

Properties of composites based on polyamide 10.10 reinforced with carbon fibers

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Abstract: The test results of carbon fiber composites based on two, different, commercially available, bio-based polyamide 10.10 grades are presented in this paper. The discussed materials differ in their impact resistance, strength and stiffness and, to a lesser extent, in water absorption, which are advantageous properties that make them suitable for different structural applications.

Keywords: biocomposite, polyamide 10.10, water absorption, reinforcement efficiency.

Właściwości kompozytów na bazie poliamidu 10.10 wzmocnionego włóknami węglowymi

Streszczenie: W pracy zaprezentowano wyniki badań kompozytów z włóknem węglowym bazujących na dwóch różnych dostępnych na rynku biopochodnych poliamidach 10.10. Opisywane materiały, różniące się wytrzymałością, modułem sprężystości, udarnością i innymi właściwościami fizycznymi, mogą znaleźć odmienne zastosowania konstrukcyjne.

Słowa kluczowe: biokompozyt, poliamid 10.10, absorpcja wody, efektywność wzmocnienia.

Producing conventional polymers like polyethylene, polypropylene, polyamide, poly(ethylene terephthalate) or polyurethanes from renewable resources is one of the goals of modern polymer science. Amongst the currently known biopolymers, biopolyamides derived from castor oil, e.g. polyamide 10.10 (PA 10.10), provide one of the most sophisticated materials [1]. Being obtained from renewable plant sources, PA 10.10 should be considered a special material for demanding, green-thinking consumers. The first sectors that began to introduce biopolyamides and their composites were the automotive and electronics industries. Biopolyamides are also used in sports equipment, in the clothing industry and as coating materials. Due to the legislative limits on CO₂ emission, depletion of fossil fuels and rising prices of oil, biobased polyamides can be seen as eco-friendly materials comparable to various petrochemical plastics. Some may say that the non-biodegradability of biopolyamides is a disadvantage that makes them less attractive than biodegradable, plant based polymers. But this is incorrect. Nowadays, biodegradability makes sense only for limited applications, especially for products with short life

cycle like packaging and some other consumer goods. For durable, structural, long-term applications and products exposed to changing atmospheric conditions, more stable materials are needed. As biopolyamide matrices are not biodegradable, the addition of carbon or glass fibers is not an obstacle, in contrast to biodegradable polymer matrices.

Biopolyamides and their composites can be an important supplement for commonly used polyamides. Their advantage is not only their biobased content but that they also possess additional features (e.g. low density and low water absorption), which make them suitable to fill the gap between polyamide 6, polyamide 12 and their modified grades. There are, however, only several studies on PA 10.10 composites present in the literature and many of them focus on the tribological properties of the materials that are not discussed in this paper [1–9]. An example can be the work of Liu T. *et al.* [7]. The authors tested PA 10.10/montmorillonite nanocomposites prepared by melt-compounding followed by compression molding. The nanocomposites exhibited improved stiffness and onset temperature of decomposition compared with neat biopolyamide. Similar results were obtained by Zeng *et al.* for multiwalled carbon nanotube-reinforced PA 10.10 composites [8]. Rajesh and Bijwe used short fiber reinforcements or microparticles for the modification of bio-based polyamide 11 (with properties similar to PA 10.10). They prepared composites filled with short glass fibers (20 wt %) and copper or bronze powders (6 wt %) processed by extrusion and followed by injection molding [9]. They also reported a major increase in the mechanical

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properties, hardness, friction and wear properties for the composites. Furthermore, the static and dynamic test results of PA 10.10 composites containing low amounts of different short fiber fillers were reported previously in [1]. Polyamide 10.10 was also mentioned in a patent as one of the matrices for producing polyamide composites modified with polycarbodiimides filled with carbon fibers [10].

In the current study, two types of commercially available PA 10.10 were investigated as matrices of carbon fiber composites adequate for structural purposes with high strength, preserved high elasticity and reduced water uptake compared to traditional engineering plastics and their composites.

