SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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PRELIMINARY STUDY ON FABRICATION AND CHARACTERIZATION OF
COMPATIBILITY HA/TPU COMPOSITE FILAMENT FOR BONE SCAFFOLD

by

MOHAMAD FITRI AZIM BIN MOHD ARIFF

Supervisor: Dr Nurazreena Binti Ahmad

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **'Preliminary Study on Fabrication and Characterization of Compatibility HA/TPU Composite Filament for Bone Scaffold'**. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of   Mohamad Fitri Azim Bin Mohd Arifff   Signature:

Student:

Date: 19 August 2022

Witness by

DR. NURAZREENA AHMAD
PPK Bahan & Sumber Mineral
Universiti Sains Malaysia

Supervisor: Dr Nurazreena Binti Ahmad   Signature:

Date: 19 August 2022

ACKNOWLEDMENTS

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LIST OF ABBREVIATIONS

TPU   Thermoplastic polyurethane

HA   Hydroxyapatite

PCL   Polycaprolactone

CA   Contact Angle

MFR   Melt Flow Rate

FTIR   Fourier-Transform Infrared Spectroscopy

TGA   Thermogravimetric Analysis

DTG   Derivative Thermogravimetry

FDM   Fused Deposition Modeling

SEM   Scanning Electron Microscopy

LIST OF SYMBOLS

°C   Degree Celsius

%   Percentage

wt%   Weight percentage

g   gram

mg/min   milligram per min

µm   micrometer

KAJIAN AWAL MENGENAI PEMBUATAN DAN CIRI-CIRI FILAMEN KOMPOSIT HA/TPU MENGIKUT KESESUAIAN PERANCAH TULANG

ABSTRAK

Objektif penyelidikan ini adalah untuk membuat dan mencirikan filamen komposit hidroksiapatit/ poliuretana termoplastik (HA/TPU). Filamen komposit HA/TPU ialah matriks polimer TPU dengan penambahan HA sebagai pengisi bioseramik. Parameter yang dikaji dalam penyelidikan ini ialah peratusan berat berbeza pengisi HA (10, 15 dan 20 wt%) dalam filamen HA/TPU. Tiga komposit HA/TPU dan satu bahan rujukan TPU tulen telah dibuat. Untuk menilai kebolehlaksanaan filamen komposit HA/TPU untuk digunakan sebagai filamen dalam kaedah pencetakan "3D Fused Deposition Modeling" (FDM), Sudut Sentuhan air (CA), Kadar Aliran Lebur (MFR), Spektroskopi Inframerah Transformasi Fourier, (FTIR) dan Analisis Termogravimetrik (TGA) digunakan untuk pencirian. Keputusan CA menunjukkan bahawa, kebolehbasahan HA/TPU dengan 20% berat mempunyai nilai sudut sentuhan air tertinggi iaitu kira-kira 67°. Sementara itu, tiada perubahan ketara antara dua filamen komposit HA/TPU yang lain dan filamen TPU tulen. Keputusan MFR menunjukkan bahawa TPU tulen mempunyai nilai MFR yang jauh lebih rendah jika dibandingkan dengan HA/TPU dengan 20% berat HA. Analisis FTIR menunjukkan bahawa polimer berkongsi empat puncak utama: puncak getaran regangan CH_2, jalur amida I, puncak getaran regangan -NH dan puncak getaran regangan -NH (jalur amida II). Graf TGA menunjukkan peratusan pengekalan berat pada suhu tinggi antara 300°C hingga 350°C untuk TPU tulen dan 250°C hingga 450°C untuk TPU dengan 20wt% HA.

PRELIMINARY STUDY ON FABRICATION AND CHARACTERIZATION OF COMPATIBILITY HA/TPU COMPOSITE FILAMENT FOR BONE SCAFFOLD

ABSTRACT

The objective of this research is to fabricate and characterize hydroxyapatite/ thermoplastic polyurethane (HA/TPU) composite filament. HA/TPU composite filament is a matrix of TPU polymer with addition of HA as bioceramic filler. The parameter investigated in this research is the different weight percentage of HA filler (10, 15 and 20 wt%) in HA/TPU filaments. Three composites of HA/TPU and one pure TPU reference material were fabricated. To evaluate the feasibility of HA/TPU composite filament to be used as filament in Fused Deposition Modelling (FDM) or 3D printing method, water Contact Angle (CA), Melt Flow Rate (MFR), Fourier Transform Infrared Spectroscopy, (FTIR) and Thermogravimetric Analysis (TGA) were used for characterization. CA results shows that, the wettability of HA/TPU with 20 wt% has the highest water contact angle value of roughly 67°. Meanwhile, there are no notable changes between the other two HA/TPU composite filaments and pure TPU filaments. MFR results show that pure TPU has considerably lower MFR value when compared to HA/TPU with 20 wt% of HA. FTIR analysis shows that the polymers shared four major peaks: the CH_2 stretching vibration peak, the amide I band, the -NH stretching vibration peak, and the -NH stretching vibration peak (amide II band). TGA graph shows a weight retention percentage at high temperatures ranging from 300°C to 350°C for pure TPU and 250°C to 450°C for TPU with 20wt% HA.

CHAPTER 1

INTRODUCTION

1.1 Background Research

Originally, the term Fused Deposition Modeling (FDM) or 3D printing refers to a procedure in which binder material is placed layer by layer onto a powder bed. FDM refers to a larger range of techniques such as 3D printing, binder jetting, material extrusion, and the roll- to-roll process (Sood A. K., 2012). Layer-by-layer manufacturing refers to several approaches that use computer-generated or aided imaging software (CAD) to reconstruct a model, as well as fast prototyping that uses solid freeform fabrication (SFF) of design. By manufacturing flexible and robust 3D-printed structures, three-dimensional printing can greatly contribute to the field of biomedical applications (Grogan S. P., 2015). One of several best components to replace this soft, strong 3D-printed structure and sensor would be a composite material composed of polymers and ceramic materials. A kind of polyurethane (PU) known as thermoplastic polyurethane (TPU) has outstanding elastic and tear-resistant qualities as well as a medium tensile strength. The inclusion of ceramic components increases the mechanical strength of the composite, resulting in a flexible yet soft and sturdy 3D-printed structural scaffold aside from improving the mechanical characteristics of the composite (Park T. J., 2008). Introducing into TPUs as main composite material, through the development of variable density and stiffness, 3D-printed structure physical qualities may be tailored, enabling the management of the reaction value with respect to the sole design of planar load (Kasovic, 2020). Another behavior that points out TPUs is due of its hygroscopic, viscoelastic, and hyperelastic properties, whereby the printed TPUs does not display intuitive behaviour (Collini, 2021). TPU has been employed as a cutting-edge mixture in the electrospinning process to create synthetic tissue for an aortic heart valve. To continue, various

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research improved the parameters for manufacturing TPU using a 3D printer before employing it for various soft tissue engineering scaffold applications (Fallahiarezoudar, 2022).

