



Faculty of Resource Science and Technology

**Fabrication of Polylactic Acid/Wax/Polyethylene Glycol Composite
Filament for Fused Deposition Modeling (FDM)**

Mohammad Rahmat bin Derise

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Fabrication of Polylactic Acid/Wax/Polyethylene Glycol Composite Filament
for Fused Deposition Modeling (FDM)

Mohammad Rahmat bin Derise

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DECLARATION

I hereby declare that all the work presented in the thesis entirely my own work. The thesis has not been accepted for any degree and is not concurrently submitted in the candidature of any other degree.



Mohammad Rahmat bin Derise

Date: 15 June 2020

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ABSTRACT

Three-dimensional (3D) printing is an emerging technology that can be used to build a complex 3D object with low cost for prototyping, modeling or production via solidification or deposition. Waxes are usually used in the manufacturing of 3D objects specifically involving molding and casting. The lost-wax casting process is extensively utilized for manufacturing metal alloy objects from automotive parts to fine jewellery. However, waxes are only useful for the manufacturing of molds and not the end products. Therefore, the aims of this study to develop a new build material for fused deposition modeling (FDM) 3D printer by utilizing polylactic acid (PLA) as the matrix, wax as filler material and polyethylene glycol (PEG) as the plasticizer. The effects of wax and polyethylene glycol loading on tensile properties and characteristics of PLA/wax composites were investigated. Tensile properties of PLA/wax composites were determined according to ASTM D638 and for characterization, the morphology of the composites was analyzed via Scanning Electron Microscopy (SEM), water absorption (ASTM D570), melting point determination (MS-ISO 3146:2004) and melt flow index (MFI) (ASTM D1238). The tensile properties of PLA/wax composites decreased with the increase of the wax loading. Results showed significant improvement in elongation at break while tensile strength and elastic moduli decreased with increasing PEG content. The SEM micrographs show the PLA phase becoming discontinuous as the wax loading increases. The addition of PEG improves the compatibility between PLA and wax and the composites become more homogenous. PLA/wax with addition 5 wt.% and 8 wt.% PEG was selected since it showed good tensile properties and characteristics. Both composites were successfully extruded at 230°C in filament production with filament diameter 1.73 mm (PLA/wax/5 wt.% PEG) and 1.71 mm (PLA/wax/8 wt.% PEG). A cube was successfully printed with printing and platform temperature 180°C and

50°C respectively via FDM by using these two composites. The quality of 3D cube printed using the selected composites was comparable with the control (commercial PLA filament and neat PLA filament). However, some layers show poor bonding between adjacent layer and layer thickness variation defects that cause by inconsistent filament diameter. Therefore, it is important to further the study on optimization of extrusion parameters during filament production to produce consistent filament diameter since inconsistent diameter will affect the printing quality.

Keywords: 3D printing, fused deposition modeling (FDM), PLA/wax composites, polyethylene glycol (PEG)

***Pembuatan Komposit Polilaktik Asid/Waks/Polietilen Glikol Filamen untuk Permodelan
Depositi Bercampur***

ABSTRAK

Percetakan tiga dimensi (3D) adalah teknologi baru yang boleh digunakan untuk membina objek 3D kompleks dengan kos rendah untuk prototaip, pemodelan, atau pengeluaran melalui pemejalan atau pemendapan. Waks biasanya digunakan dalam pembuatan objek 3D yang khusus melibatkan pencetakan dan pemutus. Proses pemutus waks yang hilang digunakan secara meluas untuk pembuatan objek aloi logam dari bahagian automotif hingga barang kemas yang halus. Walau bagaimanapun, waks hanya berguna untuk pembuatan acuan dan bukan produk akhir. Oleh itu, matlamat kajian ini untuk membangunkan bahan binaan baru untuk pemodelan depositi bercampur (FDM) pencetakan 3D dengan menggunakan polilaktik asid (PLA) sebagai matriks, waks sebagai bahan pengisi dan polietilen glikol (PEG) sebagai pemplastik. Kesan penambahan waks dan polietilen glikol pada sifat-sifat tegangan dan ciri-ciri komposit PLA/waks telah disiasat. Ciri-ciri komposit PLA/waks ditentukan mengikut ASTM D638 dan untuk penciriannya, morfologi komposit dianalisis melalui Mikroskop Pengimbasan Elektron (SEM), penyerapan air (ASTM D570), penentuan titik lebur (Malaysian Standard ISO 3146: 2004) dan indeks aliran leburan (MFI) (ASTM D1238). Ciri-ciri tegangan PLA/waks komposit menurun dengan meningkatnya penambahan waks. Kemudian, keputusan menunjukkan peningkatan yang ketara dalam pemanjangan pada pemecahan manakala kekuatan tarik dan elastik moduli menurun dengan kandungan PEG yang semakin meningkat. Mikrograf SEM menunjukkan fasa PLA menjadi tidak berterusan apabila kandungan waks meningkat. Penambahan PEG meningkatkan keserasian antara PLA dan waks dan komposit menjadi

