Mechanical Performance Under Various Conditions of 3D Printed Polylactide Composites With Natural Fibers

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Abstract

In the study, polylactide-based (PLA) composites modified with natural particles (wood, bamboo, and cork) and with different levels of infilling (100%, 80%, and 60%) obtained by additive methods were tested. The effect of type fiber, infill level and crystallization rate on the mechanical properties were investigated by using tensile, flexural, and impact tests. The materials were subjected to mechanical tests carried out at 23 and 80 °C. Furthermore, hydrothermal degradation was performed, and its effect on the properties was analyzed.

The addition of natural fillers and different level of infilling result in a similar level of reduction in the properties. Composites made of PLA are more sensitive to high temperature than to water. The decrease in Young's modulus of PLA at 80 °C was 90%, while after 28 days of hydrodegradation ~ 9%. The addition of fibers reduced this decrease at elevated temperatures. Moreover, the impact strength has been improved by 50% for composites with cork particles and for other lignocellulosic composites remained at the same level as for resin.

1. Introduction

For more than three decades, there has been a substantial increase in interest in products developed using additive manufacturing (AM). Presently, AM has revolutionized the manufacturing industry as it enables rapid manufacturing of products while simultaneously reducing cost [1] [2]. One of the most commonly used AM techniques is fused deposition modeling (FDM), which involves successive overlapping of layers of filaments; the production occurs without additional processing of the material, which allows to reduce waste during production [3]. This technology has enabled to develop prototypes with complex shapes, which is otherwise difficult to obtain by traditional techniques (injection molding) [4]. However, the production by AM requires a continuous flow of materials, which can be disturbed during the filament application process. The lack of isotropy of products can significantly affect the mechanical properties of the tested materials; hence, new solutions to improve this method are being constantly investigated, such as nozzle and platform temperature, printing speed, height of layer deposition, raster angle of infill pattern, build orientation, and addition of particles [5] [6]. To date, many works has been published on the relationship between the filament system and each other 0°/90° or 45°/45° [7]. Depending on the position of the filaments in relation to each other, the materials exhibit different properties, for example, materials with a 45°/45° filament system have higher values of mechanical properties than those with a 0°/90° filament system [8]. By optimizing the methods at the production level, it is possible to design a product with superior properties.

The development of AM also led to the development of other agents blended with the materials used in this technique. The most commonly used materials in FDM are thermoplastic polymers: acrylonitrile butadiene styrene, polyetherimide, polylactide (PLA), polycarbonate, and polymethylmethacrylate [9] [10]. Because of concerns related to environmental pollution, PLA is gaining popularity as an alternative to synthetic polymer materials. PLA is a biodegradable, biocompatible polymeric material. This material is

not only environmentally friendly, but it also has properties comparable to those of petrochemical polymers [11]. In addition, its melting temperature is relatively low, which makes its use in FDM cost-effective.

To change characteristics and additionally to reduce costs, composites with the addition of fibers or particles are often formed to reduce the production cost of the material, as is the case in traditional processing methods. Modifications of filaments can also be carried out in AM. It is reasonable to reinforce PLA with natural fillers containing lignocellulose such as wood, hemp, flax etc. (the material remains 100% biodegradable). According to previous literature, the addition of natural fillers improves the stiffness of composites while reducing tensile or flexural strength [12]. However, the addition of lignocellulosic fillers to polymer composites generates a material with a relatively high value of mechanical properties to density, while further reducing its cost.

Despite the many advantages of biodegradable polymers, during their processing and service life some disadvantages appear. Biodegradable polymers have faster water absorption capacity than petrochemical polymers. The penetration of water inside the biodegradable polymer composite affects its structural stability, leading to breakage of the polymer chains [13]. This process is further accelerated by factors such as temperature, time of exposure to water and modifications [14]. These factors are mainly important for materials intended for medical applications (surgical screws, blood vessel prostheses, sutures, bone anastomoses, etc.). Because PLA is widely used in the field of medicine, it is crucial to conduct tests that measure the impact of the aquatic environment on PLA-based materials. Studies have shown that the level of water absorption increases and the value of mechanical properties decreases with increased duration of contact of composites with the aquatic environment. It was also observed that as the water temperature increases, the water absorption rate of the material increases, which causes a corresponding decrease in the value of mechanical properties [15]. Moreover, because fibers such as lignocellulose are hydrophilic in nature, the addition of fillers containing these fibers accelerates the process of water absorption into biodegradable composites [16]. To date, only a few studies have been published on the negative impact of water on the mechanical properties of 3D-printed polymer materials, including factors such as the degree of crystallization, degree of infilling, and addition of natural fillers [17].

In the present study, PLA-based composites reinforced with natural particles (wood, bamboo, and cork) were prepared using 3D printing. In addition, neat PLA materials with varying degrees of infills (100%, 80%, and 60%) were prepared. The novelty of the present study is the comparison of the impact of the addition of natural fillers and the different degree of infilling on the mechanical properties of composite materials in various operating environments such as ambient temperature, elevated temperature (80°C), and immersion in saline solution at 38°C. In addition, two states of composite materials were tested: semi-amorphous and crystalline. For this purpose, various mechanical tests (tensile strength, bending, and impact) were conducted. These studies are important for the development of the field of materials science and manufacturing techniques. To the best of the authors' knowledge, no direct comparison of all

the above mentioned aspects has been performed; thus, the present study may further expand the area of potential applications of these composites.

2. Materials And Methods

2.1. Composites filaments and sample preparation

The filaments of neat PLA and PLA composited reinforced with 30 wt.% of wood particles (W), 2 bamboo fibers (B) and cork (C) were provided by PriMat 3D sp. z o.o. (Poznan, Poland). The diameter of filament was 1.75 mm, regardless of filament type. Standard dumbbell samples in accordance with the ISO 20753 standard (15×4×90) were produced by the FDM printer Zortrax M300 manufactured by Profound3D (Exton, PA, USA). The key printing parameters were the same for all tested samples and were following: platform temperature: 50°C, nozzle temperature 210°C, printing speed: 60 mm/s, nozzle diameter: 0.4 mm, infill pattern: linear and layer height: 0.2 mm. Additionally, in this study for composites the infill was adjusted to maximum value (100%) and for neat PLA from 100%, 80% and 60%, and the raster angle was 45 °/−45°, regardless of type. Figure 1 shows difference in the surface of samples and raster angels.

2.2. Characterization of composites

2.2.1. Physico-Mechanical tests

Density was obtained by measuring dimensions and mass using the RADWAG WAS 220/X (Radom, Poland) electronic analytical balance following the immersion method according to the ISO:1183-1 standard.

In order to study mechanical properties tensile, bending and impact tests were performed. The tensile (ISO:527 standard) and flexural (ISO:178 standard) properties were studied by using the universal MTS Criterion Model 43 testing machine (Eden Prairie, MN USA). The displacement rate was fixed to 10 mm/min and 5 mm/min for tensile tests and three-point bending tests, respectively. The impact strength was measured by the Charpy test using by Zwick/Roell MTS-SP testing machine (Ulm, Germany) on un-notched samples according to the ISO:179 standard. The applied energy on nu-notched samples was 1.5 J.

All mechanical tests were performed under vary testing condition:

- - at ambient temperature (+ 23°C ± 2), which was reflected to the control group;
- - at elevated temperature (+ 80°C) in the temperature chamber (Instron), to asses impact of high temperatures.