EXPERIMENTAL PART

Materials

Two, different, commercially available polyamide 10.10 products were selected for testing as composite matrices: Hiprolon[®] 211, Suzhou HiPro (now Arkema), marked further in the text as HP, a plasticized compound for cable applications with crosslinking agent and a basic PA 10.10 grade Vestamid[®] Terra DS16, Evonik Industries (marked as VT). Hiprolon 211, selected because of its high deformability, was filled with 10 wt % and 30 wt % chopped carbon fibers PANEX[®] 35 from Zoltek Corporation (marked as HP10CF and HP30CF respectively). Vestamid Terra DS of higher strength and stiffness than Hiprolon 211 was reinforced with 20 wt % and 40 wt % of the fibers (marked as VT20CF and VT40CF). Silane surface treatments on carbon fibers were performed in Grupa Azoty S.A. in Tarnow. The difference in fiber content between HP and VT based materials was dictated by the desire to present diverse possibilities of biopolyamide/carbon fiber composites use: in durable but flexible and impact resistant products (plasticized PA 10.10 grade with low carbon fiber content) and for applications demanding high specific strength and stiffness (unplasticized PA 10.10 composites).

Specimen preparation

Standard, dumbbell type specimens were produced in Grupa Azoty in Tarnow, Poland, by compound extrusion using a MARIS TM 30VI twin-screw extrusion line followed by injection molding (Engel ES 200/40 HSL injection molding machine). The following injection molding parameters were set for the process: the temperatures of barrel zones and die were: 200–210 °C for Hiprolon 211 and its composite with 10 wt % carbon fibers and 220–240 °C for its composite with 30 wt % carbon fibers. For Vestamid Terra DS the temperatures were 220–230 °C and for its composites with 20 wt % and 40 wt % of carbon fibers the temperatures were: 220–240 °C and 230–250 °C, respectively. Injection pressure and holding

pressure were set at 110 MPa. Because, according to Feng J.H. *et al.* [11], the glass transition temperature (T_g) of pure polyamide 10.10 is 58 °C, the mold temperature was 60 °C for all of the composites.

Methods of testing and calculations

— To determine the mechanical properties of the chosen polyamide 10.10s and their composites, tensile tests were conducted on specimens conditioned for 30 days at 22 °C and 50 % RH according to PN-EN ISO 527 under standard conditions with constant crosshead speed of 10 mm/min using universal testing machine MTS Criterion type 43. 30 kN. The test speed was set to 10 mm/min. The tensile modulus (E_t), tensile strength (σ_M) and strain at break (ε_B) were determined.

— The density of the materials was measured by a hydrostatic method. The results of the tensile tests and density measurements were used for further calculations.

Theoretical moduli of elasticity of the tested composites were calculated based on the principles of fibrous composite micromechanics [12, 13].

Assuming the most advantageous situation with fiber alignments perpendicular to the load axis, the composite modulus of elasticity equals:

$$E_c = VF_f E_f + (1 - VF_f) E_m \quad (1)$$

And for the parallel alignment:

$$E_c = \frac{1}{\frac{VF_f}{E_f} + \frac{1 - VF_f}{E_m}} \quad (2)$$

where: E_c , E_f , E_m — modulus of elasticity of composite, fiber and matrix, VF_f — fiber volume fraction.

Equations (1) and (2) were used to find the theoretical „window” of the properties for the tested composites — the window between the E_t values for the fibers lying perpendicular and parallel to the load axis. With the known densities of the matrices and fibers, the volume fractions of the fibers were calculated for particular mass fractions using a simple mathematical transformation. The densities and tensile moduli of neat polyamide matrices were obtained from the test results (see Table 1). The parameters of carbon fibers Panex[®] 35 used as reinforcement were taken from the producer data (Zoltek Carbon Fiber company). The carbon fiber density was assumed to be $\rho = 1.81 \text{ g/cm}^3$, and the tensile modulus was $E_t = 242 \text{ GPa}$. It should be noted that equations (2) and (4) are dedicated mainly to composites of fiber length greater than the critical length. In addition to factors such as length, volume, orientation and mechanical properties of the fibers and the matrix, other effects that affect the reinforcement should not be neglected. These are: the shape, the quality of the fiber surface and the adhesion between the fiber and matrix.