lebih homogen. PLA/waks dengan tambahan 5% berat dan 8% berat PEG dipilih kerana ia menunjukkan ciri-ciri dan sifat-sifat tegangan yang baik. Kedua-dua komposit berjaya diekstrud pada suhu 230°C dalam pengekstrusan filamen dengan filamen diameter 1.73 mm (PLA/waks/5 wt.% PEG) dan 1.71 mm (PLA/waks/8 wt.% PEG). Kubus berjaya dicetak dengan suhu percetakan dan platform 180°C dan 50°C masing-masing melalui FDM dengan menggunakan kedua-dua komposit ini. Kualiti kubus 3D yang dicetak menggunakan komposit yang dipilih adalah sebanding dengan kawalan (PLA komersial PLA filamen). Walau bagaimanapun, beberapa lapisan menunjukkan ikatan yang lemah antara lapisan yang berdekatan dan ketebalan lapisan tidak sama yang disebabkan oleh diameter filamen yang tidak konsisten. Oleh itu, adalah penting untuk mengkaji lebih lanjut mengenai pengoptimuman parameter pengekstrusan semasa penghasilan filamen untuk menghasilkan diameter filamen yang konsisten kerana diameter yang tidak konsisten akan menjejaskan kualiti percetakan.

Kata kunci: Pencetakan tiga dimensi, pemodelan deposisi bercampur, komposit PLA/waks, polietilen glikol

TABLE OF CONTENTS

	Page
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iii
ABSTRAK	v
TABLE OF CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREVIATION	xvi
CHAPTER 1: INTRODUCTION	1
1.1 Introduction	1
1.2 Problem statement	2
1.3 Objectives	3
1.4 Scope of the study	4
CHAPTER 2: LITERATURE REVIEW	5
2.1 3D printing.....	5
2.2 Different 3D printing technologies.....	6
2.2.1 Selective Laser Sintering (SLS).....	6
2.2.2 Stereolithography (SLA).....	7

2.2.3 Fused Deposition Modeling (FDM).....	9
2.3 Common filament material for fused deposition modeling (FDM)	12
2.3.1 Polylactic acid (PLA).....	12
2.3.2 Other common materials	12
2.4 Previous researches on composite filaments that utilize wax as a constituent materials	17
2.5 Previous researches on polylactic acid (PLA) composites with the addition of polyethylene glycol (PEG) as plasticizer	18
2.6 Filler and plasticizer in polymer composites	19
2.7 Parameters for fused deposition modeling (FDM) filament.....	22
2.7.1 Tensile testing	22
2.7.2 Scanning Electron Microscopy (SEM)	24
2.7.3 Water absorption	25
2.7.4 Melting point.....	26
2.7.5 Melt flow index (MFI)	27
2.8 Filament extrusion	28
2.9 Tensile properties and characteristics of common commercial filament for fused deposition modeling (FDM).	30
CHAPTER 3: MATERIALS AND METHODS	32
3.1 Introduction of the methodology	32

3.2 Composites preparation	34
3.3 Preparation of test specimen.....	34
3.4 Tensile testing.....	36
3.5 Scanning Electron Microscopy (Morphology)	38
3.6 Water absorption test	38
3.7 Determination of melting point	38
3.8 Melt Flow Index (MFI) test	38
3.9 Filament extrusion	41
3.10 3D printing via FDM technique by using PLA/wax composites	41
3.11 Quality of 3D printed object by using PLA/wax composites (dimensional accuracy layer height consistency)	41
CHAPTER 4: RESULTS AND DISCUSSION.....	42
4.1 Preparation of PLA/wax composites	42
4.1.1 Effect of polyethylene glycol loading (PEG) on the feedstock of PLA/wax composites	42
4.1.2 Effect of wax loading on the feedstock of PLA/wax composites	45
4.2 Tensile properties of PLA/wax composites.....	46
4.2.1 Effect of polyethylene glycol (PEG) loading on the tensile properties	47
4.2.2 Effect of wax loading on the tensile properties.....	52
4.3 Scanning Electron Microscopy (SEM) analysis (morphological properties).....	55

4.3.1 Effect of wax loading on the fractured surface of composites.....	55
4.3.2 Effect of polyethylene glycol (PEG) on the fractured surface of composites.....	59
4.4 Water absorption test	60
4.4.1 Effect of polyethylene glycol (PEG) loading on the water absorption	60
4.4.2 Effect of wax on the water absorption	63
4.5 Determination of melting point	65
4.6 Melt Flow Index (MFI) test	68
4.7 Filament extrusion	72
4.8 3D printing via FDM technique by using PLA/wax/PEG composites.....	75
4.9 Quality of 3D printed object by using PLA/wax composites (dimension error and layer height consistency)	76
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	81
5.1 Conclusions	81
5.2 Recommendations	82
REFERENCES	84
APPENDICES.....	94

