Polish Society of Composite Materials
Polskie Towarzystwo Materiałów Kompozytowych

23: 1 (2023) 56-63

COMPOSITES THEORY AND PRACTICE
ISSN: 2084-6096
ISSN (online): 2299-128X

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Received (Otrzymano) 22.12.2022

EVALUATION OF PROPERTIES OF POLYMER-CERAMIC FILAMENTS MODIFIED WITH ALUMINOSILICATES FOR USE IN 3D PRINTING

A study was conducted on selected nanoclay fillers, i.e. montmorillonite (MMT) or halloysite (HNT) in polylactic acid (PLA) pellets for the manufacture of filaments for 3D printing. A 1-3 weight fraction of the filler was used. In order to compatibilize the nanofiller with the PLA, two methods were employed to facilitate dispersion of the nanoclay particles: using prewetting of the nanoclay in dichloromethane (DCM) and introducing a short-chain plasticizer (polyethylene glycol, PEG200) during the homogenization process. The effectiveness of filler dispersion was verified by performing thermal analysis, i.e. thermogravimetry and differential scanning calorimetry (DG/DSC), as well as by microscopic observations. The processability of the obtained nanocomposite filament was verified for the finished products manufactured from both of the materials by FDM printing. Mechanical strength and impact tests were conducted on the printed samples. The results showed that the prints made from the nanocomposite filaments have better tensile strength (by 25 and 10% for PLA/HNT and PLA/MMT, respectively) compared to prints made from the pure polymer filament.

Keywords: nanoclays, fused deposition modeling, 3D printing, additive manufacturing

INTRODUCTION

Additive manufacturing (AM) technologies, including the most popular fused deposition modeling (FDM), make it possible to obtain spatial objects with unique geometry and diverse properties. Better and more advanced 3D printers are appearing on the market, allowing the use of an ever-wider range of various materials, not only based on plastics, but also metals or ceramics [1]. Additive technologies are increasingly employed by various industries, e.g. automotive, construction, but also more specific areas such as medicine or aviation [2-4]. Importantly, by using optimized geometry of the internal filling of the product, a significant reduction in the weight of the element can be obtained, but also the mechanical properties of the product can be significantly improved by directional arrangement of the filling. Thanks to this, additive manufacturing methods can greatly reduce the costs and significantly shorten the time of introducing a new product to the market [5]. A good argument for using 3D printing may also be the fact that by utilizing these methods, companies are able to reduce the amount of material waste to a minimum and reduce energy consumption. Research results have shown that material waste in additive manufacturing methods is reduced by 40% compared to traditional methods and from 95 to 98% of material waste can be recycled [6].

In order to increase the practical use of manufactured plastic products, numerous attempts are being made to modify polymer filaments by introducing the admixtures of other materials in the form of fibers or solid particles. The latter include the application of nanoadditives that can significantly change the properties of the pure matrix. Filaments utilized in 3D printers are made of thermoplastic materials, but not every material will be suitable for rapid prototyping (RP), and a material that will be suitable for filament production may not be suitable for printing and vice versa. This is mainly due to the melt flow index (MFI), the value of which should not be lower than 10 g/10 min, and the higher the MFI value, the faster the material passes through the printer's nozzle and enables printing at a higher speed [7, 8]. An important element of the applicability of filaments is also their ovality and dimensional tolerance, which should not be greater than +/–0.02 mm because larger deviations cause changes in the volume of the filament, which affects the quality of the printed surface [1, 7]. Filaments are usually produced in two diameters, 1.75 and 2.85 mm, and during the forming process they should not undergo thermal degradation so as to maintain their mechanical properties and the ability to precisely reproduce geometric shapes.

One of the promising groups of additives applied as polymer filament modifiers in FDM technology are metallic and ceramic particles. The former are employed as a modifying phase for polymers such as acrylonitrile

butadiene styrene (ABS), polylactide (PLA) or polyamide (PA), while Fe, Cu, Al or W particles are most often used as metallic fillers. It was found that the presence of an additive in the form of copper or iron particles in an ABS filament causes a significant reduction in the coefficient of thermal expansion, an increase in the thermal conductivity, storage modulus and Young's modulus [9, 10]. In turn, it was shown that the addition of tungsten to the polycarbonate (PC) matrix increases dielectric permittivity, the X-ray attenuation coefficient and the impact strength [11]. Commercial filaments also often use metal alloy particles, i.e. brass and bronze for purely aesthetic purposes. Generally, the disadvantage of using filaments reinforced with metallic particles is the very fast wear of the printing nozzle, which requires the use of abrasion-resistant materials [12].

