Effect of wood/basalt hybridization on crystallization and mechanical properties of PLA

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Abstract. In this study hybrid composites based on polylactide were reinforced with wood and basalt fibres. Composites have undergone physical and mechanical tests and the water absorption after 1 and 14 days as well as the effect of biodegradation on strength properties have been determined. Additionally the effects of annealing and temperature of tests on mechanical properties were investigated. The addition of fibres considerably increased the susceptibility of the tested composites and for composites with addition of 7.5 wt% of each wood and basalt fibres increased by more than 35% at +23°C and was by 12 times higher at 80°C. Heat treatment of composites positively influenced the results, mainly at elevated test temperatures. For pure PLA, the increase in Young's modulus was over 22 times (from 157 MPa to 3473 MPa). The addition of fibres resulted in a reduction of the differences between the materials before and after annealing. Impact strength was more than double for composites after heat treatment at room temperature.

1. Introduction

In recent years, biodegradable polymers have become more and more popular especially in the scientific research, due to their excellent mechanical properties, comparable to petrochemical polymers. An additional advantage of biodegradable polymers is their source of origin (renewable resources and nontoxic to the human body) and the fact that after the end of their life cycle they decompose into products naturally occurring in nature. Polylactide (PLA) is the most commercially used polymer in this group. PLA has been used in many fields, as a drug delivery, tissue engineering, and biodegradable fibres. However, due to the good mechanical properties, it is also increasingly used in other industries, such as automotive or aerospace. In these areas of application, fibres are often used to improve mechanical properties. Mainly, in the case of biodegradable composites the fibres come from natural sources, which not only improve their properties, but additionally leave the material completely biodegradable. The most common fibres reinforcing biodegradable polymers are fibres consisting of lignocellulose and hemicelluloses. In literature, the most common lignocellulosic fibres which reinforce the polymers are flax, hemp, jute, kenaf, and abaca [1,2]. Unfortunately, fibres containing lignocelluloses have some disadvantages, such as heat or water sensitivity, as well as poor adhesion due to their high hygroscopicity compared to hydrophobic polyolefin matrices. Moreover, the addition of natural fillers makes them difficult to manufacture due to the fact that natural fillers, mainly those containing lignocellulose, are heat-sensitive components [3]. An alternative to lignocellulosic fibres are mineral fibres, naturally occurring in nature, which after incorporation into the polymer do not impair its biodegradability. The new natural reinforcement of polymer composites
is basalt. Basalt fibres (BF) are characterized by excellent mechanical properties and high thermal resistance. They form a bridge between the most commonly used synthetic fibres, i.e. glass and carbon fibres. In comparison with glass fibres (GF), they have higher mechanical properties and higher thermal and chemical resistance, and compared to carbon fibres (CF), although they have lower strength and stiffness, they are cheaper and have better thermal and chemical resistance.

To accelerate the crystallization and improve crystallinity of PLA in order to increase the properties, numerous strategies have been employed, for instance, by blending, copolymerization, and manipulation of the processing. One of the most commonly described in the literature procedure to increase the crystalline phase in PLA is the addition of a nucleating agent, however, in the case of medical applications of PLA composites, this process is ruled out because often the nucleating agents are not biocompatible. Therefore, the appropriate selection of parameters during injection becomes an alternative and, as results from earlier tests, an effective attempt to increase the degree of crystallinity. Therefore, tailoring PLA’s crystallization behaviour has been identified as an important step in manufacturing in order to improve the properties [4]. The improvement of PLA properties by means of heat treatment is the subject of research by scientists. All works show that this process will significantly improve the strength properties of polymers. Srithep et al [5] investigated the effect of annealing time and temperature on the crystallinity and heat resistance of injection moulded PLA. Their study showed that after annealing at 80°C for 30 min improved mechanical properties - 17% of tensile strength.