LIST OF TABLES

		Page
Table 2.1	Printing parameters of common filament materials for FDM (Horvath, 2014)	16
Table 2.2	The role of each binder system constituent for FDC filament (Onagoruwa et al., 2001)	18
Table 2.3	Standard tests of tensile testing (McKeen, 2012)	23
Table 2.4	Standard tensile strength and characteristics of FDM filament	31
Table 3.1	Composition of composite designation to study the effect of polyethylene glycol (PEG) loading	36
Table 3.2	Composition of composite designation to study the effect of wax loading	36
Table 4.1	Tensile properties of PLA/wax composites with different content of polyethylene glycol (PEG)	48
Table 4.2	Tensile properties of PLA/wax composites with different content of wax	53
Table 4.3	Water absorption of PLA/wax composites with different polyethylene glycol (PEG) content for 30 days	62
Table 4.4	Water absorption of PLA/wax composites with different wax content for 30 days	64
Table 4.5	Melting point (range) of PLA/wax composites with the addition of different polyethylene glycol (PEG) content	66
Table 4.6	Melting point (range) of PLA/wax composites with different wax content	68
Table 4.7	Melt flow index (MFI) of PLA, PLA/wax composite and PLA/wax composites with different PEG content	70
Table 4.8	MFI of PLA/wax composites with different wax content	72
Table 4.9	The extrusion temperature and cooling method for the production of filament	74

Table 4.10	3D printing parameters for commercial PLA filament, neat PLA and PLA/wax composites	76
Table 4.11	Dimensional errors of 3D printed cube (10 mm × 10 mm × 10 mm). Samples measurements (averaged results), dimensions in mm	77
Table 4.12	The layer height of 3D printed cube (outer surface)	78

LIST OF FIGURES

	Page
Figure 2.1	Selective laser sintering (SLS) technology (Junji, 2013) 7
Figure 2.2	Stereolithography technology (Junji, 2013) 8
Figure 2.3	Fused deposition modeling (FDM) technology (Bual & Kumar, 2014) 10
Figure 2.4	The typical tensile test specimen, showing a reduced gage section and enlarged shoulder (Davis, 2004) 23
Figure 2.5	Instron Universal Testing Machine and example of molded and cut film test specimen (McKeen, 2012) 24
Figure 2.6	Schematic diagram of the filament extruder used for filament production (Nájera et al., 2018) 28
Figure 2.7	Filament extrusion line process 29
Figure 3.1	Flowchart summary of the methodology for the study 33
Figure 3.2	The fabrication process of PLA/wax/PEG composites 35
Figure 3.3	Dimensions of tensile test specimens (ASTM D638 Type IV) 37
Figure 3.4	Setup for extrusion of filament 40
Figure 4.1	PLA/wax composites prepared by melt blending method with different percentage of plasticizer. (a) neat PLA (control), (b) PLA/PEG composites (100/0/5), (c) PLA/wax (95/5/0), (d) PLA/wax/PEG (95/5/3), (e) PLA/wax/PEG (95/5/5), (f) PLA/wax/PEG (95/5/8), (g) PLA/wax/PEG (95/5/10), (h) PLA/wax/PEG (95/5/13), (i) PLA/wax/PEG (95/5/15) 44
Figure 4.2	PLA/wax composites prepared by melt blending method with different wax loading. (a) PLA/wax composite (95/5/0) with no addition of polyethylene glycol (PEG), (b) PLA/wax composite (95/5/5) with the addition of 5 wt.% PEG, (c) PLA/wax composite (90/10/5) with the addition of 5 wt.% PEG, (d) PLA/wax composite (85/15/5) with the addition of 5 wt.% PEG 46
Figure 4.3	Example of a tensile test specimen. (a) neat PLA and (b) PLA/wax composites with addition 5 wt.% of PEG 47

Figure 4.4	Effect of the polyethylene glycol (PEG) loading on the tensile strength of the PLA/wax composites	49
Figure 4.5	Effect of the polyethylene glycol (PEG) loading on the elastic moduli of the PLA/wax composites	50
Figure 4.6	Effect of the polyethylene glycol (PEG) loading on the elongation at break of the PLA/wax composites	52
Figure 4.7	Effect of wax loading on the tensile strength of PLA/wax composites	53
Figure 4.8	Effect of wax loading on the elastic Moduli of PLA/wax composites	54
Figure 4.9	Effect of wax loading on the elongation at break of PLA/wax composites	55
Figure 4.10	SEM micrographs of (a) neat PLA and (b) PLA/PEG (100/05)	56
Figure 4.11	SEM micrographs of (a) PLA/wax composite (95/5/0), (b) PLA/wax/PEG composite (95/5/3), (c) PLA/wax/PEG composite (95/5/5), (d) PLA/wax/PEG composite (95/5/8), (e) PLA/wax/PEG composite (95/5/10), (f) PLA/wax/PEG composite (95/5/13) and (g) PLA/wax/PEG composite (95/5/15)	58
Figure 4.12	SEM micrographs of (a) PLA/wax composite (95/5/0), (b) PLA/wax/PEG composite (95/5/5), (c) PLA/wax/PEG composite (90/10/5) and (d) PLA/wax/PEG composite (85/15/5)	60
Figure 4.13	The effect of polyethylene glycol (PEG) loading on the water absorption of PLA/wax composite for 30 days	62
Figure 4.14	Water absorption from day 1 until day 30 of PLA/wax composites at different polyethylene (PEG) loading	63
Figure 4.15	The effect of wax loading on the water absorption of PLA/wax composites for 30 days	64
Figure 4.16	Water absorption from day 1 until day 30 of PLA/wax composites at different wax loading	65
Figure 4.17	Melting point (range) of PLA/wax composites with the addition of different wt.% of PEG	67
Figure 4.18	Melting point of PLA/wax composites with the addition of 5wt% PEG	68