In the second group of ceramic additives for polymer filaments, chalk or other soft ceramic additives are most often used, affecting the aesthetics of commercial filaments. At the laboratory level, research is being carried out on the use of Al_2O_3 added to the polyamide 6 (PA6) matrix and it was found that the PA6/Al_2O_3 composite filament is characterized by a reduced value of the friction coefficient with an increase in the additive content (up to 14% by weight) [13]. In turn, the addition of $BaTiO_3$ particles affects the dielectric permittivity, causing its increase in the ABS/$BaTiO_3$ composite [10, 14]. PLA or PLGA (polyglycolide-co-polylactide) filaments filled with hydroxyapatite or tricalcium phosphate can, in turn, be used to print fully biodegradable and bioactive scaffolds [9]. Unfortunately, as in the case of metallic particles, ceramic particles also require the use of a nozzle made of materials resistant to abrasive wear [12].

On the other hand, a very promising group of materials used as fillers in polymer filaments is nanoparticles. It includes, among others, carbon nanotubes (CNT), graphene, graphite, metallic and ceramic nanoparticles, and AgO, TiO_2 [14-18]. Nanoparticles are an example of a nanometric phase modifying filaments. The nanoparticles introduced into the ABS matrix are responsible for a significant increase in the mechanical strength of the filament compared to the pure polymer filament, but for the ABS/TiO_2 filament, much lower roughness compared to the pure ABS filament was achieved [18]. The main problem with the use of nanoparticles, which hinders their practical application in the processing of filaments, is their excess surface energy, resulting in a tendency to agglomerate. In practice, this is associated with difficulties in the homogenization and even distribution of the nanoadditive in the filament, which, with a low filler content (1-5% by weight), means a decrease in the properties of the entire filament. Instead of fulfilling the role of a reinforcing phase in the nanocomposite, the nanoparticles are then the phase that weakens the filament by creating defects [9]. Various solutions to this problem can be found in the literature from chemical modifications of the nanoparticles resulting in their greater compatibility with the matrix, to multi-stage homogenization methods [1, 2]. However, both ways are too expensive for industrial applications, especially since the cost of the nanoparticles themselves is also a factor that discourages potential interest in new material solutions, e.g. for nanocomposite filaments.

Currently, the cheapest nanoparticles are nanoclays, i.e. layered aluminosilicates, the cost of which in 2020 was not higher than $ 4/kg, and owing to their chemical structure and diversified morphology (flakes, tubes), may exhibit variability in their physicochemical properties that should facilitate homogenization in the polymer matrix [4]. In the presented work, we focused on the production of a nanocomposite filament based on commercial polylactide (PLA) with a filling in the form of natural aluminosilicate nanoparticles. Two types of aluminosilicates were used in the study: hydrophilic montmorillonite (MMT) and hydrophobic halloysite (HNT) from the Dunino deposit. These clays had already been used in the previous work of the authors of the present study [19-21], but what is new is the application of physical or chemical modifications to achieve better compatibility between the polymer matrix and the nanoparticle.

The nanoclays used in this work are characterized by different chemical composition and morphology; MMT is a sodium-calcium layered aluminosilicate doped with iron, which agglomerates strongly in aqueous media [19]. Halloysite, on the other hand, is an aluminosilicate composed of different morphological forms: lamellar, disc-shaped and tubular [20]. The size of the nanoclay varies, depending on the form, from 3-12 nm in the smallest element. Halloysite has a smaller tendency to agglomerate, which is related to its lower polarity [21]. The obtained filaments were subjected to the calibration process and their homogeneity as well as the structural changes occurring after the extrusion process were monitored by means of thermal methods (DSC/TG). The filaments were then utilized to print samples in filament deposition modeling technology, and the printed shapes were subjected to mechanical and microscopic investigations to determine the properties of the finished products.

