CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

In this research, the methodology is divided into three phases. They are Phase 1: PHB/UDMA resin blend formulations; Phase 2: 3D printing of PHB/PMMA for the characterizations; and Phase 3: Fabrication of 3D printed arm cast using selected composition. Table 3.1 shows the list of apparatus and materials, meanwhile Table 3.2 shows the list of equipment used in this research.

3.2 Apparatus and Materials

Table 3.1: List of Apparatus and Materials.

No.	Apparatus/Materials	Amount/Quantity
1.	Magnetic bar	6
2.	Amber Vials	6
3.	Desiccator	1
4.	Dropper	1
5.	Weighing boat	6
6.	Polyhydroxybutyrate (PHB) powder	100g
7.	UDMA resin	200g

Table 3.2: List of Equipment.

No.	Equipment	Brand/Manufacturer/City/Country
1.	Viscometer	DVNext Rheometer, AMETEK Brookfield, Middleborough, MA, USA
2.	Universal testing machine (UTM)	Instron 5566, Instron Corporation, Norwood, MA, USA
3.	Impact testing machine	Instron Ceast 9050, Instron Corporation, Norwood, MA, USA
4.	Fourier-Transform Infrared (FTIR)	Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA
5.	Field-Emission Scanning Electron Microscopy (FESESM)	JSM-IT800 Schottky, Jeol Ltd., Akishima, Tokyo, Japan
6.	X-Ray Diffraction (XRD)	Miniflex 600, Rigaku Corporation, Akishima Tokyo, Japan
7.	Thermogravimetric Analysis (TGA)	TGA/DSC 3+, Mettler Toledo, Columbus, OH, USA
8.	SLA 3D printer	Form 3+, Formlabs, Somerville, MA, USA
9.	Ultraviolet (UV) cure machine	Wash & Cure Machine 2.0, Anycubic, Shenzhen, China

3.3 Phase 1: PHB/UDMA Resin Blend Formulation

3.3.1 Preparation of PHB/UDMA Resin Blend

PHB powder bought from Biomer Biopolyesters (Germany) was used as additives while UDMA resin was purchased from Formlabs (United States). 20g of UDMA resin was measured by using analytical balance and poured into each of amber vial. Then, PHB powder were weighed according to their composition shown in Table 3.3 and put into the vials. The solution mixture was then stirred using magnetic stirrer at room temperature and 300 rpm. After leaving the solution stirring for two hours, the homogenous mixture solution was ready for viscosity measurement.

Table 3.3: Weight Percentage (%) of PHB Incorporated within UDMA Resin.

Name	Mass (g)	
	PHB	UDMA
0 wt. % of PHB/UDMA	0.00	20.00
3 wt. % of PHB/UDMA	0.60	20.00
7 wt. % of PHB/UDMA	1.40	20.00
11 wt. % of PHB/UDMA	2.20	20.00

3.3.2 Viscosity of PHB/UDMA Resin Blend

The resulting solution mixture comprised of four amber veils; 0, 3, 7 and 11 wt. % of PHB/UDMA resin blends were undergone viscosity measurement using DVNext rheometer. The spindle size and speed were equipped with RV-04 and at 50 rpm respectively. Figure 3.1 shows the measurement set-up of the equipment.

Figure 3.1: Viscosity Measurement of 11 wt. % of PHB/UDMA Resin Blend Formulation.

3.4 Phase 2: 3D Printing and Characterizations of 3D Printed PHB/UDMA

The design of 3D model for each characterization was constructed in computer-aided design (CAD) software called Blender and saved as standard-triangulated language (.stl) file. Then, a slicer called PreFrom was used to convert the .stl file into .Form file type. Table 3.4 shows the printing parameters set-up in the Preform software.

Table 3.4: The Optimized Parameter Settings for PHB/UDMA Resin Blends.

Parameters	Value
Layer thickness (mm)	0.05
Normal exposure time (s)	60
Bottom exposure time (s)	60
Off time (s)	1
Bottom layers	8

The resin blends that had been formulated were used to print the varied composition of PHB/UDMA by using SLA 3D printer for mechanical, structural, morphological and thermal characterizations. After printing process, the samples were washed and cleaned with isopropanol to remove any uncured resin. The samples were then cured at 60 °C for an hour using ultraviolet (UV) cure machine. SLA 3D printer and UV cure machine are shown in Figure 3.2.