Figure 4.19	Effect of PEG loading on the MFI values of PLA/wax composites	70
Figure 4.20	Effect of wax loading on the MFI of PLA/wax composites	72
Figure 4.21	A filament of FDM technology extruded via single screw extruder (a) neat PLA filament, (b) PLA/wax/PEG (95/5/5) filament and (c) PLA/wax/PEG (95/5/8) filament	74
Figure 4.22	The SEM micrographs of the outer surface of 3D printed cube by using (a) commercial PLA filament, (b) neat PLA, (c) PLA/wax composites (95/5/5 wt.% PEG) and (d) PLA/wax composites (95/5/5 wt.% PEG)	79

LIST OF ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
CAD	Computer aided design
DLP	Digital light projection
EBM	Electron beam melting
FDM	Fused deposition modeling
kN	Kilonewton
LOM	Laminated object manufacturing
MPa	Mega Pascal
PC	Polycarbonate
PEG	Polyethylene glycol
PLA	Polylactic acid
PPSF	Polyphenylsulfone
SLA	Stereolithography apparatus
SLS	Selective laser sintering
STL	Standard Tessellation Language
T _g	Glass transition temperature
T _m	Melting point
UV	Ultraviolet
°C	Degree Celsius
2D	Two dimensional
3D	Three dimensional

%	Percentage
wt. %	Weight percentage
cm	centimeter
mm	millimeter

CHAPTER 1

INTRODUCTION

1.1 Introduction

Recently, three-dimensional (3D) printing is an emerging technology that can be used to build a complex 3D object with low cost for prototyping, modeling, or production via solidification or deposition (Cuiffo et al., 2017). The concept of 3D printing is straightforward where a 3D model is formed by starting with nothing where the build material has added a layer at a time until the 3D object is completed. 3D printing technology is also known as additive manufacturing (Horvath, 2014; Christiyan et al., 2016). There are different 3D printing technologies that were developed and the common techniques are stereolithography apparatus (SLA), fused deposition modeling (FDM) and selective laser sintering (SLS) (Fafenrot et al., 2017).

Among these three technologies, FDM is one of the most popular 3D printing technology that works with low-cost thermoplastic such as polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) as build material (Dudek, 2013). The build material for FDM is usually supplied in filament form, where the thermoplastic filament is extruded via a heated liquefied nozzle using feedstock filaments from a spool. The filament is deposited in patterns determined by translated computer-aided design (CAD) files and construct a 3D object layer by layer on the platform (Novakova-Marcincinova, 2012; Alvarez et al., 2016; Cuiffo et al., 2017). FDM has great advantages compared to other 3D printing technologies since it easy to handle and low-cost Aw et al. (2018).

1.2 Problem Statement

Waxes are common in the manufacturing of 3D objects specifically involving molding and casting. The lost-wax casting process is widely used for fabricating metal alloy objects from automotive parts to fine jewellery. However, in lost-wax casting, waxes are only useful to fabricate the molds and not the end products. The potential usage of wax as a build material in the manufacturing of 3D objects is not extensively studied especially in FDM technology.

According to D'Angelo *et al.* (2014), build materials available for 3D printing (FDM) is limited as compared to build materials for traditional manufacturing methods (injection molding or milling). The development of novel build materials is necessary to broaden the potential of this technology. The development of wax composite that incorporates wax in the thermoplastic matrix may offer the possibility of introducing new composite material in FDM. There were studies in developing new build materials for FDM technology. One of the new build materials that was developed by the researchers was Iron-ABS composite filament (Sa'ude *et al.*, 2014) that utilize paraffin wax as surfactant materials. Other than that, Onagoruwa *et al.* (2001), developed a binder system for fused deposition of ceramic (FDC) filament. Wax was used as one of the binder constituents in the formulation of this filament. The wax in the FDC filament assists to decreases the viscosity of this filament formulation. Even though previous studies about the utilization of wax in the formulation of composites filament were conducted but there is limited data/research available particularly dealing with the deposition of wax composite via the heated liquefied nozzle of FDM machine.