MATERIALS AND METHODS

The polymer matrix of the filament was polylactide (PLA) Ingeo™ Biopolymer 3251D manufactured by NatureWorks, in the form of granules. According to the manufacturer's data, the polymer is characterized by a relatively high flow coefficient, which should translate into the easier formation of thin-walled elements [22]. Montmorillonite MMT K-10 from ACROS Organics and halloysite (HNT) from the Polish Dunino deposit were applied as fillers/modifiers, the basic data of which are presented in Table 1. All the parameters included in Table 1 are from our research carried out for this work.

TABLE 1. **Selected properties of aluminosilicates used in filaments**

Material	pH	Zeta potential [mV]	CEC* [mol/100 g]	Loss of ignition [%]	Composition [%]
HNT	5.9	-41.8±0.2	11.0±0.6	15.39	70% halloysite (plate-like and nanotubular grains) 5% quartz, 12% kaolinite
MMT K10	3.5	-35.6±0.2	28.4±1.2	21.15	68% montmorillonite 29% quartz 2% muscovite

*CEC – cation exchange capacity

Nanocomposite filament manufacturing

Two types of homogenization were employed, after which, the polymer pellets and the aluminosilicate nanopowders were dried for 8 hours at 80°C and for 12 hours at 120°C, respectively. The first method of homogenization consisted in the addition of MMT K10 in an amount not exceeding 1-3 wt.% in relation to the weight of the dry polymer, kept for 4 h in dichloromethane (DCM, pure Avantor SA), and then mechanical mixed on rollers. The production of filaments by the second method consisted in the direct use of the previously obtained pellets (pure or pre-modified with nanoadditives) on a 3devo extruder (3devo B.V, the Netherlands) and was based on the addition of a plasticizer, which was PEG 200 (Sigma-Aldrich), in an amount not exceeding 2 wt.% relative to the dry weight of the polymer. As in the first method, polymer pellets with MMT K10 and HNT Dunino aluminosilicates treated with PEG were homogenized on rollers. In this case, also to improve the homogeneity of the filler, a Zamak-Skawina single-screw extruder was utilized. In both cases, the mass plasticized in the extruder was wound onto a spool using a Filabot Spooler winder. A schematic diagram of the manufacture of the HNT/MMT modified filaments is shown in Figure 1.

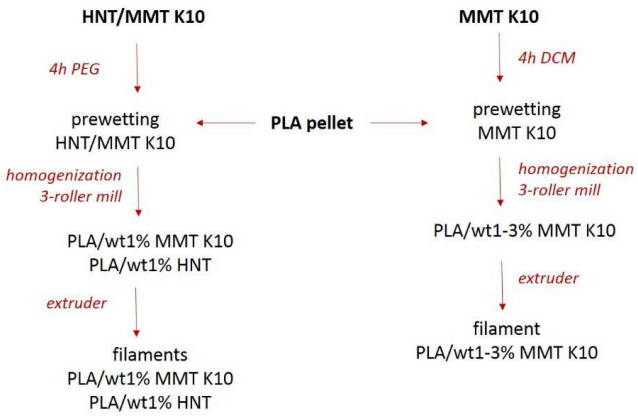


Fig. 1. Schematic diagram of manufacture of HNT/MMT filament based on PLA matrix

The prepared nanocomposite filaments were subjected to a static tensile test (Zwick/Roell 1445 Retro-Line) at the speeds of 1 mm/min and 5 mm/min to determine the modulus of elasticity and tensile strength, respectively. Mechanical strength tests were also carried out on ready-made printsin the form paddles (Fig. 2a) in accordance with the recommendations of ISO 527-1 and ISO 527-2 [23, 24]. In all the tests, the material without the nanoadditive was taken as a reference. Impact testing was also carried out bar-shaped finished prints (Fig. 2b), using the Charpy method for the edge impact variant. Samples recommended by ISO 179-1 [25] without a notch were used, with a hammer arm length of 380 mm and weight of 7.8 kg, support spacing of 22 mm, and the angle of inclination in the starting position of 161°. Ten repetitions were performed for each of the materials used in the mechanical tests. From this, the mean result and standard deviation were determined.