— In addition to the tensile tests, three point flexural tests were also conducted for the compositions according

to PN-EN ISO 178. Flexural modulus (E_f) and flexural stress (σ_f) or stress at 3.5 % strain were determined. The Charpy impact test (PN-EN ISO 179-1:2010) was carried out on unnotched specimens using a Zwick 5.5 HIT.

– In order to observe the structures of the composite fractures, scanning electron microscope images were acquired on the gold-sputtered tensile-test fracture surfaces of the specimens using a JEOL ISN5510LV microscope.

– As water absorption has a significant impact on polyamide behavior and stability, it was also measured (PN-EN ISO 62:2008) for the tested materials after one day and 7 days of incubation. The percentage change in mass (c) of the tested specimens after immersion in water was calculated using the formula:

$$c = \frac{m_2 - m_1}{m_1} \cdot 100 \% \quad (3)$$

where: m_1 – the mass of the test specimen after initial drying and before immersion, m_2 – the mass of the test specimen (mg), after immersion.

To access the plasticizing effect of water on the material mechanical properties, a tensile test for materials soaked in water was performed after 7 days of incubation.

– DSC tests were performed at the Poznan University of Technology, Faculty of Chemical Technology, Poland using a NETZSCH model DSC-200 with computer software for test analysis. The measurements were made on samples of 7.0–7.5 mg obtained from a central part of the injection molded standard dumbbell-shape specimens. All the samples were heated to 250 °C and held in a molten state for 5 min (to remove prior thermal histories), followed by cooling to 20 °C. Heating and cooling rates were equal to 10 °C/min. The heating was conducted twice to evaluate the DSC curves from the second melting procedure and gain broad information about pure polyamides and their composites. An empty pan was used as a reference.

Crystallization and melting parameters such as: crystallization temperature T_c , melting temperature during first and second melting T_{m1} and T_{m2} correspondingly, melting enthalpy ΔH_m and degree of crystallinity X_c were determined. Degree of crystallinity of polyamide and polyamide composites were calculated using the following equation [14]:

$$X_c = \frac{\Delta H_m}{(1-\phi)\Delta H_m^0} \quad (4)$$

where: ΔH_m – melting enthalpy (J/g), ϕ – weight % of the filler in the composite (%), ΔH_m^0 – the mean melting enthalpy of fully crystalline PA 10.10, which equals 244 J/g [15, 16].

The DSC curves noted during cooling and second heating were used to determine the degree of undercooling of the polymer. The degree of undercooling is the temperature difference of melting and the temperature at which crystallization takes place at maximum speed [17]:

$$\Delta T = T_{m2} - T_c \quad (5)$$

where: T_{m2} – the melting temperature of the polymer determined from DSC curve of the second heating (°C), T_c – the crystallization temperature determined from the DSC curve of the cooling (°C).

RESULTS AND DISCUSSION

Basic mechanical properties

The purpose of carbon fiber introduction to polymer matrices is mainly to provide high specific strength and modulus of elasticity of the composites to make them suitable for load-bearing applications. In the case of the current study, two ideas were investigated engaging a biobased polyamide matrix and short carbon fibers to present versatile possibilities of their use: (I) to obtain low density, high strength and stiffness composites with a VT matrix competitive with traditional structural thermoplastic composites and (II) to propose low filler content HP composites of improved strength properties preserving high impact strength and providing flexibility of products manufactured with their use such as: products adapted to the human body (e.g.: orthoses, elements of sport shoes), damping pads, springs and others. Thus, the influence of carbon fiber addition on VT and HP matrices was investigated in tensile, flexural and Charpy impact tests. The properties of the tested materials obtained in the tensile tests and Charpy impact tests are presented in Table 1, as well as the results of density measurements, while their flexural properties and examples of the flexural curves are shown in Table 2 and Fig. 1, respectively. The introduction of short carbon fibers to biopolyamide matrices resulted in an expected large increase in the mechanical properties. The mechanical properties of Vestamid Terra DS (VT) and its composites make it particularly suitable for many structural applications. It is also important to emphasize the low density of all of the tested materials, which eventually gives them high specific properties. The plasticized biopolyamide grade (HP) composites exhibit improved strength and tensile modulus of