Not only the addition of one type of fibre or heat treatment of PLA composites can significantly improve their properties. In recent years, the method of hybridizing composites has become an increasingly popular method of reinforcing polymer composites. This method consists in introducing at least two different components into the matrix. In the case of biodegradable polymers, the production of reinforcing fibres is important. Therefore, the simultaneous addition of two natural fibres, which are wood fibre and basalt fibre, causes not only the attribution of properties, but also leaves the material environmentally friendly. Therefore, this work concerns hybrid WF/BF composites. WF will be responsible for the increase of stiffness and density reduction of composites, while BF for the increase of mechanical properties. In addition, the influence of cold crystallization on the mechanical properties of the hybrid composites was determined. So far, the effect of hybridization of lignocellulosic and mineral properties on PLA has not been investigated.

2. Methodology

2.1. Materials

Polylactide grade PL1003 manufactured by Nature Plast (Isf, France). This polymer has the following properties: density — 1.24 g/cm³; fluidity index (190°C/2.16 kg) — 35 g/10 min; tensile modulus — 3500 MPa; un-notched Charpy impact strength — 16 kJ/m²; and thermal resistance (HDT B) — 55°C.

Wood fibres (Lignocel C120) manufactured by J. Rettenmaier&Söhne GmbH, (Rosenberg, Germany). The particles size is 70-150 μm.

Chopped basalt fibres (BCS17-6.4-KV16) provided by Basaltex Inc. (Wevelgem, Belgium) whose diameter amounted to 17 μm, length to 6.35 mm, density to 2.67 g/cm³, tensile modulus to 84 GPa, and tensile strength to 1 180 MPa;

Biocomposites:

PLA biocomposites were obtained using an injection moulding equipment Engel ES 200/40 HSL (Schwertberg, Austria). Injection moulding was carried out in the laboratory of plastics technology operating under GrupaAzoty SA (Tarnów, Poland). The size of the samples was 10x4x150 mm (dumb-bell shape).

Additionally, some of the injection moulded samples underwent isothermal heat treatment at 80°C for 1 h. Samples were placed to hot oven and they were hold between two glass sheets to prevent their deformation.
2.2. Method of testing

2.2.1. Density. The density of the produced composites was measured using the hydrostatic method at room temperature on a scale type RADWAG WAS 22 W, (Radwag, Radom, Poland) according to EN ISO 1183. The samples were measured in ethanol medium.

2.2.2. Morphology of fracture surfaces. Scanning electron microscope (SEM) analysis was conducted to describe the nature of failure and explain damage morphology employing low vacuum microscope JEOL 5510LV. The examined samples fractured during the tensile test were coated with a thin gold layer using vacuum coater (Carington) before observation.

2.2.3. Impact strength. The un-notched Charpy impact strength (\(a_{cl}\)) was measured using Zwick/Roell MTS-SP (Ulm, Germany) testing machine with a 1.5 J hammer.

2.2.4. Mechanical properties. The tensile test was performed by virtue of universal MTS Criterion Model 43 testing machine. The tensile test was performed with a constant cross-head speed of 5 mm/min, and the elongation was determined using the MTS axial extensometer and crosshead displacement. Furthermore, the test was run at room temperature (+23±2°C) and at decreased (-23°C) and elevated (+80°C) temperature range, which reflected the lowest and highest temperatures at which PLA composites can find practical application. Before the test, the samples had been conditioned and at the test temperature for 60 minutes.

The reported average data were based on the results of the tests concerning at least five standardized samples, along with calculated standard deviations to evaluate test reproducibility.

2.2.5. Hydrolytic degradation. The standardized samples were subjected to hydrothermal aging. They were immersed in a saline solution (2 wt. % salt) at 40 °C, to simulate human body environment. The samples were removed from the tank after 1 day and 14 days. The water remaining on the surface was wiped with a tissue paper and weighed. Finally, the water uptake was calculated as the mass difference, expressed as a percentage with the following formula:

\[
M_t = \left[ \frac{W_t - W_0}{W_0} \right] \times 100
\]

where \(M_t\) - percentage of water content, \(W_t\) - instantaneous weight of the sample, and \(W_0\) - initial weight of the sample.

Additionally, the tensile test was performed after 7 and 14 days of hydrothermal aging.

