Novel hybrid composite based on bio-PET with basalt/carbon fibre

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Abstract. The aim of this work was to evaluate the possibility of manufacturing hybrid composites based on one of the latest generations of bio derivative polyethylene terephthalate with equal amounts of basalt and carbon fibres. This combination of two types of fibres gives the opportunity to obtain synergistic strength and performance properties. Samples obtained by injection moulding were characterized by morphological, mechanical (tensile, flexural, impact) and processing (softening temperature, thermal expansion and shrinkage) properties. Light-weight and bio-based hybrid composites based on bio-PET matrix with already 10 wt% basalt fibres and 10 wt% carbon fibres are characterized by more than 90 % increase in tensile strength and they have almost four times increase in the modulus of elasticity at a wide range of temperatures. Due to the good mechanical properties of hybrid composites, they can be successfully used in various industry sectors, mainly for consumer goods, household appliances and in automotive industry. Products made of bio-based sources pose a significantly lower threat to the environment than those from petrochemical sources.

1. Introduction

Exhausting sources of crude oil and an increase in public awareness about environmental protection have significantly influenced the interest of academic and industrial society in bio-based materials. However, still composites based on polyesters, polyamides and other types of polymers, which are derived from petroleum oils are often used in various industries. The production capacity of bio-based polymers represented only a 2% share of the total polymer production in 2013 and will increase to 4% by 2020 [1]. PET is the most commonly used semi-aromatic polyester. It is the fourth-most-produced plastic [2], with a global supply of more than 19.8 million tons in 2012 [3]. PET has been widely used as beverage bottles, food containers, fibres and fabrics, packing films, photographic and recording tapes, engineering resins, and so on [4]. However, alarming information about exhausting sources of crude oil has become an impulse to replace PET with a bio-based polymer. A competitor for PET is its counterpart produced from renewable sources- bioPET. BioPET accounts for 26% of the total production of bio-based composites. The biggest producer is Coca-Cola®, which uses for production of their bottles bioPET based on ethylene glycol (EG) and terephthalic acid (TA), which are produced from vegetable sugars [5]. Although bioPET has many advantages, its biggest disadvantage is the price of 2.25 €/kg, which is about 30% higher than traditional petrochemical polymers [6].

In light of this context, polymer composites are modified more and more often by the addition of fibres. BioPET modifications are not often described in the literature and most often the reinforcement composites are by introducing nanoparticles or lignocellulose fibres. In the work of Jang et al [7]...
bioPET (ECOZEN T95 with 9% mean biomass content) with the addition of nano-clay in the content of 0 up to 5 wt% has been tested. Studies have shown that with the increase in nano-clay content, the thermal and mechanical properties of the tested composites have decreased. After the additional introduction of supercritical carbon dioxide (scCO₂), the highest composites properties were obtained, exceeding the values obtained for neat bioPET. It was concluded that the addition of scCO₂ proved to be an effective exfoliation agent. Another work based on bioPET was the work of Montava-Jorda et al [8] who added cotton textile waste (CTW) from 1 to 10 wt% to bioPET provided by NaturePlast. The highest properties were obtained for composites with an addition of 3-5 wt% of CTW. The addition of CTW in each case increased the rigidity and hardness of composites, however, with increasing fibre content, ductility and toughness decreased. Improving bioPET properties as shown by research is not an easy task. Reinforcing polymer composites with one type of filler does not always give such results; therefore, more and more attention is focused on the production of hybrid composites. The purpose of combining two or even more fibre types in a single composite is to maintain the advantages of both fibres and improve the disadvantages. Therefore, the aim of this research work was to develop, for the first time, hybrid composites based on bioPET reinforced with basalt/carbon fibre. The main goal was to increase the mechanical and processing properties. The samples made using injection moulding were subjected to the characteristics of basic physical and mechanical properties, and additionally Vicat softening point, shrinkage and thermal expansion were determined.