Additionally, samples for mechanical tests were heat treated to increase the degree of crystallinity. In this process samples were placed in a furnace at 85°C for 60 min between two glass plates to prevent their deformation. This process is justified in the case of PLA because it has a semi-amorphous state during

production. Upon heating the material above cold crystallization temperature and its slow cooling, a crystalline phase material is formed.

2.2.2. Hydrolytic degradation

For the calculation of water absorption, samples were immersed into the saline solution (distilled water with 0.9 wt.% of NaCl) at 38°C (physiological temperature) to create human body environment. The measurements were carried out in accordance with the modified ISO:62 standard, which was adopted as hydrothermal aging environment, modifying the temperature and water specifications to the desire aging condition. The samples were kept in saline for 1, 7 and 28 days. The water absorption rate of the samples was calculated by the following equation: percentage of solution content [%] = $(W_t - W_0)/(W_0) \times 100$, where W_t stands for the instantaneous weight of the sample and W_0 for the initial weight of the sample.

To determine the influence of water uptake on the basic mechanical properties of the specimens which were incubated for 28 days in water, a tensile test was performed. This study was conducted to consider to two conditions: physiological temperature and water absorption.

2.2.3. Morphological study

The fracture morphology of all the samples after tensile test were evaluated by scanning electron microscopy (SEM) (JEOL JSM5510LV,Tokyo, Japan) operating at 20 kV in low vacuum. Prior to imaging the specimens were gold-sputtered by using an auto vacuum coater (Cressington,Watford, UK). This study gave information about filler distribution and showed main characteristics of the filament orientation on breakthroughs.

2.2.4. Statistical analysis

At least five measurements for each material were performed and average values and the relative standard deviation were calculated. The statistical analyses with Analysis ToolPak in Excel (2016) such as one-way analysis of variance (ANOVA) and subsequent t-test at significant levels of $p < 0.05$ were considered to be statistically significant.

3. Results

3.1. Physico-Mechanical properties

Table 1 summarizes the used abbreviations, density and specific properties of PLA composites. It seems obvious that with a decrease in the degree of filling in materials, its density decreases. This relationship was also observed in these studies, where the following trend has been noticed: PLA100%>PLA80%>PLA60% and PLA/C > PLA/W > PLA/B. It should be emphasized that the addition of fibers had a greater impact on the decrease in density than the lower degree of PLA filling. The density of the tested composites decreased with the addition of natural fibers due to the closed morphology of lignocellulosic fibers and its lower density compared to the matrix [18]. In addition, as can be seen in the SEM pictures (Fig. 6), the composites are characterized by insufficient adhesion between the fiber and the

matrix, which increased the number of voids in the material – higher porosity. The effect of this phenomenon is a decrease in the volume fraction of neat polymer and thus decrease the density of composites. Moreover, AM itself causes an increase in discontinuities between individual layers and the extra inclusions increase them even more. However, it should be emphasized that these defects did not affect the repeatability of the results, as the standard deviation was less than 5%.

In the case of composites dedicated engineering applications, not only a single property, but a ratio of two dependencies is taken into account during the selection of the material. Because today's market expects materials of high stiffness and relatively low weight, in this work the ratio of Young's modulus value to density was determined. The addition of natural fillers decreased the specific values of the tested composites. The highest specific modulus was observed for neat PLA (3.02 MPa/(kg/m^3); density 1.23 g/cm^3); however, a slightly lower value (2.07 MPa/(kg/m^3)) was recorded for PLA/B where the lowest density was met (1.13 g/cm^3). The decrease in the specific properties for composites with the addition of lignocellulosic fibers was lower than 50% and amounted to: PLA/B – 31%; PLA/W – 37% and PLA/C – 48%. Despite similar density values of composites filled with natural fibers and with vary infilling levels, PLA80% and 60% showed a decrease of more than double in specific modulus (difference in density > 8%). In this case, the result was affected by a significant decrease in Young's modulus, caused by discontinuities in the material that generated additional stress concentrations areas.

Table 1
Abbreviations of tested composites, density and specific modulus of PLA composites

Sample	Abbreviation	Density [g/cm^3]	Specific Modulus [MPa/(kg/m^3)]
Polylactide with 100% infill	PLA100%	$1.23^{\pm 0.01}$	3.02
Polylactide with 80% infill	PLA80%	$1.22^{\pm 0.01}$	1.30
Polylactide with 60% infill	PLA60%	$1.19^{\pm 0.02}$	1.24
Polylactide with wood fibers	PLA/W	$1.17^{\pm 0.01}$	1.89
Polylactide with bamboo fibers	PLA/B	$1.13^{\pm 0.01}$	2.07
Polylactide with cork particles	PLA/C	$1.19^{\pm 0.02}$	1.55

3.2. Tensile properties

The selected stress-strain curves for the tested materials are shown in Fig. 2 (a) composites tested at ambient temperature and (b) at elevated temperature (80°C). At 23°C in the first stage, the strain was proportional to the stress (Hooke's law) up to the yield stress. At both 23°C and 80°C, neat PLA100% showed the highest stress. At 80°C, a significant increase in elongation was observed up to over 30% (PLA 100%), and the stress decreased by more than half compared to that at ambient temperature. This

effect was caused by the test temperature above T_g of PLA (~ 60°C) where the amorphous regions experience transition from rigid state (solid) to more flexible (rubbery) state [19]. With an increase in temperature, the ability to move the polymer chain increased, which resulted in significant elongation and reduction in strength values. At high temperatures, the polymer chains are reorganized and arranged along the load. Consequently, the material became more susceptible to plastic deformation [20].

Natural fillers had a more negative effect on the values of mechanical properties than filling levels at 80°C. This relationship was most likely caused by partial crystallization of neat PLA during the test (higher crystallization rate, higher mechanical properties). Neat semi-amorphous PLA (immediately after production) has greater ability to form crystals during the temperature annealing process than composites with natural fibers, as reported in literature [21]. In addition, as shown in Fig. 2b, no visible differences were noted between neat PLA after heat treatment and neat PLA without heat treatment (as observed at 23°C); this finding also confirms the possibility of the crystallization process for semi-amorphous samples during tests conducted at 80°C.

To better discuss the results Table 2 presents the selected data obtained during the static tensile test (tensile strength, Young's modulus and strain at break). The reduction in both the level of infilling and the addition of natural fillers caused a significant decrease in the values of mechanical properties, regardless of the test temperature. Deterioration of tensile strength for all modified materials was at a similar level and the obtained values were in the range – 19.2 to 26.3 MPa (ambient temperature) and – 8.2 to 21.1 MPa (elevated temperature). Both the addition of natural fibers and the reduction in the degree of infilling of composites reduced the value of tensile strength by approximately 50%. The highest decrease was noted for PLA 60% – 55% while the lowest for PLA/B – 39% (ambient temperature).

