

# 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. For that purpose, tensile properties of the neat biopolymer and its composites in their conditioned state were determined. Tensile tests in a wide range of temperatures (from -170°C to 100°C) were also performed. As the results showed, strong effect of reinforcement was obtained for all of the composites at all temperatures. Both synthetic and natural fibers can be successfully used as long-chain biopolyamide fillers in order to improve its stiffness, strength and heat resistance. The results of this work can be used in a designing process of structural materials. Such biocomposites could be applied in the automobile industry, consumer goods sector or medical devices.*

## **Keywords**

*bio-polyamide, biocomposite, renewable sources, flax fiber, glass fiber, carbon fiber*

## **1. Introduction**

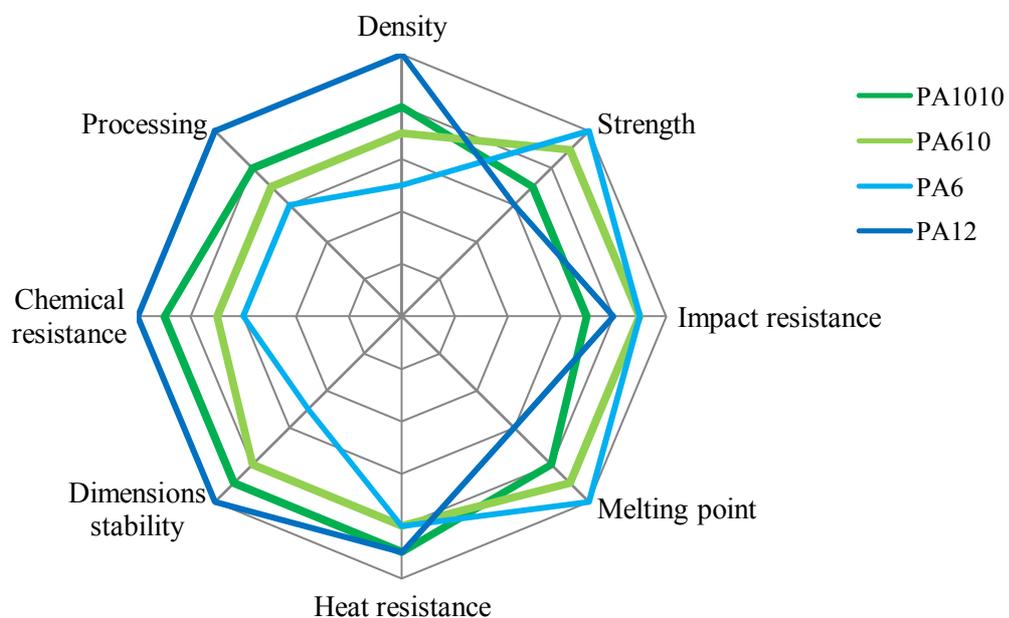
Polyamides are one of the most commonly used engineering thermoplastics. Recently more and more partially or fully biobased polyamides are entering the plastic market. These materials are more sophisticated than most of the other currently known biopolymers. A variety of bio-grades has been already offered by such companies like Arkema, Basf, DuPont, EMS-Chemie, DSM, Evonik or Suzhou Hipro. Among these grades there are homo- and copolymers.

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  $\epsilon$ -caprolactam. Likewise, glucose may be used as feedstock to produce PA 4 by fermentation to glutamate, its decarboxylation to GABA, which is then heated to produce 2-pyrrolidone and finally by ring-opening polymerization of 2-pyrrolidone. However, production of biopolyamides from carbohydrates is not yet cost-effective [1]. Copolymers (eg. PA 1010, PA 610) may be manufactured by polycondensation of various diamines and dicarbonic acids. Currently, most of diamides used in bio-polyamide production are still petrochemical origin but there are also examples of biobased ones (eg. DMDA). Among the natural dicarboxylic acids applied in bio-polyamide manufacturing, sebacic acid is the most common [2].