2. Methodology

2.1. Materials

The materials used in this investigation were bio-based PET (ECOZEN® BS 400 – SK chemicals, Korea) carbon fibre (Zoltek PX35, Toray Group, USA) with nominal diameter of 7.2 μm, length of 4 mm and basalt fibre (Basaltex BCS17-6.4-KV16, Basaltex, Belgium) with nominal diameter of 17 μm, length of 6.35 mm. Standard dumbbell samples were injection moulded using the Engel ES 200/40 (Engel Austria, Schwertberg) machine after compounding fibre and bioPET by means of a twin screw extruder. The temperatures in the subsequent zones ranged from 230°C to 260°C and the injection speed ranged from 60 to 90 mm/s.

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 22W, (Radwag, Radom, Poland) according to EN ISO 1183. The samples were measured in ethanol medium.

2.2.2. Water absorption. Water absorption was carried out according to ASTM D570-98 standard. The specimens of bioPET and composites were immersed in distilled water at room temperature and weighed after 1 and 30 days using electronic weighing balance (RADWAG WAS 22W). Samples were removed from water bath and their weight was measured after surface drying using tissue paper. Water absorption was calculated using equation:

\[ \%W = \frac{W_n - W_0}{W_0} \times 100 \]

where \( W_0 \) is the initial weight of the sample, \( W_n \) is the weight of the saturated sample, \( \%W \) gives the percentage increase in weight

Additionally, to assess the influence of absorbed water all compositions were tested in a conditioned state and after 30 days of soaking in water.

2.2.3. Mechanical properties. Specimens of mechanical testing were conditioned at 22°C/50% relative humidity for at least 80 h according to ISO 291 for test room conditions. Tensile tests were carried out according to PN-EN ISO 527-1:2012. MTS Criterion Model 43 testing machine (MTS Systems Corp.,
Eden Prairie, MN, USA) with maximum load range of up to 30 kN and with a traverse speed of 5 mm/min was used. For the accurate measurement of displacement allowing the determination of the tensile modulus, an MTS 634.31F axial extensometer was used. In addition to the tensile tests and three-point flexural tests were also conducted for the compositions according to PN-EN ISO 178:2011. Machine control was carried out from the level of an MTS TestSuite TW software 1.0 (MTS Systems Corp., Eden Prairie, MN, USA). Charpy impact test was carried out in accordance with PN-EN ISO 179-2 standard using Zwick/Roell MTS-SP (Zwick Roell Group, Ulm, Germany) testing machine. The average un-notched impact strength was calculated. The mechanical tests were performed at various temperatures of potential application. Tests were carried out at −24, 22 and at 80°C using the temperature chamber (Instron, Norwood, USA).

2.2.4. Processing properties. The softening point was determined by the Vicat method (PN-EN ISO 306:2014-02) by Ceast 6510 (Pianezza, Italy) machine using method A50 with a force of 10 N and a heating rate of 50°C/h. The percentage linear shrinkage (LS) of the specimen was calculated as:

\[
LS = \frac{L_1 - L_2}{L_1} \times 100\%
\]

where, LS is linear shrinkage, L₁ is selected dimension in the mould [µm] and L₂ is the same dimension measured on the mould at a certain temperature and pressure [µm]

2.2.5. Composite morphology. SEM structure images were taken on tensile-test fracture surfaces of specimens using scanning electron microscope JEOL JSN5510LV (JEOL Ltd., Tokyo, Japan). The accelerating voltage was 20 kV. All samples were coated with gold using Cressington 108 auto sputter coater (Cressington Scientific Instruments, Watford, UK) before observation.

2.2.6. Thermal expansion. The thermal properties of composites were performed on the NETZSCH 402 F1 Hyperion device (NERZSCH Group, Selb, Germany), where the samples were placed vertically. The dilatometric analysis consists in measuring the length of the sample (L) as a function of temperature (T). The length and temperature data were recorded and analysed with Proteus software. The samples were cooled from 30°C temperature to -60°C, heated to 140°C and finally cooled to -60°C temperature. The heating and cooling rates were kept constant at 10°C/min. The coefficient of linear thermal expansion (αL) was calculated as:

\[
\alpha_L = \frac{1}{L} \frac{dL}{dT} \text{1/K}
\]

where L is the linear dimension of the test sample and dL/dT is the rate of change in the linear dimension per unit temperature.