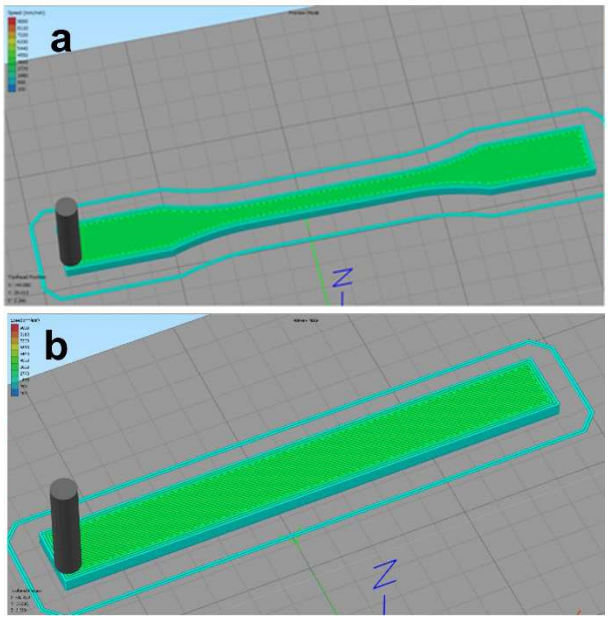


Fig. 2. Model of samples for mechanical testing prepared in the Slicer program, intended for testing: a) static tensile, b) impact strength

Thermal tests were also performed to determine the thermal durability of the filament (TG) and the degree of its crystallinity (DSC). Scanning colorimetry tests were conducted in a protective atmosphere and with a temperature rise of 10°C/min in the temperature range of 20-250°C (STA 449 F3 Jupiter by Netzsch). The printouts were made on a MakerBot Replicator 2X device under the following conditions: the diameter of the nozzle used in the printer was 0.4 mm, the height of a single layer was 0.2 mm, the filling was 100% (rectilinear filling type), the number of continuous side layers, bottom and top was 3, and the overall preset print speed was 50 mm/s. Before fabrication, both filaments were dried at about 40°C for 3 hours. The quality of the filaments and the finished prints was assessed by means of a KEYENCE VHX-900F optical microscope

with microscope software. Ten repetitions were performed for each of the materials to measure the filament size. From this, the mean result and standard deviation were determined.

RESULTS AND DISCUSSION

During the preparation of the nanocomposite filament with the addition of MMT K10, it was found that the higher the filler content, the more difficult and more random its dispersion in the volume of the pellets. The polymer pellet softened with dichloromethane was surrounded by MMT powder, which, thanks to the applied solvent, does not fall off the surface of the beads. The utilization of such a procedure facilitated the homogenization process on the extruder screw ensured that the amount of nanoclay did not exceed 1% by weight. At higher contents, agglomerates were observed on the filament surface (Fig. 3a-b, 3e-f), which significantly affected the roughness of the filament surface, which is shown in the size of the standard deviation (as well as its geometry for PLA 1.75±0.02, for PLA/1 wt.% MMT 1.75±0.12 (Table 2). Difficulties in aluminosilicate dispersion were also similar in the case of the second method, in which the addition of polyethylene glycol (PEG) plasticizer was used, whose role was to wet the nanoclay at the stage of pellet preparation for extrusion. The surface of PLA and PLA/PEG shown in Figure 3c, d is smooth compared to the nanocomposite filaments. The addition of clay increases the roughness of the filament as evidenced by the standard deviation increasing from 1.75±0.35 (for PLA/PEG) to 1.78±0.56 (for PLA/PEG/1 wt.% MMT).

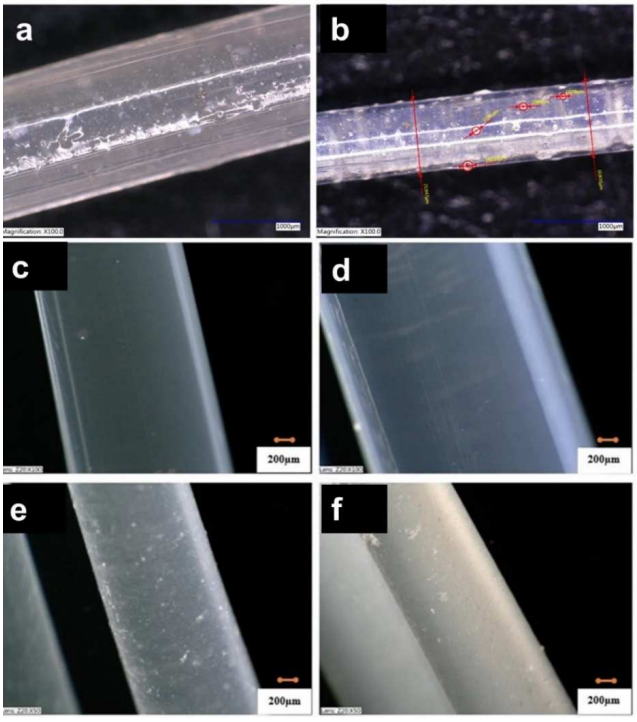


Fig. 3. Surface morphology of nanocomposite filaments: PLA/1 wt.% MMT (a), PLA/1 wt.% HNT (b), PLA (c), PLA/PEG (d), PLA/PEG/3 wt.% MMT (e), PLA/PEG/1 wt.% HNT (f)