At present, in production of commercially available biopolyamides, castor oil is used as renewable feedstock. Among other industrial plant oils, castor oil exhibits unique chemical structure and properties. It is build in almost 90% of ricinoleic acid with double bond and hydroxy group which provide possibilities for chemical modifications [2,3]. The

modifications may lead to synthesis of polyamides building blocks, such as: sebacic acid, aminoudnecane acid or decamethylenediamine (DMDA), which have been mentioned before [2,3].

In polyamides, intermolecular interactions, which determine properties, decrease with an increasing length of polymer chain. Long chain biopolyamides such as: PA 11, PA 1010 and, to a lesser extent, PA 610 have lower density, lower water absorption but also significantly lower strength and stiffness, lower melting point and continuous operating temperature than polyamides like PA 6 [2,3]. Polyamide 11 (Rilsan PA 11 from Arkema) has been commercially available for over 60 years now and applied in different industry sectors (e.g.: automotive, textile, electronics, coatings). PA 11 is fully biobased. Polyamide 1010 has similar properties to PA 11 and may be used as its substitute. Polyamide 610 consists of about 60% of renewable feedstock. It has recently met with a great interest, as it combines high mechanical properties (characteristic of PA 6) with low density and high chemical resistance (typical for PA 1010) [4]. Polyamides 610 and 1010 possess features that make them suitable to fill the gap in properties between PA 12 and PA 6 (the two important petrochemical engineering materials), which is schematically presented in figure 1.



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

In order to improve mechanical performance and thermal stability of long chain biopolyamides, different fillers, both synthetic and natural, can be used. Błędzki et. al. studied composites on a base of two biopolyamides: PA 1010 and PA 610, filled with man-made or natural (abaca) cellulose fibers (15 – 30% wt.). The fillers addition caused significant enhancement of stiffness and strength. There was also an increase of impact strength for man-made fibers and a decrease for natural filler [6,7]. Liu Z. et.al. tested PA 1010/montmorillonite nanocomposites prepared by intercalating polymerization. This nanocomposites had higher modulus of elasticity and onset temperature of decomposition compared with neat biopolyamide [8]. Similar results were obtained by Zeng et. al. for multiwalled carbon nanotubes-reinforced PA 1010 composites and by Liu T. et.al. for PA11/nanoclay composites prepared via melt-compounding method [9,10]. Rajesh and Bijwe also reported major increase of mechanical properties, hardness, friction and wear properties

of polyamide 11 filled with short glass fibres (20% wt.) and copper or bronze powders (6%), processed by extrusion followed by injection molding [3,11]

There are also a 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 [12]. Another example of commercially used bio-PA / glass fiber composite is Toyota Camry radiator end tank.

In this paper, mechanical and physical properties of commercially available biobased polyamide filled with flax, glass or carbon short fibers are presented. The aim of the study is to examine the influence of each kind of filler on the composite behaviour, and to determine whether the tested biocomposites could be applied as replacement of traditional engineering, durable polyamides, like polyamide 6.

## **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. Flax fibers, cut and low twisted roving (diameter 10-30  $\mu\text{m}$  and length of 120  $\mu\text{m}$ ) were supplied by Safilin Sp z o.o. (Poland). Glass fibers (diameter: 10  $\mu\text{m}$ , average length: 120-150) and carbon fibers (diameter: 8  $\mu\text{m}$ , average length: 80-120) were provided by Zakłady Azotowe in Tarnow (Poland). Standard dumbbell type specimens (10 x 4 x 150 mm) were produced in a two-step process. First, the Hiprolon 211 pellets and fibers were compounded on a twin-screw extruder with a gravimetric screw feeder. The thus obtained granulate was injection molded using Engel ES 200/40 HSL in Zakłady Azotowe in Tarnow. Composition of all tested materials is described in table 1.

