Kaunas University of Technology
Faculty of Mathematics and Natural Sciences

Development of 3D printing materials for patient specific applications in radiotherapy

Master's Final Degree Project

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Kaunas, 2023

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Medical physics (6213GX001)

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Summary

In this study, new 3D printing materials using PLA and different concentrations (0.5%;1%;2%) of TiO_2 have been produced. TiO_2 concentration effect on the mechanical propertiesof the X-ray irradiated newly produced materials and their suitability for patient-specific applications has been investigated. Filaments have been produced using a 3D Devo filament extruder. Attenuation properties have been simulated using the XCOM database. Samples have been irradiated with 6 MeV energy photons with 2Gy and 70Gy. These values have been selected in order to see how the mechanical properties are affected after one treatment procedure and the whole treatment. Mechanical tests were performed using the ElectroPuls® E10000 Linear-Torsion machine. The results have shown that newly designed materials can solve current solutions issues and increase the needed mechanical parameters including the Yougn‘s module, Maximum load, and tensile stress. The results have shown that newly created filaments have the potential to change currently used materials for patient-specific applications.

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Santrauka

Šio tyrimo metu naujos 3D spausdinimui skirtos medžiagos sudarytos iš PLA ir skirtingų koncentracijų (0.5%;1%;2%) TiO_2 buvo gaminamos. Taip pat buvo tiriamas TiO_2 koncentracijos poveikis naujai pagamintos medžiagos mechaninėms savybėms. Kartu buvo ištirta kaip naujai sukurtų medžiagų savybes paveikia spinduliuotė bei galimybės panaudoti šias medžiagas pacientams personalizuotose procedūrose. Medžiagos buvo kuriamos naudojantis 3D Devo filament extruder įranga. Darbo metu buvo atliekama atenuacijos savybių simuliacija naudojantis XCOM duomenų baze. Bandiniai buvo apšvitinti 6MeV energijos fotonais 2Gy ir 70Gy dozėmis. Būtent tokios dozės buvo pasirinktos siekiant įvertinti kaip kinta naujų medžiagų mechaninės savybės po vienos radioterapijos procedūros ir po viso procedūrų ciklo. Mechaninių savybių testavimas buvo atliekamas naudojantis ElectroPuls® E10000 testavimo įranga. Rezultatai parodė jog naujos medžiagos gali išspręsti problemas kylančias su dabartiniais sprendimais. Buvo pastebėtas mechaninių savybių kaip Jungo modulis, maksimali apkrova ir tempimo įtempis pagerėjimas. Rezultatai įrodė jog pagamintos medžiagos turi potencialo pakeisti šiuo metu naudojamus sprendimus pacientams personalizuotuose radioterapijos procedūrose.

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Abbreviations:

PLA **-** Polylactic Acid

ABS - Acrylonitrile Butadiene Styrene

PC – Polycarbonate

PET - Polyethylene Terephthalate

HIPS - High Impact Polystyrene

PVA - Polyvinyl Alcohol

$CaCo_3$ – Calcium carbonate

TiO_2 – Titanium Oxide

Al_2O_3 – Aliuminium Oxide

MRI –Magnetic resonance imaging

CT – Computerized tomography

FDM - Fused deposition modelling

PCL - Polycaprolactone

Introduction

Radiotherapy is one of the most common cancer treatment techniques. Radiation not only affects the cancerous regions but also can create some harm for healthy tissues. To prevent the harmful effect of such a treatment patient-specific equipment including shielding equipment(masks, bolus, and others) and immobilizations devices(stereotactic frame, patient holders) are used [1]. Currently used materials have some limitations such as material‘s availability, complicated production, lack of customization options, high production costs and prolonged irradiation time, which may lead to degradation of the mechanical properties. Recent developments in 3D printing technology have shown promising results in the sollution of the current issues, however there is a lack of suitable 3D printing materials. Due to this reason, researchers are trying to produce new 3D printing materials by incorporating different fillers in the polymer matrix that would be suitable for the mentioned medical applications [2,3,4].

The aim of this work was to develop a new 3D printing materials for medical applications and evaluate their performance under high-energy photon exposure.

In order to achieve this aim following goals have been set:

1. To develop a procedure for the extrusion of Polylactic Acid + Titanium dioxide filaments and fabricate 3D printing filaments containing different filler concentrations.
2. To print out experimental samples from newly developed filaments and evaluate their mechanical properties.
3. Using the XCOM database to simulate X-ray attenuation properties of the new materials.
4. To investigate high and low-dose radiation impact on the newly developed materials.

1. Literature overview

1.1. Ionising radiation in the medicine

Ionizing radiation is used for different applications including radiation medicine, industry or agriculture [5,6,7]. Besides, its advantages, the application of the usage of ionizing radiation can cause unwanted effects such as radiation-induced health problems or reduced performance of components while talking about the equipment. Due to this reason unnecessary exposure should be limited. The most common and easy way is to use shielding [5,8].

When selecting suitable shielding materials different mechanisms of radiation interaction with objects should be taken into account. While talking about the high energy photons there are three main interactions with matter processes: Compton scattering, photoelectric absorption and pair production. The occurrence probability of each process depends on photon energy, and the shielding material [9,10]. Photon interaction with matted is determined by attenuation coefficient μ, which directly depends on the energy of the incident radiation and shielding material properties. The perfect shielding material should attenuate the radiation with the minimal possible impact on the material‘s physical, mechanical, and thermal properties [4].

High atomic number (Z) materials are the best choice for high-energy radiation shielding applications. Lead is one of the most suitable shielding materials, however, it is toxic, and it‘s utilization is very problematic. Another lead limitation is the difficult manufacturing process and its limitations in terms of shape and size. All these disadvantages are indicating the necessity of finding a suitable substitute for lead as the shielding material [11,12].

It is supposed that the substitute for lead besides its shielding properties should be safe, lightweight, durable, possesses good chemical and mechanical stability, and be easily customizable [4]. In the past decades polymer composites including high atomic number fillers were deeply investigated as the potential shielding materials [13]. However, the majority of the investigated materials were manufactured using traditional casting and molding methods which had numerous limitations such as speed of the manufacturing process, final cost of the product and high amount of the remaining waste [14].

In medical field patient specific applications such as immobilization devices[1], phantoms[15,16] boluses [17] and shielding equipment are extremely important[3,12]. However, these applications are also suffering from limited customization according to the patient‘s needs and long and expensive manufacturing processes. The mechanical and radiation performance of currently used materials also needs further improvement [3,18].

Radiotherapy is one of the cancer treatment procedures. Since this method explores the treatment of cancerous tissues and tumors with the prescribed dose, precision and accuracy of the dose delivery are of great importance [19,20,21]. According to the international commission of Radiation, 95% of all the prescribed doses should be delivered to the CTV (clinical target volume)[18]. To ensure the exact dose is delivered at the required tissue depth and area additional safety equipment is being used. Such equipment is made of materials whose radiation attenuation properties are close to human tissue attenuation [3,22,23]. However, it should be noted that every individual has different body and organ structures, which means that the procedures and treatment plans for each person must be individualized. Due to this reason, the equipment used for the procedures must be customized. Phantoms, Bolus, and Immobilization devices are the most commons examples of equipment where 3D printing technologies advantages can be used these days [3,24].

Bolus. The surface dose (skin dose) is much lower than the maximum radiation dose, this phenomenon occurs because of the build-up effects which are happening between D_{max} and surfaces regions[18]. In cases where the treatments are performed for superficial tumors, this effect causes issues, since is supposed that D_{max} is delivered at the skin surface. To prevent possible issues and optimize the amount of delivered dose boluses are used [25].

The main function of bolus is to increase the maximum dose on the skin surface. It is achieved by altering the received dose deph on the skin. The application of boluses contributes to the adjustment of the D_{max} for superficial tumors [26]. To provide their function boluses should be made from materials that have similar radiological properties as human tissue. Due to this reason, a couple of materials to produce boluses are used: water[27], different types of wax[28,29], thermoplastic[30] and others.

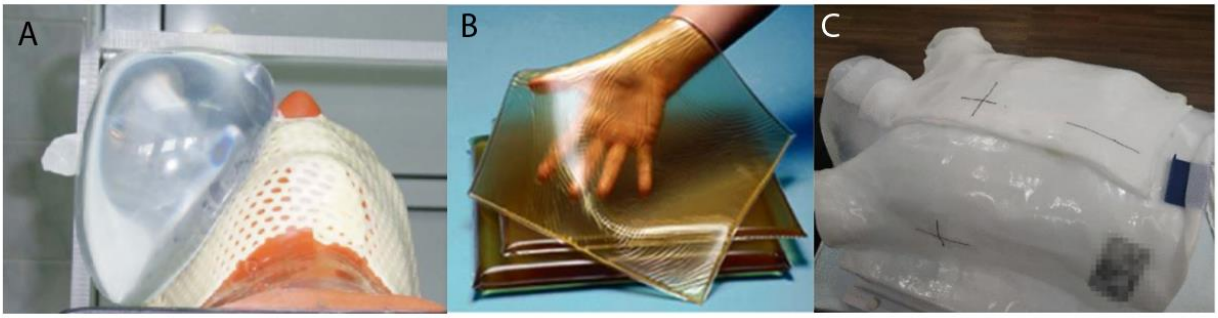

Fig.1 Different type of boluses. A – Water bolus [31] B – Superflab [25] C – Thermoplastic bolus [30]

All of these materials have their own advantages and disadvantages. Water-type boluses are easy to produce and maintain. However, they are not practical and convenient to use. Besides, it is hard to customize them according to every patient [18]. Plate boluses for instance have limitations in accuracy, precision and maintenance during the procedure [32]. 3D printing and its recent developments have shown the potential to solve current issues with the new materials and personalize the usage of the boluses.

Immobilization devices. Radiotherapy despite positive treatment results for the cancer regions can have a negative side impact on healthy tissues. The dose must be localized in the tumor site. Due to this reason during the treatment, it is a must to ensure that patients are moving as little as possible. To minimize the movement immobilization devices are being used. They can be separated into two main categories: Invasive and non-invasive[33].

Invasive fixation requires surgical intervention and fitting. For example, a stereotactic frame is considered to be invasive fixation equipment since it is being fixated on the person while putting the holder inside the person‘s body [34]. The invasive fixations are a method that provides discomfort for the patients, requires additional human resources to be used, and increases the chance of a possible infection [33].

Non-invasive fixation is the most preferred option since it is more convenient for the patient and does not require additional actions such as small surgeries. While considering the neck and head regions previously discussed bolus is an example of a non-invasive solution. However, the bolus solution has its issues. Firstly accuracy highly depends on the operator‘s experience, secondly, a person‘s weight loss due to the treatment can make it difficult to prevent movement in the same bolus. Besides, the process of making the boluses are time-consuming and it can be claustrophobic for the patients[28,35]. Another uncertainty of this solution is the accuracy, some researchers showed extremely good accuracy up to 1mm while others argue that such accuracy is not possible[33].

Phantoms. Different types of phantoms are used in the standard dosimetry procedures before radiotherapy sessions. The measurements are the must procedure to ensure that the treatment plan is suitable and the dose would distribute on the tumor site as theoretically expected. Standard practice is to use standard shape phantoms where the dose fluence is measured. Afterward, the difficult reconstruction mechanisms are used to recalculate the data from the phantom (as it was on a patient) as it would be *In Vivo (Inside the patient's body)*. To make the whole process easy and simple s scientists have started to use patient-specific phantoms which have the same geometry (including pathologies) as the patient [36,37]. Currently, the technology faces challenges such as the limitation of materials that have similar mechanical and radiological properties(attenuation coefficient) as real human tissue. Another challenge is the possibility to have the fast and cost-efficient production of patient-specific phantoms with the accurate and patient-like geometry. [2,36,37].