TABLE 2. **Utility properties of nanocomposite filaments**

Material	Average filament diameter [µm]	Variation coefficient [%]
PLA/1 wt.% HNT	1.75±0.71	4.1
PLA/1 wt.% MMT	1.79±0.34	4.7
PLA/PEG/3 wt.% MMT	1.72±0.63	3.9
PLA/PEG/1 wt.% HNT	1.78±0.56	6.9
PLA/PEG	1.75±0.35	3.4
PLA	1.75±0.02	0.4

The larger amount of MMT additive (3 wt.%) is better distributed in the polymer when PEG is used as a factor facilitating the distribution of nanoclays in the PLA/PEG/MMT or PLA/PEG/HNT filaments, but as a result, a material with greater shape variability and greater roughness is obtained compared to the previously proposed method of clay homogenization by means of the organic solvent DCM. Similar problems were signaled in the literature on the subject, but they concerned other nanometric fillers, i.e. $CaCO_3$, TiO_2 or modified MMT (C93A, C30B) [17, 18, 26-28]. According to Mohapatry et al., the addition of PEG 200 or PEG 6000 worked well in the initial process, where the first stage of homogenization took place in a twin-screw extruder, and the role of PEG was to assure greater flexibility of the extrusion process [28, 29]. The authors indicate that processing problems were related to the different melting temperature of PEG in relation to the PLA matrix, as well as nanoclay sedimentation with a higher proportion of PEG. In our research, a constant amount of low-molecular PEG (2 wt.%) at a constant proportion with nanoclay facilitated its homogenization on the PLA pellet, even when it was performed only in one step by extrusion. The performed thermal tests showed, however, that PEG may interfere with the maintenance of properties such as the strength or crystallinity of the filament. In the case of the PLA/PEG/3 wt.% MMT and PLA/PEG/1 wt.% HNT nanocomposite filaments, the addition of PEG lowers the glass transition temperature (by 8°C for PLA/PEG and by about 9°C for PLA/PEG/3 wt.% MMT compared to pure PLA), while neither the presence of PEG nor the presence of nanoclay affected the melting point of PLA. The above changes were not observed in the materials in which DCM was used as a factor facilitating the distribution of nanoclay (Table 3). It is rather the effect of the additive on the crystallinity of the nanocomposite filament that is observed here, which strongly depends on the form of the nanoclay: flakes (MMT) or flakes and tubes (HNT). The analysis of thermal tests (DSC/TG) allowed a simple method of nanoclay homogenization to be selected, with the use of a solvent as the more effective method. This method does not bring additional burdens related to the role of the plasticizer, nor does it negatively affect the softening or glass transition temperature, which makes the filament similar in behavior and processing temperatures to pure PLA filament.

The results obtained for PLA/1 wt.% MMT correspond with the data published by Coppola et al. [29], where the authors demonstrated the role of the filler as a nucleant supporting the process of polymer crystallization based on organophilized MMT (OMMT Cloisite 30B). In the studied system, similar results were obtained for unmodified nanoclay. Other authors pointed out that the nucleating effect of nanoclay was seen in the cold crystallization temperature as it was lower for neat PLA than the nanocomposite filament, which could be an indicator of an increase in crystallization temperature.