1.4 Problem Statement

Bone scaffold composed of composite material has attracted attentions for biomedical applications mainly for bone repairment and regeneration. Hydroxyapatite (HA) is chosen as the main material in bone scaffold as an inorganic ceramic which has the same chemical composition as the human bone. HA is known to be brittle, making it impossible to be used for load bearing applications. However, with the combination of polycaprolactone (PCL) and HA as composite scaffold material has increased the scaffold toleration and resistance towards the internal forces inside human bone and other biochemical reactions. This concept is similar to other medical applications consisting of polymer composite as the main structure.

The fabrication of bone scaffold by using FDM requires filament as the feed materials. It is worth noting that there are factors that influence the successful rate of 3D structure fabrication using filament. Commonly filament is produced by any extruder machine applicable in the market and based on the preferable application. As there is HA content in the filament, the brittleness resulting from the high porosity might cause failure during the extrusion process and after it solidifies to become a solid structure. Thus, varying the HA wt.% would fulfil the shortcoming. On the other hand, to apply bone scaffold into human bone, the need of HA coating is obligatory. It is worth to mention that another option for fabricate bone scaffold is by foam replication. And by using foam replication method it will increase the brittleness because once the foam is burned out it will leave a hollow space/ strut structure.

In relation to that, comparing to FDM technique, the 3D printed component (bone scaffold must be dipped in HA slurry or respective solution first before undergoing a sintering process to strengthen the structure with low porosity. The PCL content will be melted away throughout the

process and eventually provides an array of vacant space inside the bone scaffold. Hence, the final structure itself cannot withstand any load received or biochemical reaction inside human bone. In this study, a substitution of PCL material would impact the characteristic for both the filament and bone scaffold. An alternative material is suggested to overcome the hollowness and increase the strength. As stated by Jung et al. (2016), thermoplastic polyurethane (TPU) shows remarkable results in biomedical application. Its characteristics are preferable in this application when compared to PCL. It is better to have a composite of HA/TPU because the HA will be sintered together and reduces the hollowness of the strut. On the other hand, TPU is a new filament material with flexible medical grade. It might be the wise choice for low-budget FDM to cut the production cost. Another relation to that TPU shows better properties such as higher glass transition temperature (Tg) and melting temperature (Tm) compared to PCL which help to improve the capability to negate PCL's lack of functionality (Jankauskaite, 2008).

1.5 Objective

The objectives of this studies are as follows:

1.   To fabricate HA/TPU filament via extruding process with varying HA/TPU ratio to achieve desirable properties which are wettability, flow characteristic, thermal stability and chemical composition stability.

2.   To characterize HA/TPU filament in accordance with the FDM requirement and compatibility towards bone scaffold application.

1.6   Scope of Research

Pure Thermoplastic Polyurethane (TPU) pellets and Hydroxyapatite (HA) powder are used to make HA/TPU filaments. The two-roll mill technique is used to compound the material, which is then extruded before being evaluated. All raw materials are chosen in accordance with the study's requirements. The next stage is to fabricate filaments using the appropriate procedures, combine HA/TPU composites using a two-roll mill, and extrude HA/TPU filaments using an extruder machine.

HA/TPU undergoes a two-roll mill compounding process, one of the commonly used techniques. Because the compounding process is not confined to a small amount of mixture when utilizing this approach, the procedure is simplified, and a wide range of homogenous mixtures is obtained. Three composite HA/TPU compositions and one pure TPU reference material were employed. By varying HA content, the samples are divided into HA/TPU 10wt%, HA/TPU 15wt%, and HA/TPU 20wt%. The weight of each composite is fixed at 250g. Thus, there will be a 250g pure TPU, 225g TPU with 25g HA, 212.5g TPU with 37.5g HA, and 200g TPU with 50g HA since the amount is weight maximum of 250g. Before shredding, the thick layer of HA/TPU is cut into thin and tiny fragments using a cutting board. The shredding technique is used to keep the size range of HA/TPU flakes consistent. The size of HA/TPU plays an important role in maintaining a good surface and uniform heating throughout the extruding process, as well as ensuring that the characteristic is maintained at its best with a low degradation rate and does not exceed controlled factors.

3D FDM filaments were generated using an extruder with a 1.75 mm extrusion nozzle after shredding the TPU/HA composite flakes. Instead of cooling the extruded filaments with air, they are promptly cooled in a water bath, which reduces thermal deformation. The composite flakes were extruded as a HA/TPU composite filament, which was then directed to a drive wheel and coiled at a steady rate. All filaments of varying compositions were extruded at 175 °C with

input flow of 120%, and the extrusion dial speed and spooler were adjusted until the filament diameters were consistent.

Several characterization approaches are utilized to characterize the volatized HA/TPU filaments to establish possible behaviour that can be used as universal references. Water Contact Angle (CA), Melt Flow Rate (MFR), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). Their physical and chemical characterization are suggested to follow 3D printing feasibility and compatibility towards medical application.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Polymer Materials, Ceramic Materials, Composite Materials and Polymer Matrix Composite (PMC) Materials.

2.1.1 Polymer Materials

A world without plastics, or synthetic organic polymers, seems inconceivable today, even though large-scale production and use began in 1950. Although the earliest synthetic polymers, such as Bakelite, developed in the early twentieth century, plastics were not widely used outside of the military until after World War II (Geyer R., 2017). In the plastics sector, polymer is frequently used as a synonym for plastic or resin. Polymers are a class of materials that have a wide range of properties. They can be found in everyday home items, clothing and toys, construction materials and insulation, and a variety of other items. Polymers are typically classed as natural polymers and synthetic polymers, although they can also be classified as natural polymers, semi-synthetic polymers, and synthetic polymers, depending on the source (Zhang, 2022). Synthetic polymer materials are polymers produced through specific polymerization reactions employing monomers with specified structure and relative molecular weight as raw materials, primarily phenolic resin. There are numerous varieties of synthetic polymer materials, such as plastics, synthetic fibers, and synthetic rubber, that are the result of current materials science progress and are widely employed in all parts of production and life (Young R. J., (2011). The variety of polymer materials that have been synthesized and industrially produced have swiftly evolved. In the late 1960s, a slew of new products appeared, each one synthesizing a different type of plastic material, such as polyoxymethylene, polyurethane, polycarbonate, polysulfone, polyimide, and polyetheretherketone.