3. Results
The composition of bioPET produced with a mixture of basalt fibres (BF) and carbon fibres (CF) and the results of basic physical and mechanical properties are presented in table 1. The addition of an equilbrium fibre mixture increases the density of the composition slightly up to 10% at the same time improving processing properties. As can be observed, as the fibre content increased, the thermal resistance of the composites increased, while the percentage of shrinkage decreased. The highest value improvement was observed for bioPET10.10 composites - 10% and over 60% for Vicat softening point (VSP) and shrinkage, respectively. Combination of basalt and carbon fibres creates a synergistic effect on the improvement of the thermal properties of the composite. As the fibre content increases, VST increases, which is due to the restriction of the movement of PET molecular chains by fibres, the increase in the Young's modulus at elevated temperatures and the increase in thermal resistance. Modular CFs are responsible for a significant increase in stiffness, while an increase in the thermal stability rigid BFs. The reduction of shrinkage is caused by particularly long basalt fibres, which show a much smaller than the matrix shrinkage, additionally they connect the distal areas of the composite,
stabilizing its dimensions. Improvement of processing properties with a simultaneous small increase in mass significantly widens the scope of application of manufactured composites.

Table 1. Composition and basic physic and processing properties of the materials.

| Index       | Composition                                                                 | Density [g/cm³] | Vicat softening temperature [°C] | Shrinkage [%] |
|-------------|------------------------------------------------------------------------------|-----------------|----------------------------------|---------------|
| bioPET      | Neat bioPET ECOZEN® BS 400                                                  | 1.27±0.02       | 190.6±7                         | 1.2±0.3       |
| bioPET5.5   | ECOZEN® BS 400 + 5wt% BF + 5wt% CF                                          | 1.32±0.04       | 202.4±10                        | 0.65±0.01     |
| bioPET7.7   | ECOZEN® BS 400 + 7.5wt% BF + 7.5 wt% CF                                     | 1.37±0.04       | 205.7±9                         | 0.54±0.02     |
| bioPET10.10 | ECOZEN® BS 400 +10 wt% BF+ 10 wt% CF                                         | 1.41±0.03       | 209.8±12                        | 0.46±0.01     |

Table 2. Comparison of basic strength results.

| Index       | Tensile strength, [MPa] | Tensile modulus [MPa] | Energy to break [J] | Flexural strength [MPa] | Flexural modulus [MPa] | Impact Strength, [kJ/m²] |
|-------------|-------------------------|-----------------------|---------------------|------------------------|------------------------|-------------------------|
| bioPET      | 52.3±0.7                | 2 081±475             | 7.9±0.2             | 86.4±0.9               | 2 128±695              | 19.9±0.9                |
| bioPET5.5   | 76.3±1.1                | 5 864±105             | 3.8±0.1             | 126.3±1.0              | 4 860±121              | 22.8±1.3                |
| bioPET7.7   | 95.1±0.9                | 7 687±103             | 4.1±0.09            | 149.2±0.8              | 7 418±899             | 24.9±0.9                |
| bioPET10.10 | 97.1±1.2                | 9 603±4121            | 4.5±0.1             | 159.2±1.4              | 8 336±152              | 29.9±1.6                |

To determine the effect of hybridization on the mechanical properties of fibre mixtures (CF and BF) of composites based on bioPET, tensile, bending and Charpy impact strength tests were carried out (table 2). As the fibre content increased, there was a significant linear improvement in mechanical properties, this was mainly observed in the Young's modulus and bending modulus. The bioPET 10.10 composites were characterized by an almost twofold increase in tensile strength (52.3 MPa – bioPET and 97.1 MPa – bioPET10.10) and almost fivefold increase in the Young's modulus (~2 GPa – bioPET and 10 GPa – bioPET10.10). In addition, an increase in the impact strength was observed, for bioPET10.10 composites, where the growth was as higher as 50%. Mainly the increase in impact strength was caused by the addition of basalt fibres which are characterized by high values of impact resistance [9].