TABLE 3. **Thermal properties of nanocomposite materials determined on basis of DSC curves**

Material type	T_g [°C]	T_k [°C]	T_m [°C]	ΔH [J/g]	λc [%]
PLA	62.0	101	151	34.01	36.34
PLA/1 wt.% MMT	63.1	98	151	38.17	40.78
PLA/1 wt.% HNT	64.0	99	150	30.04	32.09
PLA/PEG	53.8	96	150	22.59	20.51
PLA/PEG/3 wt.% MMT	54.0	97	149	22.64	20.95
PLA/PEG/1 wt.% HNT	54.6	96	146	18.98	29.74

T_g – glass transition temperature, T_k – crystallization temperature, T_m – melting temperature, ΔH – heat capacity, λc – crystallinity

The published results of work on polymer nanocomposites with nanoclays, including MMT, indicate a significant impact of MMT on the strength of the material formed into a filament. In the work of Weng et al., the authors received an ABS-based filament with a 3 wt.% MMT content, whose tensile strength and Young's modulus were significantly higher compared to the reference filament [30]. A similar trend is indicated in the present work (Table 4), and the highest tensile strength was obtained for the PLA/1 wt.% HNT nanocomposite filament (R_m is 11.97% higher than the strength of the PLA filament), which is related to the maintenance of the circular geometry of the filament, as well as the relatively high degree of nanoclay dispersion. A strengthening effect relative to pure polylactide was also observed for the PLA/HNT nanocomposites, and higher values of the modulus of elasticity were noted for both the PLA/1 wt.% HNT and PLA/1 wt.% HNT filaments, by 74.14% and 118.1%, respectively. Slight differences in the Young's modulus values were also obtained for the nanocomposite filaments with MMT, with the addition of MMT not significantly improving the properties, and even in the case of PLA/1 wt.% MMT, the modulus of elasticity occurred to be lower by 47% than that of pure polylactide. It is worth noting that the Young's modulus values obtained in each case were characterized by large relative percentage standard deviations, which can be attributed to the difficulties in maintaining the geometry of these filaments and the agglomeration of particles in their volume. The obtained results of the mechanical tests allowed the selection of a nanocomposite filament whose mechanical and functional properties were the best (including the coefficient of variation confirming the constant geometry of the filament). The filaments with 1 wt.% HNT and with 3 wt.% MMT were used as representative materials for the test prints and printer calibration. Calibration of the printing process settings is an inseparable activity accompanying the implementation of a new filament on a 3D printer, and the selection of parameters is closely related to the type of material and the device used, which in this case was a MakerBot Replicator 2X printer with a nozzle having an output hole diameter of 0.4 mm.

TABLE 4. **Mechanical properties of nanocomposite filaments**

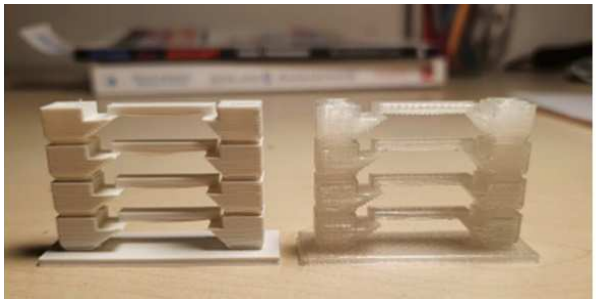
Material type	Elasticity modulus E [GPa]	Tensile strength R_m [MPa]	Elongation at break ε [%]
PLA	1160±34.66	49.3±18.03	4.2±0.81
PLA/1 wt.% HNT	2020±27.92	50.6±5.10	5.8±0.30
PLA/3 wt.% HNT	2530±24.55	55.2±6.79	3.6±0.98
PLA/1 wt.% MMT	614±13.22	47.9±2.76	3.6±2.50
PLA/3 wt.% MMT	1110±78.83	46.4±10.08	3.8±4.10

Optimization of the nozzle temperature consisted in carrying out test prints from a so-called temperature tower, i.e. an object where each shelf is printed at a nozzle temperature 5°C higher than the previous one. The process started with settings dedicated to the shelves, from the lowest to the highest: 200, 195, 190 and 185°C. This is important because the temperature is an important factor affecting the quality of the printout: too high a temperature results in an increased value of polymer flow and weakening of its properties, while too low can cause losses in the printouts and jamming of the material in the nozzle. When analyzing the test print, special attention was paid to the visual quality of the surface, all visible defects such as defects in the layers, melting or hanging threads. It was finally established that nanocomposite filaments require a nozzle temperature of 190-195°C. The same authors showed that the PLA/OMMT Cloisite B filament and print had good quality (high dispersion in the filament and in the samples printed from them). The elastic modulus of the printed nanocomposite samples was 15% higher than that of the pure PLA. The introduction of nanoclay into the matrix of the filament necessitates raising the nozzle temperature [31]. The nozzle temperature is 15°C higher than the melting temperature, which raises the elastic modulus of the printed nanocomposite.