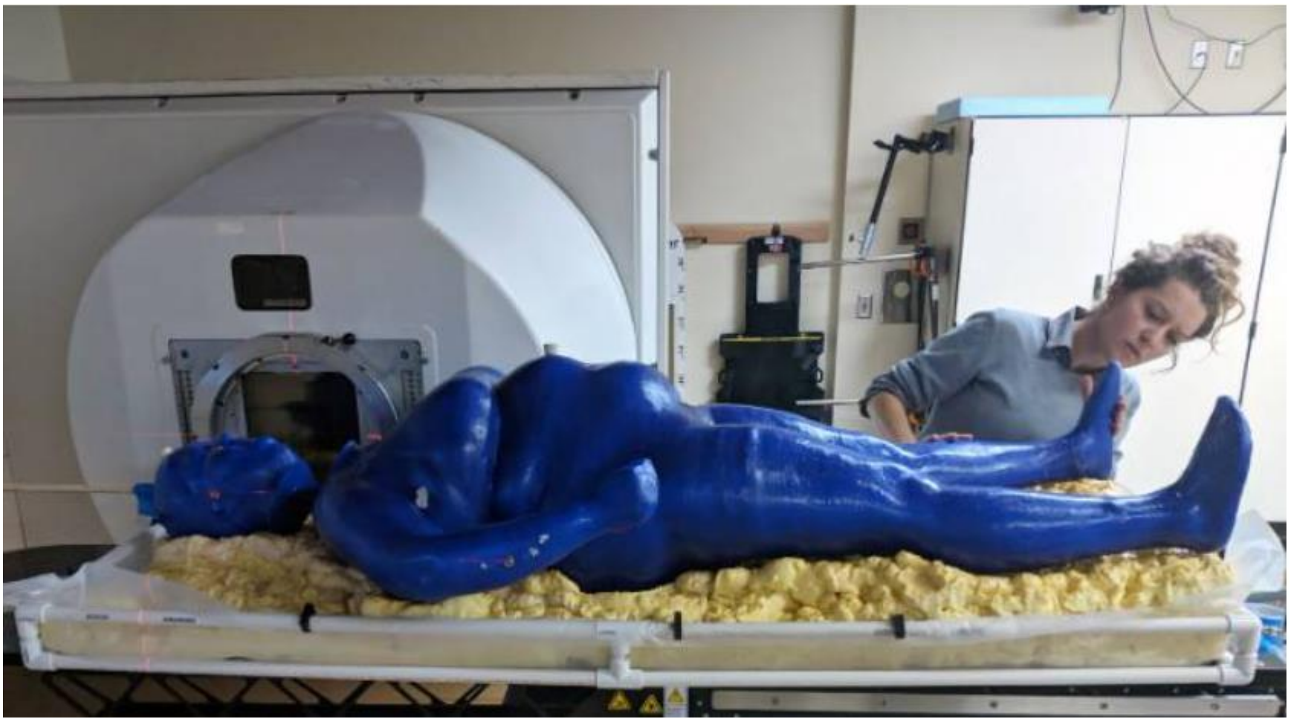

Fig 2 . 3D printed whole patient body phantom in order to evaluate radiotherapy processes [38].

1.2. Application of 3D printing materials in radiation medicine

The recent developments of 3D printing have increased the possibility to create a higher variety of light and easily customized materials that can potentially substitute the lead for shielding and help to solve current challenges for patient-specific applications such as immobilization or phantoms for dosimetry [39,40]. By using different imaging techniques it is already possible to print completely accurate parts of the patient's body according to the images reconstructed from MRI or CT scans. Such custom equipment can help to achieve the highest precision for fixation, shielding, or dosimetric applications [1,15,41].

FDM(Fuse deposition modeling) 3D printing method has become revolutionary technology in this field since of its cheap and quick production, wide object customization options, and easy usage. Besides, the materials used for FDM printing are filaments which consist of polymers with additional filler incorporated into its matrix. The filaments have relatively easy production which unlocks additional options to design new materials with improved properties and meet the needs and requirements of medical applications [42,43].

1.2.1. 3D Printing materials

3D Filaments are thermoplastics that are mostly made from polymers that can melt rather than burn in relatively low temperatures. The Filaments have the ability to be molted and solidify when cooling [44].According to the need, different polymers can be used to produce the filament. However, the polymers must be able to change their form from solid to pliable at certain temperatures. Other concerns while selecting suitable polymers, are their mechanical, and thermal properties. Also, the availability of the material and the cost need to be taken into account [45].

In the 3D printing market, Polylactic Acid (PLA); Acrylonitrile Butadiene Styrene(ABS); Nylon; Polycarbonate (PC); Polyethylene Terephthalate (PET); High Impact Polystyrene (HIPS); Polyvinyl Alcohol (PVA) are the most popular and widely researched polymers [45,46].

PLA (Polylactic Acid). The PLA was first synthesized in 1932 by heating the lactic acid under a vacuum and removing condensated water. At that time it was impossible to produce high molecular weight PLA. However these days PLA can be synthesized using different methods. PLA production has advantages such as biocompatibility, processibility, energy saving, and environmentally safe [40].

The properties of the PLA highly depend on its processing temperatures; annealing time and molecular weight. These parameters have a direct impact on the PLA crystallinity which are the main factor to impact the PLA properties such as hardness, tensile strength, stiffness, melting point, and glass transition temperature. PLA density and mechanical properties are highly dependent on the glass transition temperature [47].

It is worth mentioning that PLA is a soluble polymer. The solvents of the PLA are dioxane, acetonitrile, and chloroform. There are also solvents that PLA is partially soluble such as acetone. However, if such a solvent is heated to the boiling temperature the polymer can solve in it[48].

The PLA granules have a slightly yellowish color and have a relatively smooth surface. While talking about PLA advantages it exhibits very good barrier properties, which shows how the polymer permits gas. The PLA has a tensile modulus of around 3GPa; tensile strength of around 50MPa and an elongation break at 4%. In the market, PLA glass transition temperature stands at 50 to 80 degrees, while melting temperatures are around 170-180 degrees[47,49].

Table 1. Main properties of PLA filament[40,43,49]

Tensile strengh	49.5MPa
Flexular strengh	103MPa
Density	1.15 g/cm^3
Extrusion temperature	145-160 C◦
Glass transition temperature	60 C◦

The mechanical properties, biocompatibility, and easy production combined with the low cost of the material and easy accessibility make PLA the most commonly used polymer in various applications including medicine, automotive, and engineering [49].

While talking about the radiological properties PLA has relatively similar attenuation coefficients as ABS [50].

Table 2. Radiological properties of PLA[50]

X-ray generator‘s voltage	Linear X-ray attenuation coefficient
50kV	0.029mm^{-1}
70kV	0.024mm^{-1}
100 kV	0.021mm^{-1}

ABS (Acrylonitrile butadiene styrene). This thermoplastic mainly consists of three monomers: Acrylonitrile, Butadiene, and Styrene. Such a combination of different monomers results in a good performance in thermal resistance, lightweight; reflectivity, and mechanical strength. It is worth mentioning that the material is easy to shape [51].

The most common ABS production technique is to use polymerization through the emulsion. During this process, the mixture of the products is mixed and polymerized using special catalyzers which result in the formation of the ABS thermoplastic [52]. There are other ways to synthesize ABS however Emulsion polymerization is the most popular method.

ABS granules are yellowish in color and can be produced in various sizes and grades depending on the composition and amounts of Acrylonitrile, Butadiene, and Styrene. These thermoplastics filaments usually have such properties [53]:

Table 3. Main properties of ABS filament[51,53]

Tensile strengh	43MPa
Flexular strengh	66MPa
Density	1.04 g/cm^3
Extrusion temperature	220-260 C◦
Glass transition temperature	105 C◦

While talking about the radiological properties of the ABS different research has been done in the past 5 years. Different measurement techniques and methods have been applied to the research. However, the results are similar and the attenuation coefficient for ABS is as follows [54,55]:

Table 4. Radiological properties of ABS[54,55]

X-ray generator's voltage	Linear X-ray attenuation cofficient
50kV	0.020mm^{-1}
70kV	0.018mm^{-1}
100 kV	0.016mm^{-1}

PET (Polyethylene terephthalate). Another common material is polyethylene terephthalate (PET). PET is available in amorphous and semi–crystalline forms. This material is produced by a transesterification reaction between Ethylene glycol and dimethyl terephthalate. PET thermoplastic has good chemical stability and good mechanical strength. Besides, the material is easy to be processed and relatively cheap due to this reason it is very common in the industry [56]. PET in different forms is very often found in our daily life since it is the main material for the packing industry and plastic bottles [57]. Another PET advantage is its recycling ability. Plastic bottles waste can be reused for new filament production. However, the mechanical properties are worse as compared to the newly produced filament [58].

Table 5. Main properties of PET filament[59]

Tensile strengh	42.5-63.6MPa
Flexular strengh	82MPa
Density	1.38 g/cm^3
Extrusion temperature	265-300 C◦
Glass transition temperature	70 C◦

The radiological properties of PET material are as follows;

Table 6. Radiological properties of PET [8]

X-ray generator's voltage	Linear X-ray attenuation coefficient
59.9kev	0.19 mm^{-1}
80kev	0.17 mm^{-1}
136kev	0.14 mm^{-1}

1.2.2. Additives to 3D printing materials

3D printing is still new and fast-evolving technology. Increased technical possibilities and new challenges for material-specific applications have have shown a new demand for 3D printing materials. Depending on the 3D printing technology different forms of polymers and polymer mixtures are used. One of the easiest ways to improve and enhanced printing material properties is to use different additives [60].

Polymer fillers depending on their origin are separated into two main categories: Synthetic fillers and natural fillers [61].

3D printing materials may be natural minerals or synthetic chemical compounds. In order to use them as fillers, materials must be specifically treated. Examples of natural fillers are $CaCo_3$; Starch; Wood flour [62].

Synthetic fillers are formed during chemical synthesis or chemical processing of the raw material. Examples of such fillers are TiO_2; Al_2O_3[63].

According to the composition, fillers are also divided into organic and inorganic. Inorganic fillers have the subgroup of oxide, hydroxide, salts, metals, and silicates. Organic ones are represented by natural materials[61].

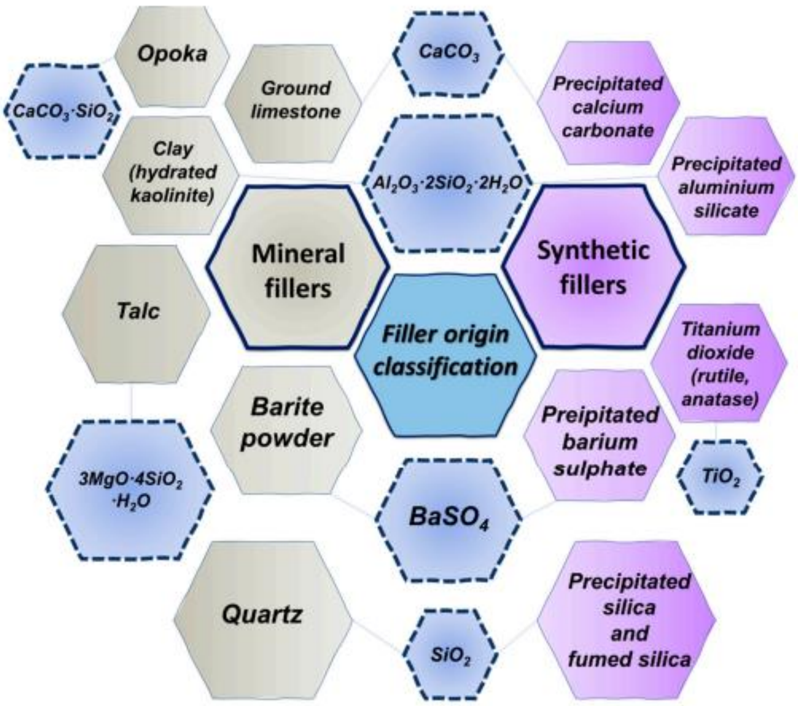

Fig 3. Fillers clasification [61]

Nowadays scientist have a particularly huge interest in natural additives such as Cellulose[64]; Mono Wall Carbon Nanotubes (MWCN) [65] ; $CaSO_4$ [66]; MgO [67] ; $CaCo_3$[68] ; $BaSO_4$ [68]; TiO_2[69].

TiO_2 (Titanium Dioxide) is one of the most common fillers used in the polymer matrix. This filler has a high surface area per particle size and highly effective pigment. It was also investigated that TiO_2 particles have a free hydroxyl group which increases aggregation tendency. Also, it improves the dispersion of the filler in the polymer composites [70].