To determine mechanical properties of the biopolyamide and its composites tensile tests were conducted according to PN-EN ISO 527, with an universal testing machine (Insight 50 MTS with MTS axial extensometer) with a constant crosshead speed of 10 mm/min. Elastic modulus ( $E_t$ ), tensile strength ( $\sigma_M$ ) and strain at break ( $\epsilon_B$ ) were determined. The tests were performed 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. Charpy impact strength ( $a_{cN}$ ) was obtained from notched specimens using Zwick HIT5.5P. Materials density ( $\rho$ ) was measured by hydrostatic method. Absorption of water (at 20°C) was calculated after 1 day, 7 and 30 days of soaking, according to PN-EN ISO 62:2000. In order to observe the composite structures, SEM images were made on the gold-sputtered tensile-test fracture surfaces of specimens using JEOL JSN5510LV.

## **3. Test results**

### **3.1 Mechanical properties at room temperature**

Tensile properties like tensile strength, modulus of elasticity and elongation at break of tested materials are presented in table 1. Strong effect of reinforcement was obtained for all of the composites. Tensile strength was above 2 and 3 times higher for 10% and 20% wt. of carbon fiber content respectively, than for neat bio-polyamide. The 20% of flax fibers addition caused the same strength increase as 10% of glass fibers filling (about 26%). The most positive achieved effect of fibers adding was the significant improvement of stiffness of composites at low fillers weight content: from 2 and 4 times for 10 and 20% of flax fibers to

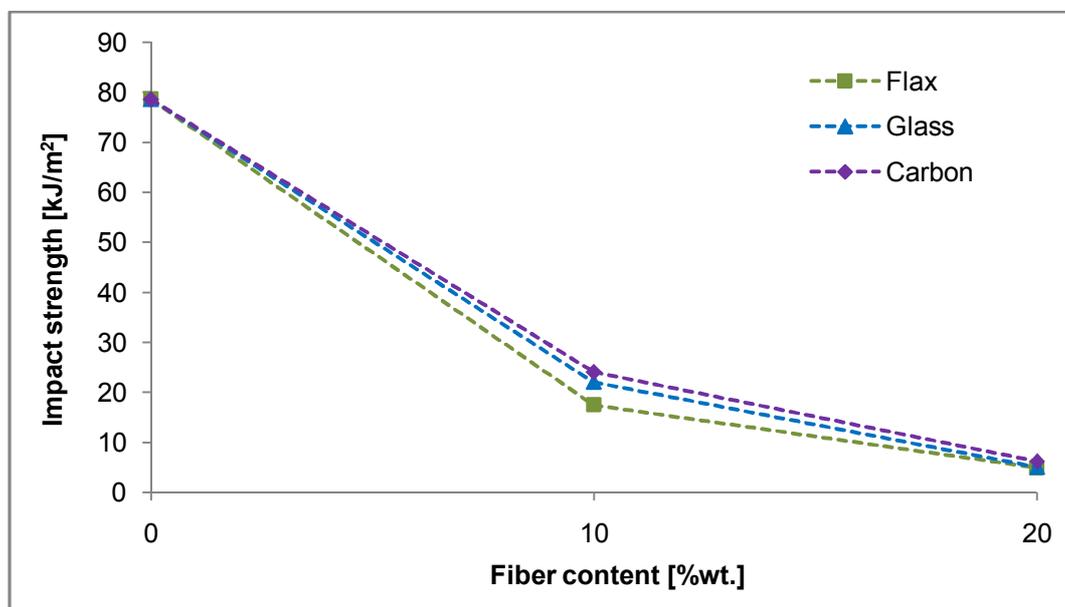
even 18 times for 20% of carbon fibers. Thus the biocomposites modulus of elasticity values are similar or higher than for well-known neat polyamide 6 [3]. For comparison purposes, properties of an exemplary PA 6 Tarnamid T-27 produced in Azoty Tarnów, Poland are also listed in table 1 as well as in table 2 and figure 6 [13].

