorbed water but still their tensile strength is higher than for wood flour composites (see Table 1).

Natural fiber composites can be used in many applications owing to various desirable properties including high specific strength, high specific stiffness [13]. Unfortunately, natural composites — especially those based on thermoplastic biopolymers — are more sensitive to heat and moisture when operating in a changing environment and varying conditions of usage.

Influence of temperature

When a polymer specimen is tension tested at elevated temperatures, its modulus of elasticity and strength decrease with increasing temperature because of thermal softening. In a polymeric matrix composite, the matrix-dominated properties are more affected by increasing temperature than the fiber-dominated properties [14]. It is especially important for composites based on thermoplastic PHB with thermal properties like for Biomer P226 (T_g — approx. 9 °C, melting point — approx. 175 °C, TMV — approx. 53 °C).

In Figure 3, the comparison of elongation curves for PHB and its composites with kenaf fibers and wood flour tested in higher temperature (40 °C) is presented. We can

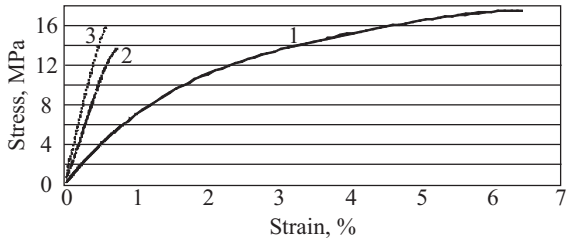

Fig. 3. Comparison of tensile curves (stress-strain) for PHB filled with wood flour or kenaf fiber determined in 40 °C: 1 — PHB, 2 — PHB filled with wood flour, 3 — PHB filled with kenaf fiber

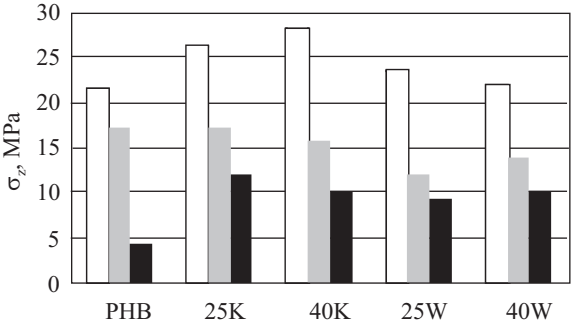

Fig. 4. Comparison of tensile strength of biocomposites with wood flour or kenaf, determined at various temperatures: □ — 23 °C, ■ — 40 °C, ■ — 60 °C

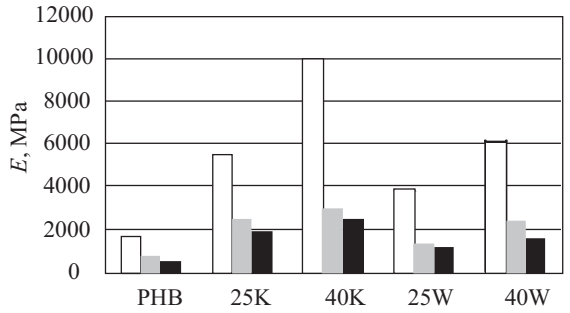

Fig. 5. Comparison of modulus of elasticity of biocomposites with wood flour or kenaf, determined at various temperatures: □ — 23 °C, ■ — 40 °C, ■ — 60 °C

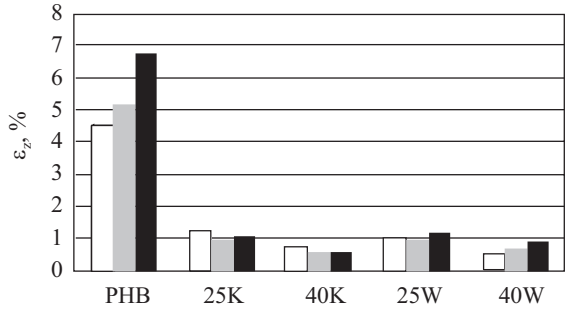

Fig. 6. Comparison of strain at break of biocomposites with wood flour or kenaf, determined at various temperatures: □ — 23 °C, ■ — 40 °C, ■ — 60 °C

observe the effect of increasing stiffness as a result of adding natural fibers to PHB matrix in higher temperature.