2.1.2   Ceramic Materials

Ceramic is employed in components that are exposed to severely harsh environments (high stresses, creep, wear, corrosion, impact, and very high temperatures) in general (Peng, 2018). They are used in thermal protection systems, such as refractory linings for the metal and cement industries (Pinto & Braulio, 2012). One of the most rapidly developing areas of modern materials science for medicine is the development of ceramic materials based on calcium phosphates. These biocompatible materials can be employed in medicine as porous matrices for replacing missing or injured bone tissue or as cell culturing substrates (Huang J., 2022). These porous and textured ceramics can be made using a variety of techniques, including compaction, sol–gel, extrusion, hydrothermal synthesis, and gel casting. Among these procedures, compaction is one of the most used methods for producing porous ceramics. As a result, a pore-former or porogen agent must be added to the initial mixture. The resultant ceramic products have considerable mechanical strength as well as a highly porous texture (Dabir S., (2017). It should allow for the filtering of contaminants in high-flow rate water to generate drinking (tap) water.

Ceramics based on hydroxyapatite are frequently made from HA powder that has been manufactured using various processes. Among these, two major groups of approaches should be mentioned: water-containing syntheses and anhydrous syntheses. One of the most major uses for porous HA is controlled drug release in bone abnormalities such as bone cancers or osteoporosis (Logigan, 2022). Porous HA granules or scaffolds filled with medicines ensure localised and prolonged drug release, which accelerates bone repair (Suchanek W.,1998). Custom-made porous HA scaffolds are also generally utilized as a gap filler to heal bone deformities by encouraging bone in growth, particularly when conventional procedures have failed. Quarto et al. 2001, for example, implanted HA scaffolds seeded with in vitro grown autologous bone marrow cells in patients of different ages to cure major bone abnormalities (4–7 cm) of the ulna, humerus, and tibia similarly as shown in Figure 2.1.
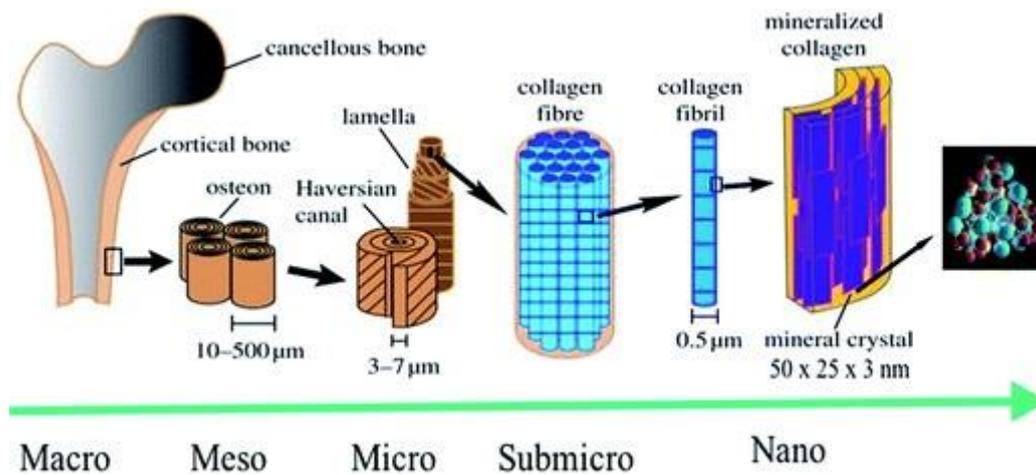
Figure 2. 1: Bone's hierarchical structure at various size scales. The microstructure of cortical bone is made up of osteons with Haversian canals and lamellae, whilst the structural units at the nanoscale are collagen fibers made up of bundles of mineralized collagen fibrils (this figure was modified from the work of Zhang et al. and Rho et al.).

To increase mechanical qualities or impart controllable restorability, HA can be used alone or in combination with other polymers such as poly(lactic-co-glycolic) acid (PLGA), poly (L- lactic acid) (PLLA), and polycaprolactone (PCL) in the creation of 3D scaffolds (Haider A, 2017).

2.1.3 Biomaterials

Biomaterials must be compatible with the human body since the human system's sensitivity might impact the structure's properties. The primary purpose of a bone scaffold is to promote bone cell migration to aid bone formation or to serve as a replacement component for a broken section. To avoid any negative effects on human bone, a toxicity-free element in the bone scaffold should be used. Hydroxyapatite is a common substance that has a similar composition to human bones (HA). Since the presence of HA is insufficient to hold the scaffold structure together, HA is added as a filler to thermoplastic polyurethane (TPU), which will supposedly become an advanced composite. Finally, this composite is formed into a filament- like structure

in accordance with the FDM specifications. The manufacturing of HA/TPU composite filament as a filament is thoroughly investigated to be suitable for FDM with low defect or failure rates. It's worth mentioning that the HA/TPU filament's characterization will have a significant impact on this research. According to Jung et al. (2016), TPU is relevant and more suited for bone scaffold due to its exceptional ability to generate bone tissue. Furthermore, because TPU's rate of degradation can be controlled, it has been shown to have improved biocompatibility and hemocompatibility. He also mentioned that TPU is the preferred filament material for fabricating sophisticated 3D structures with FDM.

2.1.4 Biomaterial Ceramics

Owing to its excellent structural capabilities, attractive appearance, great biocompatibility, and chemical inertness, biomaterial ceramics have been widely used in the medical fields. There are two types of bioceramics: bioactive and bioinert. Aluminum oxide, partly solidified zirconium oxide, and pyrolytic carbon are typical examples of bioinert ceramics used in medical settings today, whereas a variety of calcium phosphates and surface-active bioglasses are examples of bioactive ceramics. The common characteristic of those bioceramics comes in corrosion resistance, high mechanical strength and outstanding tribological aspects (Mirzaali, 2022). Aluminum oxide, zirconium oxide, titanium dioxide, silicon nitride, pyrolytic graphite, and diamond-like carbon are now interested in materials of load-bearing implants thanks to their qualities in terms of tensile strength and fracture toughness (Ivanova, 2014).

In past few years, attention in silicon nitride or called as nierite is up driving as an advanced ceramic material having high compressive and flexural strengths, relatively high fracture toughness, extremely low friction coefficient, strong corrosion resistance. It has presently been developed for a wide range of medicinal uses as it complies the common criteria needed. These applications include wave guides for medical diagnostics, microtubes for intelligent neural circuits, micro-spectroscopic imaging devices, photonic ICs, optical biosensors, novel dental

implants, spinal intervertebral spacers, tissue engineering scaffolds, antibacterial and antiviral coatings, and others.