As the material itself, TiO_2 is also known as Titania and is the transition metal oxide type. This material is naturally occurring and can be found in mineral forms such as Rutile, Anatase, and Brookite [71]. TiO_2 is used as a white color pigment for different paints, printing ink, electronics components, and filaments. TiO_2 is widely used because its properties can vary depending on the need. It is possible because properties are highly dependent on the particle size and form. Another feature that makes TiO_2 interesting for the scientist is that its properties also depends on the polymer matrix it is in [71].

This filler is non-toxic, cheap , and easily accessible. Besides, since it has the ability to change its properties according to the material matrix this filler is seen as an option to be used in the new materials designed to solve current challenges in the medical application of ionizing radiation [71,72].

Composites of Polylactic acid (PLA) and Titanium oxide (TiO_2) has antimicrobial activity, high chemical stability, and suitable mechanical properties [73]. The researchers have shown that incorporating TiO_2 particles in the polymers has enchanted the polymer properties significantly [74].

$CaCO_3$ (Calcium Carbonate). Calcium carbonate or simply regular chalk. Throughout the years $CaCo_3$ is one of the most commonly used fillers in production worldwide and the plastic industry is not an exception [75].

$CaCO_3$ is an odorless, white powder (can be a colorless crystal) with a density of 2.71g/cm^3. This material has a melting temperature of 825C$^\circ$, also $CaCO_3$ is practically not soluble in water [76].

Calcium carbonate is used as a filler so widely for a couple of reasons. Firstly, it is very easily acquired and has a lot of possible source throughout the globe which makes the material cheap and have a sustainable supply chain. Another huge advantage is that $CaCO_3$ helps to increase the hardness, durability, adhesion, and impact resistance of the end product. Besides, most of the time adding the $CaCO_3$ improves the end surfaces of the material[77].

While talking about radiological properties the $CaCo_3$ is investigated to be used as a high dose dosimeter since while it is affected by the irradiation it forms free radicals which can be detected using Electron paramagnetic resonance (EPR) method [78]. It is also worth mentioning that photon mass attenuation coefficient of $CaCo_3$ is 0.0772 ± 0.0022 while photon energy is 661.6 keV [79].

While considering the possible additives and polymer compounds some parameters need to be carefully evaluated.

The surface energy of the interaction between polymer and additive. High surface energies can result in the dispersion which leads to inferior mechanical properties. The best way is when the additive interacts with the polymer matrix. While interaction happens in such a manner the surface energy is minimum[80].

Aggregation of the fillers. Aggregation is the process when smaller particles combine into bigger particles with higher density [81]. The aggregation is based on the particles forces of the attraction including hydrogen bonding; acid/base interactions and similar. Sometimes this process can be used as an advantage during the production of polymers. However, in many cases, it is disadvantageous because big-size particles are not able to interact with the matrix properly and can deteriorate the material properties [80].

Dispersability of the fillers. Dispersability is a process during which the additive distributes in the solution. Fillers such as TiO_2 have shown poor dispersibility properties in the polymer matrix. Due to this reason, scientists have researched different methods to improve this feature [69,82].

To minimize these issues different processes have been developed on how additives can be incorporated into the polymer matrix. Solution mixing; melt mixing in-situ polymerization, are the most common ones[73].

Solution mixing. During such a procedure filler are being dissolved in the solvent. Separately the polymer solution is being prepared. After the whole solutions are ready they are mixed using an ultrasound batch [68,83].

In situ polymerization. his is the method when adding the nanofiller to the polymer triggers the polymerization of the solution. During the polymerization process, a whole new polymeric junction occurs between the filler and the monomer which results in the creation of a new composite [84].

Melt mixing. These methods are based on the mixing of the polymer solution while it is heated during the process. Firstly, the needed temperature (depending on the used polymer) is achieved. When the polymer starts melting the shreds are rotated to disperse the added filler and the solution itself. During this process, the composite components and fillers are incorporated at the same time[83].

It is also worth mentioning that additives such as TiO_2 need additional surface treatment before incorporation in order to achieve homogenous dispersion in the matrix [73].

1.3. Manufacturing of filaments containing additives

As mentioned previously 3D filaments consist of two main components thermoplastic(Polymer) and different fillers. Thermoplastic is most often present in small grain-like pieces called pellets. On the other hand fillers, most of the time is in the form of powders or similar pellets.

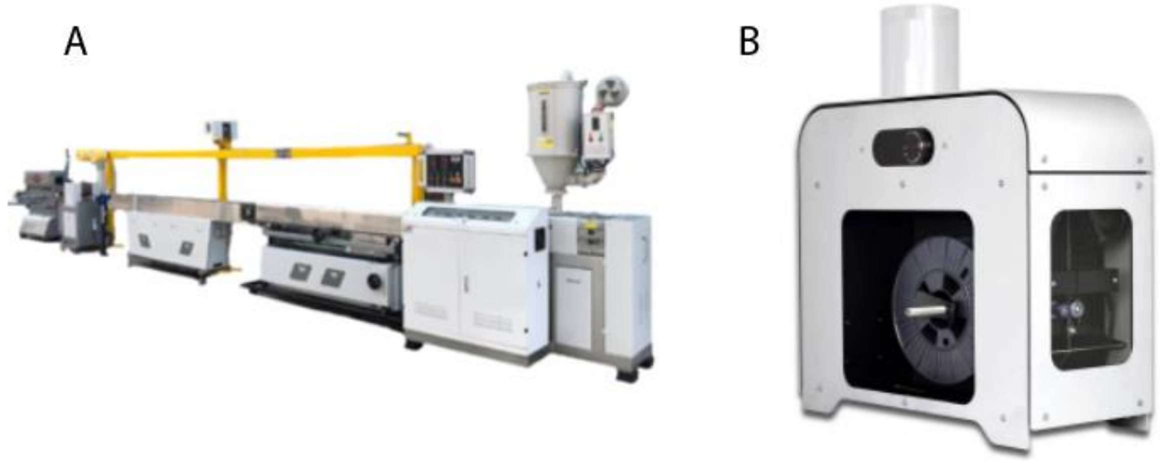

Fig 4. Different types of extruders. A – Commercial type; B- Desktop

All of the extruders have similar structures. However, according to the model, they can be adjusted and designed differently. These main components are: Turning screws, Hopper, Heaters, Thickness measurement systems, spooling systems, fans[85,86].

The whole process begins by inserting raw materials polymer and filler into Hopper (Figure 5) where they are melted using high temperatures at different zones. Different temperatures in all of the zones are applied.The material is pushed by the screw forward applying pressure. Then the materials are molded and cooled by the fans, the molded materials go to the measuring system where the needed thickness is achieved by regulating the screw speed accordingly [85,87].

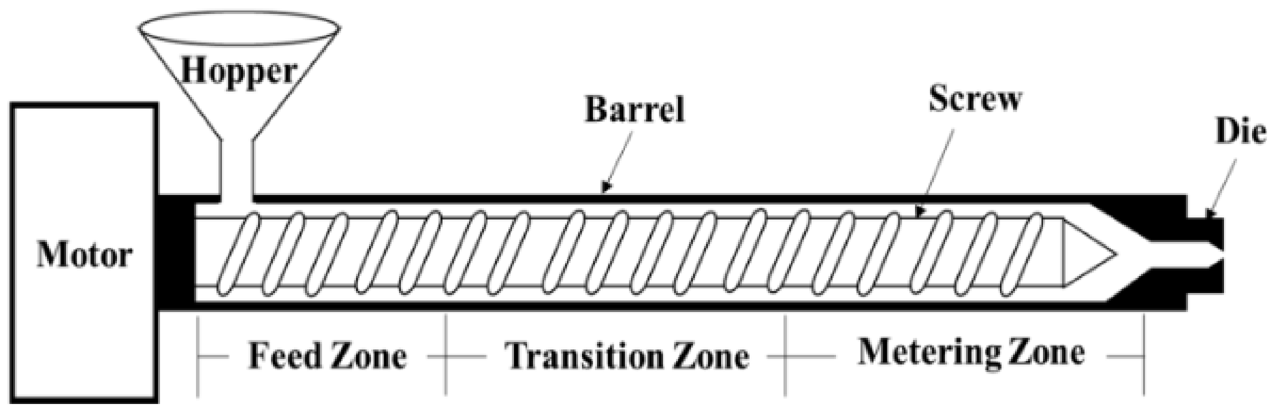

Fig 5. General scheme of the extruder [86]

There are different options how raw material can be processed with filler before the extrusion process. Polymers can be mixed together with the powder form fillers by making the powder cover the thermoplastic pellets. Another option is to melt the polymer using an additional solver and temperature to incorporate the fillers inside the matrix of the polymer. For such as mixing mechanical stirring or ultrasound mixing are being used according to the filler type[76,88,89]. Some authors have been investigating the influence of mechanical properties while drying the polymer pellets in a special dryer before the extrusion process. However, such a method is relatively long and has not shown extraordinary improvement in the mechanical performance of the thermoplastics [90].

1.4. 3D printing

There are three main 3D printing technologies: SLA(Stereolithography); SLS(Selective laser sintering); FDM (Fused deposition modeling) [87]. All of these methods have advantages and disadvantages.

FDM. Such type printers are the most common 3D printers nowadays. This type of 3D printer is based on thermoplastic(filaments) melting properties. Melted filaments are extruded through the nozzle and adhere to the build plate. The nozzle move around the built plate in the positions described in the program code called G Code. G code holds information about the positions and thickness of each layer. In such a way layer by layer, the final object is produced [91,92,93].

Standard FDM printers have the same basic structure: Filament feeder and holder, nozzle, extruder, cooler, printing bed, and positioner [87,94].

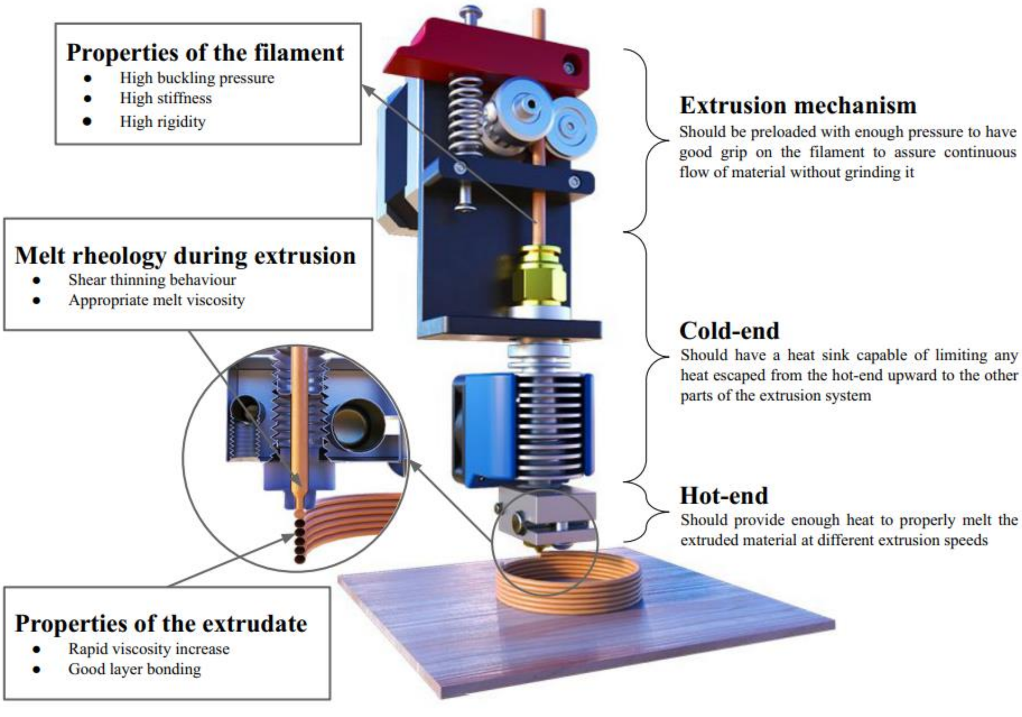

Fig 6. Scheme of regular FDM printer [94]

The FDM-type 3D printers have a lot of advantages over other types. First of all, FDM printers are desktop printers and they do not need a special working area. Also, they are easy to use and production speed is relatively fast. Besides, there are a lot of different filaments which can be easily used according to the needed specifications of the final object. The costs of the final product are also relatively small [93].

However, drawbacks of this type printers are the small accuracy of the small details of the object and relatively poor surface finish. Also, the number of objects produced in a single printing process is limited by the size of the build plate[87,93].