In the next stage of device calibration, the print quality of the calibration cubes was assessed (Fig. 4b), thanks to which it became possible to check and determine important parameters such as appropriate layer width, adhesion of the layers to the substrate and the quality of the first layers, the filament extrusion multi-

plier, or maintaining the set dimensions of the printout. The areas most prone to defects (corners, edges and flat surfaces) as well as the quality of the paths were analyzed. It is known from the literature on the subject that the gaps between the material paths indicate too little extruded filament as a function of time, while overmolded, injected filament indicates too much. As a result of the tests, a lower printing speed was selected (from 60 to 50 mm/s) and it was decided to widen the path width relative to the reference filament (from 0.4 to 0.48 mm).

a)



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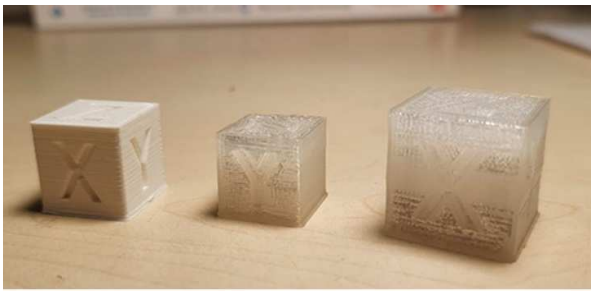

Fig. 4. Calibration prints made of PLA-based nanocomposite materials: temperature tower (a), calibration cube (b). Matte prints were made of PLA/3 wt.% MMT filament, and clear prints were made of PLA

Based on the conducted research on the selection of the parameters of the printing process, samples with a rectangular cross-section of PLA filament and PLA with nanoclay additives were produced and their mechanical properties were measured, the results of which are presented in Table 5. By analyzing the course of the stress-strain curves, one can notice the high plasticity of this material, which flows after reaching a strain of less than 4%, is visible on the graph as a decrease in the recorded stress. In reality, however, there is strong deformation on the cross-section of the samples and the formation of a neck, whose cross-section strongly decreases. Therefore, for a full analysis of the averaged stress in this region, it would be necessary to precisely measure the decreasing cross-section and relate it to the force value, which would certainly show the real, significantly higher stress values, and thus the final stress at break.

In addition, it can be stated that the stress-strain curves obtained from the tensile test for the investigated nanocomposite material samples reveal their different character: the curve for the PLA/3 wt.% MMT sample has a course typical for a brittle material (similar to the course for pure PLA), while the curve for PLA/1 wt.% HNTs indicates, as mentioned earlier, a shape corresponding to a plastic (ductile) material. The printed paddle-shaped samples, as also mentioned, had a significantly higher modulus of elasticity (25% higher for PLA/1 wt.% HNT and 10% higher for PLA/3 wt.% MMT); neverthless, the higher stiffness of the PLA/1 wt.% HNT results in lower strain at break of the material, which is known from literature reports concerning materials without multi-stage homogenization [16].

TABLE 5. **Mechanical properties of nanocomposite prints**

Material type	Elasticity modulus E [GPa]	Tensile strength R_m [MPa]	Elongation at break ε [%]	Impact strength [kJ/m^2]
PLA/1 wt.% HNT	1.67±16.7	48.4±3.4	3.4±0.2	32.41±12.99
PLA/3 wt.% MMT	1.46±24.7	47.5±3.3	9.8±0.5	27.89±9.09
PLA	1.33±13.5	46.7±2.9	6.5±0.3	25.78±4.55

Better results in terms of the possibility of deformation of the finished prints can be obtained by using the addition of the PEG plasticizer at the stage of preparation of the nanocomposite pre-granulate with the MMT filler [26, 28, 29]. Its type and proportion can strongly influence the deformation value of the finished materials. This procedure, however, causes a decrease in the strength of the material and a significant decrease in the Young's modulus, which in some applications may be a factor disqualifying the product in terms of quality. Similar to Mohapratra et al., in the presented research the selection of the aluminosilicate filler plays a key role, which can significantly affect the change in the mechanical properties of the filament and the finished product [26]. In another work, the authors using commercial nanoclays, i.e. Cloisite 30B, as fillers for a PLA-based filament obtained a slight increase in the Young's modulus of the nanocomposite filament [32]. Better enhancement of the mechanical properties of nanocomposite filaments with MMT was noted in a paper in which PLA-based blends with a small loading of nanoclay (1 to 5 wt.%) and Joncryl - a multifunctional chain extender were used [30, 32, 33]. Grigora et al. showed that PLA/Jonacryl filaments successfully enhanced the molecular weight, melt flow index, complex viscosity, and improved the printability as well as the mechanical behavior of PLA. The presence of 4 wt.% MMT resulted in better mechanical properties: a higher Young's modulus compared to neat PLA filament [33].