In Figures 4—6, comparison of tensile strength, modulus of elasticity and strain at break determined at various temperatures (23 °C, 40 °C and 60 °C) is presented. Adding natural fiber caused an increase of tensile strength for PHB composites in higher temperature compared to pure polymer (Fig. 4). The addition of natural fiber, especially kenaf, improved up to three times modulus of elasticity consequently in increasing temperatures (Fig. 5). Strain at break increased only for pure PHB under higher temperatures, for composites it stayed at the same level (Fig. 6).

The interface in any fiber-matrix composite system is responsible for transmitting stresses from polymer to the fibers. This stress transfer efficiency largely depends on the fiber-matrix interface and mechanical properties of the fiber and polymer [15]. Fig. 7 and Fig. 8, show a comparison of an effect of filling thermoplastic matrix — Biomer P226 with 40 % of wood flour and kenaf fibers. We can observe that the differences between morphology of chosen natural fibers — longer and more stiffness kenaf fiber seem to be more coherent and breaks perpendicularly to the polymer matrix. On the fractured surfaces after elongation test, we can observe that some fibers are pulled out from the matrix, but most of them are still tightly linked to the matrix. It is an effect of developed surface of fibres and good adhesion and that is a reason of increased strength of composite.

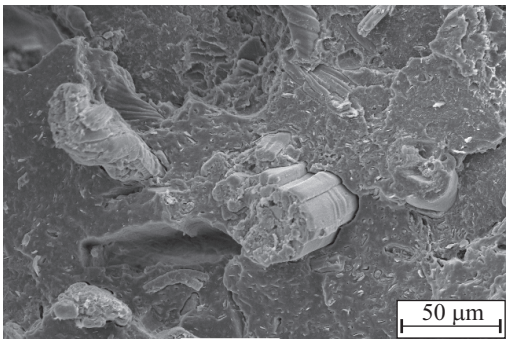

Fig. 7. SEM image of fracture at ambient temperature after elongation of PHB filled with 40 wt. % of kenaf fiber

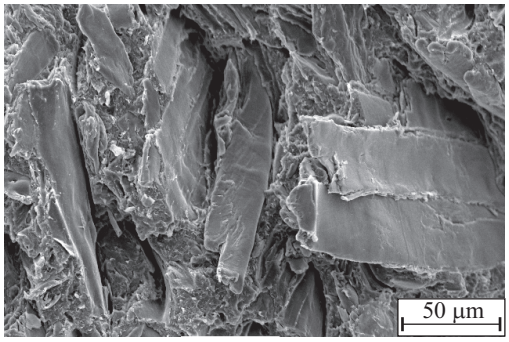

Fig. 8. SEM image of fracture at ambient temperature after elongation of PHB filled with 40 wt. % of wood flour

CONCLUSIONS

This study has shown that biocomposites based on thermoplastic biodegradable PHB filled with natural fibers, both from renewable material, can be an interesting alternative to conventional polymeric material based on gas or oil modified by hand-made fiber like glass or carbon.

In case of adding kenaf fiber (without special aperture) to PHB we can observe improvement of mechanical properties compared to wood flour which has special preparation. It is confirmed by increasing modulus of elasticity up to five-times and 30-proportional increase of tensile strength for PHB filled with 40 % of kenaf fiber. The increase of tensile strength and SEM images observations confirm good adhesion between natural fibers and PHB. In comparison to composites based on thermoplastic starch, this increase is lower [16, 17]. However, the advantage of composites based on PHB is the higher stability of properties under the garden compost treatment and in water, which can create new opportunities of applications.

It seems that these biocomposites can be processed with classical plastic machines like injection molding machine or conventional extruders. It is important that it requires less electric energy with the same efficiency of processing because melting temperature of thermoplastic biopolymers like PHB is lower than polyolefines or other traditional plastic (PCV, PS or PA).

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