The purpose of this research is to develop new thermoplastic/wax composite filament as a build material for FDM technology that utilizes polylactic acid (PLA) as the matrix, wax as a filler and polyethylene glycol (PEG) as the plasticizer. PEG was chosen as a plasticizer for PLA/wax composite because previous researchers have shown that the addition of PEG had successfully overcome the brittleness and broaden PLA's application. An investigation of optimum composition was explored on the mixing ratio of constituent material by using a melt blending technique. The performance of PLA/wax/PEG composite in the tensile testing, water absorption, melt flow index (MFI), thermal (melting point) and morphological properties will be investigated. The promising PLA/wax/PEG that met the standard properties of filament were chosen to be used in the filament production and 3D printing via FDM technology.

1.3 Objectives

The study of the fused deposition modeling (FDM) by using PLA/wax composites consists of three main objectives which are:

- i. To investigate the plasticizing effect of polyethylene glycol and wax loading effect on tensile properties, morphological, water absorption, melting point and melt flow index (MFI) of PLA/wax/PEG composites.
- ii. To fabricates polylactic acid/wax/PEG composite filament for fused deposition modeling (FDM) application.
- iii. To validate the quality of 3D object print using selected PLA/wax composites filament, commercial PLA filament and neat PLA filament via fused deposition modeling (FDM).

1.4 Scope of the study

This study focused on the fabrication of PLA/wax/PEG composites filament for application in fused deposition modeling (FDM) technology. The wax used in this study was supplied by Shell MDS, Bintulu Sarawak, Malaysia with the congealing point 102-106°C. Then, only one plasticizer was used in this study which is polyethylene glycol (PEG). The major part of the study presented in this thesis is focused on the effects of wax loading and PEG loading on tensile properties and characteristics of PLA/wax/PEG composites and the application of these composites' filament in FDM technology. The tensile properties (ASTM D638) and characteristics of PLA/wax/PEG composites such as water absorption (ASTM D570), morphological (Scanning Electron Microscopy Analysis), melting point (Malaysian Standard ISO 3146:2004, Method A: Capillary tube), melt flow index (MFI) (ASTM D1238) were determined to select the composites that have potential as a build material for FDM technology. The selected PLA/wax/PEG composites were applied in FDM technology to print a 3D object. The quality of 3D printed objects using the selected PLA/wax/PEG composites was evaluated and compared to commercial PLA filament based on these three aspects; dimensional accuracy, quality of the outer surface of 3D printed object and layer height accuracy.

CHAPTER 2

LITERATURE REVIEW

2.1 3D Printing

Three-dimensional (3D) printing, also known as additive manufacturing (AM), produces 3D objects in a layer-by-layer on the platform. The example of 3D printing technology such as stereolithography apparatus (SLA), laminated object manufacturing (LOM), selective laser sintering (SLS), fused deposition modeling (FDM), digital light projection (DLP) and electron beam melting (EBM) (Tao et al., 2017). Nowadays, these 3D printing technologies are attractive for various applications in fields of architecture, medical, aerospace, automotive, education and fashion industries (Chiulan et al., 2017; Tao et al., 2017).

3D printing is a technology used for the rapid fabrication of 3D models directly from a digital design which is computer-aided design (CAD) files (Leigh et al., 2012). Additive manufacturing basically started with nothing and made 3D objects continuously by fuses layer by layer of material on the printing platform until it fully created (Leigh et al., 2012; Horvath, 2014). Most of the rapid prototyping processes can build a 3D object from a wide range of build materials. The materials to be selected depending on the type of 3D printing technology used (Leigh et al., 2012).

2.2 Different 3D Printing technologies

2.2.1 Selective Laser Sintering (SLS)

Selective laser sintering is the selective binding technologies that build a 3D model from a powder by using heat or binding agents to bind the particles of powder together (Horvath, 2014). Horvath (2014); Chiulan et al. (2017) mentioned that in SLS system, the desired design of the 3D model is imported to the printer and then, an infrared laser beam is used to fuses the build material in the form of powder into thin layers, one layer at a time. According to Chiulan et al. (2017), thermoplastic polyurethanes (TPU), polyamides, ceramic and metal powder are the common build materials for this technology. After the first layer is fused to a platform, the platform goes down one layer of thickness and the powder from the powder delivery system is applied across the building platform to form a new layer of powder to be sintered onto the previous layer (Dudek et al., 2013; Horvath, 2014; Chiulan et al., 2017). This process of sintering is repeated, and the completed 3D model is detached from the SLS system. Then, to remove any trace of powder the 3D model is brushed and sandblasted (Chiulan et al., 2017).

According to Horvath (2014), the advantage of the SLS technique is the powder also acts as supporting material for this 3D printing technique. Therefore, a more complex and detailed design could be achieved. However, the build material can be hard to handle, and this type of printers tend to be expensive. The technology of selective laser sintering (SLS) as shown in Figure 2.1.

