Castor oil bio-polyamide
reinforced with natural and synthetic short fibers

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Abstract
This paper presents selected results of the research on biocomposites of a long-chain polyamide (Suzhou Hipro Polymers, China) obtained from castor oil, filled with 10 and 20 wt.% of glass, carbon and flax fibers. Tensile properties of the neat biopolymer and its composites were determined in a wide range of temperatures (from -170°C to 100°C). As the results showed, both synthetic and natural fibers can be successfully used as long-chain bio-polyamide fillers in order to improve its stiffness, strength and heat resistance. Such biocomposites could be applied for example in automobile industry, electronic devices and other industry sectors.

Keywords
bio-polyamide, biocomposite, renewable sources

1. Introduction
Polyamides are one of the most commonly used engineering, construction thermoplastics. It is a group of polymers with methylene groups -CH₂- and amide groups -NH-CO- in their backbone chain. All polyamides (PA) are designated with numbers that represent the number of carbon atoms in their monomers. That means that the higher the numbers, the longer the polyamide chain units [1].

Recently more and more partially or fully biobased polyamides are entering plastic market. These materials are more sophisticated than most of the other currently known biopolymers. A variety of bio-grades has been already offered by such companies like Arkema, Basf, DuPont, EMS-Chemie, DSM, Evonik or Suzhou Hipro. Among these grades there are homopolymers (fig. 1) and copolymers (fig. 2) [3].

![Fig. 1. General chemical formula for homopolyamides, where X equals polyamide number minus 1 (e.g.: X=5 for PA 6, X=10 for PA 11) [3]](image1)

![Fig. 2. General chemical formula for copolyamides, where X equals the number of carbon atoms in diamine (first PA number) and Y equals the number of carbon atoms in dicarboxylic acid (second PA number minus 2) in the monomer (e.g.: X=6, Y=8 for PA 610, X=10, Y=8 for PA 1012) [3]](image2)
Homopolyamides are manufactured either by polycondensation of aminocarbonic acids or by ring-opening polymerization of lactams. The first route is used in production of castor oil based PA 11. The other production pathway may be used for example to obtain bio-PA 6 from fermentative generated ε-caprolactam, but at the moment biopolyamide production from sugars is not cost-effective. Copolymers (eg. PA 1010, PA 610) may be manufactured by polycondensation of various diamines and dicarboxylic acids. Currently, most of diarnides used in bio-polyamide production are still petrochemical origin but there are also examples of biobased ones [3,4].

Almost all of the mono- and co-polyamides that are commercially available at the moment are produced mainly from castor oil and those are long-chain polyamides. The most important are PA 11, PA 1010 and PA 610. PA 1010 and PA 11 are fully biobased and PA 610 contains about 60% wt. of renewable source raw materials [4]. These polyamides possess features that make them suitable to fill the gap in properties between PA 12 and PA 6 (the two well-known and important petrochemical engineering materials), which is schematically presented in figure 1 [5].

![Fig. 1. A map of properties of two main bio-polyamides PA 1010 and PA 610 and traditional engineering polyamides [5]](image)

There are few examples of long-chain biopolyamides composites already present in the market which have been applied in automotive and sport industry. The Hans Sport Series 2 Device, one of HANS device models (head and neck support devices) a safety item in car racing sports is made of a composite of PA 1010, PA 610 (from DuPont company) and carbon or glass fibers. It is convenient, light-weight and offers all the same safety performance as the other models [6]. Another example of commercially used bio-PA / glass fiber composite is Toyota Camry radiator end tank.

2. Materials and methods of testing
The composites presented in this study consists of a long-chain polyamide compound from castor oil, Hiprolon 211 (Suzhou Hipro Polymers, China) filled with 10% and 20% wt. of
flax, glass or carbon fibers. Standard dumbbell type specimens were produced by compounding extrusion followed by injection molding.

To determine mechanical properties of the biopolyamide and its composites tensile tests were conducted according to PN-EN ISO 527 under standard conditions at room temperature and also at 100°C using thermal chamber mounted between the jaws of tensile machine and at low temperature (approx.: -170°C) on specimens cooled in liquid nitrogen. Vicat softening point and the materials density were also measured.

3. Test results
Table 1 presents composition of all tested materials, their density and Vicat softening temperatures (VSP) [7]. For comparison purposes, properties of an exemplary PA 6 Tarnamid T-27 produced in Azoty Tarnów, Poland are also listed in table 1[8].