**Table 1.** – Tested materials composition and their tensile properties measured at room temperature

Matrix	Fiber type, content [wt%]	Index	$\sigma_M$ [MPa]	$E_t$ [MPa]	$\varepsilon_B$ [%]
bio-PA Hiprolon 211	-	Hpr	26,7	350	277
	Flax, 10	Hpr/10F	27,9	725	137
	Glass, 10	Hpr/10G	33,9	2060	90
	Carbon, 10	Hpr/10C	71,1	4000	10
	Flax, 20	Hpr/20F	33,4	1445	29
	Glass, 20	Hpr/20G	41,9	3600	4
	Carbon, 20	Hpr/20C	91,7	6521	7
PA 6 Tarnamid T-27	-	PA6	45*	1100*	280*

\*producer data (Azoty Tarnow, Poland) [13]

Low fiber content composites preserved good ductile properties: high elongation at break and, as can be seen in figure 2, satisfactory impact resistance. The impact strength values of the 20% wt. fibers composites are at the level of those of common PA 6 (for Tarnamid T-27,  $a_{cN} = 12 \text{ kJ/m}^2$  according to producer data [13]).



**Fig. 2.** Charpy impact strength, notched, of neat bio-polyamide and its composites

### 3.2 Tensile properties at high and low temperatures

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 [14].

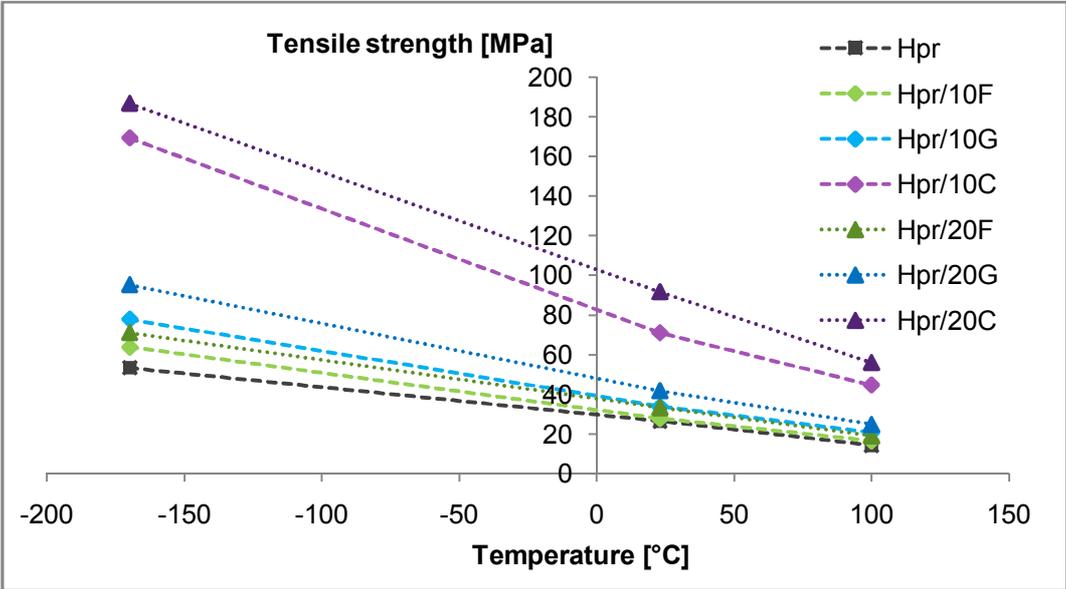


Fig. 3. Tensile strength of tested materials at -170°C, 23°C and 100°C

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. It should be emphasized that the dashed lines shown in figures 2 - 5 show only a tendency of changes in properties but cannot be treated as describing function behaviour.