SLS. The selective laser sintering method is based on particle fusion into a 3D model using a high-power laser. Particles are fused into the 3D object using a laser layer by layer[95].

Heaters, a build chamber, a powder delivery system, a recoater, a laser (often a reasonably inexpensive CO_2/Diode laser), and an X-Y scanning mirror make up a standard SLS printer[96].

SLS printers are good solution for super difficult geometry objects and models produced with this technology have good mechanical properties. However, there are limited options of suitable materials for the SLS printers also the processes are expensive. Additional treatment after the production of the objects is also needed, the equipment is huge and needs a special working place. These disadvantages make this method only suitable for mass production such as automotive parts or implants[95,96,97].

SLA. Stereolithography 3D printing method is based on the polymer resin property to photopolymerize. During this process, the UV light initiates the formation of free radicals in the resin which forms polymer chains by connecting with monomers and each other[98,99]. Due to these chains formation material state changes from liquid to solid.

Standard SLA printer have structure as follows: UV or Laser source; Scanning galvanometers; moving build plate; Resin vat; Scanning mirrors[87,100].

SLA printers exhibit extremely good accuracy and precision for small details and have the best resolution from all of the 3D printer types. However, it also has limitations. Firstly, the amount of possible resins is limited and these materials are toxic. Also after the printing process, the object needs to be additionally treated with Polyvinyl alcohol and cured with a UV source. Another disadvantage of SLA is the price of resins. It is relatively high and the whole production process is relatively long. On the other hand, such a solution already has its market which is Dental models and action figures[98,100,101,102].

1.5. Properties of 3D printed materials

The 3D printing material creation is a very precise and sophisticated procedure. In order to investigate how different amounts of various additives contribute to the final material properties different tests are being done. The testing methodology is done not only at the RnD stage but also at the mass industry production[85,103,104].

The majority of the tests are focused on mechanical parameters such as elongation strength, tensile strength, Young‘s module and similar. The mechanical testing standards for plastics are ASTM D638 and ISO 527-2. The measurement methods covered by these standards focus on measuring Young‘s module, Yield Stress, and Elongation on the brake. The sample used for these standards is a dog bone shape with fixed dimensions and thickness in the standard. It is relatively easy to manufacture such a specimen with 3D printer [105].

Besides the mentioned standards ASTM D790 and ISO 178 are used in order to determine the flexure of the filament. These standards equalize the 3-point bending method which helps to evaluate the flexural module, flexural strength, and strain break [105,106].

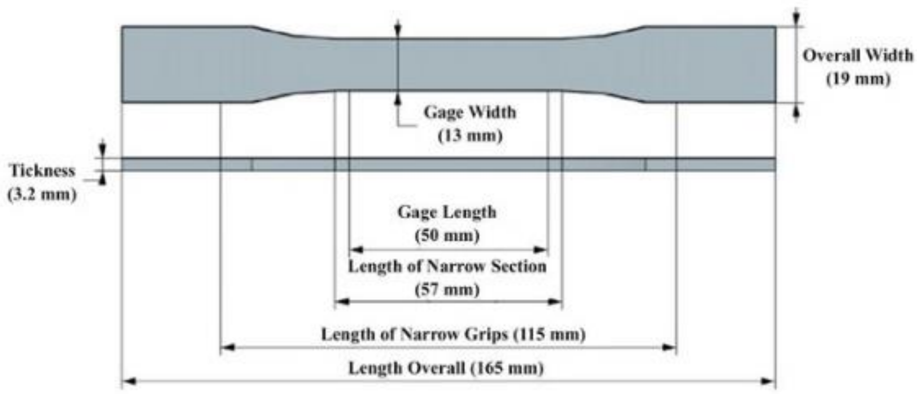

Fig 7. Mechanical testing sample [107]

Another important specification for filaments is water absorption. Sometimes because of the nature of some additives filament can have increased water absorption which is harmful and can reduce the lifetime of the printed component. In order to evaluate this parameter testing according to the standard ASTM D570 is done[108]. This test standard is based on the relatively simple measurement, the round form samples are placed in the desiccator to remove as much water as possible from them. After this procedure samples are weighted. Then they are put in distilled water and left to shrink for 24 hours. Afterward, the samples are weighted and the results are compared with the ones gathered before the procedure[109].

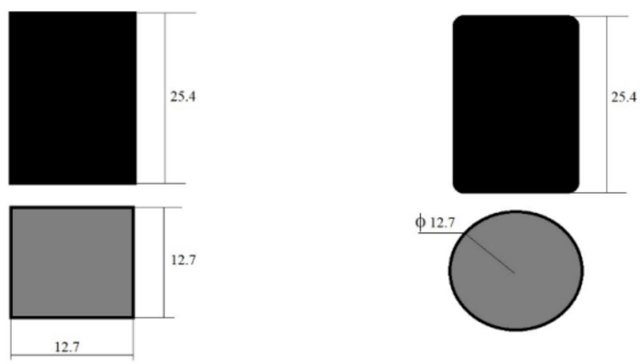

Fig 8. Possible sample forms for ASTM D570 test [110].

The last of the testing methods are the printing tests. Such a testing method helps to evaluate how different filaments result in the properties of the end print. There are different testing models for this purpose, however, they are testing the same parameters. Accuracy, overhang, details, bridging, extrusion, printing temperature. Of course, all of these parameters depend not only on the filament material but also on the settings of the 3D printer. Due to this reason, these calibration models are used to evaluate the compatibility of the printing parameters with the filaments and filament properties [100,111].

Fig 9. Different 3D printing test prints. A – Benchy; B- All in one; C – Cali Cat; D – Phil A. Ment

2. Experimental part

2.1. Fabrication of 3D printing filaments containing additives

Fabrication of 3D printed samples has been performed in the 3D printing laboratory at the Physics Department of Kaunas University of Technology.

Fabrication of the new PLA filaments with different concentrations of TiO_2 additives has performed. The main materials for the fabrication were: PLA granulates (3Devo) ; TiO_2 (Sigma Aldrich). Also for purging purposes, we have used the Devo Clean purge granules (3Devo).

Table 7. Produced filament composition

	PLA+TiO2 0%	PLA+TiO2 0.5%	PLA+TiO2 1%	PLA+TiO2 2%
PLA	100%	99.5%	99%	98%
TiO2	0%	0.5%	1%	2%

The filament has been produced using filament extruder 3D devo filament maker „Precision 450".

Before every filament fabrication, the purging process must have been performed in order to clean the remaining particles from previous extrusion processes. The purging procedure was performed in the following order:

1. The 3D devo filament maker was turned on and left until it is heated to the required temperature of 180C˚.
2. While the filament maker is warming up some settings were adjusted. The hopper sensor was turned off in order to let the filament maker run with an empty hopper.
3. The cooling fans are set to 0% and directed toward the exit.
4. The filament sensor must be covered by paper or cardboard to save it from being damaged or contaminated during the purging process.
5. When these preparation steps are completed the purging can be started.
6. Firstly the hopper needs to run completely empty until there are no leftovers from the previous material. Afterward, a small amount of purging material (around 40-60g) is added.
7. The purging material will go through the system and come off the extruded as in normal filament production. When the first portion is all used, add an additional amount of around 100-200g.
8. After around 15 minutes the purging material mix with leftover particles will be visible coming out of the extruder. It can be seen in the change in color and structure.
9. When the purging process is in motion changes in the RPM can be started. Change the RPM every minute from 2 to 15 RPM.
10. After doing step 9 for 10 minutes the purging material starts to come out clean (White color). This indicates that the filament extruder is clear and ready for the new process.

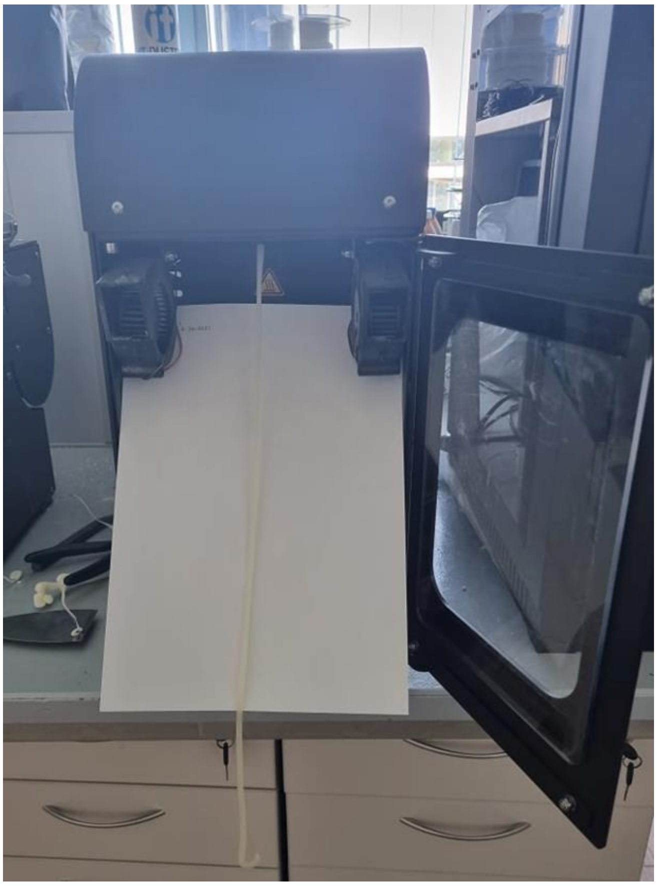

Fig 10. Purging process

When the purging process is done fabrication of the filament material can be started. During each fabrication, we produced 80g of each filament composition. This amount was selected because it takes time for the diameter to stabilize during the filament extrusion. The fabrication procedure was done as follows

1. The required amount according to the composition of the PLA granules and additives are weighted and added in the same laboratory vessel.
2. The vessel is closed by the sheet of paper and the whole mixture is shaken in order to granules become covered in the powder additives.
3. Once the granules are fully covered by the powder additives they are added to the 3D Devo filament maker. Filament makers are set on PLA preset properties: 1.75mm diameter; 4th zone temperature 170C˚; 3th zone temperature 185C˚; 2nd zone temperature 190C˚; 1st zone temperature 170C˚; 3.5 RPM screw rotating speed.
4. When the filament starts to be formed through the extruder it is taken mechanically and extended to go through the diameter measurement system.
5. After the diameter became stable the filament is extended to the spooling sector and the spooling process starts. Once the tension is enough the filament is left to be spooled automatically. The process goes on until there is enough granules in the hopper.

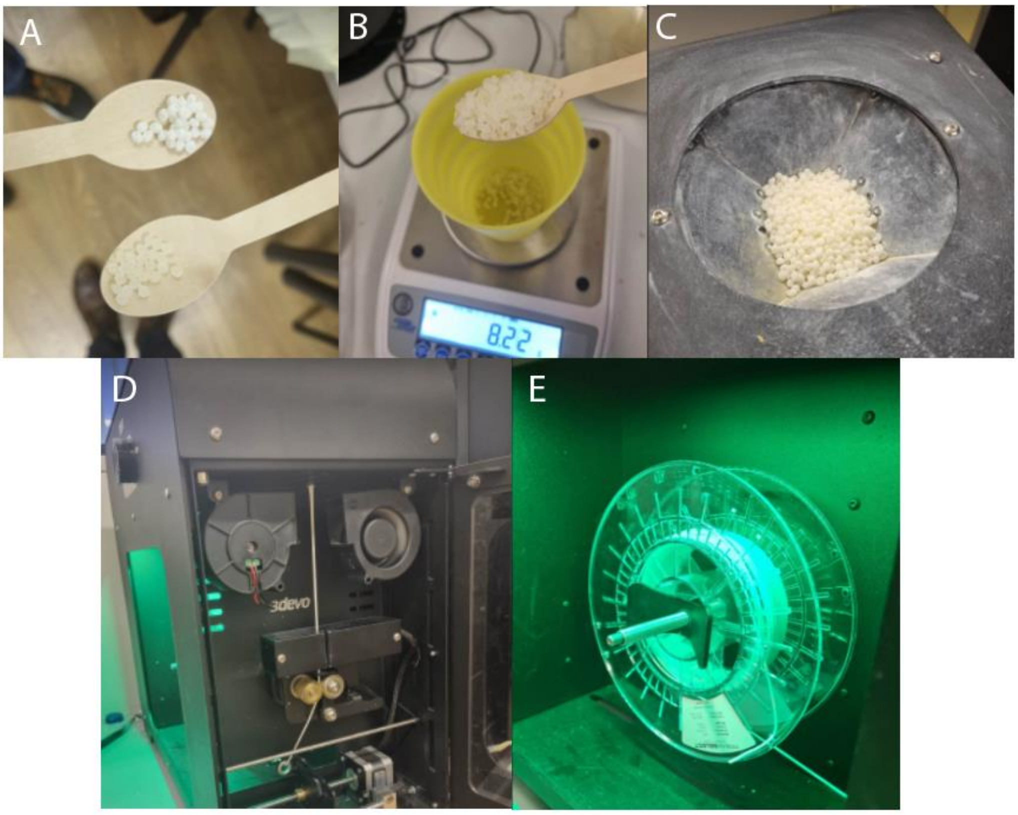

Fig 11. Fabrication steps. A-Difference between PLA and PLA +TiO_2; B-Weigting; C- Granules in the hopper; D-Extrusion procedure; E-Spooling procedure

When extrusion has finished the spool of newly created filament material is ready to be used.