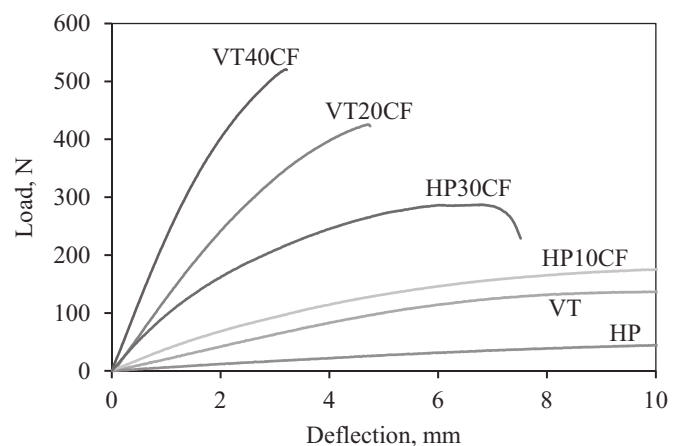
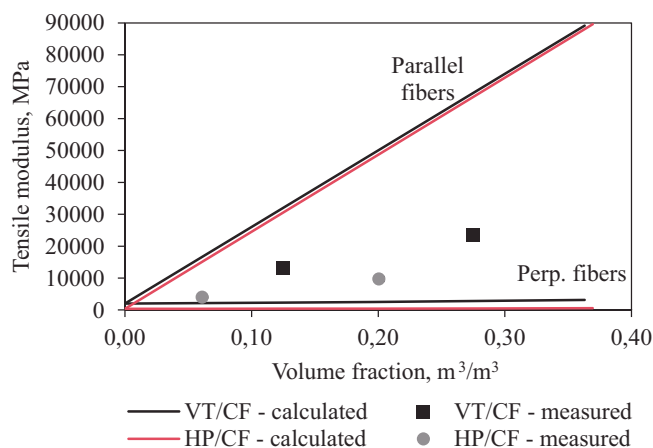


Fig. 1. Example flexural curves for the tested materials

Table 1. Physico-mechanical characterization of the tested materials

Material	Density, g/cm ³	Tensile strength, MPa	Tensile modulus, MPa	Strain at break, %	Unnotched Charpy impact strength, kJ/m ²
VT	1.031	51.4 ± 1.5	2030 ± 39	89.0 ± 1.1	unbroken
VT20CF	1.122	158.0 ± 2.4	13252 ± 216	4.5 ± 0.2	28.5
VT40CF	1.219	184.9 ± 3.5	23645 ± 578	3.8 ± 0.3	24.6
HP	1.060	26.7 ± 1.2	350 ± 11	277 ± 20	unbroken
HP10CF	1.070	71.1 ± 1.9	4000 ± 60	10 ± 1.9	unbroken
HP30CF	1.181	102.8 ± 2.6	9714 ± 495	6.2 ± 0.4	78.6

**Fig. 2.** Comparison of theoretical and measured tensile modulus vs. volume fraction for VT and HP composites

4000 MPa (HP10CF) and 9714 MPa (HP30CF), preserved a high ability to deform and high impact strength (the composite filled with 10 wt % of carbon fibers was not broken during the Charpy unnotched impact test — see: Table 1).

Further analysis of the mechanical properties was done to find what is the efficiency of reinforcement for the tested materials compared to the effect that can be theoretically obtained under the ideal conditions of long-fiber reinforced composites with ideal interfacial interactions. The curves in Fig. 2 show the tensile modulus of the composites as a function of volume fraction of carbon fibers based on the theoretical (calculated) and ex-