Figure 3.2: UV Cure Machine (Left) and SLA 3D Printer (Right).

Then, the 3D printed samples were left for 24 hours inside a desiccator at room temperature. After that, the samples were tested for tensile and impact measurements by using UTM and impact testing machine, respectively for mechanical properties. The

3D printed samples were also analyzed using FESEM, FTIR, XRD and TGA as shown in Figure 3.3.

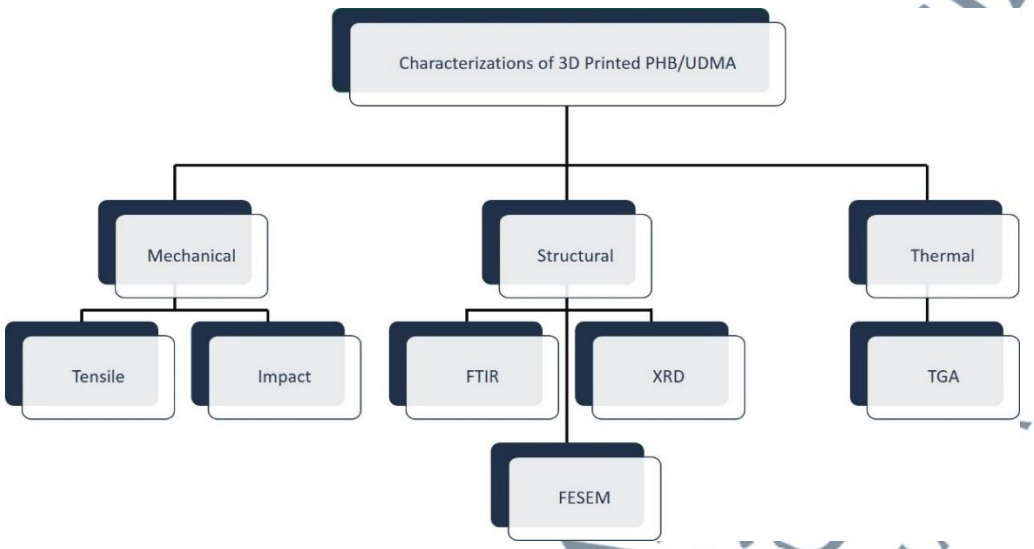

Figure 3.3: The Characterizations of 3D Printed UDMA and Varied Compositions of PHB/UDMA.

3.4.1 Tensile

Tensile properties such as tensile stress, tensile strain and Young's modulus were determined by using UTM. The machine was equipped with a crosshead speed of 5 mm/min and loaded with 10 kN load cell. The sample was designed concordance to the guidelines provided by American Society for Testing and Materials, ASTM D-638 (Type-V). Tensile tests were measured using a dog-bone shape according to ASTM D-638 (63.5 mm × 9.53 mm × 3.2 mm). Triplicate samples were printed for each composition of PHB/UDMA resin blends. A total of 24 samples obtained for tensile measurements and half of them represent for after a day and 30 days of aging. The data obtained through Blue Hill software. Figure 3.4 shows the tensile samples of 3D printed PHB/UDMA at different compositions before tested.

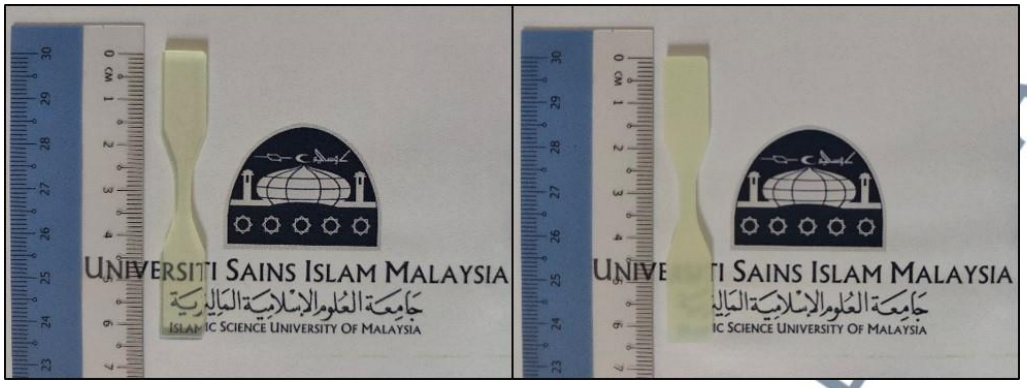

Figure 3.4: Tensile Samples of 3D Printed Pure UDMA (Left) and 3D Printed of 11 wt. % PHB/UDMA.