One of this work tasks was to successfully produce new filaments with planned compositions (See Table 7). The fabrication of these new materials was successful.The resulting filaments have been smooth and relatively straight however there were some regions of the filament which had been thicker. These regions are called Blops and need to be removed mechanically since they are too thick to move into the 3D printer extruder. The tendency of these regions occurrence has been noticed when the tension of the extruder was not strong enough also for the higher concentration of the additives in the filaments. Besides it was noticed that the Blops amount was also higher when the filament extruder was not cleaned properly after the previous extrusion.

The example of the produced PLA filament containing TiO_2 is provided in Fig. 12.

Fig 12. Example of the produced filament with TiO_2

The next step of the work was to create 3D-printed samples for each of the newly created materials. We have selected to produce five pieces of ISO 527 standard samples and also the sample in the form of a cube for different tests. All of the printing samples were designed and sliced using Z-Suite software.

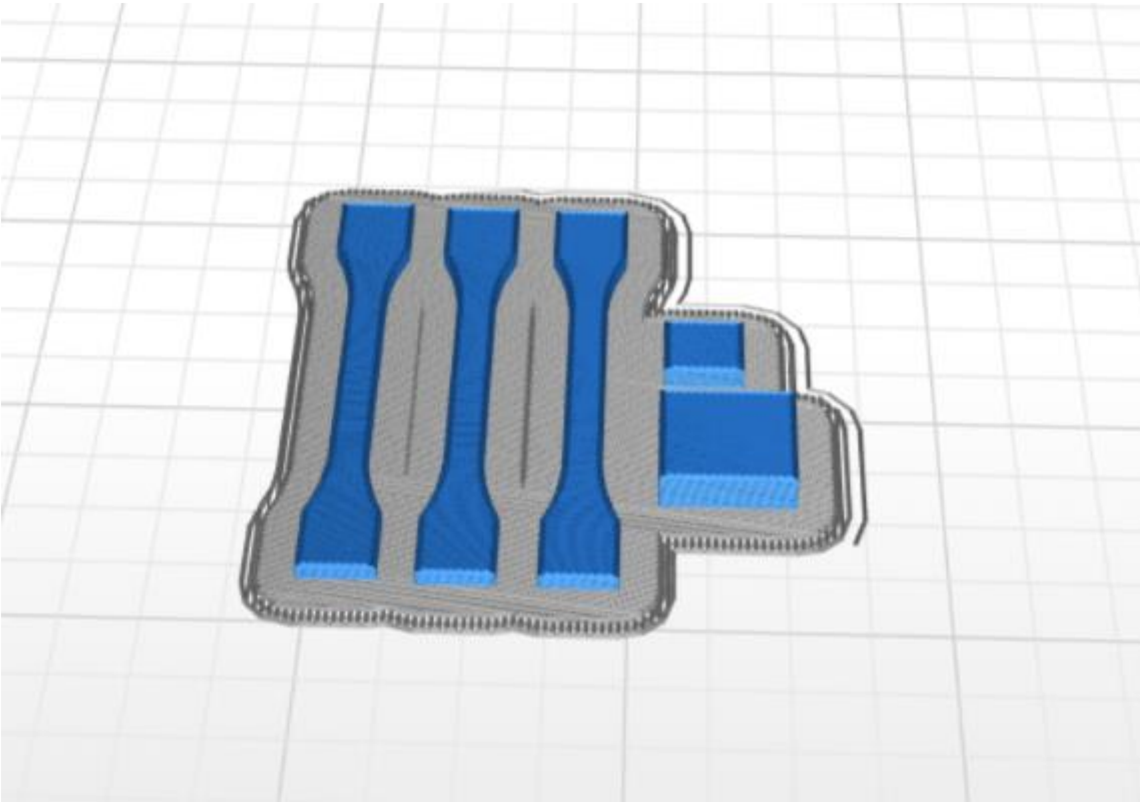

Fig 13. Model of the printed test samples in the Z-SUITE software

The samples were printed using the Zortrax M300 3D printer. The printing parameters were used as they would be for a preset of regular PLA material with 0.29 mm layer, solid infill, and automatically generated raft and supports.

The whole printing process was also done as a regular process of 3D printing. The selected material was loaded into the printer and the needed STL file was selected.

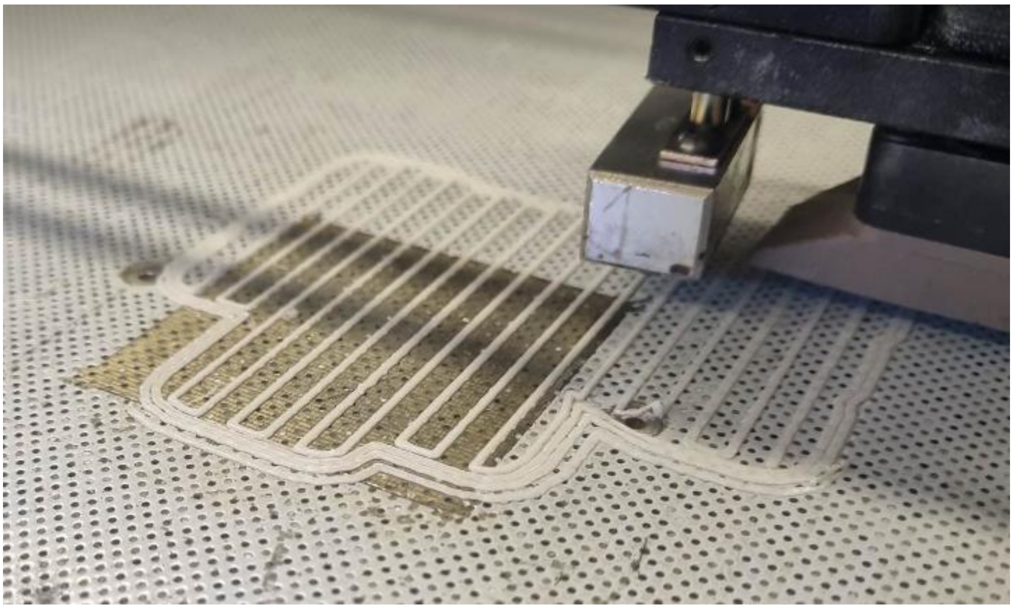

Fig 14. 3D printing process of the test samples

After the samples were printed the raft have been taken off and the samples were separated into different bags for easier tracking and also to be prepared for further experimental steps.
From each of the newly produced filaments, five pieces of ISO 527 samples were produced. Samples have been named in the following structure:
Filler type + PLA and % of the filler in the composition (0.5%/1%/2%) + sample number (1-5). Each sample has been irradiated to the corresponding dose.

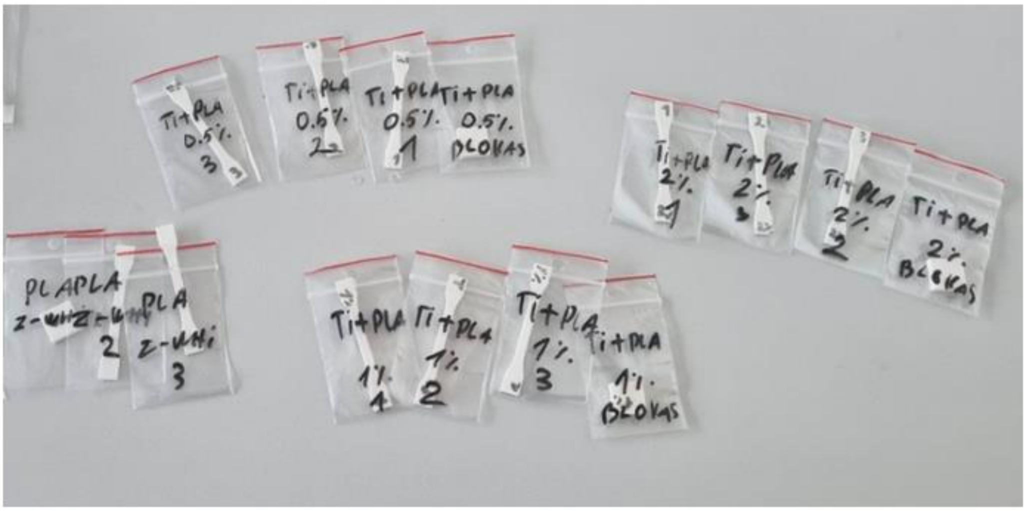

Fig 15. Some of the printed and sorted samples.

2.2. Irradiation of experimental samples

3D printed samples were irradiated in medical linear accelerator VARIAN CLINAC DMX at Lithuanian University of Health Sciences Oncology Clinics. Samples were irradiated using 6MeV photons. Different doses between 2 Gy and 70 Gy were applied for each of the samples. The selection of doses was based on the fact that 2 Gy is a dose in a single irradiation fraction and 70 Gy is possible maximum dose for the whole treatment cycle of patient. It should be noted, that one of the samples was left as a reference (without any irradiation) for each newly formed filament.

2.3. Investigation of the mechanical properties of samples

The irradiation impact on the mechanical properties has been evaluated. All of the samples have been terminated and the performance of their mechanical properties and irradiation effect are discussed

The tensile testing was performed in the Dynamics laboratory at the Laboratory Centre of the Kaunas University of Technology. Mechanical tests were performed according to the ISO 527-1:2019 standard.

The ElectroPuls® E10000 Linear-Torsion machine was performing experimental tests. This machine is an all-electric test instrument designed for dynamic and static testing on a wide range of materials and components. It includes Instron® advanced digital control electronics, bi-axial Dynacell™ load cell, Console software, and the very latest in testing technology – hassle-free tuning based on specimen stiffness, electrically operated crosshead lifts, a T-slot table for flexible test set ups and a host of other user-orientated features. The linear and rotational motion, static and dynamic fatigue (frequency up to 100Hz) test system is designed to study the mechanical properties of materials in environments of various temperatures (-70 ÷ +350°C) with linear (10kN, ±30mm) and rotational (100Nm, ± 135° or ± 16 revolutions) with motion loads that can act together and separately.

Fig 16. ElectroPuls® E10000 Linear-Torsion equipment

The tested specimens were fixed using self-tightening clamps. The specimens were extended alongside the major longitudinal axis at a 1.0000 mm/min speed until sample fractures. Gauge length L_0 = 25mm. During the testing, the sustained load and elongation are also being evaluated.