Table 2
Tensile properties of PLA composites

Tensile properties	Condition	Thermal treatment	Composites					
			PLA 100%	PLA 80%	PLA 60%	PLA/W	PLA/B	PLA/C
Tensile strength [MPa]	+ 23°C	NO	42.9± 3.9	20.6± 2.6	19.2± 1.4	24.7± 0.5	26.3± 0.6	24.1± 1.1
		YES	58.5± 0.7	21.6± 1.0	20.7± 0.9	25.2± 0.7	27.3± 0.2	25.1± 0.4
	+ 80°C	NO	21.1± 0.6	15.6± 0.6	12.9± 0.8	8.2± 0.7	9.6± 0.6	9.9± 0.5
		YES	23.9± 2.5	14.2± 0.5	13.5± 0.6	7.9± 0.5	8.4± 0.6	9.3± 0.7
Tensile Modulus [MPa]	+ 23°C	NO	3742± 74	1585± 95	1470± 87	2213± 26	2334± 112	1844± 51
		YES	3926± 100	1711± 94	1524± 45	2296± 27	2359± 51	2021± 18
	+ 80°C	NO	392± 89	330± 16	292± 30	325± 7	386± 17	247± 7
		YES	366± 21	358± 25	332± 70	322± 10	302± 8	211± 12
Elongation at break [%]	+ 23°C	NO	6.4	3.4	4.6	3.6	7.1	6.4
		YES	2.6	2.7	2.6	3.3	4.8	5.7
	+ 80°C	NO	30.1	17.2	14.5	14.1	13.7	21.3
		YES	22.4	21.1	25.3	15.7	18.8	25.5

In general, three factors have impact on the results obtained during the tensile tests of fiber reinforced composites: initial fiber/matrix strength, fiber length, and fiber/matrix adhesion. In the case of fiber reinforced composites, it is expected that the fibers which usually have a higher stiffness than the polymer matrix will carry the load applied to the matrix. However, the condition of sufficient fiber/matrix adhesion must be met. As was already reported, the addition of unmodified natural fibers is leading to decrease in strength [22]. In this study, insufficient fiber/matrix adhesion confirmed by SEM (Fig. 6) and empty spaces in the material had a negative effect on the mechanical properties. The first reason is due to the hydrophilic nature of the fibers and the hydrophobic nature of the matrix, which prevents the formation of strong bonds between the components. Furthermore, during the FDM process, the incorporation of fibers creates higher empty spaces between the applied layers [23].

The modification of PLA also had a negative effect on the stiffness of the tested composites. Lowering the degree of filling in composites had a more negative effect on the Young's modulus

values than the addition of natural fibers. Moreover, in the case of Young's modulus, the differences in decreases in the values to pure PLA were higher than in the case of tensile strength. The following decrease was observed: PLA/B (38%) > PLA/W (41%) > PLA/C (51%) > PLA80% (58%) > PLA60% (61%).

As PLA is known to occur in various forms from amorphous to the crystalline phase, the more the amount of the crystalline phase, the higher is the value of the mechanical properties of materials. Consequently, various methods have been used to increase the degree of crystallinity: addition of fillers or heat treatment [24]. Therefore, heat-treated materials were also considered in the study to achieve higher mechanical results.

As shown by previous research of the authors of the presented work, the PLA after annealing (heat treatment) increases the amount of the crystalline phase and thus increases the value of the mechanical properties [25]. The highest improvement in properties was recorded for neat PLA (over 35% for tensile strength). After the thermal treatment, neat 3D printed PLA had higher values of mechanical properties as those of PLA produced by traditional methods (injection molding) [26]. The addition of natural fibers did not significantly change the tensile strength after crystallization (max. improvement was 10%). This shows that despite the increase in the degree of crystallization, the negative effect of natural fillers still persists. This occurs due to the formation of stresses at the borders of the matrix and filler. Moreover, it is possible that this is by reason of increasing loss of adhesion due to shrinkage of the PLA matrix during crystallization, which could increase the lack of fiber/matrix adhesion.

In addition, elongation at break after crystallization was reduced more than doubled. The reduction in elongation indicates an increase in material stiffness, which is confirmed by the improvement in Young's modulus value. All tested materials showed an increase in the modulus of elasticity for heat-treated materials. However, it should be noted that the higher improvement for tensile strength than for Young's modulus was registered.

Negative effects of elevated test temperatures were observed in the present study. Neat PLA showed a decrease in tensile strength by approximately 50%, while composites with the addition of fibers recorded a decrease by 3 times (from 24.7 ± 0.5 MPa to 7.9 ± 0.5 MPa for PLA/W). The decrease in Young's modulus was even higher, with approximately 90% for neat PLA and approximately 80% for composites. Because of the relatively low T_g, the values of the mechanical properties of PLA decreased drastically as the material became more plastic. At high test temperatures, the increase in the crystalline phase did not affect the results.

The results show that both the introduction of natural fillers and the reduction of the filling density have a similar effect on the mechanical properties of 3D printed polymer composites. Although a decrease in mechanical properties was observed, it should be noted that the results are comparable with other commonly used composites (polypropylene, polyethylene, etc.) produced by injection molding [27][28]. In all these cases, the main advantage of the produced composites is the reduction of polymer matrix content, which constitutes both an economic and an environmental benefit. In addition, the use of bio-

based materials in combination with 3D printing techniques (waste reduction) further increases the above-mentioned benefits.

3.3. Flexural properties

The properties obtained during the three-point bending test are very important, because they combine different stresses, i.e. compression and tension. Phenomena occurring during the bending test depends on the position: the upper layer is subjected to compression while the lower layer to tension. Therefore, in the bending test, good fiber/matrix adhesion is not as significant as the fiber orientation. The more parallel the fibers are arranged in the matrix, the higher the flexural properties.

Similar relationships as in the tensile test were noticed in the three-point bending test (Fig. 3). However, the results obtained during the bending test are twice as high as during the tensile test. This fact is related to the aforementioned mechanisms that occur during tests. In addition, as can be seen in the SEM pictures (Fig. 6), the fibers are distributed mostly parallel in the matrix, which means that the fibers are more resistant to applied load.

For both composites with a reduced infilling content and with the addition of natural fillers, the properties of flexural strength and flexural modulus have decreased. No significant differences were observed in the results of flexural strength composites with natural fillers (45.3 MPa- 51.2 MPa). However, their decrease compared to neat PLA was about 50%. A similar situation occurred in flexural modulus. The decrease in properties is caused by the increase in the porosity of the composites produced by inadequate interfacial bonding. The results obtained coincide with the results of the work of composites with natural fillers obtained by FDM [23].

A higher decrease in properties was noted for composites with a lower degree of filling, for flexural modulus it was up to 3 times lower. At elevated temperatures, the decrease in all values remained at the same level for each of the composites. This indicates a greater influence of temperature on mechanical values than the amount of filling or type of filler.

The influence of the degree of crystallization of composites is also visible. Along with the increase in the degree of crystallization, the mechanical properties increased at 23°C, the highest differences can be seen in the case of neat PLA, the increase was about 20%. At 80°C composites reported lower properties after heat treatment than before. As with tensile properties, this is due to the formation of crystallites when tested at high temperatures.

3.4. Impact properties

For fiber-reinforced composites during loading, the impact strength component is affected by fiber pull out or breaking of fibers. As reported in the literature, composites with longer fibers that pull out have higher impact strength values, while composites with short fibers have significantly reduced impact strength values [29]. In composites with the same fiber content, shorter fibers occur more than long ones,

which implies means that short fibers generate more stress concentration areas at the fiber ends. Impact strength results for composites were presented in Table 3.