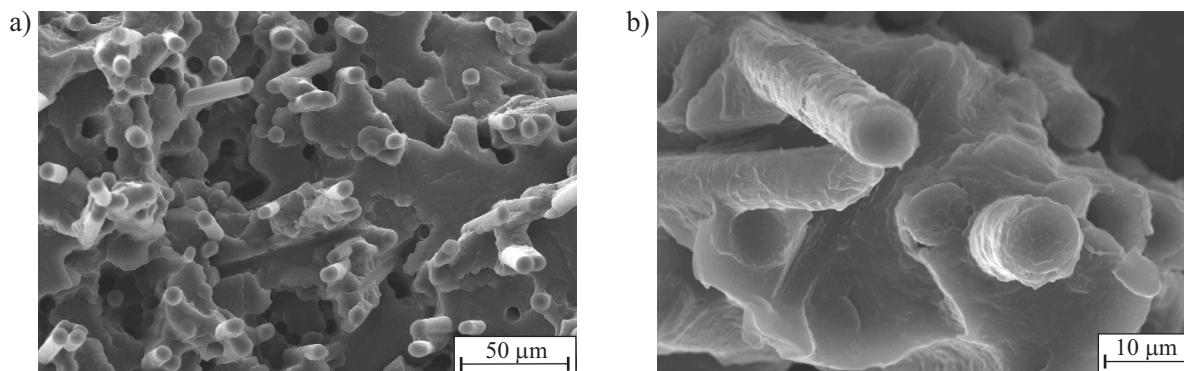
perimental data. Although high increases in tensile strength and modulus were observed for Hiprolon 211 (HP) composites compared to neat matrix (Table 1), the results in Fig. 2 show that the efficiency of reinforcement is lower than for VT composites. For the reinforcement in the form of short fibers that are prone to breaking and further shortening during processing and that are injection molded, the results obtained for VT/CF composites (20 wt % and 40 wt %) should be considered as satisfactory.

Table 2. Flexural strength and modulus of tested materials

	Flexural strength, MPa	Flexural modulus, MPa
VT	62.5 ± 9.7*	1676 ± 210
VT20CF	231.1 ± 11.5	10494 ± 246
VT40CF	283.0 ± 14.1	19830 ± 367
HP	17.6 ± 0.6*	436 ± 31
HP10CF	82.1 ± 0.1*	3169 ± 48
HP30CF	158.8 ± 3.9	8243 ± 494

* For VT, HP and HP10CF materials strength at 3.5 % strain was shown instead of flexural strength because of their high elasticity, acc. ISO 178 recommendations.

A confirmation of these statements can be found also in Fig. 3 and 4 showing the microstructure of the tensile test fracture surfaces of composites of VT filled with 40 wt % carbon fiber and HP with 10 wt % of the fibers,

**Fig. 3.** SEM images of tensile test fractures of VT40CF composites

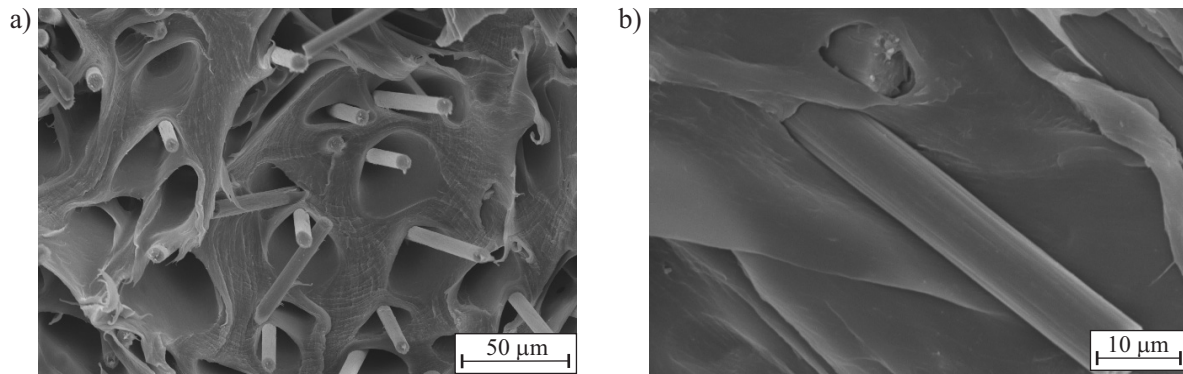


Fig. 4. SEM images of tensile test fractures of HP10CF composites

respectively. Unplasticized polyamide VT showed good adhesion to carbon fibers (Fig. 3b). We can see a positive effect of broken fibers but there are also some voids as an evidence of fibers being pulled out. The HP matrix does not cover the surface of the carbon fibers tightly (the surface of carbon fiber is smooth — Fig. 4b) and thus the lower efficiency of reinforcement in this case can be expected, compared to VT composites. The differences in the structure and deformation of the matrices shown in those pictures are also dictated by the difference in the amount of carbon fibers (10 wt % and 40 wt %) and the tensile properties of the matrices. For HP10CF, a high strain at break was achieved ($\epsilon_B = 10\%$) — the fibers are more extensively pulled out from the matrix than for VT composites.