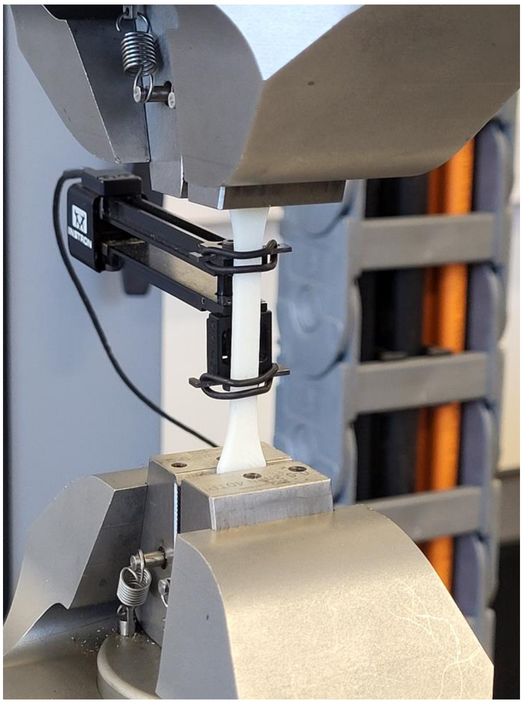

Fig 17. Sample during the tensile tests

2.4. Simulation of the attenuation properties of the experimental samples

3D materials used in procedures with high doses of irradiation tend to degrade. To prevent such a degradation materials suppose to be irradiation resistant and their attenuation change due to the irradiation suppose to be minimal [4]. To theoretically evaluate newly produced filaments attenuation properties XCOM database [4,5] was used for the theoretical simulation. In the data base simulation was selected for the mixtures with the manually entered energies.

3. Results

The theoretical simulation of the attenuation properties of the newly produced 3D printing materials has been performed in order to assess the changes of the mass attenuation coefficient in fillament materials containing different amounts of TiO_2 filler and compare these results with the attenuation properties of human tissue and polyccapralctone (material which is commonly used for the production of fixation masks). The assessment resultas are provided in Fig.18.

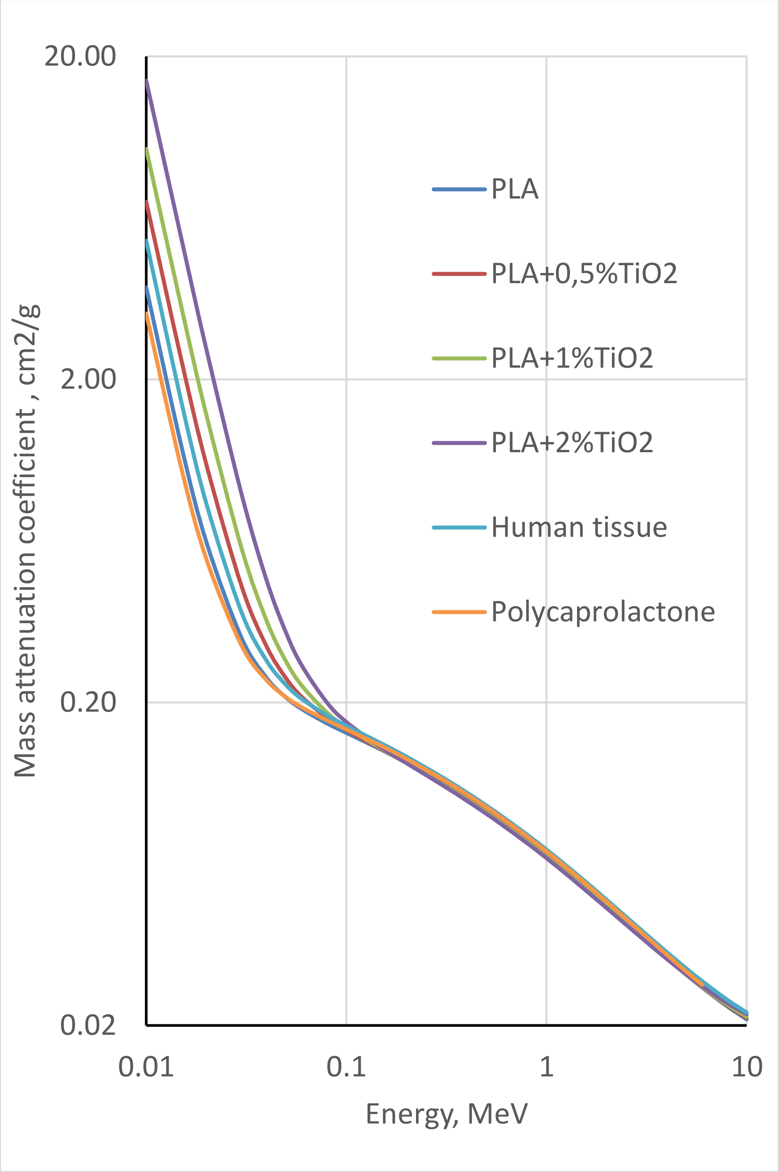

Fig.18. XCOM simulated mass attenuation coefficients of the newly produced fillaments. The attenuation coefficient of human tissue and of polycaprolactone (commercial fixation mask‘s material) are indicated for the comparison

Table 8. Comparison of the total attenuation for different concentrations

TiO_2 concentration , %	Total attenuation coficient, cm^2/g
0%	0.0262
0.5%	0.02626
1%	0.02632
2%	0.02644
Human tissue	0.02741
Polycaprolactone(mask material)	0.02672

It could be seen, that increasing the filler concentration corresponds to the increased attenuation coefficient, even the changes are small due to small concentrations of the filler. It was found, that the observed increasement follows linear trend. Reffereing to other authors who have investigated similar compositions, it could be stated that the obtained experimental measurement resuldmeasurement results of materials attenuation indicated values that were <2.5% [4] lower than simulated ones. In general, it can be seen that filaments with the TiO_2 filler have attenuation properties similar to the currently used mask material (Polycaprolactone). The attenuation values are still lower than human tissue, however further increases in the filler concentration might enhance the values to be relatively closer to the human tissue values. It is important to mentioned that the attenuation properties for small energies are better than a human tissues.This result indicates that newly developed filaments are suitable for procedures requiring small energies since they are blocking small energy irradiation better than human tissues, but do not prevent high energy photon transfer to the deeeper layers of patients body.

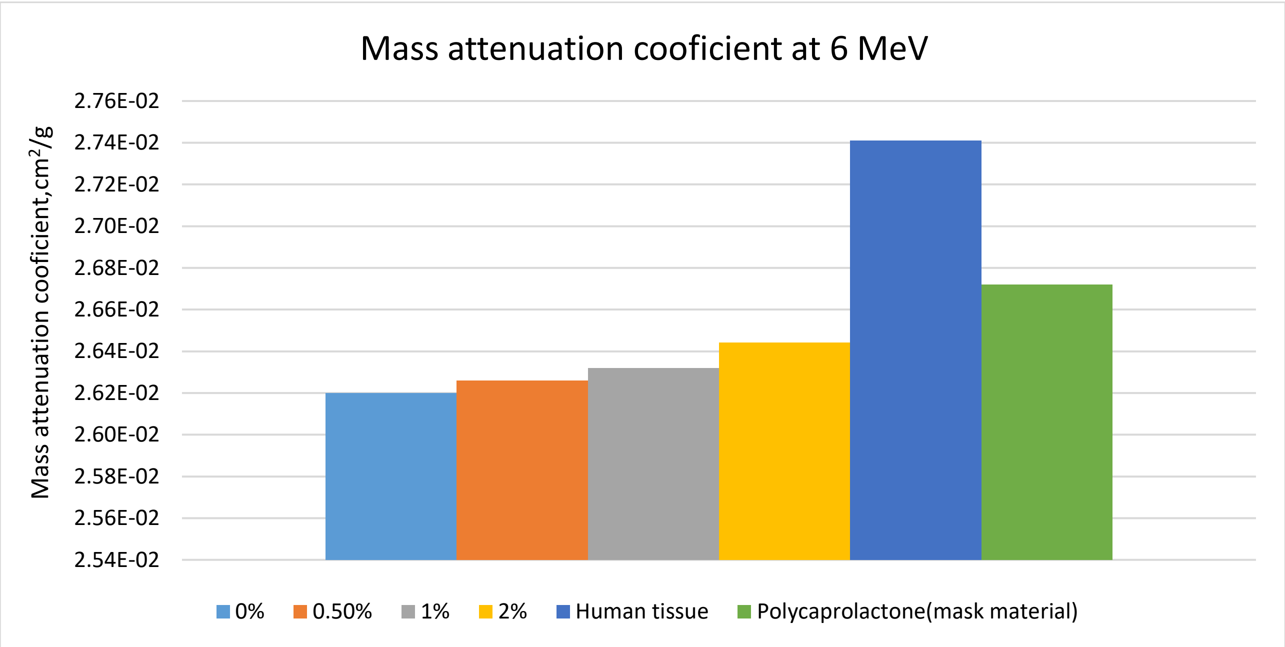

Fig 19. XCOM database simulated mass attenuation coefficients of investigated materials at 6 MeV

The attenuation coefficient is an important property for the materials used in applications such as custom masks; shielding. Materials exhibiting such properties can block irradiation and save non-treated zones by saving them from additional irradiation. Currently, available filaments attenuation coefficient needs to be improved since it is lower than currently used standard materials. Simulation results suggest that TiO_2 usage as a have the potential to solve these challenges and make 3D materials more suitable for such an application.

Mechanical testing results can be discussed on the base of the standard Stress-Strain curve[112].

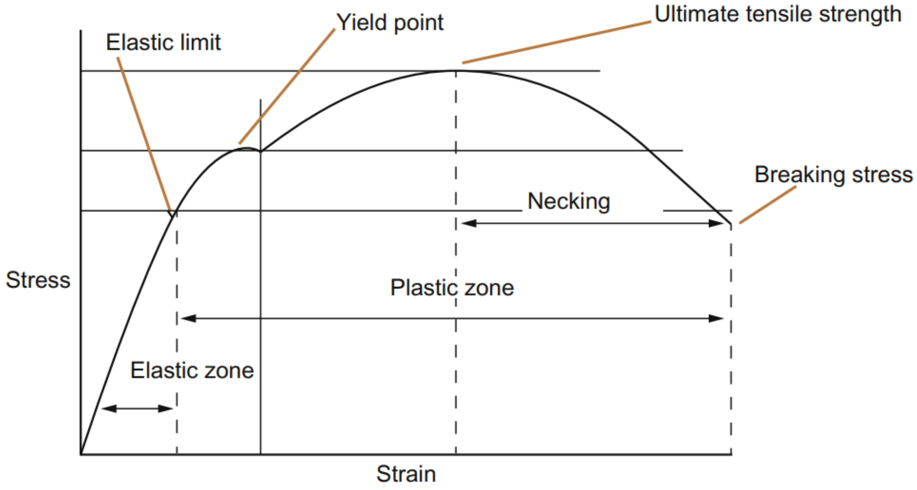

Fig 20. Example of the Stress- Strain curve [112]

The stress-strain curve helps to identificate how the sample reacts while applying increasing tensile stress. It indicates the maximum tensile strength which is possible to achieve before breaking the sample. Elastic properties can also be indicated from such a measurement. From the provided data in the graph, Young's modulus (E) is calculated by having a ratio of tensile stress(σ) to tensile strain (ε). However, the provided example is the ideal measurement and not all of the samples show such clear results [112].

The results of Tensile tests of the produced samples are provided below.