Table 3
Impact strength of PLA composites with vary infills and fillers

Impact strength [J/cm^3]						
Samples	PLA100%	PLA80%	PLA60%	PLA/W	PLA/B	PLA/C
without thermal treatment	$10.4^{\pm 0.4}$	$7.5^{\pm 0.6}$	$7.9^{\pm 0.2}$	$9.4^{\pm 0.9}$	$9.1^{\pm 0.2}$	$22.3^{\pm 0.7}$
after thermal treatment	$19.6^{\pm 0.7}$	$10.7^{\pm 0.2}$	$10.4^{\pm 0.4}$	$12.4^{\pm 0.9}$	$12.3^{\pm 0.5}$	$25.0^{\pm 0.7}$

In the present study, composites with the addition of wood and bamboo fibers showed similar values of mechanical properties as those of pure PLA; this finding indicates no negative impact of natural fibers on the impact properties. According to the literature, the addition of natural fillers to polymer composites results in a reduction of impact strength [30]. It should be emphasized that in this paper the results of impact strength are higher or at a similar level as the matrix. The impact strength of PLA/C composites was improved by more than twice (from 10.87 kJ/m^2 to 22.1 kJ/m^2).

Similar to the values of properties obtained during the tensile and bending tests, the impact strength values increased after thermal treatment. The most obvious gain effect caused by the increase in the amount of the crystalline phase was noted for neat PLA 100%.

The reduction in the degree of filling decreased the impact strength value by approximately 30% for both PLA 80% and 60%; however, no significant differences in the results ($p > 0.05$) were noted for the different levels of filling (80% and 60%).

3.5. Influence of hydrolytic degradation on mechanical properties

In the field of biodegradable polymers, hydrolytic degradation and its impact on changing mechanical properties of materials have a very important role. Several factors determine water absorption of composite materials: type of polymer matrix, type and content of fillers, adhesion matrix/filler, and test temperature [31]. In this study synergic effect of water and temperature was studied. Figure 4 shows the change in weight of the composites during immersion in saline at 38°C.

As observed for modified composites, the highest mass increase occurred in the first stage; subsequently, saturation occurred after 7 days (when the daily weight gain of the samples was less than 0.01%), and the mass remained constant for up to 28 days.

The mechanism of water absorption in these studies is not in accordance with Fick's law of diffusion. There is no three-stage sorption course distinguished: rapid increase in the first phase and sorption release followed by saturation [32]. This is most likely caused by capillarity phenomena, which was

caused by fiber swelling. In addition, as other researchers indicate, this phenomenon may be associated with the leaching of polymer particles, which leads to weight loss [33].

The highest water absorption was shown by PLA 60% (8.1%) and PLA 80% (7.8%). This was because of a lack of material continuity due to the bulk region in the material, as observed in Fig. 6. PLA 100% showed the greatest density of material and hence the lowest water absorption value (~ 1%). Because PLA is hygroscopic in nature, it can absorb approximately 1% water horizontally [35]. According to previous literature, lignocellulose-containing additives are susceptible to water absorption due to their hydrophilic nature (presence of many hydroxyl groups). The results of the present study also confirmed this fact. PLA/B (5.7%) showed the highest water absorption in the group of lignocellulose fiber-reinforced composites. This is not only because of the strong hydrophilicity of PLA/B that has a significant impact on water absorption, but also due to the fibers around which additional microchannel spaces are formed through which water can flow. In the group of composites reinforced with fillers, PLA/C (4.28%) had the lowest water absorption rate. This relationship results from the cellulose content in the fibers. The higher the cellulose content, the higher the water absorption capacity. The content of cellulose in individual fillers used in the research is: 40–50% for wood, 40–55% for bamboo and 12–25% for cork, which corresponds to the results obtained in this study PLA/B > PLA/W > PLAC [34]. Moreover, higher water uptake capacity by wood than by cork has already been reported by other studies [27].

Figure 5 shows the results of tensile strength and Young's modulus after hydrodegradation of the composites. The tensile strength value for composites immersed for 28 days at + 38°C decreased by approximately 5% and 20% for neat PLA and composites with natural particles, respectively. Lower decrease in the mechanical properties of neat polymer are associated with a greater ability to plastic deformation than for fibers-reinforced composites. Furthermore, natural fillers containing lignocellulose have a high water absorption capacity, which causes them to swell (increase in size), which contributes to the formation of cracks in the matrix [35]. In addition, water flowing into the material caused the fibers to detach from the matrix, which further contributed to the reduction of fiber/matrix adhesion. During the tensile test of materials subjected to water immersion, lignocellulosic fillers induce additional stress that reduces the values of mechanical properties (expansion and contraction of fibers during water absorption).

However, in the case of Young's Modulus the decrease was about 10% for all tested materials. As mentioned earlier, composite stiffness is not as dependent on fiber adhesion as it is in tensile strength. Additionally, a slight decrease in the stiffness of the materials could be caused by an increase in the degree of crystallinity of the material, because of immersion in water at 38°C.

A similar tendency was observed for samples after heat treatment. By comparing the results obtained during tests at 80°C, it can be concluded that biodegradable composites are more susceptible to high temperatures than to water. This is particularly evident for Young's Modulus, where neat PLA subjected to high temperature showed a decrease of approximately 90% at elevated temperatures.

3.6. Microstructure

Figure 6 shows the fractured surface of the composites after the tensile test. As shown in the figure, the addition of natural fillers changed the characteristic of the breakthrough from ductile to fragile. As already mentioned, the decrease in the values of mechanical properties for composites with 80% and 60% infilling was caused by a lack of material continuity and gaps between the applied filaments (higher porosity of materials) what can be seen in Fig. 6. Each natural fiber used in the present study has a different structure. Wood fibers are the widest, and the width reaches approximately 800 μm; additionally, the adhesion between the matrix and the fiber is poor. Bamboo fibers are the longest, and their filamentary structure can be observed in the figure. A black rings around the bamboo fibers occur, which indicates poor adhesion and deformation. However, because of the length of bamboo fibers, the value of the properties of composites with these fibers are the highest compared to those of the other tested materials. In addition, the differences among the distances between the filaments are the lowest for PLA/B, because of the higher viscosity of the material and the predominant elastic fraction, which causes impeded flow and directly affects the interlayer bonding.

4. Conclusion

The mechanical behavior of PLA based composites in different states and conditions were investigated in this study. Studies have shown that both the effect of changing the amount of filling and the addition of natural fillers have a similar effect on mechanical properties. Heat treatment of manufactured composites increase their mechanical performance. Despite the decrease in mechanical properties after hydrolytic degradation, mechanical properties remain at a high level, which generates their potential use in long term applications. In addition, the composites were characterized by high impact strength values comparable with neat PLA, and in the case of cork composites, improvement constituted 50%.

In summary, the work presents the results obtained through the use of various techniques for the modification of biodegradable 3D printed materials. The obtained data will allow to design material with the expected properties at an early stage of engineering design. As a results of the work, the impact of lignocellulosic particles has a different effect on the mechanical properties than in the case of injection-molded polymer composites. The addition of lignocellulosic fibers to injection-molded polymer composites generally improves their Young’s modulus, while in the case of 3D printed composites it lowers their mechanical properties. However, the relatively high obtained mechanical properties compere to the density of composites with natural fillers and the low decrease in mechanical properties after hydrolytic degradation indicate their potential application in various industry sectors (medicine, furniture, decorations, automotive industry and so on).

