CHAPTER 1

INTRODUCTION

1.1 Research Background

Plastic is a material comprised of a wide range of synthetic or semi-synthetic polymer typically derived from petrochemicals that are malleable and can be molded into desired objects. The rapid advancement of technology has improved quality of human-life significantly. Adversely, it has also doubled waste generation. According to a statistic, nearly 300 million tonnes of plastic wastes are produced annually (Vuleta, 2022). Poor practices of waste management and inefficient recycling technologies have exacerbated this environmental issue (Kibria et al., 2023). Therefore, the pursuit of renewable polymers for sustainable products acts as the drive for the progress of biopolymers in recent years (Okolie et al., 2023).

Polymers from renewable resources have gained significant attention due to the environmental awareness and the realization of limited petroleum resources. Biopolymers such as polylactic acid (PLA), chitosan, gelatin and polyhydroxyalkanoates (PHA) could offer several benefits as they are abundance in nature, non-toxic and less expensive (Mukherjee & Koller, 2023; Nicolescu et al., 2023; Guillén-Carvajal et al., 2023). Among other biopolymers, PHA has a special characteristic which is it being a thermoplastic polyester (Turco et al., 2021). PHA comprises of a group family of biodegradable polyester that are produced from various types of microorganisms for intracellular carbon and energy storage purposes (McAdam et al., 2020). Polyhydroxybutyrate (PHB) is a short chain length of PHA and the most commonly used in the commercial product due to its mechanical properties that are comparable with the petroleum-based plastic such as polypropylene and polyethylene (McAdam et al., 2020). Even though PHB has many desirable properties, there are myriad obstacles that need to be addressed such as its brittleness, thermal instability and tendency to crack and fracture (Ramos et al., 2022).

The mechanical performance and processability of PHB could be improved through several methods such as chemical modification, thermal and drawing process and blending with other natural or synthetic polymers (Yeo et al., 2018). Among these paths, the cheapest and most efficient way for obtaining new materials with improved mechanical performance is by blending with other natural or synthetic polymers. However, the synergistic composition between two constituent of polymers that will act as filler and matrix must be at optimal condition, so that both materials' properties could be fully utilized in accordance with the application.

Acrylate or methacrylate based resin monomer such as bisphenol A-glycidyl methacrylate (Bis-GMA), bisphenol A diglycidyl methacrylate ethoxylated (Bis-EMA), triethylene glycol dimethacrylate (TEDGMA) and urethane dimethacrylate (UDMA), will undergo a cross-linking process which is photopolymerization upon being exposed towards a light source (Bagheri & Jin, 2019). Among these resin, the former two could generate after-products of degradation that is said to be proven to have an estrogenic effect towards human's health (Bakopoulou et al., 2009). The by-product is called bisphenol-A (BPA). Therefore, UDMA is formulated as BPA free acting as an alternative to eliminate that risk (Szczesio-Wlodarczyk et al., 2021a). The selection of UDMA as a matrix and PHB as a filler using polymer blending technique is very crucial so that the properties of both materials could be utilized. Acrylate and methacrylate monomers can polymerize due to their vinyl functional group, which undergoes a radical polymerization (Gziut et al., 2023). The photoinitiator will generate reactive species when excited at specific wavelength in the UV spectrum. These reactive species initiate the polymerization of the monomers. Both monomers are commonly found in the 3D printing photopolymer resin.

Studies on 3D printing or also known as additive manufacturing have been progressing rapidly in medical sector (Aimar et al., 2019). It has been utilized to fabricate medical devices including implants, prostheses, orthoses and scaffolds (Kermavnar et al., 2021). This technology has a hidden potential that could revolutionize the way orthopedic surgeons treat their fracture-bone patient. Orthopedic cast is typically made up from fiberglass and plaster of Paris (PoP) (Ekanayake et al., 2023). However, there are several complications that could arise from the usage of traditional cast for instance inflammation due to the poor ventilation design, pressure sores as the cast may not well-fitted and thermal injury attributed from the cast removal (Guida et al., 2019). Therefore, personalized treatment for each individual patient could be executed especially for those who has uncommon anatomy by using 3D printing as a tool for the fabrication of cast (Y. Chen et al., 2020). In addition, it allows for the fabrication of intricate design according to specific needs of individual desire, economical approach for small-scale production and much shorter time for fabrication.

1.2 Problem Statement

Stereolithography (SLA) comprises of three key components which are photopolymer resin, SLA 3D printer and computer-aided design (CAD) file. Every commercialized resin has its own specific viscosity. The printability of a 3D structure highly depends on the viscosity of the photopolymer resin itself so that the resin must be able to flow back at the center of vat/tank for succeeding layer to continue printing.

Therefore, the viscosity of the resin must be within the range of printability to obtain a fine 3D printed structure.