Table 1. – Tested materials composition with their density and Vicat softening point

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Filler, content [% wt.]</th>
<th>Index</th>
<th>Density [g/cm³]</th>
<th>VSP [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biopolyamide (Hiprolon 211)</td>
<td>-</td>
<td>Hpr</td>
<td>1,05 [7]</td>
<td>168 [7]</td>
</tr>
<tr>
<td></td>
<td>Flax fiber, 10</td>
<td>Hpr/10F</td>
<td>1,06 [7]</td>
<td>172 [7]</td>
</tr>
<tr>
<td></td>
<td>Flax fiber, 20</td>
<td>Hpr/20F</td>
<td>1,08</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>Glass fiber, 10</td>
<td>Hpr/10G</td>
<td>1,1 [7]</td>
<td>174 [7]</td>
</tr>
<tr>
<td></td>
<td>Glass fiber, 20</td>
<td>Hpr/20G</td>
<td>1,16</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>Carbon fiber, 10</td>
<td>Hpr/10C</td>
<td>1,07 [7]</td>
<td>180 [7]</td>
</tr>
<tr>
<td></td>
<td>Carbon fiber, 20</td>
<td>Hpr/20C</td>
<td>1,1</td>
<td>186</td>
</tr>
<tr>
<td>PA6 (Tarnamid T-27)</td>
<td>-</td>
<td>PA6</td>
<td>1,14*</td>
<td>195*</td>
</tr>
</tbody>
</table>

*producer data (Azoty Tarnów, Poland) [8]

For almost all of tested materials (except of Hpr/20G) density values were lower than for PA 6 [8]. Flax fiber addition resulted in the lowest density increase, which was expected. Natural fibers are well-known as weight reducing fillers.

Vicat softening point is the temperature at which standardized flat-ended needle penetrates the specimen to the depth of 1 mm under specific load and heating rate conditions (PN-EN ISO 306:2002). It can be used to compare heat resistance (heat-softening properties) of different thermoplastics. The increase of VSP for tested composites was significant. They are more resistant to deformation at high temperatures than neat bio-polyamide. It is also expected that further increase of fiber content may increase VSP value of the composites to the level of PA 6. For 20%wt. carbon fiber filled polyamide the value was even 18°C higher than for neat bio-polyamide and only 9°C lower than for PA6 [8].

To initially determine both thermal and mechanical properties of the composites, tensile tests were conducted at different temperatures. The results (tensile strength and modulus of elasticity) are shown in figures 3 and 4.

When a polymer specimen is tension tested at elevated temperatures, its modulus and strength decrease with increasing temperature because of thermal softening. And there is an opposite effect when the testing temperature is lowered. In a polymeric matrix composite, the matrix-
dominated properties are more affected by temperature changes than the fiber-dominated properties [9].

![Tensile strength graph](image1)  
**Fig. 3.** Tensile strength of tested materials at -170°C, 23°C and 100°C

However, in case of the tested materials, changes of tensile strength (fig. 3) and modulus of elasticity (fig.4) with temperature change were not proportional for the neat biopolymer and its composites. There was an effect of higher strength increase for composites at -170°C and 100°C than for room temperature tested specimens. At all test temperatures strong effect of reinforcement for all of the fibers filled biopolyamide was noticed [7].

It should be emphasized that the dashed lines shown in figures 3 - 4 show only a tendency of changes in properties but cannot be treated as describing function behavior.

![Modulus of elasticity graph](image2)  
**Fig. 4.** Modulus of elasticity of tested materials at -170°C, 23°C and 100°C
4. Conclusions

In order to improve mechanical performance and thermal stability of long chain biopolyamides, different fillers, both synthetic and natural, can be used. Even low fiber content (10%) provides significant improvement of these properties which are crucial for construction materials. Addition of carbon and glass fibers causes high increase of Vicat softening point or stiffness and strength of the composites in different temperatures. Addition of 20%wt. of flax fibers gives similar effect as 10% wt. glass fiber filling. Bio-polyamide/flax composite is the most eco-friendly among all tested materials as it is derived entirely from plant resources.

These and previous [7] test results proves that bio-polyamide composites are acceptable as construction materials and can be used as an alternative to conventional plastics for different industry sectors.

References