The presented results suggest in what direction should be guided further research on 3D printed polymer composites. It is important to increase the fiber adhesion to the matrix. This effect can be achieved by introducing smaller natural particles (nano or micro scale) or by adding a plasticizer. With the addition of a plasticizer, one should consider the use of natural composition (leaving 100% biodegradable material) or the final use of material for engineering products whose 100% biodegradation is not required.

Taken together, additive techniques are a dynamically developing group of manufacturing processes. However, the methodology of research on polymeric composites produced using the FDM is not well systematized [38]. Mechanical tests presented in this paper can provide predictions regarding the influence of different modification of composites (level of infill, fillers and pre-post-processing techniques) on mechanical behavior. In addition, our study took into account the behavior of composites in various environments (temperatures and hydrolytic degradation). Such an extensive and systematic presentation concerning a “difficult” polymer such as PLA (low Tg, biodegradation, high production cost, etc.) is the reference for detailed evaluation of other materials. The modifications and methodology contained in this work will not only serve for the investigation of model PLA system, but also for other petrochemical matrices that are less sensitive to the aquatic environment and elevated temperatures.

To sum up, the research presented in the paper shows how 3D printed polymer composites can be modeled by changing various components, i.e. type of filler, degree of filling or rate of crystallization (pre or post processing).

Declarations

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Conflicts of interest/Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and material

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations. Specific (or example) data may be sent on request by the corresponding author.

Code availability

Not applicable

Authors' contributions

All authors contributed to the study conception and design. Material preparation, investigation and data collection were performed by Karolina E. Mazur, Aleksandra Borucka, Paulina Kaczor, Szymon Gądek and Stanisław Kuciel. The first draft of the manuscript was written by Karolina E. Mazur and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

References

1. Wang J, Li H, Liu R et al (2018) Thermoelectric and mechanical properties of PLA/Bi0·5Sb1·5Te3 composite wires used for 3D printing. Compos Sci Technol 157:1–9. https://doi.org/10.1016/j.compscitech.2018.01.013
2. Sang L, Han S, Li Z et al (2019) Development of short basalt fiber reinforced polylactide composites and their feasible evaluation for 3D printing applications. Compos Part B Eng 164:629–639. https://doi.org/10.1016/j.compositesb.2019.01.085
3. Bekas DG, Hou Y, Liu Y, Panesar A (2019) 3D printing to enable multifunctionality in polymer-based composites: A review. Compos Part B Eng 179:107540. https://doi.org/10.1016/j.compositesb.2019.107540
4. Cisneros-López EO, Pal AK, Rodriguez AU et al (2020) Recycled poly(lactic acid)–based 3D printed sustainable biocomposites: a comparative study with injection molding. Mater Today Sustain In Press. https://doi.org/10.1016/j.mtsust.2019.100027
5. Carlier E, Marquette S, Peerboom C et al (2019) Investigation of the parameters used in fused deposition modeling of poly(lactic acid) to optimize 3D printing sessions. Int J Pharm 565:367–377. https://doi.org/10.1016/j.ijpharm.2019.05.008
6. Yao T, Deng Z, Zhang K, Li S (2019) A method to predict the ultimate tensile strength of 3D printing polylactic acid (PLA) materials with different printing orientations. Compos Part B Eng 163:393–402. https://doi.org/10.1016/j.compositesb.2019.01.025
7. Pyl L, Kalteremidou KA, Van Hemelrijck D (2018) Exploration of specimen geometry and tab configuration for tensile testing exploiting the potential of 3D printing freeform shape continuous carbon fibre-reinforced nylon matrix composites. Polym Test 71:318–328. https://doi.org/10.1016/j.polymertesting.2018.09.022
8. Yao T, Ye J, Deng Z et al (2020) Tensile failure strength and separation angle of FDM 3D printing PLA material: Experimental and theoretical analyses. Compos Part B Eng 188:107894. https://doi.org/10.1016/J.COMPOSITESB.2020.107894
9. Kuo CC, Liu LC, Teng WF et al (2016) Preparation of starch/acrylonitrile-butadiene-styrene copolymers (ABS) biomass alloys and their feasible evaluation for 3D printing applications. Compos Part B Eng 86:36–39. https://doi.org/10.1016/j.compositesb.2015.10.005
10. Velu R, Raspall F, Singamneni S (2019) 3D printing technologies and composite materials for structural applications. In: Green Composites for Automotive Applications. pp 171–196
11. Sui T, Salvati E, Zhang H et al (2019) Probing the complex thermo-mechanical properties of a 3D-printed polylactide-hydroxyapatite composite using in situ synchrotron X-ray scattering. J Adv Res 16:113–122. https://doi.org/10.1016/j.jare.2018.11.002
12. Quiles-Carrillo L, Montanes N, Garcia-Garcia D et al (2018) Effect of different compatibilizers on injection-molded green composite pieces based on polylactide filled with almond shell flour. Compos Part B Eng 147:76–85. https://doi.org/10.1016/j.compositesb.2018.04.017

13. Olewnik-Kruszkowska E, Burkowska-But A, Tarach I et al (2020) Biodegradation of polylactide-based composites with an addition of a compatibilizing agent in different environments. Int Biodeterior Biodegrad 147:104840. https://doi.org/10.1016/j.ibiod.2019.104840
14. Gil-Castell O, Badia JD, Ingles-Mascaros S et al (2018) Polylactide-based self-reinforced composites biodegradation: Individual and combined influence of temperature, water and compost. Polym Degrad Stab 158:40–51. https://doi.org/10.1016/j.polymdegradstab.2018.10.017
15. Fukushima K, Tabuani D, Dottori M et al (2011) Effect of temperature and nanoparticle type on hydrolytic degradation of poly(lactic acid) nanocomposites. Polym Degrad Stab 96:2120–2129. https://doi.org/10.1016/j.polymdegradstab.2011.09.018
16. Bismarck A, Aranberri-Askargorta I, Springer J et al (2002) Surface characterization of flax, hemp and cellulose fibers; Surface properties and the water uptake behavior. Polym Compos 23:872–894. https://doi.org/10.1002/pc.10485
17. Dorati R, Pisani S, Maffeis G et al (2018) Study on hydrophilicity and degradability of chitosan/polylactide-co-polycaprolactone nanofibre blend electrospun membrane. Carbohydr Polym 199:150–160. https://doi.org/10.1016/j.carbpol.2018.06.050
18. Hao LC, Sapuan SM, Hassan MR, Sheltami RM (2018) Natural fiber reinforced vinyl polymer composites. In: Natural Fibre Reinforced Vinyl Ester and Vinyl Polymer Composites. pp 27–70
19. Awal A, Rana M, Sain M (2015) Thermorheological and mechanical properties of cellulose reinforced PLA bio-composites. Mech Mater. https://doi.org/10.1016/j.mechmat.2014.09.009
20. Gil-Castell O, Badia JD, Kittikorn T et al (2014) Hydrothermal ageing of polylactide/sisal biocomposites. Studies of water absorption behaviour and Physico-Chemical performance. Polym Degrad Stab 108:212–222. https://doi.org/10.1016/j.polymdegradstab.2014.06.010
21. Kuciel S, Mazur K, Hebda M (2020) The Influence of Wood and Basalt Fibres on Mechanical, Thermal and Hydrothermal Properties of PLA Composites. J Polym Environ. https://doi.org/10.1007/s10924-020-01677-z
22. Lee KY, Bharadia P, Blaker JJ, Bismarck A (2012) Short sisal fibre reinforced bacterial cellulose polylactide nanocomposites using hairy sisal fibres as reinforcement. Compos Part A Appl Sci Manuf 43:2065–2074. https://doi.org/10.1016/j.compositesa.2012.06.013
23. Xiao X, Chevali VS, Song P et al (2019) Polylactide/hemp hurd biocomposites as sustainable 3D printing feedstock. Compos Sci Technol 184:107887. https://doi.org/10.1016/j.compscitech.2019.107887
24. Bai H, Huang C, Xiu H et al (2014) Enhancing mechanical performance of polylactide by tailoring crystal morphology and lamellae orientation with the aid of nucleating agent. Polymer 55:6924–6934. https://doi.org/10.1016/j.polymer.2014.10.059
25. Kuciel S, Romańska P (2018) Hybrid composites of polylactide with basalt and carbon fibers and their thermal treatment. Materials (Basel). https://doi.org/10.3390/ma12010095
26. Arao Y, Fujiura T, Itani S, Tanaka T (2015) Strength improvement in injection-molded jute-fiber-reinforced polylactide green-composites. Compos Part B Eng 68:200–206.