Due to the fact that bioPET reinforced composites can be used in various industrial sectors, where temperatures ranging from -50 (outdoor parking lots) up to 125°C (under the hood), mechanical tests have been carried out at temperatures: -24°C and +80°C [10]. In figure 1, the values obtained during the tensile test were presented: tensile strength (left) and Young modulus (right) at three temperatures. The highest properties were observed at reduced temperatures, while the lowest at +80°C. The decrease in strength properties is slightly different between different test temperatures, which proves bioPET stability at extreme temperatures, which may indicate a higher degree of crystallinity of the tested composites. Polymers with high crystallinity have a higher glass transition temperature T_g (T_g is 67°C for amorphous PET and 81°C for crystalline PET) and have higher modulus, toughness, stiffness, tensile strength, hardness and more resistance to solvents, but less impact strength [11].

Table 3 shows the values obtained during the three-point bending and Charpy impact strength without notch at three temperatures. Similar relationship as in the case of tensile strength was obtained during the bending test. The highest values were achieved at reduced temperatures for the highest fibre content. Along with the increase of fibre content, the bending strength and the module increase by about 2 times and by 3.5 times, respectively for bioPET10.10 composites. In the case of the impact strength value, the highest values were obtained at elevated temperatures, this is related to the increase
in the plasticity of the materials. At elevated temperatures, along with the increase in fibre content, the values of impact strength decreased, due to higher stiffness.

![Graph](image.png)

**Figure 1.** Comparison of tensile properties: tensile strength (a) and Young modulus (b) at three temperatures.

| Index          | Flexural strength [MPa] | Flexural modulus [MPa] | Impact Strength [kJ/m²] |
|----------------|-------------------------|------------------------|------------------------|
| bioPET -24°C   | 93.8±0.8                | 2 222±195              | 13.1±0.5               |
| 22°C           | 86.4±1.0                | 2 128±121              | 19.9±1.2               |
| 80°C           | 81.9±1.3                | 1 861±129              | 25.5±1.4               |
| bioPET 5.5 -24°C | 141.7±1.1             | 5 255±165              | 16.0±1.4               |
| 22°C           | 126.3±1.0               | 4 860±121              | 22.8±1.2               |
| 80°C           | 109.5±0.9               | 4 061±189              | 26.6±2.1               |
| bioPET 7.7 -24°C | 162.2±1.5             | 6 731±175              | 16.1±1.2               |
| 22°C           | 149.2±1.0               | 7 418±121              | 24.9±1.7               |
| 80°C           | 110.6±1.6               | 5 122±139              | 25.1±1.8               |
| bioPET 10.10 -24°C | 179.5±1.8            | 8 344±205              | 13.1±1.4               |
| 22°C           | 159.2±1.0               | 8 336±121              | 19.9±1.1               |
| 80°C           | 128.9±2.1               | 7 724±129              | 20.1±2.9               |

Table 3. Results of bending and impact test at three temperatures.

![Table 3](image.png)

**Table 4.** Water absorption of the tested composites.

| Time          | bioPET | bioPET 5.5 | bioPET 7.7 | bioPET 10.10 |
|---------------|--------|------------|------------|--------------|
| 1 day [%]     | 0.07   | 0.065      | 0.063      | 0.06         |
| 30 days [%]   | 0.26   | 0.24       | 0.22       | 0.20         |

Table 4 presents the results of water sorption for the tested composites after 1 day and 30 days of soaking. As can be seen, the addition of fibres caused a decrease in water sorption. As the fibre content increases, the amount of water taken up by the material decreases. For bioPET10.10 (0.20%) the difference between bioPET neat (0.26%) after 30 days was 0.06% (table 4). Additionally, the influence of water sorption after 30 days on strength properties was examined (figure 2). After 30 days, it can be observed a decrease in strength properties. The reduction of mechanical properties after 30 days of hydrothermal aging is the effect of water sorption at the fibre boundaries and stress relaxation between the fibres and the matrix, and disintegration of chains due to the reduction of the molecular weight of the polymer matrix. Under the influence of water macromolecular chains break with gradual decrease of molecular weight, up to monomers. However, it is worth noting that the
decrease in properties was slight to a maximum of 5%.