3.4.2 Impact

Fracture toughness or impact strength were measured by using impact testing machine with nominal impact energy at 11 J. The sample data set were also the same as tensile measurement, where 12 samples were prepared each for after a day and 30 days of aging. The sample was designed and printed according to American Society for Testing and Materials, ASTM D-256. Impact tests were measured using a rectangular shape with a V-notch according to ASTM D-256 (63.5 mm × 12.7 mm × 3.2 mm). Figure 3.5 shows the impact samples of varied 3D printed PHB/UDMA before tested.

Figure 3.5: The Impact Samples for 3D Printed Pure UDMA and Varied Composition of PHB/UDMA.

3.4.3 Fourier Transform Infrared (FTIR)

A Fourier Transform Infrared spectrometer was used to analyze absorption spectra within a range from 400 cm^{-1} until 4000 cm^{-1} of PHB powder, UDMA resin and varied composition of 3D printed PHB/UDMA. An absorption band of 1637 cm^{-1}, corresponding to C=C double bonds in the methacrylate groups, was used for the quantitative determination of unreacted methacrylate groups. Meanwhile, the peak intensities were compared to an internal standard, the C-C aromatic absorption band at 1608 cm^{-1} which did not participate in the polymerization reaction. The absorption at those peaks were also utilized to evaluate the degree of double bond conversions (DC %) according to the following Equation (3.1) (Moldovan et al., 2019):

$$\text{Degree of conversion (\%)} = \left[1 - \left(\frac{(1637\ cm^{-1}/1608\ cm^{-1})}{(1637\ cm^{-1}/1608\ cm^{-1})}\right)\right] \times 100 \quad (3.1)$$

3.4.4 Field-Emission Scanning Electron Microscope (FESEM)

Field Emission Scanning Electron Microscope (FESEM) was used to obtain surface morphology of 3D printed PHB/UDMA. FESEM images were acquired at an accelerating voltage of 0.50 kV under 1000X. The surface morphological was used to determine the miscibility of the polymer blend between PHB particles and UDMA matrix.

3.4.5 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) was utilized to evaluate the degree of crystallinity of PHB powder and varied of 3D printed PHB/UDMA. The instrument was operated under a voltage of 40 kV, a current of 15 mA and Cu K_α radiation (λ=0.154 nm). The range

angle for scanning was from 2.5° until 30° with a 10°s/step. The crystallinity index (CI) for PHB powder and 3D printed PHB/UDMA were calculated using OriginPro software according to the Equation (3.2):

$$\text{Crystallinity Index (\%)} = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks}} \times 100 \quad (3.2)$$

3.4.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out with a Mettler-Toledo TGA/DSC 3+ system. All analyses were performed with a 10 mg sample in aluminum pans under a dynamic nitrogen atmosphere between 30 and 700 ℃. The experiments were ran at a scanning rate of 20 ℃/min.

3.4.7 Statistical Analysis

Using the Statistical Package for the Social Sciences (SPSS v.21), tensile properties and impact strength measurements were statistically analyzed. After determining that the data were in line with a normal distribution ($p > 0.05$), two-way analysis of variance (ANOVA) was used to examine the relationship between the compositions of PHB content (wt. %) within UDMA based resin and the aging duration of varied 3D printed PHB/UDMA towards mechanical properties.

3.5 Phase 3: Fabrication of 3D Printed Arm Cast

7 wt. % of PHB/UDMA resin formulations was selected according to the data analysis acquired from Phase 2. A patient model was instructed to maintain his elbow on the relative support whilst his fingers were on the hand support for at least 60 s to acquire 3D mesh. Then, the 3D mesh was continued for further reconstruction in the 3D software (Blender). During this stage, the generation of holes created to increase

ventilation to avoid irritation instead of conventional cast that fully was encased around the treated area. The fabrication of the 3D printed arm cast had been performed by using SLA 3D printer.