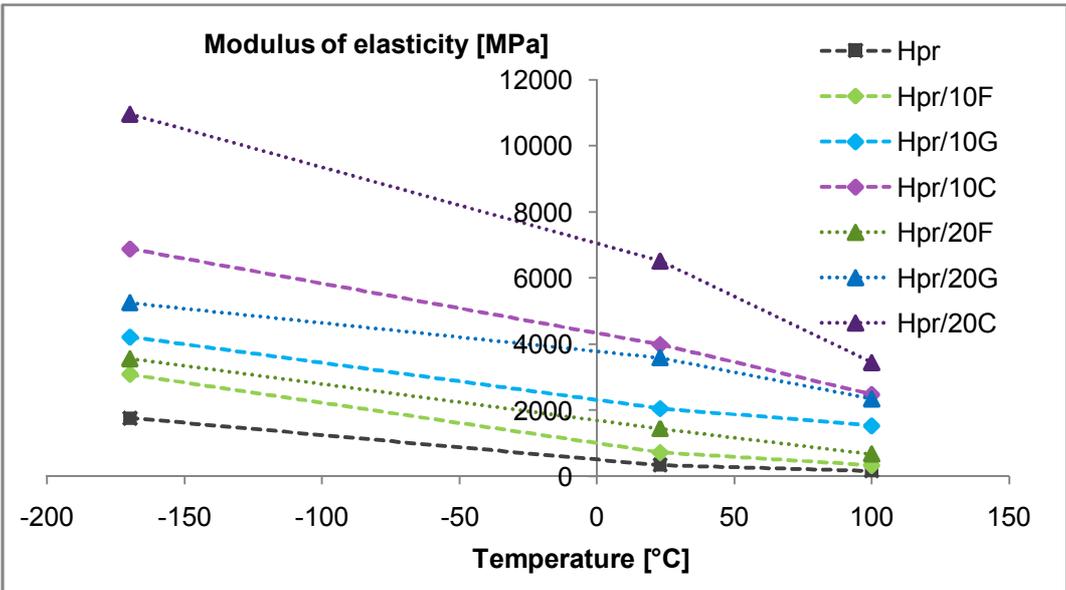
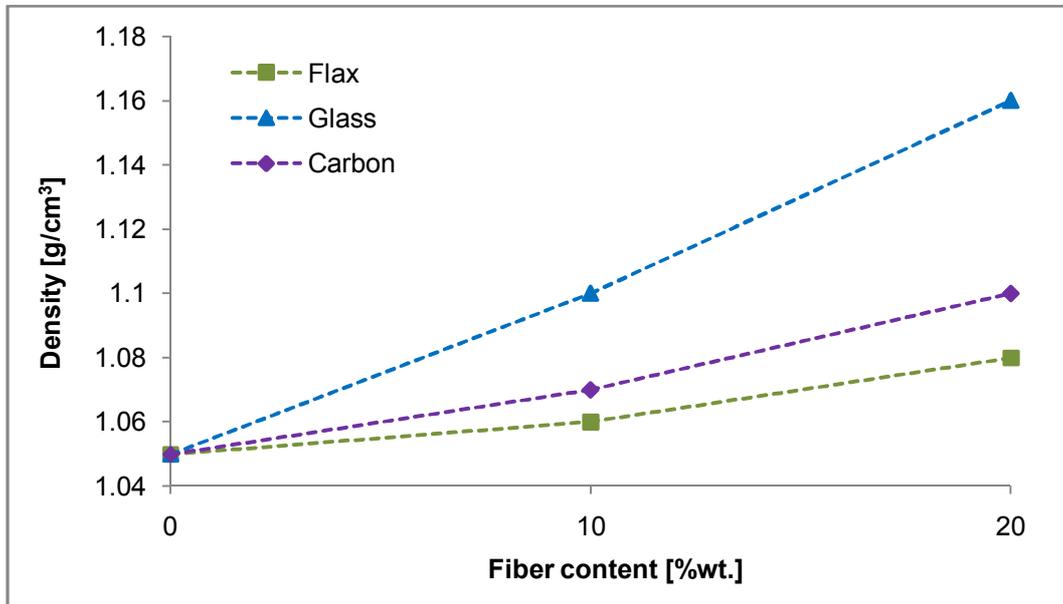


Fig. 4. Modulus of elasticity of tested materials at -170°C, 23°C and 100°C

### 3.3 Physical properties

One of the important advantages of long-chain bio-polyamides and their composites is their low density. The densities of neat bio-polyamide and composites are shown in figure 5. For almost all of tested materials (except of Hpr/20G) density values were lower than for PA 6 (for Tarnamid T-27  $\rho=1,14 \text{ g/cm}^3$  [13]). Flax fiber addition resulted in the lowest density increase, which was expected. Natural fibers are well-known as weight reducing fillers.