Water absorption and its influence

Lower water absorption is one of the important advantages of long-chain polyamides, also polyamide 10.10, compared to polyamide 6, polyamide 4.6, *etc.* [1]. An obvious reduction in water absorption is observed for the composites with increasing content of non-absorbable carbon fiber filler, which can be seen in Fig. 5 showing the results of water absorption measurements per-

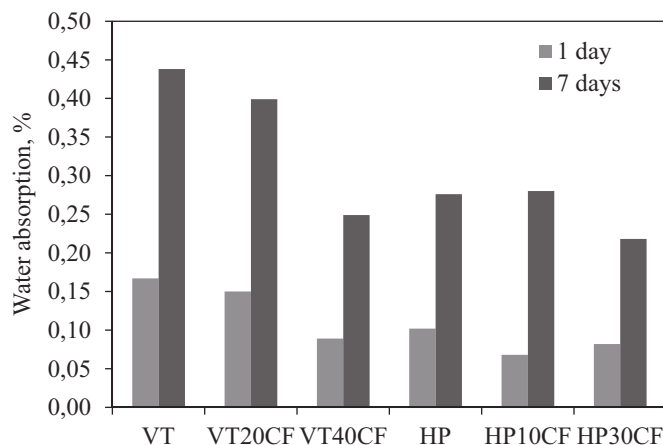


Fig. 5. Water absorption after 1 day and 7 days of incubation for the tested materials

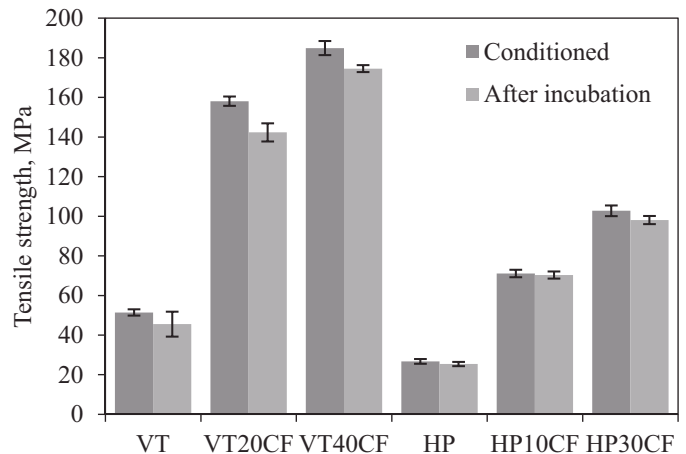


Fig. 6. Comparison of tensile strength of the materials in the conditioned state and after 7 days of incubation in water

formed after 1 day and 7 days of incubation for all of the tested materials. Also, we notice a higher absorption of water for the neat, unplasticized polyamide VT and its composite VT20CF than for HP matrix. This confirms a well-known effect that a plasticizer and crosslinking agent reduces the water absorption of so modified polymers. A small plasticizing effect of absorbed water on the biopolyamide mechanical properties can be seen in Fig. 6 showing the changes of tensile strength after 7 days of soaking. The results are in agreement with the water absorption values for the materials and the changes are greater for VT polyamide and its composites than for HP based materials. A similar effect was observed in changes of modulus of elasticity. The decrease in the mechanical properties are very little, up to approx. 10 % for VT and approx. 5 % for HP and their composites, which is a very satisfactory result for polyamide-based structural materials.