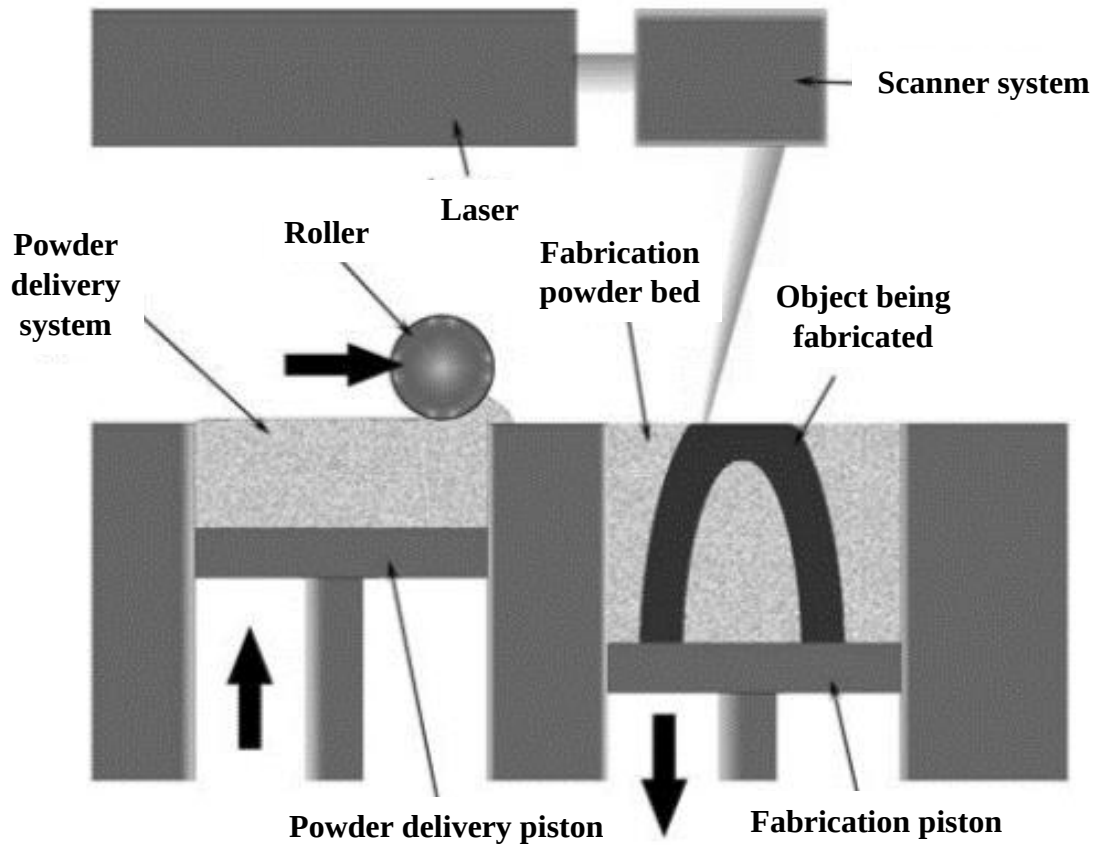


Figure 2.1: Selective laser sintering (SLS) technology. (Junji, 2013)

2.2.2 Stereolithography apparatus (SLA)

Stereolithography apparatus (SLA) is the selective solidification technique where the 3D object is built from a liquid tank by selectively applying energy in order to harden the liquid material a layer at a time. SLA technique is quite similar to SLS, where the first layer is built on the build platform and the platform descends one layer of thickness into the liquid tank. Stereolithography apparatus (SLA) applies an ultraviolet (UV) light to change the state of liquid resin into a solid-state with a laser, or occasionally a digital light projection (DLP) imager, in order to solidify an entire layer at a time (Horvath, 2014). A laser beam traces the slices of an object on the surface of this liquid resin and it is hardened and builds one layer of the object on the platform. After the laser beam has drawn a two-dimensional (2D) path

on the platform surface, the solidified layer is lowered into the resin bath and the 3D object is completed by repeat the same process for each layer (Hamod, 2014).

According to Horvath (2014), the completed 3D object is requiring to be cured after that, and the build material which is liquid resin is can be untidy to handle in this process. Currently, a desktop SLA 3D printer is available in the market. However, the cost is more expensive compared to the filament-based printers (fused deposition modeling, FDM). Figure 2.2 shows the stereolithography (SLA) technology.