*Fig. 5. Density of tested materials*

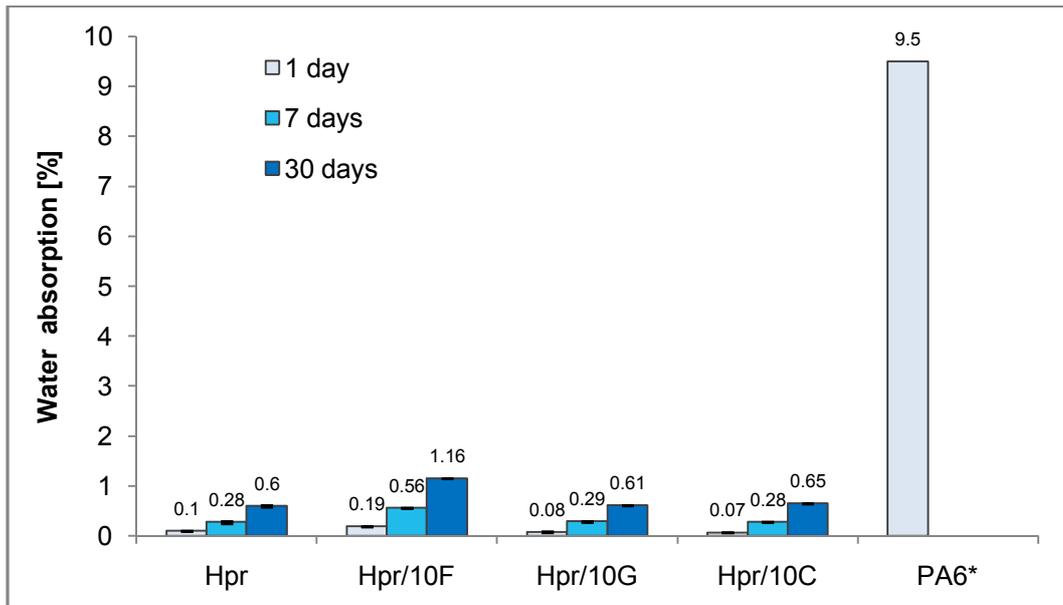
Engineering materials aside from superior mechanical properties should exhibit high thermal properties. Introduction of fillers usually enable the composite to work at higher temperatures than neat polymer. As can be seen in table 2, addition of fillers, especially carbon or, to a lesser extent, glass fibers resulted in the noticeable increase of Vicat softening point [3]. It is expected that further increase of fibers content may increase VSP value of the composites to the level of PA 6.

*Table 2. – Vicat softening point of biopolyamide matrix and its 10% wt. fiber filled composites*

Index	Hpr	Hpr/10F	Hpr/10G	Hpr/10C	PA6*
VSP [°C]	168	172	174	180	195

\*producer data (Azoty Tarnow, Poland) [13]

Water absorption of neat bio-polyamide and its composites calculated after 1,7 and 30 days of soaking is shown in figure 6. As it was expected, lignocellulosic flax fibers caused a considerable increase of absorbability, while for carbon or glass fibers there were no major changes in the absorption value [3]. Nevertheless, the Hpr/10F composite still absorbs less water after 30 days soaking than polyamide 6 (Tarnamid T-27, Azoty Tarnów) after 24 hours exposure (1,8% according to tarnamid t-27 producer data) [13].