The other competitor of bioceramic is hydroxyapatite (HA). This bioceramic is osterconductive where it allows bone growth to an acceptance level of human bone growth rate with limited bioactivity (Siniscalco D. et al., 2019). It has drawn a lot of interest as a potential replacement material for bone. Because of interactions between the bone tissue and the biomaterial driven by its chemical similarity to the mineral portion of bone, whereby a strong contact forms after implantation.

2.1.5 Composite Materials and Polymer Matrix Composite (PMC) Materials

Composites are structures created by fusing two or more materials having dissimilar physic mechanical characteristics (Kaczmarek, 2018). One component is the matrix that holds the composite together, and the other is the construction material that gives the composite its strength. A suitable mix of the constituent materials and their orientation results in a material with qualities that are impossible to produce using traditional ways of manufacturing homogeneous materials (Trzepieciński, 2021). The characteristics of the component phases, the volume percentage of the phases, the method of distribution of the dispersed phase in the matrix, and the geometric aspects of the dispersed phase all influence to the composite strength. Metal-based composites and non-metal (polymer, ceramic) composites are classified according to the matrix type. Composites reinforced with fibres or particles or in a dispersion way exist depending on the type of reinforcing component. Metal matrix composites (MMC), ceramic matrix composites (CMC), aramid fibre-reinforced plastics (AFRP), and polymer-based composite materials (carbon fibre-reinforced plastics CFRP, glass fibre-reinforced plastics, GFRP) are the most common types of composite materials. When low weight and great durability are the most important application criteria, aramid fibre-reinforced polymer (AFRP) composites are used. Compared to AFRP composites, CFRP composites have a substantially higher rigidity.

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The desire to make a thermoplastic matrix composite stem from its inherent nature, which is diametrically opposed to that of a thermosetting matrix, namely the material's ability to be recycled. TPCs may offer more fatigue resistance than thermoset-based alternatives such as fiber-reinforced epoxies and vinyl esters, due to the higher toughness of the matrix. This method involves injecting a low-viscosity resin into a mould with pre-placed dry fibres, followed by a curing step. Because thermoplastic polymer melts have a high viscosity, reactive processing is required, a low-viscosity monomer melt is injected between the fibres, along with an activating system, if necessary, followed by in situ polymerization of the monomer to form a linear polymer with a sufficiently high molecular weight (Van Rijswijk, 2006).

2.2   Polymer Properties

Polymers have a bunch of properties that evaluate the specific specification for an application. The characteristic of its own is available to distinguish by testing a preferable method. Several important properties of polymers are divided into three sections which are physical, chemical, and mechanical. In physical properties, the study from polymer bodies would point out some crucial characteristics such as the tensile strength, hardness (resistivity), crystallinity (polymers arrangement), thermal expansion (expands or contracts of polymer chain), elasticity (stretching mechanism) and heat capacity (capability to negate heat) or even heat conductivity. As for the chemical properties of a polymer, such information about interaction between reactive groups (carbonyl group presents on monomer chains) and adhesion where the surface of interaction occurs on its surfaces. On a single mechanical strength of polymers would discover some hidden properties such as toughness, Young's Modulus, percentage of elongation and cross-linking. Those characteristics are capable of determining the choice of application that can be implemented.

2.2.1 Tensile Strength

In a study by Valente et al. (2016) stated that the final mechanical properties of the product are also affected by the polymerization temperature whereby because of the increase in crystal formation, both the elastic modulus and the tensile strength increase. When the temperature drops, the degree of crystallization increases, but not the strength or rigidity; this is because the crystallization rate is so rapid that it keeps the caprolactam monomers within the crystallites, increasing the material's fragility. In addition to the monomer, even the reactive end sections of the chains can be blocked, resulting in not only a sudden halt in the macromolecule's growth, but also a restriction on chain interdiffusion between the amorphous and crystalline phases (Van Rijswijk K., 2006).

2.2.2 Hardness

Hard polymers are resistant to hard substances penetrating through them. They are utilized in the development of products and can tolerate wear and tear as well as indention. In the recent research by Bhaskar et al., using the shore D hardness test, the hardness of polymers is tested with a reference polymer of polylactic acid (PLA). From the research, a comparison of polylactic acid (PLA) and grafted glycidyl methacrylate (GPLA) samples, the shore D hardness exhibited an increase. Shore hardness test of 75HD and 65HD were found in PLA and GPLA, respectively as shown in Figure 2.2. When compared to PLA and GPLA, the composites had higher hardness values. This demonstrates that the layers are tightly linked and packed, resulting in significant reaction forces during the indentation. The continuous resistance supplied to the indenter from the entire structure due to the presence of the thermally activated material is the cause of the high hardness values. Furthermore, plastic composites experienced a higher tension and compression with quite sturdy reaction forces which provides a high hardness value (Butt J., 2020).
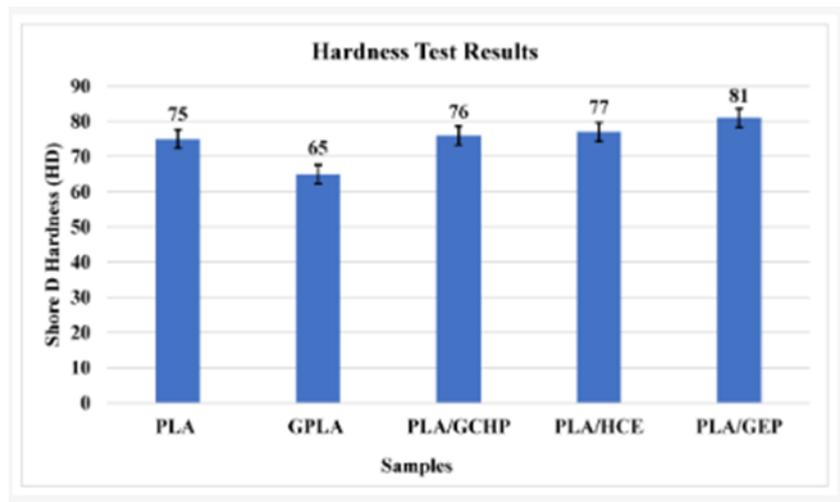
Figure 2. 2: Hardness testing values for each polymer and its composites (Shirvani H, 2022).

2.2.3 Crystallinity (Polymers Arrangement)

As they're more brittle, polymers with lower crystallinity are more useful. The type of polymeric chain arrangement influences this characteristic. Based on the chain arrangement of polymer chains the polymerization temperature capable to change the crystallinity or degree crystallization. This is demonstrated by the fact that the melting temperature tends to drop, implying that a smaller quantity of heat flow (mJ/g) is required to melt the polymer's crystalline area. The fact that the mobility of macromolecules is favored as temperature rises, resulting in a lesser chance of crystallite formation, is one of the explanations by the Van Rijswijk et al. (2006).