https://doi.org/10.1016/j.compositesb.2014.08.032
27. Andrzejewski J, Szostak M, Barczewski M, Łuczak P (2019) Cork-wood hybrid filler system for polypropylene and poly(lactic acid) based injection molded composites. Structure evaluation and mechanical performance. Compos Part B Eng 163:655–668. https://doi.org/10.1016/j.compositesb.2018.12.109
28. Monteiro SN, Lopes FPD, Barbosa AP et al (2011) Natural lignocellulosic fibers as engineering materials-An overview. Metall Mater Trans A Phys Metall Mater Sci 42:2963. https://doi.org/10.1007/s11661-011-0789-6
29. He ZL, Xu JK, Zhang L et al (2019) Dramatically enhanced tensile strength and impact toughness of polydicyclopentadiene composites by covalent bond formation between phenyl-functionalized silica and dicyclopentadiene. Compos Part B Eng 170:31–40. https://doi.org/10.1016/j.compositesb.2019.04.040
30. Oksman K, Skrifvars M, Selin JF (2003) Natural fibres as reinforcement in polylactic acid (PLA) composites. Compos Sci Technol 63:1317–1324. https://doi.org/10.1016/S0266-3538(03)00103-9
31. Valente M, Tirillò J, Quitadamo A, Santulli C (2017) Paper fiber filled polymer. Mechanical evaluation and interfaces modification. Compos Part B Eng 110:520–529. https://doi.org/10.1016/j.compositesb.2016.11.013
32. Fick A (1855) Ueber Diffusion. Ann Phys 94:59–86. https://doi.org/10.1002/andp.18551700105
33. Maslinda AB, Abdul Majid MS, Ridzuan MJM et al (2017) Effect of water absorption on the mechanical properties of hybrid interwoven cellulosic-cellulosic fibre reinforced epoxy composites. Compos Struct 167:227–237. https://doi.org/10.1016/j.compstruct.2017.02.023
34. Fernandes EM, Pires RA, Mano JF, Reis RL (2013) Bionanocomposites from lignocellulosic resources: Properties, applications and future trends for their use in the biomedical field. Prog Polym Sci 38:1415–1441. https://doi.org/10.1016/j.progpolymsci.2013.05.013
35. Pickett JE (2018) Chap. 8 – Weathering of Plastics

Figures

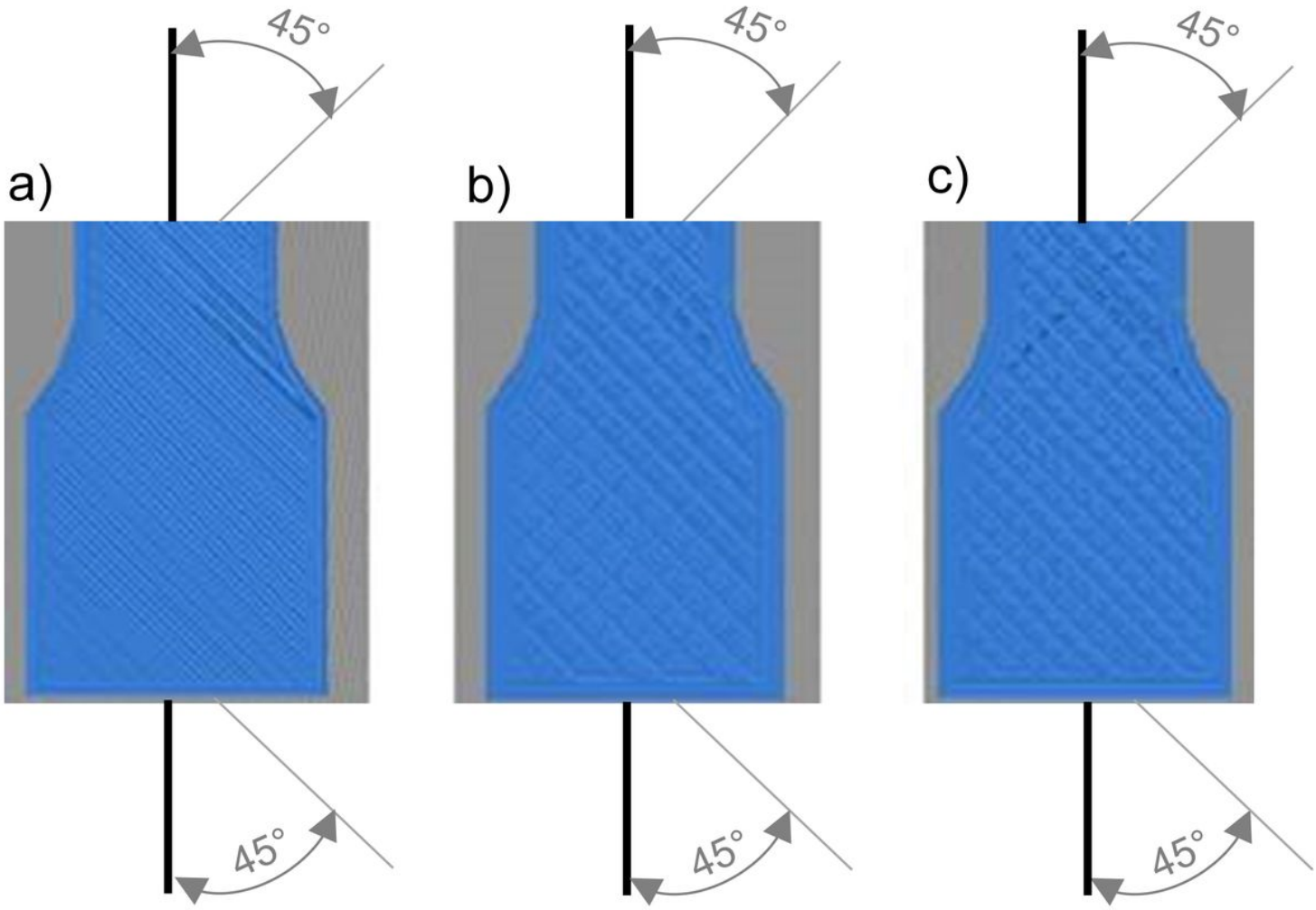

Figure 1

Appearance of designed samples with different filling levels: (a) 100%, (b) 80%, (c) 60%