3.6 Flow Chart of Research

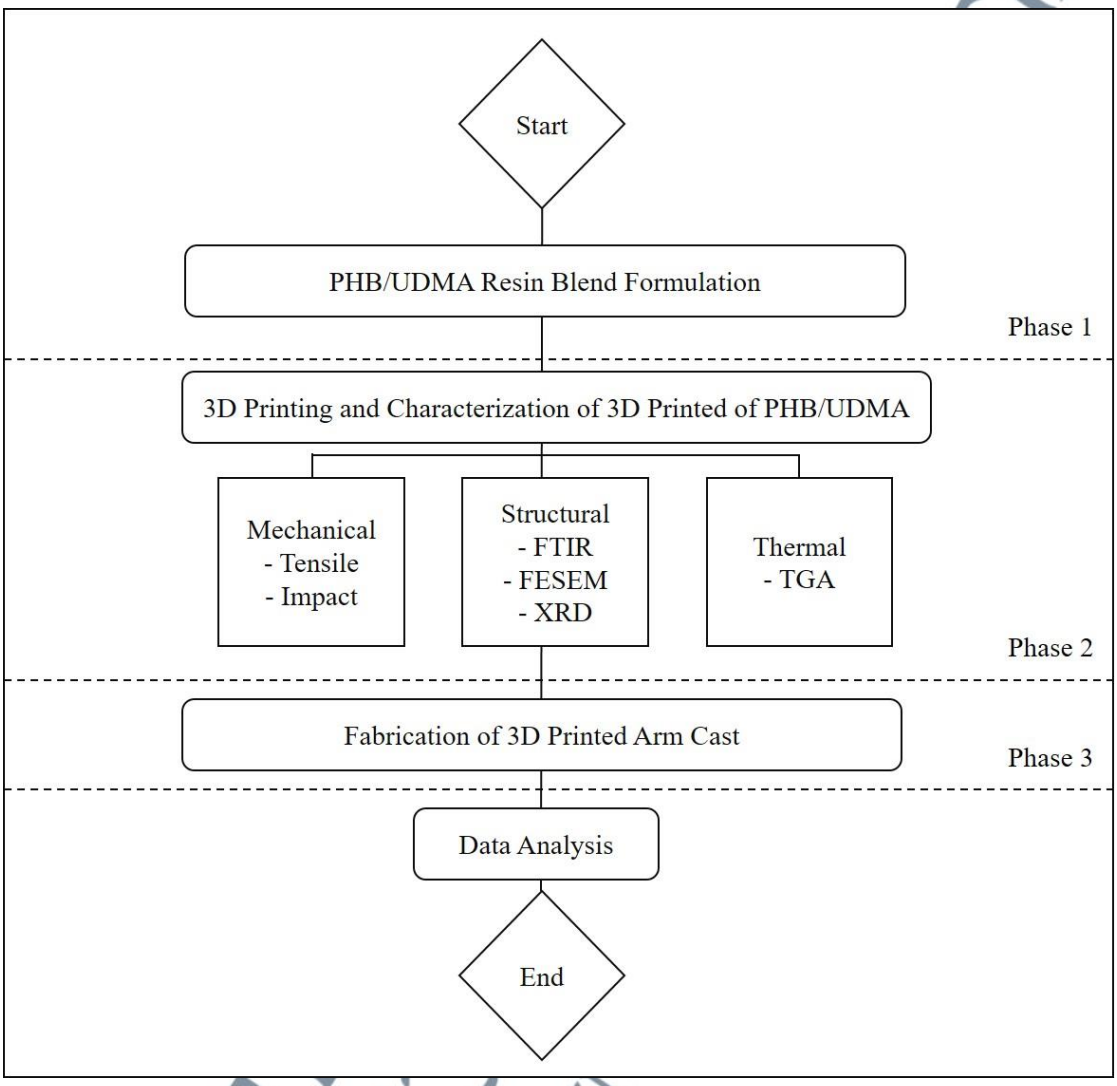

Figure 3.6: The Flow Chart of Research.