Both solid and foamed samples yielded comparable T_m high values, and it seemed to be mostly unaffected by the filler quantity and expansion ratio. The compression molding and foaming temperature (160 °C) may not have been high enough to completely melt the bigger and more perfect crystals, as shown by the consistency of the T_m high values. The second melting peak (T_m high) is made up of bigger crystallites with higher melting temperatures (Petrossian et al., 2019).
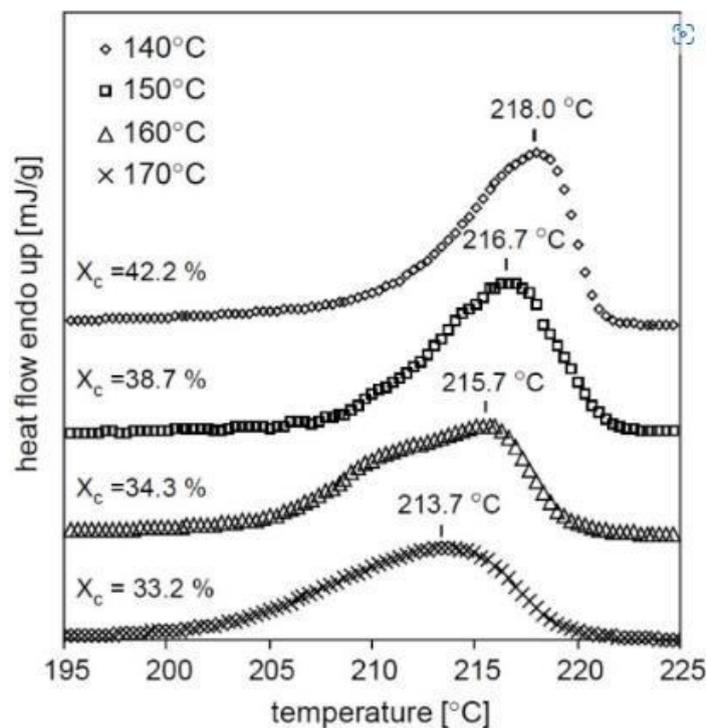
Figure 2. 3: DSC measurements of degree of crystallinity and polymer melting point for various polymerization temperatures (Bersee, 2006).

Another theory is that branch points obstruct the development of crystals, lowering the degree of crystallinity (Stavrov D., 2005). In terms of the branching process, Figure 2.4 compares the degree of crystallinity at various polymerization temperatures for two different activator and initiator formulations (1.2 mol % HDCL versus 0.6 mol % HDCL). No branching occurs below the deblocking temperature (160 °C), and a higher activator concentration results in a bigger number of polymer chains and, as a result, a lower molecular weight. As previously stated, a lower molecular weight results in a higher degree of crystallinity. However, above the release temperature, a larger activator concentration induces a considerable increase in branching, resulting in poorer crystallinity (Rossitti I., 2022).
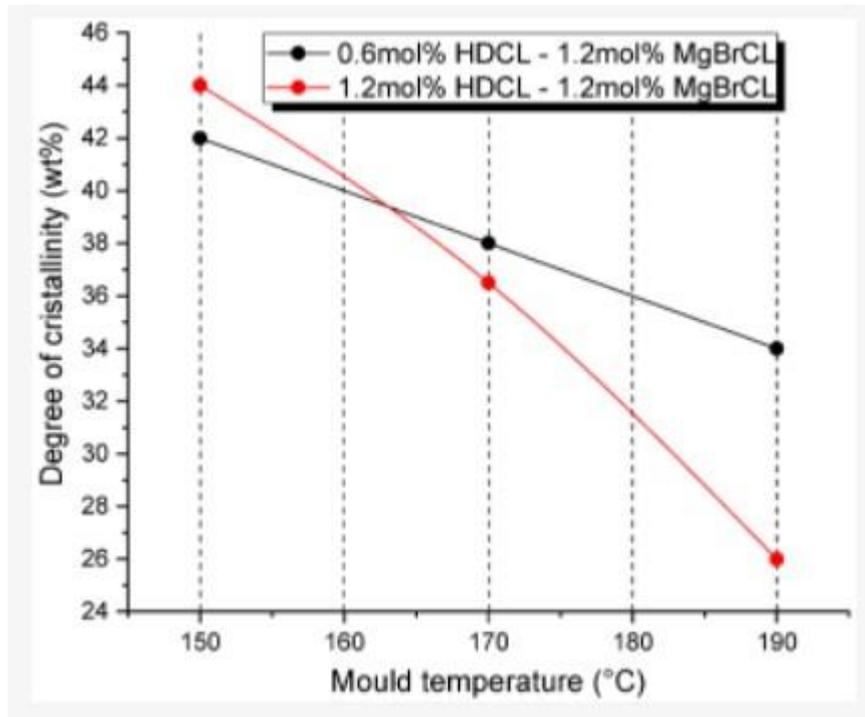
Figure 2. 4: Crystallinity at varied mould temperatures for two distinct activator concentrations

(L. Brügge-Mann GmbH & Co. KG. Bruggemann, 2022).

2.2.4 Thermal Expansion (Contracts and Expands of Polymer Chains)

The extent to which a polymer expands or contracts when subjected to heat or cold is measured by this property. A study by Zaldivar R. J. et al. the coefficient of thermal expansion (CTE) for each construction orientation specimen was determined using the TA Instruments TMA. For each sample set, tests were conducted in three principal directions (axial (x), transverse (y), and through-thickness (z). For Sample Sets A-D, a TMA was used to quantify the linear thermal expansion behaviour in each of the three principal directions (axial, transverse, and through-thickness) as shown in Table 1.1. The anisotropic CTE qualities are observed in all of the configurations investigated. Because of their similarity in construction orientation, specimen configurations A and B had identical CTE along all the investigated axes, as shown in Table 1.1 In line with the fibre extrude direction, the CTE in the out of plane direction (z-axis) is approximately 64.7 m/ (mC), but only 52.7 m/ (mC) in the axial direction. In the transverse

direction, on the other hand, sample set C had the greatest CTE. These results correspond to the

fracture surface and its strain field as shown in Figure 2.5.

Table 1. 1: For various sample designations, linear thermal expansion as a function of

direction (Witkin D. B., 2017).