DSC analysis

The values of the melting and crystallization point for biopolyamides VT and HP (reference materials) and the composites with chopped carbon fibers recorded in heating-cooling-heating cycles are given in Table 3. The DSC

curves obtained for the tested materials in the cooling–second heating cycle are shown in Fig. 7 and 8. Analysis of the results showed that the introduction of carbon fibers into both biopolyamide matrices did not change the melting temperature of the composite compared to the reference sample in any significant way. It was noted, however, that in the second heating cycle double peaks appear in the melting curves. There are several possibilities for the occurrence of such multiple melting peaks. First, they could result from secondary crystallization in the amorphous regions between lamellae. Second, they might be due to recrystallization of metastable or imperfect folded-chain crystals. Third, they could also be a sign of the presence of crystals with different lamellar thicknesses [16]. Besides an amorphous phase, semi-crystal-

line polyamide can exhibit three main crystalline forms, the stable monoclinic α form, the metastable pseudo-hexagonal β form, and the unstable monoclinic γ form [18–19]. The β and γ forms may reorganize into the α form during the DSC scan. This information suggested that the main melting peak on the composites curves (Fig. 7b and 8b) could be attributed to the melting of the α -crystalline form. The smaller one probably indicates the melting of the thermodynamically unstable γ -crystalline form. The different crystalline forms have to be confirmed by X-ray analyses.

It was noticed during analysis of the crystallization temperatures (T_c) of the composites that, in the case of carbon fibers filler, there was a noticeable increase in the value of T_c compared to the reference materials and this

Table 3. Temperatures of melting (T_m) and crystallization (T_c), melting enthalpy (ΔH_m), degree of crystallinity (X_c) and values of ΔT for tested materials (1 – first heating cycle, 2 – second heating cycle)

Material	T_{m1} , °C	ΔH_{m1}	X_{c1} , %	T_c , °C	T_{m2} , °C		ΔH_{m2}	X_{c2} , %	ΔT	
VT	203.3	66.69	27.33	173.5	189.2	201.3	91.06	37.32	15.7	27.8
VT20CF	202.2	53.48	22.37	177.6	189.5	201.2	60.16	25.16	11.9	23.6
VT40CF	201.2	41.88	17.88	177.9	189.0	199.5	54.19	23.13	11.1	21.6
HP	194.2	49.52	20.30	170.3	183.0	192.7	57.36	23.51	11.7	22.4
HP10CF	192.8	45.37	18.78	171.1	182.0	192.7	55.80	23.10	10.9	21.6
HP30CF	192.1	30.99	13.09	173.7	183.7	193.3	41.36	17.48	10.0	19.6

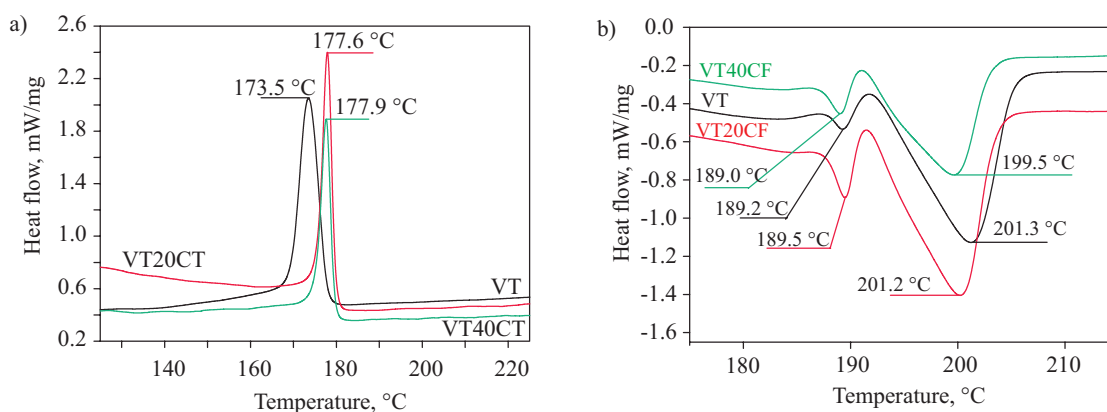


Fig. 7. DSC: a) cooling curves, b) second heating curves for the tested materials based on VT