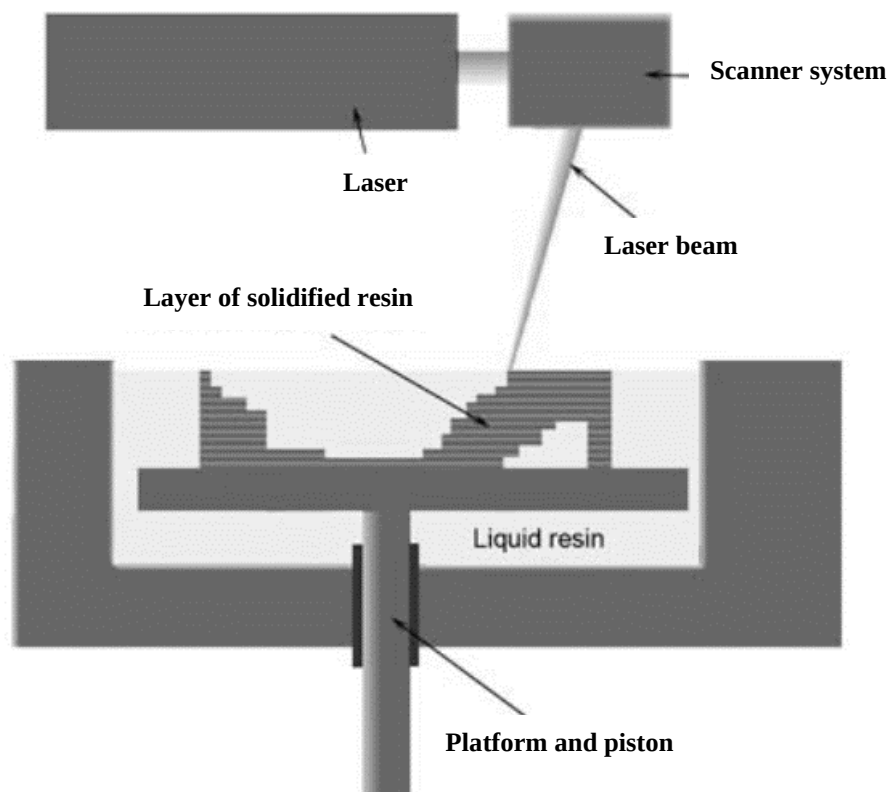


Figure 2.2: Stereolithography apparatus (SLA) technology (Junji, 2013)

2.2.3 Fused deposition modeling (FDM)

Fused deposition modeling (FDM) is one of the common 3D printing technology that was developed by Stratasys in Eden Prairie, Minnesota (Novakova-Marcincinova, 2012). FDM technology is an additive manufacturing (AM) or rapid prototyping (RP) process that builds a 3D object by using thermoplastic filaments and inserting them into a heated liquefier to be extruded via a nozzle with small diameter onto a build platform (Mireles et al., 2012). According to Onagoruwa et al. (2001), to create a positive pressure to extrude the semi-molten materials, the cold filament at the top of the liquefier will function as a piston.

The FDM head is controlled by the computer and it is moving in X-Y direction while build platform in the Z direction and this motion based on the computer-aided-design, CAD design of the 3D model (Onagoruwa et al., 2001). The nozzle FDM 3D printing comprises resistive heaters that can sustain the temperature of the build material at just above its melting point. Therefore, the thermoplastic extrudes smoothly via the nozzle and build a layer on the platform (Novakova-Marcincinova, 2012). The build material for FDM is usually supplied in filament form. There are two materials are used in the FDM machine which is build material and support material. The most commonly used materials in FDM are polylactic acid (PLA) acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyethylene terephthalate (PET) and thermoplastic elastomers (Dudek, 2013; Chiulan et al., 2017). Figure 2.3 shows fused deposition modeling (FDM) technology.

The FDM process has three steps which are pre-processing, production and post-processing (Dandgaval & Bichkar, 2016). In the pre-processing step, computer-aided-design (CAD) software is used to creates a 3D object design. The 3D object design is saved

in Standard Tessellation Language (STL) format then, exported to the FDM Catalyst software.