Specimen Configuration	CTE Axial (x)-direction (microns/(m °C)	CTE Transverse (y)-direction (microns/(m °C)	CTE Out-of-plane (z)-direction (microns/(m °C)
A	52.7	58.9	64.7
B	53.7	59.2	64.5
C	59.9	62.3	58.3
D	61.3	57.0	59.3
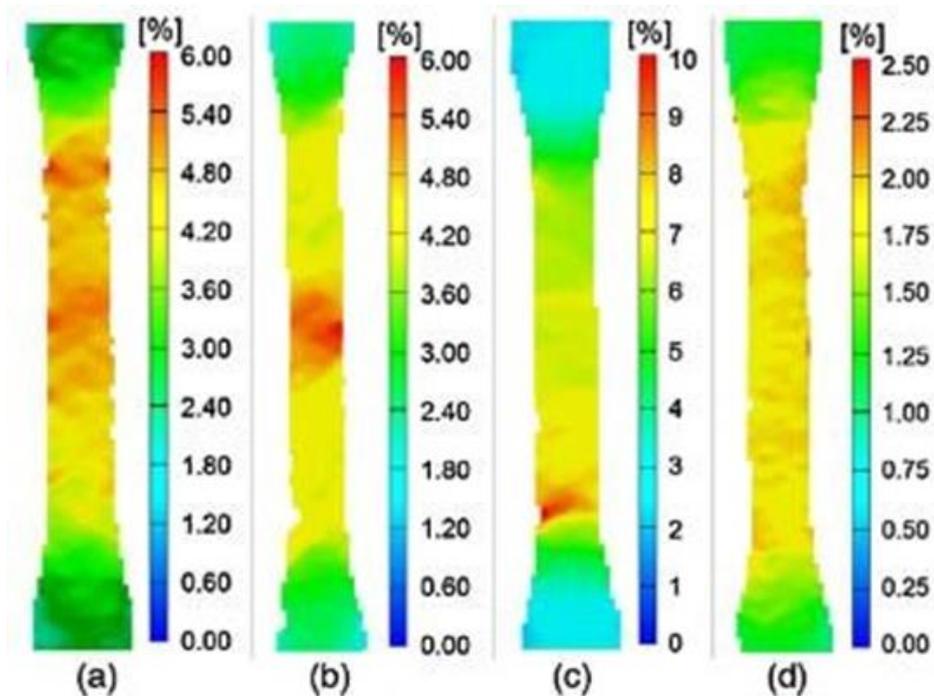
Figure 2. 5: DIC strain fields obtained prior to fracture Four different FDM materials were

tested: (a) flat-x (b) flat-y (c) edge (d) upright-z (McLouth T., 2017).

2.2.5 Interaction Between Reactive Groups (Carbonyl Group Presents on Monomer Chains)

The polarity of the monomers determines the intermolecular forces between them. The hydrogen bond is formed by the carbonyl group (amide group) located on the side chains of the monomers. Yang J. et al. (2002), studied that physical and chemical processes are involved in the degradation of acrylonitrile butadiene styrene rubber (NBR), resulting in a loss of physical and mechanical characteristic in which is supported by Zhao J. et al. (2015), statements. The major reason in having loss of those characteristics is due to small molecular additives migrating and volatilizing, and rubber molecular chains creep and relax, among other physical responses (Wang Q., 2009). The formation of oxygen-containing groups increases the polarity of rubber molecular chains, which has a significant impact on intermolecular interaction, energy distribution, and the mobility and flexibility of rubber chains, resulting in noticeable changes in the physical and chemical properties of NBR (Zeng D., 2016). Furthermore, the development of polar groups in rubber chains may have favorable or negative impacts on oxygen and other chemical species diffusion behaviours into rubber materials, promoting or inhibiting breakdown rates (Coronado M., 2014). Advanced experimental characterization methods, such as Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance spectroscopy, are used to understand changes in rubber materials at the molecular level in an indirect or qualitative way, especially for oxidation products, associated with physical or mechanical properties.

2.2.6 Adhesion

In a simple perspective, polymer adhesion is surface contact with coating, and the external environment, such as paints, influences their quality. The interatomic and intermolecular contact at the interface of two surfaces is known as adhesion. In automotive field, application of chemical groups at or near the interface, for example, influence adhesion between the polymer surface and

the paint substrate layer (Pijpers A. P., 2001). Adding an adhesion promoter, such as a chlorinated polyolefin (CPO), flame treating the polypropylene compounds, plasma treating the polypropylene to promote the creation of polar functional groups at the surface or blending in ethylene–propylene rubber (EPR), which forms a thermoplastic polyolefin, are all options for improving adhesion (Tang H., 2002). In the biomedical field, understanding adhesion principles is becoming increasingly important. Studies examine the breaking of links between human hepatoma cell lines and polymers such as polystyrene, polymethylmethacrylate, and polycarbonate, for example. The surface free energy of the polymer has been found to be the most important determinant in cell adhesion to polymer substrates, regardless of whether the surface has been coated by a protein layer (Zhao Q., 2004).

2.2.7 Toughness

The impact resistance of a plastic determines its toughness. It refers to a material's capacity to withstand fracture and deformation. Examining the region beneath the stress-strain curve for the specific polymer is a frequent technique to discuss the polymer's toughness. The mechanical test usually focuses on the polymer material's macroscopic qualities. Linear elasticity, non-reversible plastic deformation, and failure are all produced by increasing the amount of deformation over time while measuring the elastic constants strength (yield point), and toughness (fracture resistance) (Raos G., 2021). Raos G. et al. stated that polymer materials have a high toughness, which means they can withstand enormous and irreversible mechanical deformations by absorbing large quantities of energy without entirely breaking, and they may even repair when the stress is removed. Figure 2.6 depicts some of the major traits and mechanisms responsible for these qualities.
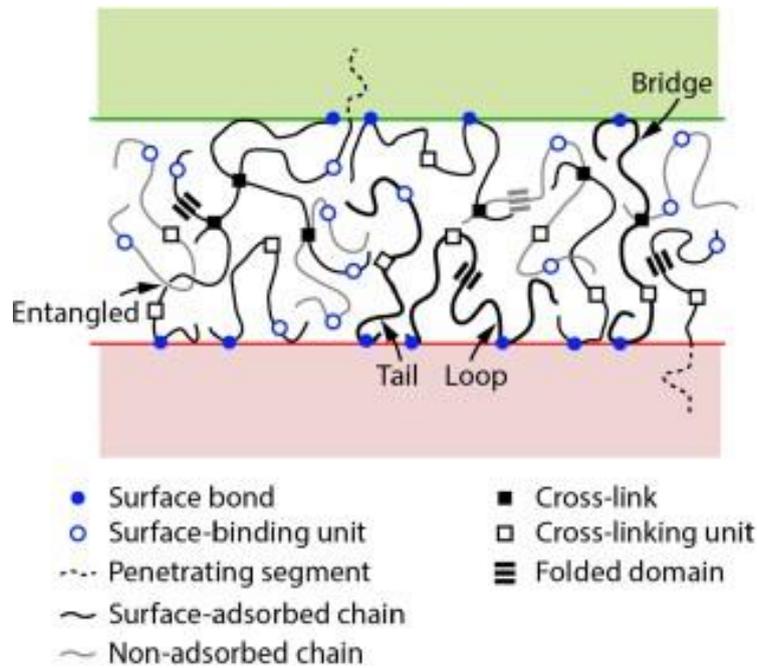
Figure 2. 6: The internal structure of an adhesive polymer film between two solid surfaces is depicted schematically, with molecular characteristics crucial to surface force production highlighted in which correspond to fracture toughness (Raos G., 2021).