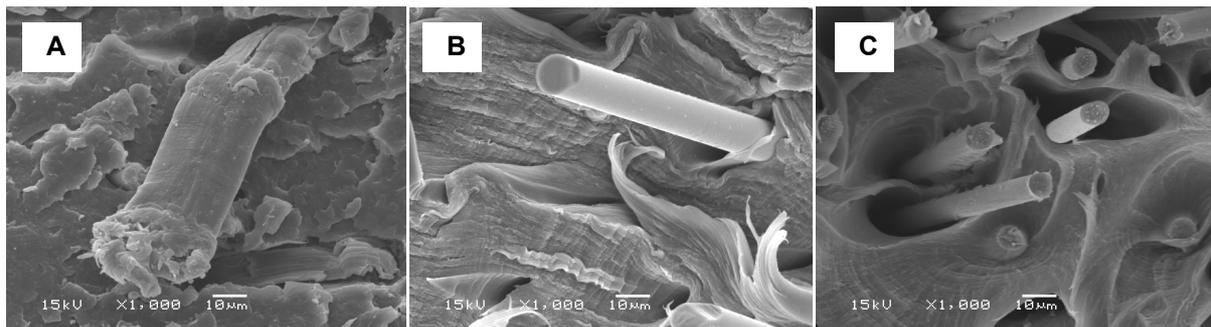
**Fig. 6** Water absorption of bio-polyamide and its 10% wt. filled composites after 1, 7 and 30 days of soaking [3]

\*Producer data, absorption of water after 1 day soaking (Azoty Tarnow) [13]

Here long-chain polyamides have a great advantage over short-chain polyamides which absorb significant amount of water and thus may show considerable dimensional changes due to moisture absorption.