It is clear, however, that the bar-shaped samples printed with nanocomposite filaments exhibited an impact strength higher than that recorded for a bar printed with pure polymer filament (Table 5). It is worth emphasizing that according to sources provided by filament manufacturers, most commercially available filaments based on polylactide have impact strength values in the range of 16-20 kJ/m^2 [26]. The literature

data show that it is only possible to achieve the obtained impact strength result with a higher concentration of the nanofiller. Moreno et al. demonstrated that the addition of nanometric $CaCO_3$ above 3 wt.% to PLA causes an almost two-fold increase in the impact strength [34, 35]. In turn, increasing the amount of calcium carbonate filling to 15 wt.% causes a significant rise in the deformation of the nanocomposite, even up to 12% [35], which was also the case in the present study. In the case of the tested nanocomposite samples with aluminosilicates, it was observed that they have more than a 16% higher impact strength compared to samples printed with neat PLA filament, despite the higher tensile modulus and the discontinuous nature of the stress-strain curve (Fig. 5). Moreover, in the case of nanocomposites, a lower value of the relative standard deviation is observed for the investigated samples, which confirms the repeatable nature of the filament and the prints made based on it (Table 5).

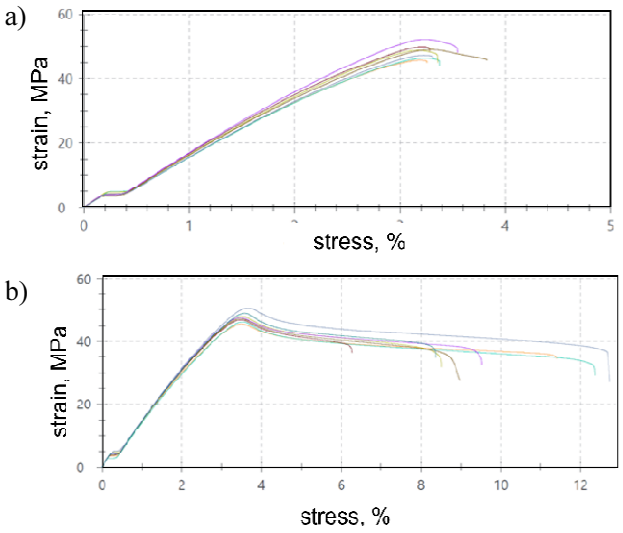

Fig. 5. Stress-strain curves in tensile test for paddle-shaped samples printed from nanocomposite filaments: a) PLA/3 wt.% MMT and b) PLA/1 wt.% HNT

CONCLUSIONS

The form of one-stage homogenization of PLA pellets with aluminosilicate proposed in the work makes it possible to prepare a nanocomposite filament and directly extrude nanocomposite materials without using any process such as melt mixing or nanocomposite masterbatch fabrication. The effectiveness of its formation in the 3D printing process strongly depends on the form and nature of the aluminosilicate as well as the amount of nanoadditive used and the application of DCM solvent to facilitate homogenization of the nanoclay. From the practical point of view, the most important feature of the filament that determines its potential use is maintaining a smooth surface and uniform geometry of the nanocomposite filament, which in the case of the examined materials was achieved for two out of the six systems. The investigated filaments PLA/1 wt.% HNT and PLA/3 wt.% MMT were used to calibrate the printer and make paddles-shaped and bar-shaped samples. The printed products from the nanocomposite filaments were characterized by satisfactory (often improved) mechanical properties, i.e. tensile strength, stiffness modulus and impact strength, without a loss of print quality of the elements.

Acknowledgments

This work was funded by a subsidy from the Ministry of Education and Science for AGH University of Science and Technology in Kraków, project No 16.16. 160.557-5

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