**Figure 2.** Comparison of tensile test result immediately after injection (red) and after 30 days of soaking in the water (blue).

**Figure 3.** SEM images of the bioPET composites with basalt and carbon fibres (the fracture after elongation test): (a) bioPET 5.5, (b) bioPET 10.10, (c) bioPET 5.5 and (d) bioPET 10.10.

SEM was carried out to evaluate the state of dispersion and adhesion of BF and CF in bioPET matrix. Micrographs of the fractured surfaces of tensile specimens are presented in figure 3(a) bioPET 5.5 at 1000x magnification – area of developed fracture of bioPET with broken carbon fibre, figure 3(b) bioPET 10.10 at 1000x magnification – area of mixing basalt and carbon fibres -one broken basalt fibre and “whole” after pulling out of any carbon fibre on ductile fracture of bioPET figure 3(c) bioPET 5.5 at 2000x magnification a group of parallel carbon fibres, figure 3(d) bioPET 10.10 at 2000x magnification - a single basalt fibre in the bioPET matrix. Fractured specimens after elongation test are characterized by a combined characteristic from a brittle fracture (for higher addition of fibres).
to a ductile fracture (for bioPET 5.5 with ‘pull out’ effect for parts of BF). Various cross sections of BFs were observed with measured diameter of basalt fibre: 16-23 μm. SEM images indicate better adhesion to CF than BF. On CF, it can be seen the residual of the matrix and much lower in the pull out phenomenon than in the case of BF. Additionally, good fibre adhesion is confirmed by durability tests.

The values of linear coefficient of thermal expansion of tested materials have been presented in table 5. Neat bioPET had the highest value. This is due to the fact that thermoplastic polymers have high coefficients of linear thermal expansion due to weak secondary bonds between the chains. While the filler content added to the polymer matrix increased, the linear coefficient of thermal expansion decreased. It decreased almost three times. This is a positive phenomenon due to the dimensional stability of elements made of such composites, better possibility of their cooperation and accuracy of fixing.

Table 5. Results of dilatometry test.

| Index      | Linear coefficient of thermal expansion \( \alpha \times 10^{-6}, 1/K \) | Softening temperature \( ^{\circ}C \) | Maximum of extension \( \% \) | The shrinkage start temperature \( ^{\circ}C \) |
|------------|-------------------------------------------------|-------------------------------------|-----------------|---------------------|
| bioPET     | 8.88                                           | 104.5                               | 0.66            | 128.3               |
| bioPET 5.5 | 3.14                                           | 107.3                               | 0.25            | 150.8               |
| bioPET 7.7 | 2.70                                           | 108.1                               | 0.24            | 151.1               |
| bioPET 10.10 | 2.73                                      | 108.1                               | 0.21            | 154.8               |

4. Conclusion

The conducted research confirmed the possibility of producing an effective reinforcement for bioPET matrix by carbon and basalt fibres added simultaneously. The strength increase for the bioPET 7.7 composites was up to 85% and the tensile modulus increased almost four times. The impact strength remained constant, thermal resistance increased and the technological shrinkage decreased twice. Such composites become an attractive materials for technical products operating at elevated temperatures. To sum up, polymers from renewable sources are an attractive structural material that is not inferior to traditional polymers the from crude oil or gas. Due to the environmental protection requirements and the objective necessity of using renewable raw materials, research on new types of polymers available on the market due to the modern achievements of material engineering should be developed.

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