2.2.8 Young's Modulus

It is the ratio of tensile stress and tensile strain. A recent work conducted by Rodrguez-Panes et al. compared the tensile mechanical characteristics of Polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) specimens generated using an FDM 3D printer. The impacts of infill density, layer thickness, and printing orientation on the mechanical characteristics of 3D printed specimens were examined in this work. The findings of this investigation revealed that the mechanical characteristics of ABS printed specimens varied less than those of PLA specimens. The mechanical characteristics of 3D printed specimens were most affected by infill density. The researchers discovered that the pattern and print orientation had no influence on the Poisson ratio and Young's modulus of elasticity of 3D printed ABS specimens based on the Figure 2.8 (Zou, 2016). Another study by Wickramasinghe et al. observed that infill density had the biggest influence on the mechanical characteristics of 3D printed specimens.

Meanwhile, in ABS specimens, both shear characteristics, modulus of elasticity and shear yield strength, varied substantially more than 30%. According to Mazzanti et al. and various researchers that have explored the mechanical characteristics of 3D printed specimens utilizing FDM technology and come with results similarly to Figure 2.7 as quoted by Nguyen H. T. (2022).
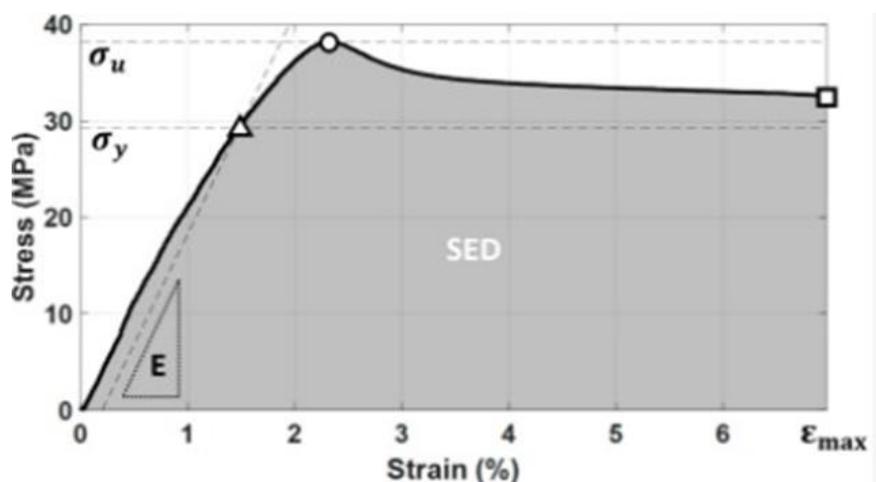
Figure 2. 7: A typical stress–strain curve derived from tensile tests performed on the specimens described in this article (Nguyen H. T., 2022).
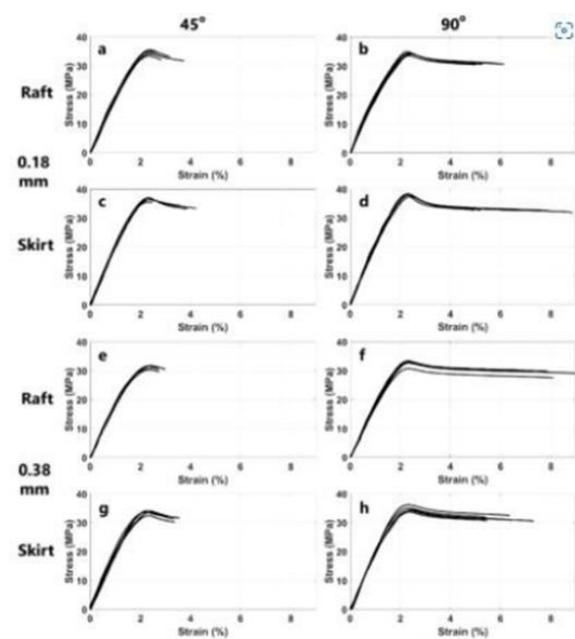
Figure 2. 8: Stress–strain curves of each set of inspected specimens were measured. Each type was evaluated with five specimens: (a) R-45-0.18 mm, (b) R-90-0.18 mm, (c) S-45-0.18 mm,

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(d) S-90-0.18 mm, (e) R-45-0.38 mm, (f) R-90-0.38 mm, (g) S-45-0.38 mm, and (h) S-90-

0.38mm (Nguyen H. T., 2022).

2.2.9 Elasticity

Polymer networks are made up of long polymer chains that are crosslinked to produce a massive three-dimensional macromolecule. All polymer networks have great elasticity, or the capacity to undergo substantial reversible deformations under relatively low applied stress. A polymer network is made up of long polymer chains that are crosslinked to produce a massive 3D macromolecule. High elasticity is the most distinguishing attribute of polymer materials, and it is linked to the most fundamental characteristics of perfect chains discussed in the previous lecture. Rubbers are extremely elastic polymer compounds that are commonly used in everyday life. Single-molecule of the elasticity of a single chain may be tested using Atomic Force Microscopy (AFM-FS) test. With an atomic-molecular spatial resolution, AFM can identify intermolecular forces. As a nondestructive testing approach, this nanomechanical characterisation methodology is widely used in a variety of applications, including those involving electronics, semiconductors, polymers, biology, and biomaterials (Caglayan, 2014). In related to that study, it measures the force required to keep two units of the same chain apart. The force-distance connection is nonlinear, and it may be modelled using a modified version of one of the traditional chain elasticity models, such as the freely rotating chain, freely jointed chain, or worm-like chain (Raos G., 2021).

2.2.10 Degradation

One of the primary elements that might negatively impact the quality of recycled plastic material is polymer degradation. A material degrading imply that it loses its capacity to be processed, its mechanical or thermal capabilities, its electrical and optical qualities, or its attractive and aesthetic features (Kometani, 2006). Because recycled and virgin polymers have

different viscosity and density when produced the desired products, polymer degradation during processing also lowers the productivity of the recycled material. Many elements, including shear stress, temperature, humidity, pH, the presence of oxygen, UV radiation, and the presence of other technical additions, have an impact on degradation (Sawaguchi, 2019). It is crucial to understand how different polymeric materials' end characteristics are affected by their numerous extrusions. However, only a limited number of scientific publications have so far focused on actually characterising variations to the features of biodegradable types of renewable materials following numerous treatments of these materials as cited by Beltran et al. (2019).