3. Results

![Figure 1. SEM images of PLA/7.5W7.5B.](image)

In figure 1 SEM photos of PLA compositions were presented with 7.5 wt% WF and 7.5 wt% BF
without annealing at the breakthroughs. Plastic breakthrough and evenly distributed fibres are observed. There are no visible agglomerations, and basalt and wood fibres mutually intertwine. There is a clear difference between the construction of WF, which are about 150 µm and made of several microfibrils, and thin, long BF. In the case of BF, the pull out phenomenon is more visible than in the case of WF. The remains of the matrix are visible on the BF, which may indicate good fibre-matrix adhesion, which has been confirmed in mechanical tests.

Table 1 shows the density values, impact strengths determined during the Charpy test without notch and the Vicat softening point (VSP). As can be seen, there was an increase in the density of the tested composites by about 5%, however, this increase is insignificant, because the composites with only 15 wt% of BF based on the PLA matrix have a density of 1.36 g/cm³ [6]. Addition of only WF would result in lowering density, while reducing strength values, so the creation of hybrid composites allows to create a material with relatively good strength properties compared to density. The addition of fibres will not significantly affect impact values, which is a beneficial phenomenon, because the decreased in impact strength of the lignocellulosic fibres described in the literature has been compensated by the addition of BF, which are characterized by high impact strength. Whereas, materials with an increased degree of crystallization were characterized by an over-two-fold increase in the impact strength- PLA/7.5W7.5B from 21.5±0.4 to 47.7±3.2 (kJ/m²). With the increasing fibre content VST increased. It is due to the increased stiffness of composites and high thermal stability of rigid BFs. The same situations like for impact strength occurred for VSP after heat treatment. The results are more than twice higher than for untreated composites.

Table 1. Density values, Charpy impact strength and Vicat softening point depending on the state.

| Samples            | Density (g/cm³) | State            | (kJ/m²) | Vicat softening point (°C) |
|--------------------|----------------|------------------|---------|---------------------------|
| PLA                | Polylactide    | 1.25±0.01        | Semi-amorphous | 20.4±0.5     | 60.8±1.9  |
| cPLA               | Nature Plast   |                 | Crystallized   | 40.6±1.2     | 161.2±2.5 |
| PLA/3.5W3.5B       | Polylactide + 3.5/3.5 | 1.27±0.01     | Semi-amorphous | 19.9±0.3     | 71.4±1.9  |
| cPLA/3.5W3.5B      | wt.% wood/basalt |                 | Crystallized   | 42.9±1.8     | 161.5±3.1 |
| PLA/7.5W7.5B       | Polylactide + 7.5/7.5 | 1.32±0.02     | Semi-amorphous | 21.5±0.4     | 77.4±2.1  |
| cPLA/7.5W7.5B      | wt.% wood/basalt |                 | Crystallized   | 47.7±3.2     | 164.9±2.7 |

Figure 2. The values of tensile strength (left) and elastic modulus (right) depend on temperature and state.

In order to determine the mechanical properties of the produced materials, a tensile test was carried out. In figure 2. the values of tensile strength and Young's modulus have been presented in two states at different temperatures (-24°C, 23°C and +80°C). The addition of fibres resulted in a decrease in the
tensile strength, however, as the fillers increase, the results are improved. This decrease is related to the addition of lignocellulosic fibres, the addition of which reduces the tensile strength [7]. The simultaneous addition of BF will not significantly increase the tensile strength in small amounts - 3.5 wt%. On the other hand, the increase in the content of BF, which have high strength properties, equalized values in relation to PLA at extreme temperatures. The addition of fibres improved the Young's modulus values at all tested temperatures. As the percentage of fibres increases, the value of the elastic modulus increases. As research shows, both WF and BF added separately significantly increase Young's modulus [8]. The highest increase in stiffness caused by the addition of fibres occurred at high temperatures, where the difference was 88.2% and 91.7% for PLA/3.5W3.5B and PLA/7.5W7.5B, respectively. These differences are due to the glass transition temperature PLA, which is within 60°C, which makes the unmodified polymer go from a brittle to a plastic state, which increases its deformation at the expense of strength properties. The addition of fibres has increased this temperature and thus increased stiffness. It is worth noting that the highest values for both tensile strength and Young's modulus were obtained at reduced temperatures.