In other aspect, the mechanical properties of 3D printed structures always undergo degradation by aging process over the time. Hence, polymer blending technique has always been utilized because it is the most convenient and cost-effective way in tailoring the materials' properties according to a desired application. However, the inclusion of another materials within photopolymer resin will disrupt the structural properties of the final 3D structures in terms of its degree of double bond conversion (DC), crystallinity index (CI), surface morphological and thermal behavior.

Conventional method of fabrication of an object has become a concern as not all materials fit wells with those process. The traditional technique of fabrication is more preferred due to its mass production. However, the problems arise when the products come with a complex geometry and ergonomic structures in particular arm cast for fracture-bone patient. This technique could not afford to attain a certain level of complexity. In addition, this technique also produces a lot of waste materials. Hence, a sustainable and efficient technology must be adopted to fabricate the arm cast.

Nowadays, bone fractures are common skeletal injuries that could happen to anyone across the age group. Conventionally, casting and splinting have been utilized to support and immobilize broken bones. However, this conventional casting has several complications such as pressure sores due to poor casting techniques, skin irritation caused by sweating and lastly compartment syndrome that is attributed from pressure concentrated around the tissue within limited space that hinder blood circulation.

Therefore, a new approach to treat a bone fractured patient is by utilizing SLA technique to tackle these issues. Nevertheless, the materials used are also crucial in the fabrication process since they have different properties. A fine and success of 3D printed structure must be defined and evaluated first through several measurements before fabricating a 3D printed arm cast. Information generated in this research will become a pioneer in delving into the potential of 3D printing technique especially, SLA as a tool to fabricate immobilization device which is a 3D printed arm cast for broken-arm patient.

1.3 Scope of Study

The scope of this research is only limited to study the influence of PHB powder as additives incorporated within UDMA based resin towards its printability and mechanical properties of 3D printed PHB/UDMA. The printability of different PHB content (wt. %) incorporated within UDMA resin blend was determined by measuring its viscosity. The samples were prepared using stereolithography (SLA) technique. 3D printed PHB/UDMA were characterized physicochemical in terms of its mechanical, structural and thermal. The characterization was done by using universal testing machine (UTM), impact testing machine, Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and thermogravimetric analysis (TGA).

The fabrication of 3D printed arm cast using additive manufacturing has been explored attributed to its flexibility of customization. Whilst the progress of 3D printed arm cast seems have been well documented especially using fused deposition modelling (FDM) technique, the utilization of SLA technique to fabricate a 3D printed arm cast using is none found in any study before.

1.4 Objectives

Therefore, the objectives of this study are:

1. To measure the viscosity of PHB/UDMA resin blend composition through viscometer for 3D printability.
2. To characterize different compositions of 3D printed of PHB/UDMA via mechanical properties comprise of tensile (Young's modulus, tensile stress and tensile strain) and impact between after a day and a month of aging by using statistical analysis.
3. To study structural properties using Fourier-transform infrared spectroscopy (FTIR) for degree of double bonds conversion (DC), x-ray diffraction (XRD) for crystallinity index (CI), field emission scanning electron microscopy (FESEM) for surface morphological, and thermogravimetric analysis (TGA) for thermal behaviour.
4. To fabricate a 3D printed arm cast according to a selected composition of PHB and UDMA polymer blend.

1.5 Thesis Layout

Overall, the contents of this thesis writing will contain introduction, literature review, methodology, results and discussion of 3D printability and mechanical properties of PHB/UDMA resin blend in medical application for broken-arm patient.

In Chapter 1, the introduction is written as a basic concept for better comprehension of the thesis title. It introduces the main materials that are used in this research, which are PHB powder and UDMA based resin. The problem statement is also written in this part to emphasize the importance of conducting this research. Next, the objectives and scope of the study will avail the cognizance to justify the selection of materials based on scientific purposes.

Chapter 2 discusses the relation of the previous studies on the physical and chemical properties, synthesis route, benefits and challenges of PHB application. The classification of additive manufacturing into several terminologies based on their mechanism has been also elaborated in this part. Among those techniques, vat-photopolymerization has been emphasize more on its type of machines, polymerization mechanism and monomers used in the polymerization. Lastly, the integration of 3D printing in medical/health sector has also been explained further in this chapter.

Chapter 3 describes the methodology of this research of which is divided into three phases. The first would be the PHB/UDMA resin blend formulation, followed by the characterization of 3D printed PHB/UDMA and then the fabrication of 3D printed arm cast.

Chapter 4 discusses the data obtained from several measurements which are viscosity of the PHB/UDMA resin blend and their properties of different composition of PHB/UDMA comprised of mechanical, morphological, structural, crystallinity and thermal analysis. Last but not least, the fabrication of selected PHB/UDMA resin blend for medical application which is 3D printed arm casting will be elaborated more at the end of this chapter.

Finally, the last chapter of the thesis, which is Chapter 5, is the summarization according to the research's findings whilst the future recommendations have been also suggested for a better comprehension and understanding about this research.