2.2.11 Photoluminescence

The Photoluminescence (PL) spectra of $BaSrTiO_3$ and $SrTiO_3$ CNs, which were captured at an excitation wavelength of 350 nm, are shown in Figure. The emission bands of $BaSrTiO_3$ and $SrTiO_3$ have maximum values at 426 nm and have intensities of approximately 3.4 104 and 1.98 104 counts/s, respectively as in Figure 2.9. An earlier study found that the weight ratio of the two thermoplastic polymers affects where the PL band of the TPU:TPO mix is located (Baibarac, 2021). The PL band of the TPU:TPO blends consequently occurs at 486 nm and 465 nm, respectively, when the TPU:TPO mass ratio is equal to 1:1 and 2:1. The exchange reaction between the two thermoplastic polymers is being used to explain this occurrence (Nila, 2021).
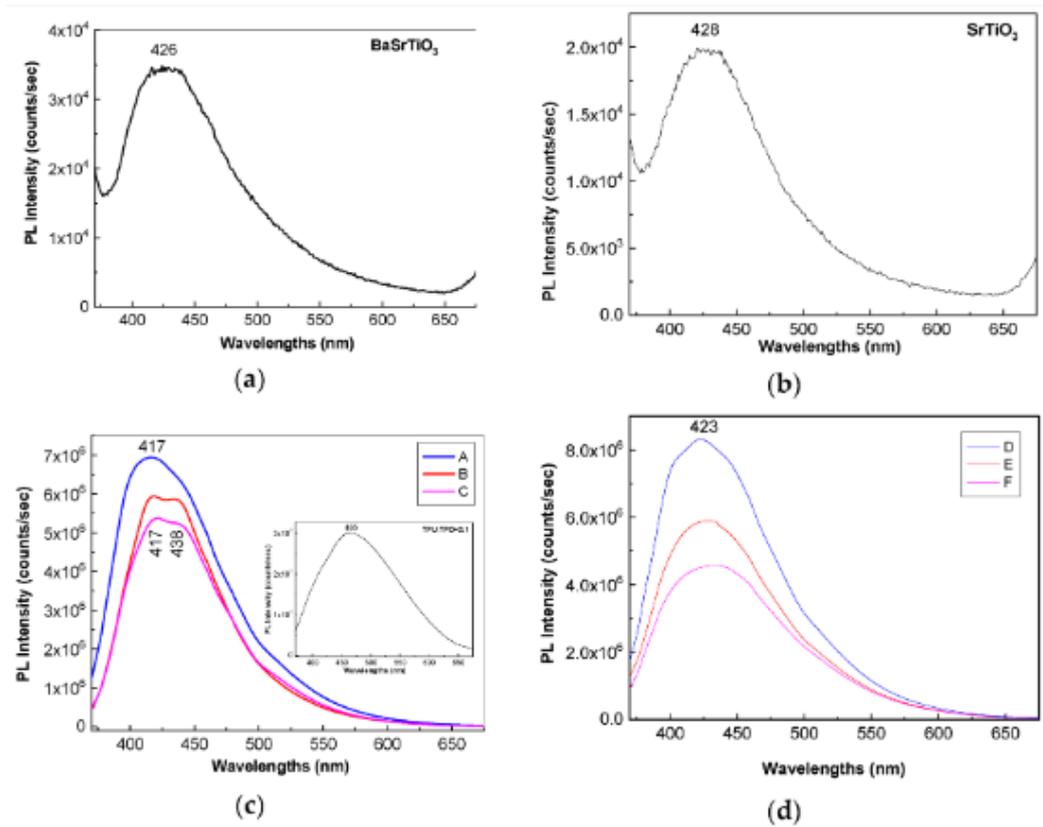
Figure 2. 9: PL spectra of BaSrTiO3, SrTiO3, and composites made of TPU:TPO thermoplastic polymers, CNs of type BaSrTiO3 (c), and SrTiO3 (b), respectively (d) (Smaranda et al., 2012).

2.3   Polymer Matrix Filament

Material extrusion printing, which accounts for most of the 3D printer market, is excellent for producing patient-specific implants and easy-to-scale manufacturing technologies. For body parts of reconstructive scaffold manufacturing, the material extrusion approach has not been fully researched. A thermal technique is used for filament fabrication rather than in chemical route because it produces solvent-free and environmentally friendly filaments with no adverse consequences (such as cell death) from solvent residuals. Thus, there is a simplest option to fabricate PMC filaments as the chemical route have inherent limitations, such as the difficult fabrication process associated with the leaching of solvent residues in the fabricated scaffolds; thus, they may not be appropriate for scaffold fabrication in hospital settings (Kim C. G., 2021). The thermoplastic biopolymers based on crystalline PLA or PCL are currently the most widely

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used "medical" filaments for FDM 3D printers. They have the features that medical devices and structures require, such as biodegradability and long-term durability. However, there are few filaments on the market that have qualities (texture, flexibility, and physical sensitivity) that may be used to replicate real tissues or organs. These are critical needs in the development of effective surgical teaching systems for surgeons and medical students using 3D printing technology. Thermoplastic polyurethanes (TPUs) with suitable design can be used as an alternative to medical filaments made of PCL and PLA. They have biocompatibility and hemocompatibility, according to the literature (Kucinska-Lipka J., 2017). Hot-melt HA/PCL filament fabrication as for example and the scaffolds produced by this approach are ongoing and yet very little information on the fabrication parameters for machines in research facilities is available (Zavrel F., 2022).

2.4 Fabrication Technique of Biomaterial Ceramics

2.4.1 Foam Replication

In fabrication of biomaterial ceramic, they all strive to create a structure with a porosity that is comparable to that of human composition. Taking fabrication of scaffold as example, the majority of bioactive glass ceramic-based scaffolds are made by utilizing the foam replication technique, which creates ceramic foams by saturating a polymer sponge with a bio-ceramic slurry. The sponge is then burned during a further heat-treatment process that also sinters the ceramic particles (Gabor A. G. et al., 2022). High porosity in this kind of scaffold is obviously linked to poor mechanical characteristics. The polymer burning method is an alternative that involves mixing organic fillers, which function as pore formers, with ceramic powders (Bellucci, 2011).

2.4.2 Sol-gel Synthesis

A first-generation biomaterial is a generation where the bioinert characteristics are altered using a variety of techniques, including adding additional bioactive qualities, modifying the surface composition and microstructure, or moving the biomaterial from the first to the second

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