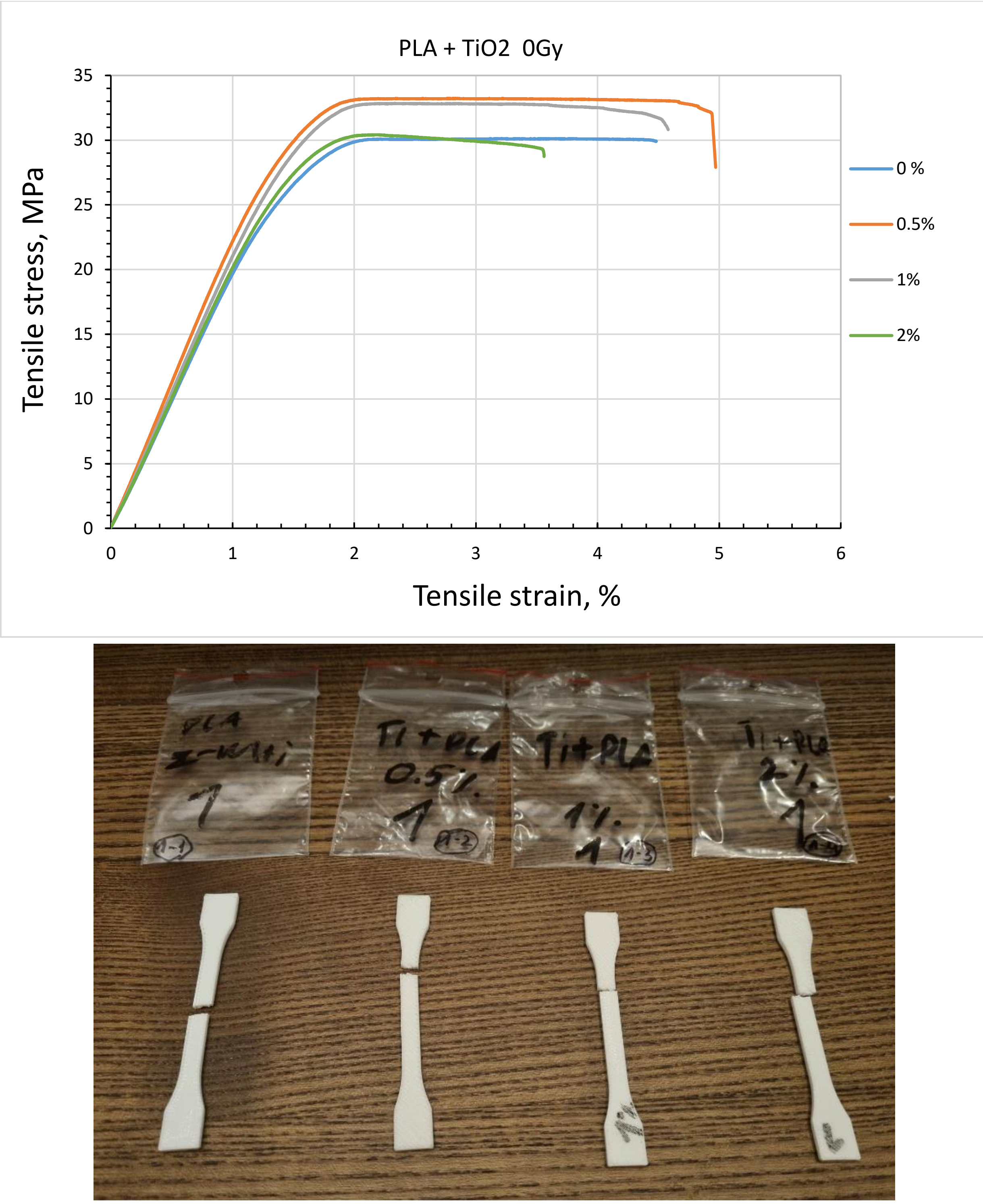

Fig 21. PLA +TiO_2 0Gy Mechanical test results

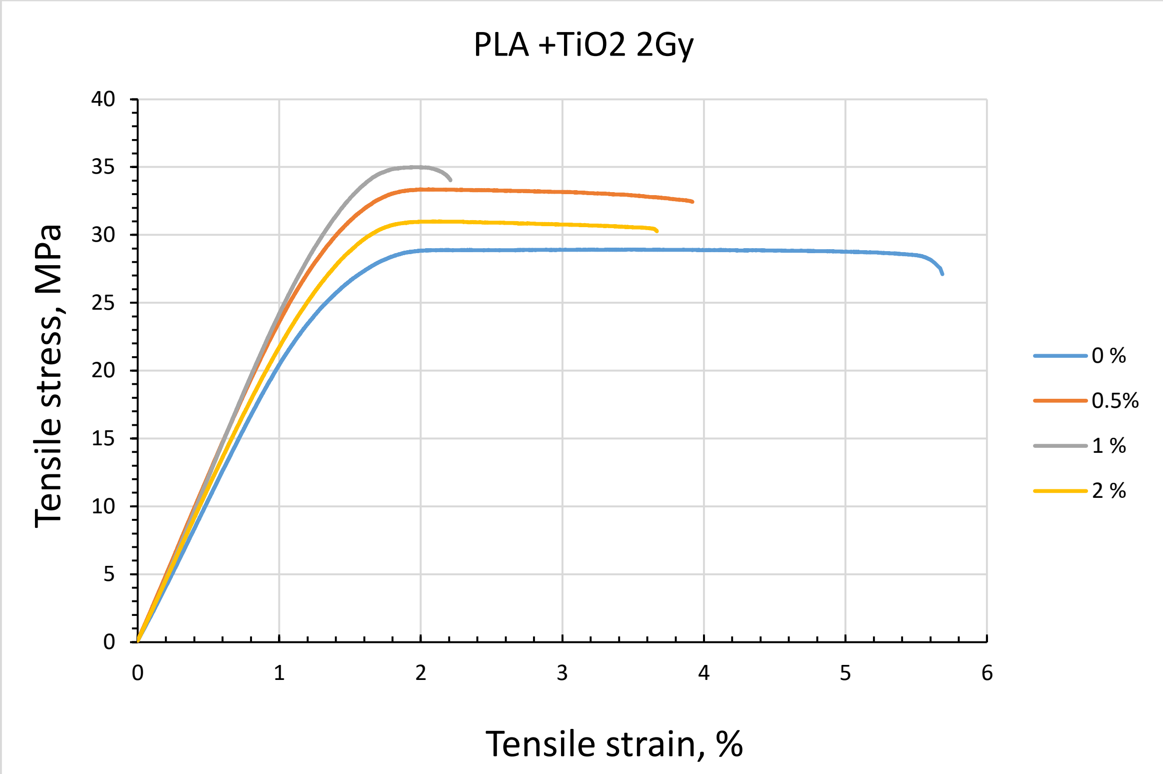

Fig 22. PLA +TiO_2 2 Gy Mechanical test results

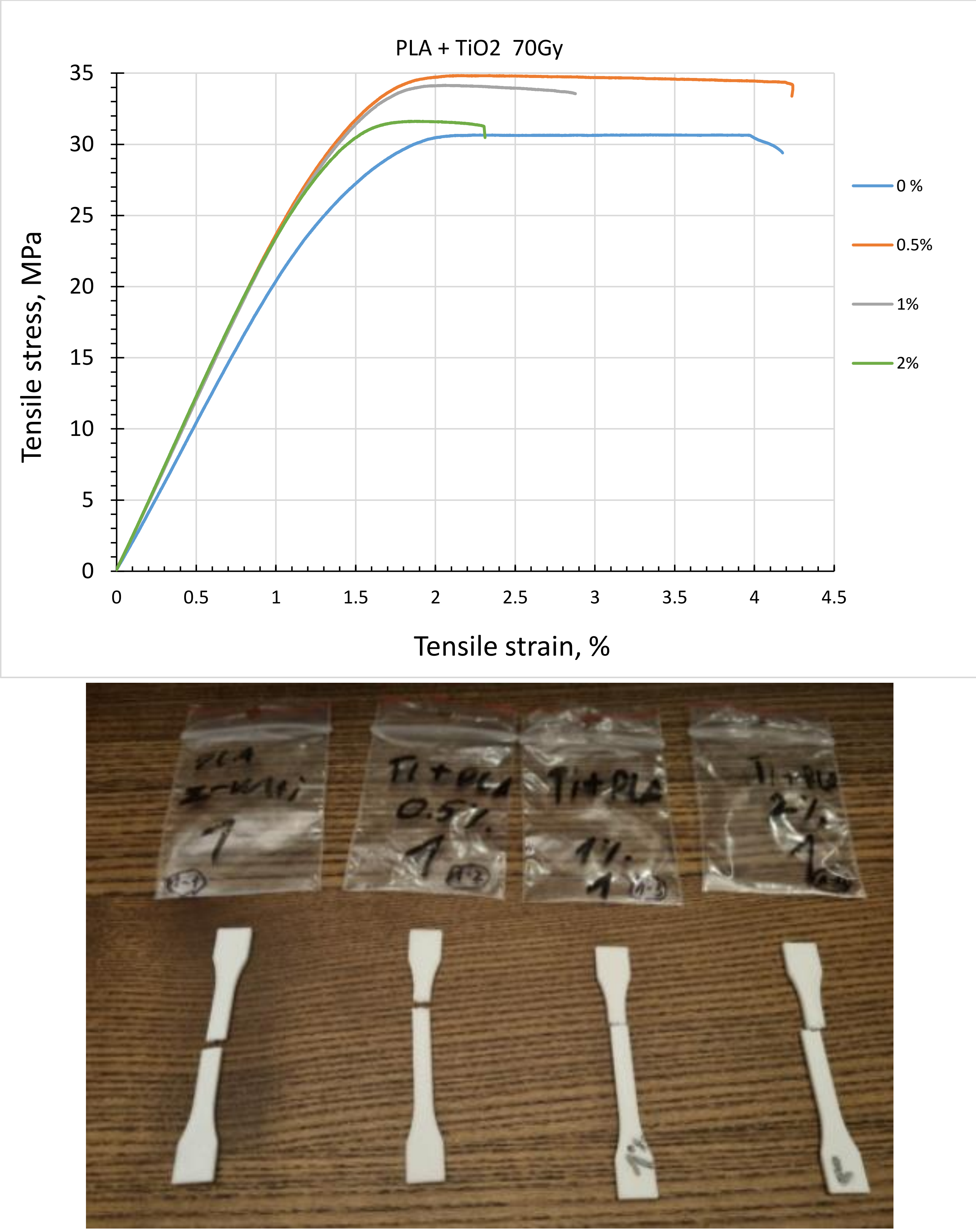

Fig 23. PLA +TiO_2 70 Gy Mechanical test results

The main properties have been discussed and evaluated separately. Since the goal was to produce a suitable 3D printing material for patient-specific applications the mechanical properties have been investigated in the small irradiation doses(2Gy) and high doses (70Gy).

3.1. Maximum load [N]

The parameter that shows the maximum load that material can withstand without fracturing. The measurement results showed that adding filler slightly increases the possible maximum load compared with the pure filament. The highest values have been measured for a filament with 1% TiO_2 concentration. It was also noticed that maximum load is not increasing linearly and goes lower by increasing concentrations of TiO_2 to 2%.

It could be explained by the formation of agglomerates of the filler particles. Agglomerates form microscopic irregularities which cause air gaps (voids) that weaken the material's performance. The agglomeration problem can be solved by using additional material which could work as a surfactant[4,113,114].

On the other hand, the situation is the same for the filament without added fillers. This indicates that decreased performance is not related only to fillers but is also affected by the irradiation dose. As discussed earlier high irradiation doses (70Gy) might induce further polymerization for the thermopolymers of filament. It might be that such a polymerization results in weakening chemical bonds and forces between polymer chains which causes a decrease in the maximum load[64,88]. Another possibility is that the properties degrade due to the material interaction with the radiation. Photoeffect and Compton scattering is the common interactions for 6MeV energy photons. During these interactions, the material degrades by losing the junctions and also decreasing the material mechanical properties.

However, it noticed that there was noticed that even with the degradation the values increased when compared to the pure PLA. Such a tendency shows material suitability for patient-specific applications, especially fixation, and shielding. In such an application the objects are used in awkward angles and difficult fixation with a high load to sustain, also it is a common problem that currently used material lack customizations and tends to break over the course of procedures.

Table 9. Comparison of the Maximum load for different concentrations

Maximum Load [N]				
Gy	PLA	PLA TIO2 0.5%	PLA TIO2 1%	PLA TIO2 2%
0	301.28	332.27	328.43	304.22
2	289.31	333.54	349.94	309.95
70	306.72	348.28	341.44	316.2

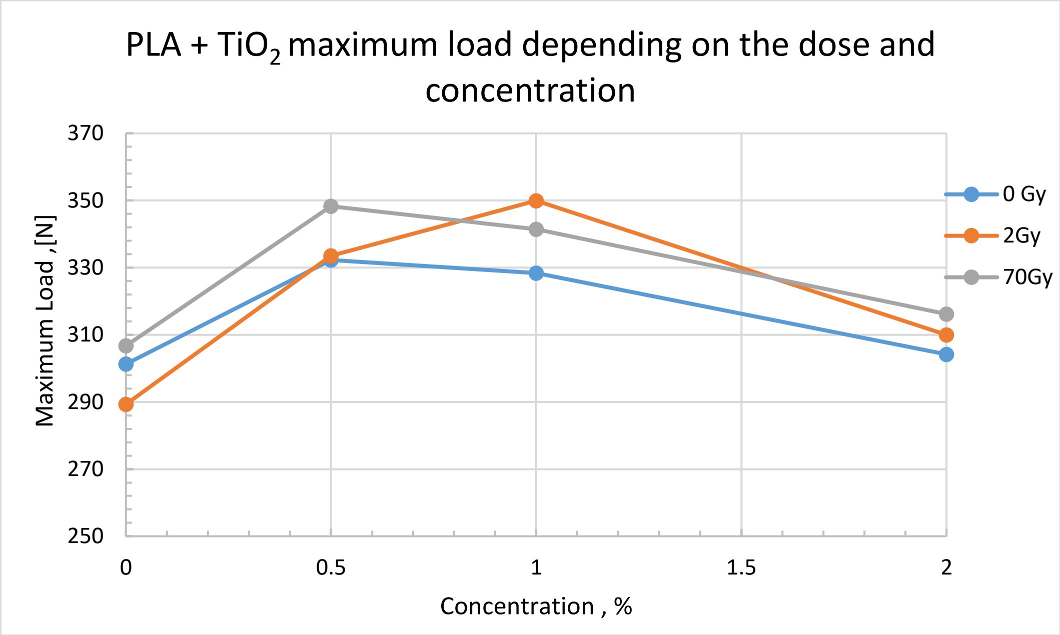

Fig 24. PLA +TiO_2 maximum load comparison graph

3.2. Tensile stress

Tensile stress shows how material resists the forces of tensile until it fractures. While evaluating tensile stress results it can be seen that the values are not varying significantly by increasing the irradiation dose.