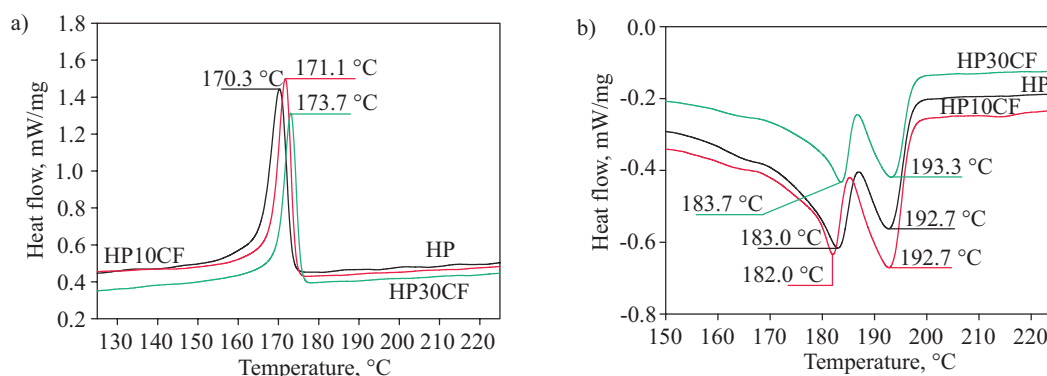


Fig. 8. DSC: a) cooling curves, b) second heating curves for the tested materials based on HPA

effect increased with higher fillers contents (e.g. 4.4 °C for VT/40CF and 3.4 °C for HP/30CF). This indicated that the addition of CFs enhanced the nucleation rate of crystallization of PA 10.10. The higher the content of carbon fibers in a matrix of polyamide, the larger the number of created nucleation sites [14–16]. Simultaneously, it was noted that the melting enthalpy and degree of crystallinity of composites was smaller compared to the unmodified PA and this effect also increased with higher filler contents. This might be due to the limitation of the mobility of macromolecule composite segments.

Studying melting and crystallization points and their impact on the performance of the injection molding process, it was noted that the introduction of carbon fibers into both biopolyamide matrices, despite the small changes of T_m and T_c , affected the value of ΔT . The values of ΔT for the tested materials are also summarized in Table 3. It can be seen that the use of carbon fibers as biopolyamide fillers resulted in a reduction of the ΔT . In the case of composites based on VT, the addition of 20 wt % chopped carbon fibers into the matrix resulted in values of ΔT that were lower than for pure biopolyamide by as much as 3.8 °C and 4.2 °C for the first and second melting peak, respectively. For composites containing 40 wt % of the filler, these differences were higher and had a value of 4.6 °C and 6.2 °C, respectively. The use of carbon fibers as the filler of HP resulted in a reduction of the ΔT of 1.8 °C and 0.8 °C for HP10CF and 1.2 °C and 2.8 °C for HP30CF (the first and second melting peak, respectively). The results therefore suggest that the use of carbon fibers as biopolyamides fillers is justified not only in terms of the performance of the composites, but also in terms of economics of the manufacturing process.

CONCLUSIONS

The use of polymers from renewable sources is beneficial to the natural human environment as it contributes to the limitation of the CO₂ emission and allows a more efficient utilization of non-renewable sources that are slowly ending. Nowadays, this is one of the most important demands of so-called “green chemistry”. There is a growing interest in durable, biobased materials of sophisticated properties intended for structural applications as shown by market leaders of various industry sectors, especially automotive, aerospace, sport and medicine.

In this study, biobased polyamide grades and their composites were tested in terms of their possible structural applications: tensile tests followed by microstructure analysis and reinforcement efficiency assessment were conducted, as well as other mechanical tests under different conditions typical for polyamides use. Additionally, DSC analysis was performed. Thus, the obtained physico-mechanical test results discussed in this paper demonstrated the feasibility of using two different commercially available polyamide 10.10 grades and their composites with short carbon fibers as new, attractive,

structural, environmentally-friendly materials. As the most beneficial features of those materials, reduced water uptake, low density and high specific strength can be listed. The tested polyamide 10.10 composites can be indicated for use in different structural applications, from more flexible and ductile (Hiproton 211 grade and its composites) to durable and stiff ones (Vestamid Teraa DS and its composites with higher carbon fiber content). Those materials, especially VT based composites, can compete with metal alloys in medium to high load bearing applications and at low to medium working temperatures. Both tested grades of polyamide 10.10 can be applied in different industrial sectors such as the automotive sector, sport, medicine or E&E.

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