The contribution of the crystalline structure, molecular mass and structure of the polymer chain is responsible for the strength properties of injected polymer composites. Therefore, in the tests, the composites were heat treated to obtain the crystalline phase. Thermal treatment of materials influenced the increase of PLA crystallinity, thus improving the tensile strength values at 23 and +80°C and slightly decreased at -24°C. The higher the temperature of the tests, the higher positive effect of crystallization was observed. The effect of crystallization on the increase in the properties of PLA composites is widely described in the literature [9]. The crystalline phase produced in PLA is stronger and stiffer than the amorphous phase. The highest improvement in properties was obtained for PLA at 80°C, increase by 50%. The increase in the crystalline phase in the composites improved the Young's modulus. In particular, this is observed in the case of elevated temperatures, where for PLA without crystallization, the decrease was over 95%, with the increase in the proportion of fibres the differences decrease. The addition of fibres made the reinforcement effect due to crystallization lower than in the case of neat PLA. Similar results were obtained by Wang et al [10], who investigated the effect of the crystallization time on the properties of PLA composites with GF (0wt%, 5wt%, 10wt%, 15wt% and 20wt%). The crystallization performed (80°C for 90 min) positively influenced the strength values of the composites. There was an increase in tensile strength and Young's modulus for pure PLA-60.4% and 34.3%, and for composites with 20wt% GF-20.6% and 35.8%, respectively.

Figure 3. Weight gain for PLA composites, tensile strength and Young's modulus after incubation in water.

Biodegradable composites absorb water more quickly than traditional petrochemical composites, therefore, in order to comprehensively characterize biocomposites, it is important to determine water absorption and its impact on mechanical properties. In figure 3 were shown weight gain (left) and
tensile properties after injection, 1 week and 2 weeks of immersion in water. The combination of hydrophilic lignocellulose fibres with non-absorbing mineral fibres allows to optimize some parameters. In the previous work, where the addition of only one type of fibre 7.5wt% WF, water absorption after 14 days was 2.15%, and 15wt% WF 3.51% [6]. Comparing these results with the results of hybrid composites, it can be noticed that the introduction of 7.5wt% WF and 7.5wt% BF resulted in a reduction of water absorption up to 1.8% and PLA/3.5W3.5B - 1.5%. The increase in the degree of crystallization will positively affect the water absorbency results for all materials tested. Similar results were obtained in the study of Kuciel et al [11]. Where the hybrid composites on the PLA matrix were tested with CF and BF (7.5/7.5 and 12.5/12.5 wt%). It has been confirmed that, both the introduction of carbon and basalt fibres as well as the increase in crystallinity reduced the possibility of water sorption. After 7 days of incubation in water for PLA12.5/12.5 after heat treatment, the water absorption was 20% lower than for the neat heat treated polylactide and as much as 50% lower than for the neat and non-heat-treated polylactide.

4. Conclusion
In the work, hybrid composites based on PLA reinforced with wood and basalt fibres with improved mechanical properties have been created. Reinforcement composites with natural fibres not only creates a material with high strength properties, but also leaves it harmless to the environment after the biodegradation process. The content of lignocellulosic fibres, which negatively influence the strength properties of composites, was compensated by the addition of basalt fibres, leaving the material still low in density. Furthermore, after the addition of fibres, water absorption decreased, and the strength properties after 14 days of soaking in water only slightly decreased. In order to increase the degree of crystallinity, heat treatment was carried out. Increased crystallization after heat treatment leads to a significant improvement in the mechanical properties of pure PLA and PLA/WB composites. Both the addition of fibres and heat treatment significantly improved processing properties (VSP). As the presented research shows, the created hybrid composites, after optimizing the production process, taking into account mainly the additional heat cycle, can be successfully used in various industry sectors. They have high mechanical properties, even after long use in water environments, which is often a problem for biodegradable composites. In addition, their advantage is the low harm to nature after the end of the life cycle, because they break down into products naturally occurring in nature.

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