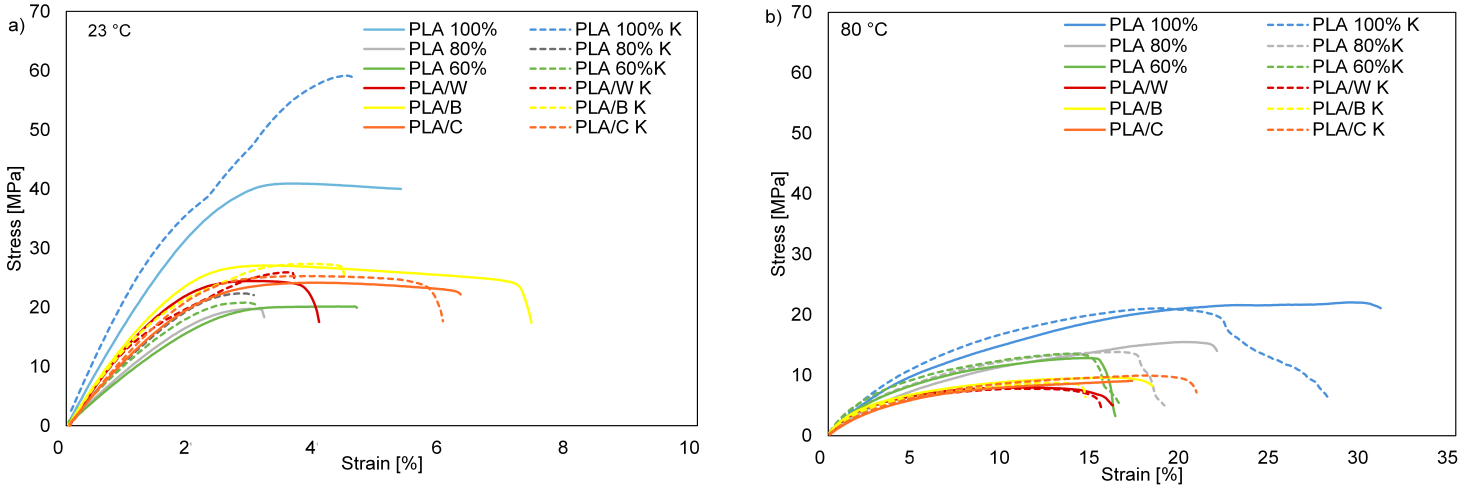

Figure 2

Tensile stress-strain curves of PLA composites with different infill and fillers a) at 23 °C and b) 80 °C (footnotes: K- after heat treatment)