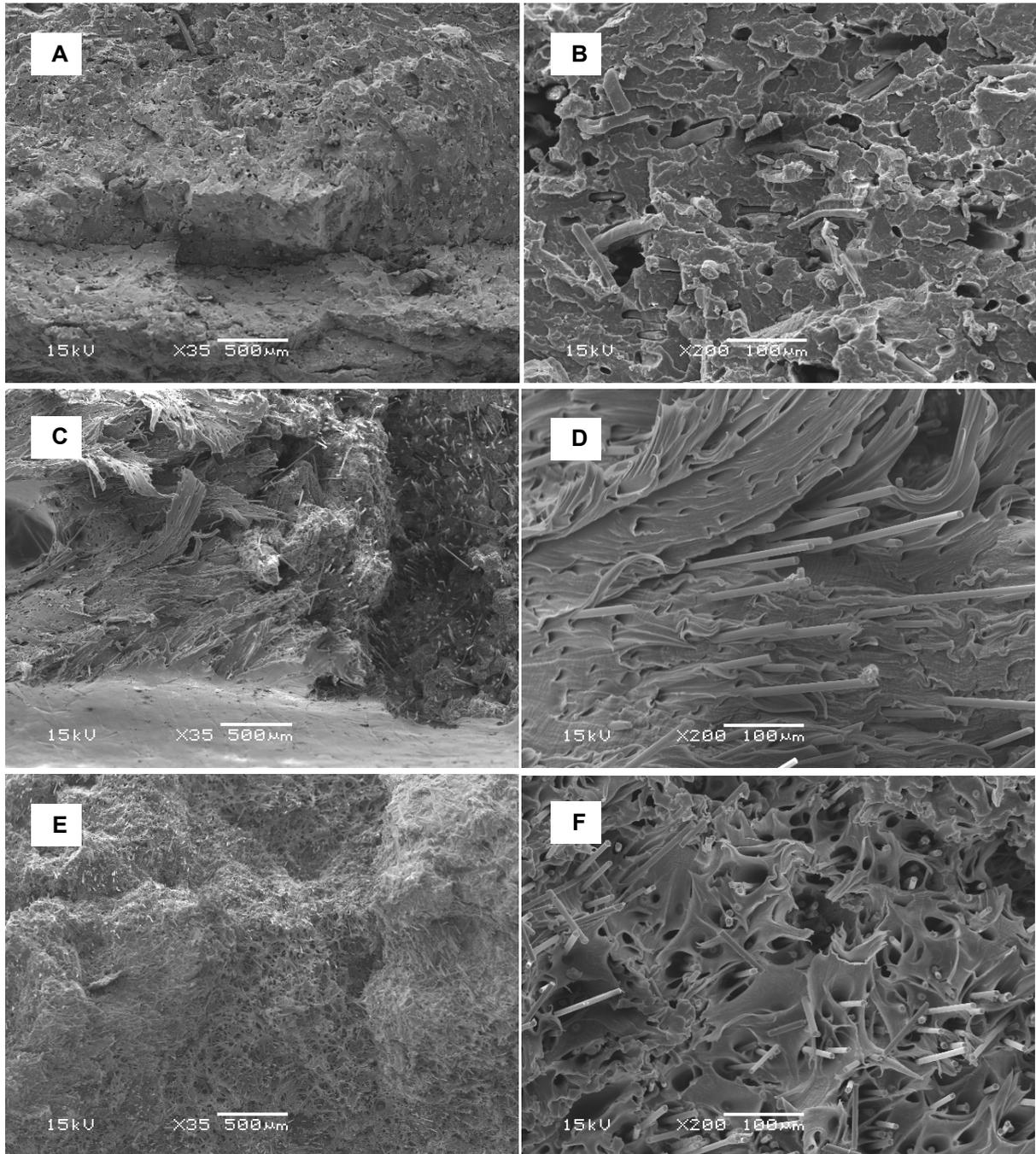
### 3.4 Microscopic observations

After the tensile tests, the microstructures of the 10% wt filled composites were analyzed. Figure 7 shows the SEM images of the composites where single fibers morphology can be seen. The same image (fig. 7a) also proves that the bio-polyamide composites can be successfully processed with natural fibers as there are no visible signs of thermal damage and deformations of the flax fiber [3].



**Fig. 8** Flax (a), glass (b) and carbon (c) fibers embedded in a polymer matrix

In figure 8 there are SEM images (with the magnification of 35x and 200x) of the composites tensile test fractures. The Hpr/10F specimen was broken in liquid nitrogen in the tensile fracture zone as its highly developed fracture surface hindered the microscopic observations. Hence the images of Hpr/10F (fig. 8 a,b) show semi-crystalline nature of bio-polyamide matrix. Although in the images in figure 8 voids left by pulled-out fibers and discontinuities at the fiber-matrix interfaces can be seen, the fiber-matrix adhesion was obtained, what can be proved by mechanical tests results (especially by the enhancement of tensile strength) [3].



**Fig. 7.** SEM images of tensile fracture surfaces of tested composites a,b – flax fibers filled bio-PA (Hpr/10L), specimen broken in liquid N<sub>2</sub> in the tensile fracture zone, c,d – composite with glass fibers (Hpr/10G), e,f – carbon fibers in biopolyamide matrix (Hpr/10G)

#### 4. Conclusion

Composites of biobased polyamide filled with different fibers may be an interesting alternative to currently used composites based on petrochemical polyamides. Their mechanical properties are comparable and high impact resistance of tested bio-polyamide composites makes them equipped to be used in the parts exposed to dynamic loading. Modification with glass fibers is more advantageous comparing with flax fibers. However, flax fiber is light-weight and its 20% wt. content provides similar reinforcement effect as 10%

wt. of glass fiber filling. Addition of flax fibers makes it possible to produce composite derived entirely from renewable raw materials with good strength and stiffness and high toughness. For manufacturing composites with natural fibers low processing temperature of bio-PA is also an advantageous feature – bio-polyamide composites can be produced at temperatures lower than the lignocellulosic fiber decomposition temperature (which is about 210°C). Composites filled with carbon fiber have a great stiffness and durability.

These features make the bio-polyamide composites acceptable as construction materials. Reinforced bio-polyamide with preserved good elasticity, low-weight and low moisture absorption can be a very attractive material for automobile sector, sport and tourism goods, medical devices or electronic and electrical industry.

### **Symbols**

$a_{cN}$	Charpy impact strength	[kJ/m <sup>3</sup> ]
$E_t$	modulus of elasticity	[MPa]
$\varepsilon_B$	strain at break	[%]
$\rho$	density	[g/cm <sup>3</sup> ]
$\sigma_M$	tensile strength	[MPa]

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