An important point is that by increasing the filler concentration there is a tendency that tensile strength is decreasing. This phenomenon was also observed by other authors [7] and can be explained by the interaction which happens between a polymer matrix and a filler. With higher concentrations of the filler, particles form agglomerates leading to higher particle size and lower volumetric particle size. Due to this interaction amount of polymer particle interactions become lower.

When the high enough concentration of the filler is achieved, the polymer chains become immobilized which results in a high stress on the point of aggregation. This additional stress creates the microfracture points which decreases the tensile stress of the final material [7].

Another possible cause is the poor distribution of the filler particles. While particles are poorly distributed they can also form structures that cause the creation of small air voids and gaps. These formed air gaps decrease mechanical properties such as tensile stress. Such an issue might be potentially solved by using smaller-size TiO_2 particles. It might have better distribution than the ones we have used in this research. However, it is only a hypothesis and needs to be experimentally confirmed or denied.

Currently used material for radiotherapy masks PCL tensile stress is around 12-30 MPa [115] in comparison our designed filaments achieved the same result even better than the maximum PCL values. It is also can be seen that the tensile property does not degrade facing high degradation over irradiation of 70Gy. This is important since 70Gy is the maximum dose that masks receive over the course of the treatment procedures. The practice shows that mask tends to break over the course. Due to this reason the ability to not degrade over time under irradiation is promising in order to solve this issue and improve the current solution.

Table 10.Comparison of the Tensile stress at Maximum Load for different concentrations

Tensile stress at Maximum Load [MPa]				
Gy	PLA	PLA TIO2 0.5%	PLA TIO2 1%	PLA TIO2 2%
0	30.13	33.23	32.84	30.42
2	28.93	33.35	34.99	30.99
70	30.67	30.67	34.14	31.62

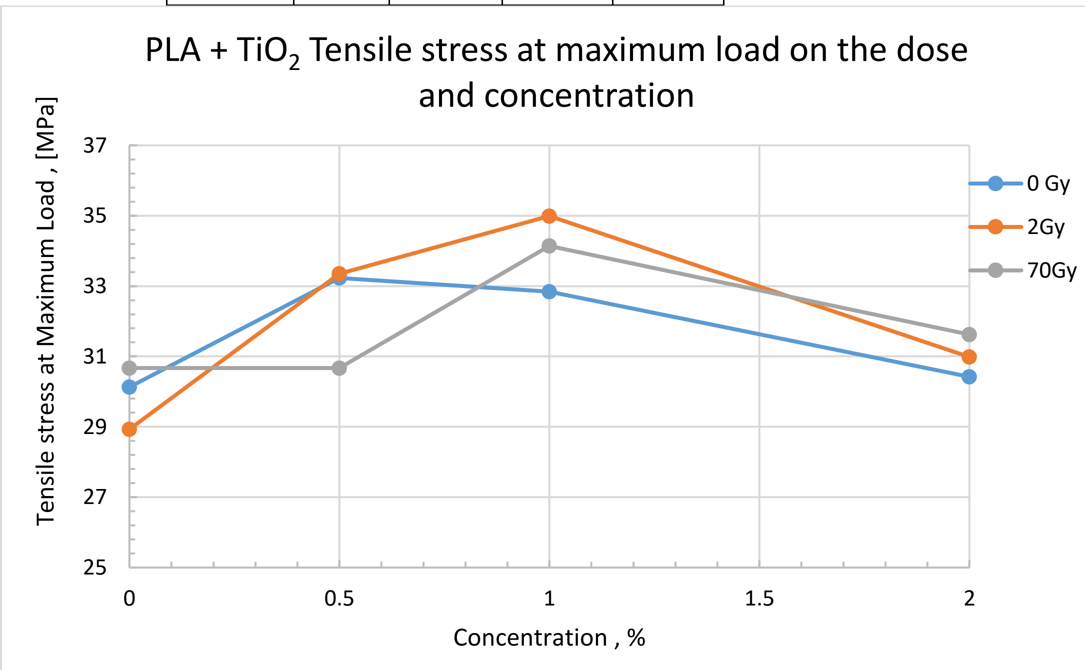

Fig 25. PLA +TiO_2 Maximum tensile stress comparison graph

3.3. Young's Modulus

Young‘s modulus is a parameter that shows the elastic properties of the material. Results have indicated that Young‘s module values are not significantly improved by the fillers. As can be seen, the compositions containing filler have a higher value compared to the PLA without the additives however the difference is very small

While evaluating the irradiation effect on the Young‘s module it can be seen that for the smaller concentrations, the higher doses have reduced this parameter. However, for the higher concentrations, it was slightly increasing together with the irradiation dose increasement. As mentioned earlier it is important that values are not degrading over the 70Gy irradiation. As it can be seen from the results the new created filaments are meeting this requirement.

Nevertheless, the improvement was noticed. Elastic properties are very important for patient-specific applications since current solutions lack such a property. Due to this reason, the new 3D material has the potential to solve this issue and substitute the current solutions.

Table 11 .Comparison of Young's Modulus for different concentrations

Young's Modulus [MPa]				
Gy	PLA	PLA TIO2 0.5%	PLA TIO2 1%	PLA TIO2 2%
0	4091.65	2260.52	2129.72	2002.47
2	2105.02	2498.19	2471.2	2289.19
70	2095.42	2095.42	2382.76	2469.64

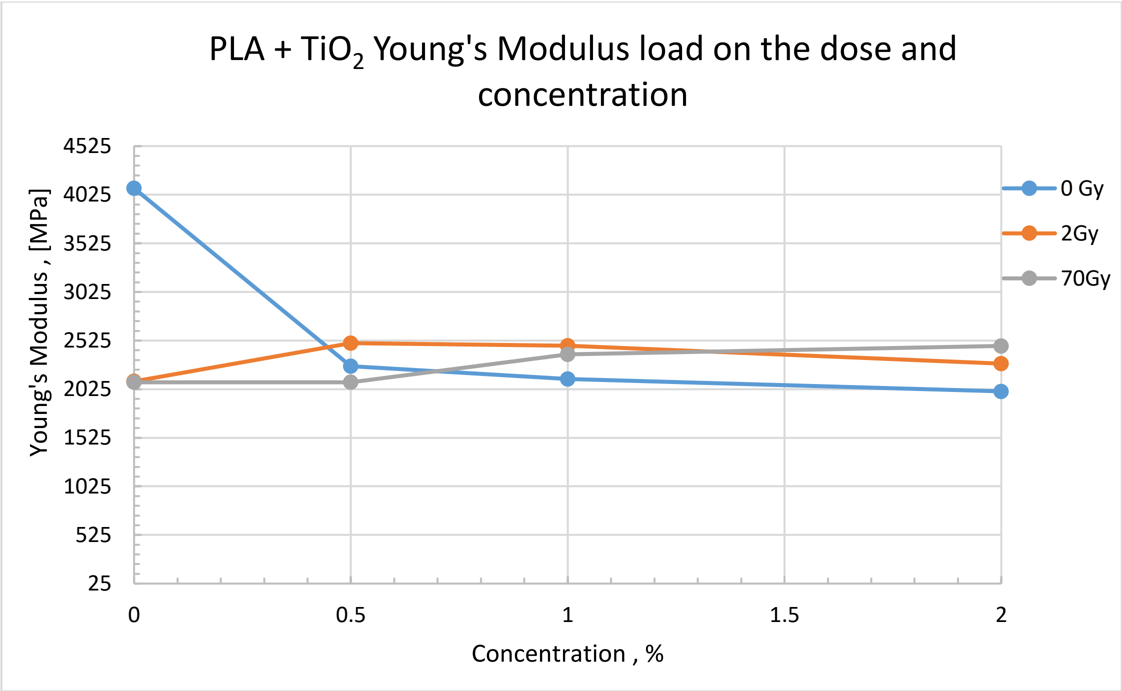

Fig 26. PLA +TiO_2 Young‘s Modulus comparison

In general, the mechanical tests have shown the potential of the newly designed filaments to improve important mechanical properties for patient-specific applications. It might be that increasing filler concentration even further the attenuation properties would be even closer to the human tissue values. While talking about the mechanical properties it already shows potential to solve current challenges since of its resistance to degradation over time under irradiation. However, increasing the filler concentration might enhance the mechanical properties even further and make the 3D printing radiology mask and other equipment the main selection.

Conclusions

Extrusion procedure for the PLA filaments containing different amounts of TiO_2 filler has been developed, adjusted, and implemented. Newly produced filaments were used for 3D printing of materials, suggested for the designing of patient‘s fixation masks during X-ray radiotherapy procedures.

XCOM database-based simulation of the attenuation properties of newly designed PLA composites containing TiO_2 has shown that the higher filler‘s concentrations were responsible for the increased X-ray attenuation of samples in the low energy region, however, attenuation coefficients at higher energies (MeV range) varied not significant in the same samples and was comparable with those obtained for human tissue and for material (polycaprolactone) which is commonly used for the fixation mask‘s design in radiotherapy, thus indicating the applicability of the new materials for the construction of patient-specific devices in radiotherapy.

Performed mechanical tests of the experimental samples fabricated out of newly developed materials revealed, that at least tensile properties of the PLA containing different amounts of TiO_2 were better, as compared to those of pure PLA. It was found that the tensile stress at maximum load indicated increasing tendency with the increased concentration of TiO_2 filler for all experimental samples independently whether they were irradiated or not. However when the filler‘s concentration was higher than 1%, tensile stress at maximum value started to decrease. Such a behaviour may occure due to possible agglomeration and worse distribution of TiO_2 particles in the polymer matrix at higher concentrations.

The performed investigation has shown that the irradiation has had an impact on the mechanical properties of the samples. The impact was higher for the samples irradiated with higher doses (70 Gy) due to the possible radiation degradation of the material. However, the mechanical properties of PLA containing TiO_2 additives remained still better than those obtained for pure PLA, in particular for 2Gy irradiated samples: tensile stress at maximum load for PLA+ TiO_2 was 34.99 MPa as compared to PLA 28.93 MPa, the maximum load for PLA+ TiO_2 was 349.94 N as compared to PLA 289.31 N, Young‘s module for PLA+ TiO_2 2105.02 MPa as compared to PLA 2498.19, and for 70 Gy irradiated samples: tensile stress at maximum load for PLA+ TiO_2 was 34.14 MPa as compared to PLA 30.67 MPa, the maximum load for PLA+ TiO2 was 348.28 N as compared to PLA 306.72 N, Young‘s module for PLA+ TiO_2 2469.64 MPa as compared to PLA 2095.42

Overall, the newly created PLA+TiO_2 composites have shown promising results and indicated the potential to exchange polycaprolactone when designing radiotherapy masks and/or other patient-specific immobilization devices, since their mechanical properties almost do not degrade over time under high energy irradiation and materials are more robust for its reuse during the whole radiation treatment procedure which may contain > 30 fractions (the mask will be set and removed from the patient 30 times). The possibility to apply 3D printing for the fabrication of patient-specific devices (masks) will contribute to the individualization of patients' treatment.

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