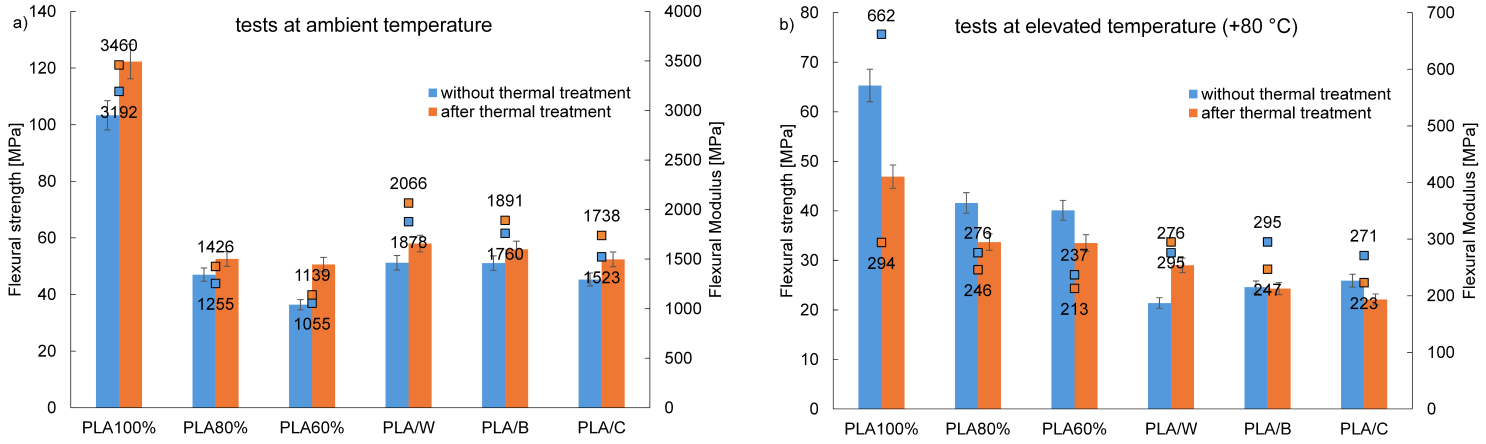

Figure 3

Flexural properties of PLA and its composites a) at 23 °C and b) 80 °C

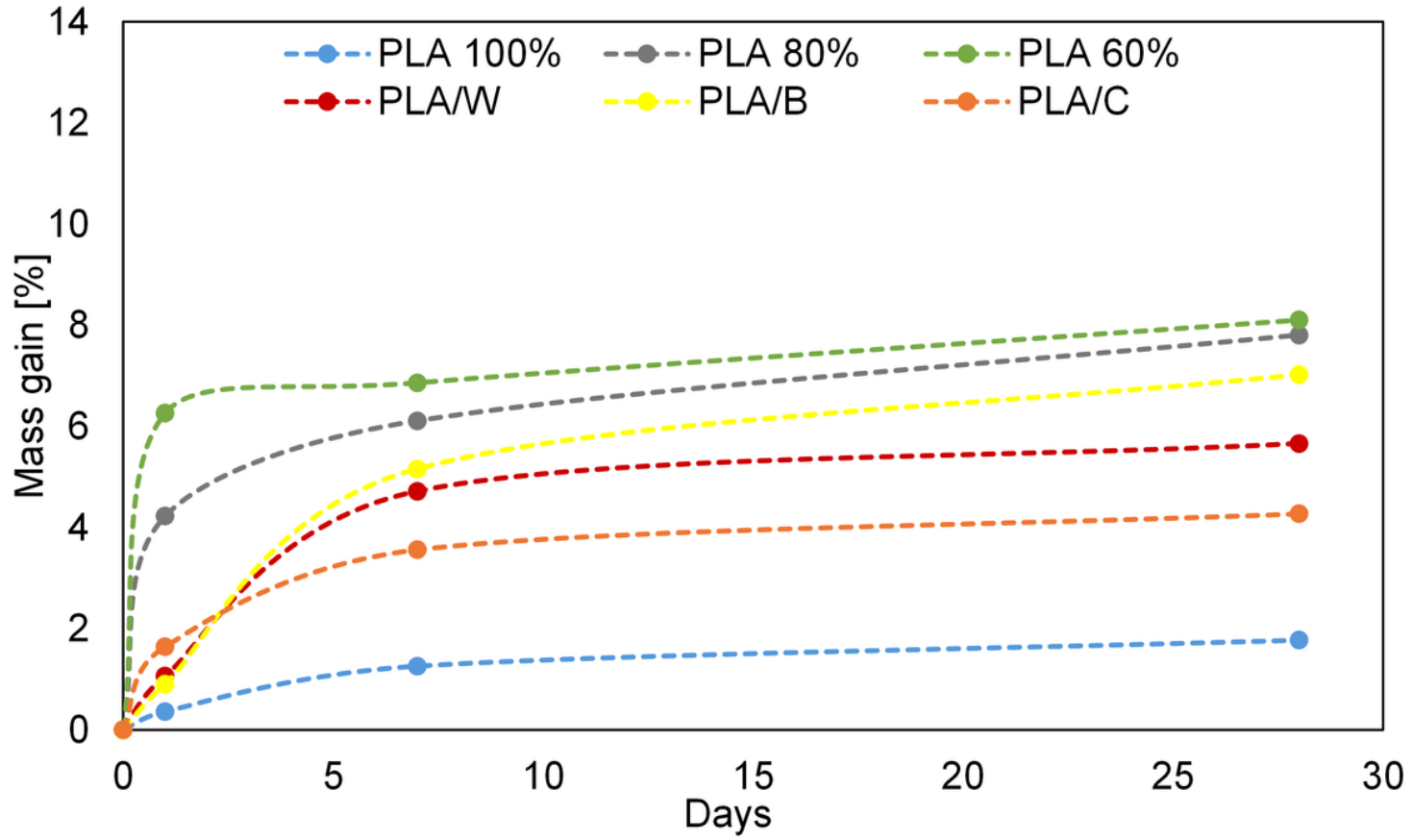

Figure 4

Water absorption of PLA composites with vary infills and fillers

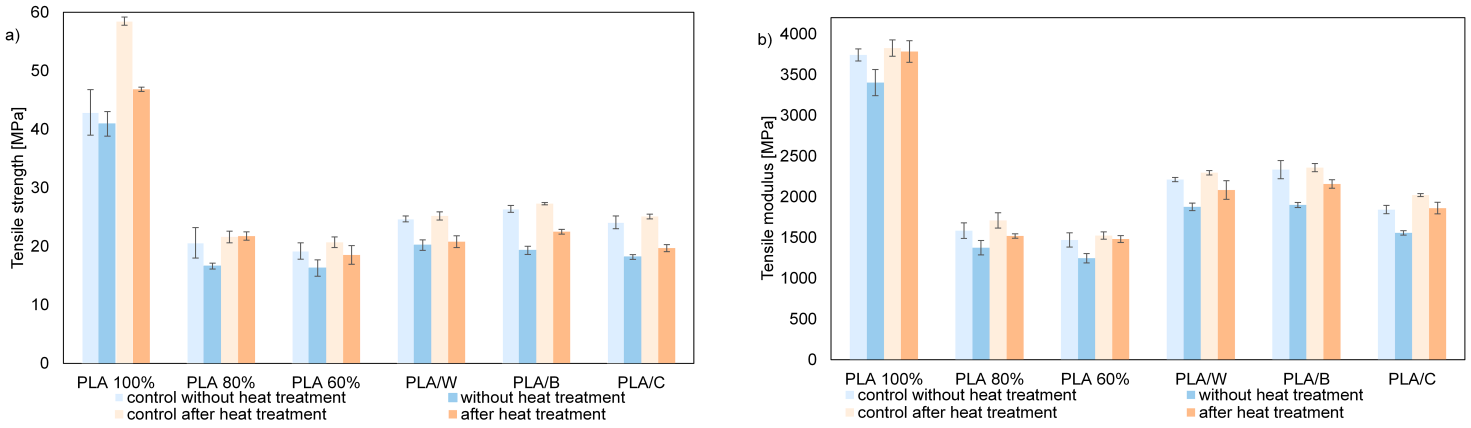

Figure 5

Change of mechanical properties of samples immediately after printing (control) and after 28 days of hydrolytic degradation: (a) tensile strength and (b) Young's Modulus

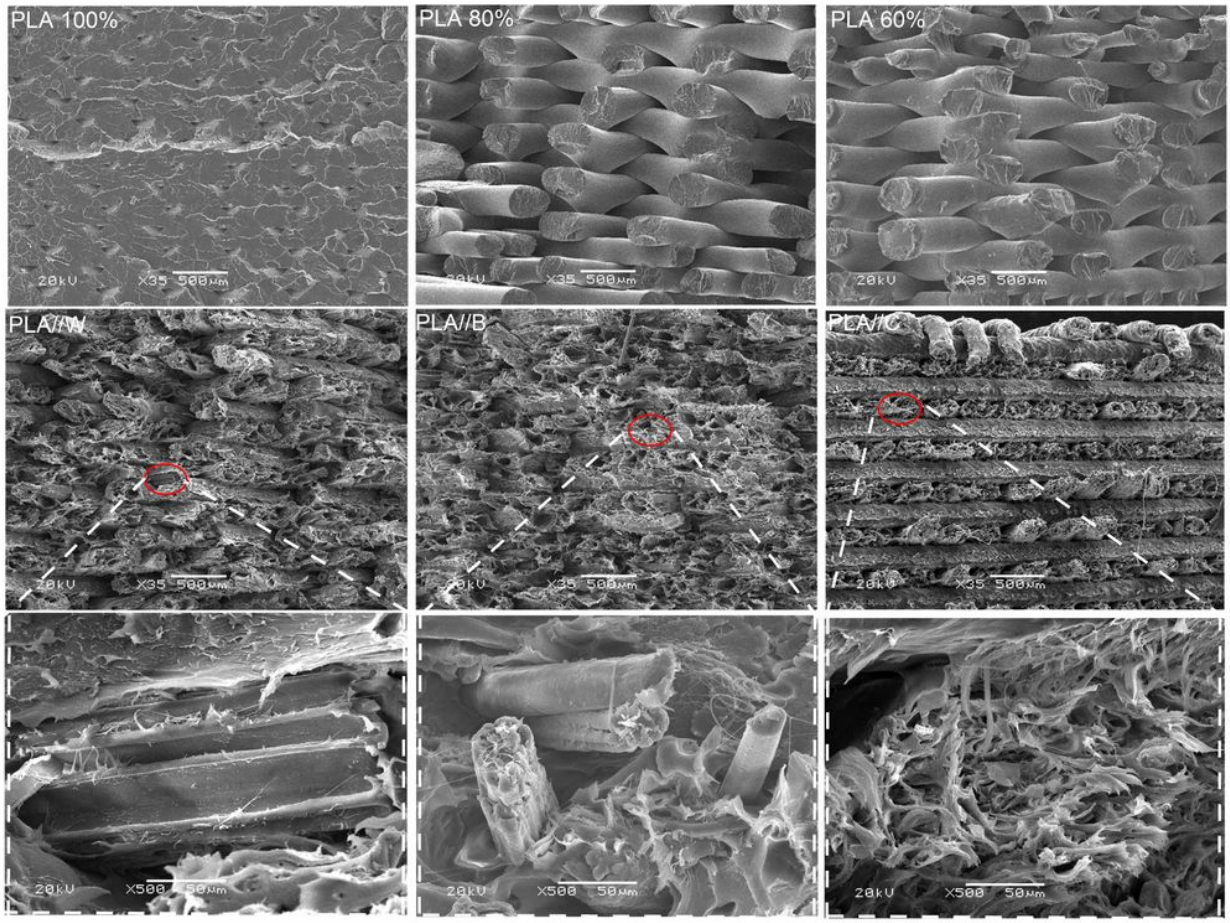

Figure 6

SEM images of fracture morphology for tested materials