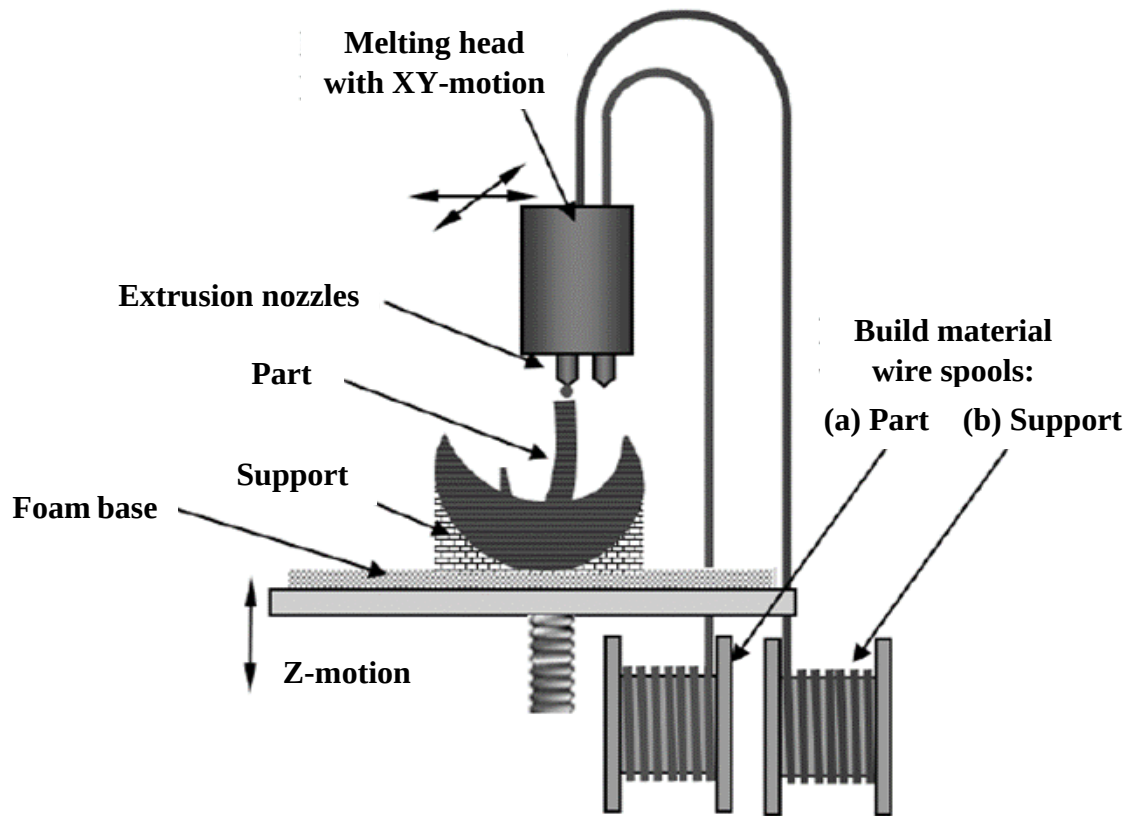


Figure 2.3: Fused deposition modeling (FDM) technology (Bual & Kumar, 2014)

STL file format tessellates the 3D section into a triangle set. This file format serves some advantages where almost all CAD systems support it, and the part geometry is simplifying by reducing it to its most basic element. Novakova-Marcincinova and Novak-Marcincin (2012) stated that the STL file is horizontally sliced into numerous thin segments after the STL file is exported to Catalyst software. These segments embody the 2D contours that the FDM process will create which, when stacked upon one another, will be similar to the original 3D object. This sectioning method is commonly used in all existing rapid

prototyping techniques. Then, the Catalyst software uses this data to create a process plan that will control the hardware of the FDM 3D printer (Novakova-Marcincinova & Novak-Marcincin, 2012).

In the production process, the semi-molten thermoplastic filament is deposited layer by layer via a heated nozzle on the build platform model where the new layer stacks on the top of the previous layer and fuses by physical interactions. The deposited materials harden immediately after flowing from the nozzle and fused to the layer below (Novakova-Marcincinova, 2012; Chiulan et al., 2017). The platform lowers, once a layer is built and then extrusion nozzle deposits a new layer until the 3D model is fully created (Novakova-Marcincinova, 2012; Aliheidari et al., 2017). Overhanging designs is required a support structure during printing and this is automatically generated. In order to print this support structure, the support material is needed. (Bual & Kumar, 2014). According to Dandgaval and Bichkar (2016) in post-processing, any supports materials attaches to 3D objects are removed and cleaned.

Wachsmuth, (2008); Lužanin et al. (2013); Alvarez et al. (2016) mentioned that recently, FDM is the most popular 3D printing technology due to some advantages over other techniques such as easy to handle, easily replaced, choice of materials, cost-effective maintenance and using a non-hazardous build material. Among all the commercially available 3D printing technology, FDM is the only one process that does not involve carcinogenic chemicals, hazardous fumes, or messy powders and it can be located in the same place with the user. Therefore, FDM being acknowledged as an “office-friendly 3D printer” (Wachsmuth, 2008).

2.3 Common filament materials for fused deposition modeling (FDM)

2.3.1 Polylactic acid

Polylactic acid (PLA) is known as thermoplastic aliphatic polyester acquire from agricultural resources usually corn (Jamshidian et al., 2010; Mansor et al., 2011; Xiao et al., 2012; Chiulan et al., 2017). PLA is made up via lactides and lactic acid monomers ring-opening polymerization, which are gained from sugar feedstock fermentation (Mansor et al., 2011). Mansor et al. (2011) stated that PLA is categorized among the biopolymers due to its renewability and degradability to nature. Nowadays, PLA emerging as an alternative material to petroleum-based polymeric material.

Polylactic acid (PLA) is commonly used as a build material in the fused deposition modeling technique (Choi et al., 2016). It can be extruded at a quite low temperature (around 210°C) which means PLA filament is easier to be extruded via the FDM nozzle compared to other build materials and as well as enables the use of less expensive printers (Horvath, 2014; Behzadnasad & Yousefi, 2016). A heated bed/platform is a part of the 3D printer where the 3D model sticks on it. It improves printing quality by helping to prevent warping and prevent poor adhesion to the heated bed. PLA does not need a heated bed/platform if the print bed is covered with blue tape. However, if the bed is covered with something else for example Kapton tape, the bed needs to be heated to a low temperature usually at 60°C to make the model stick (Horvath, 2014).

2.3.2 Other common materials

Other common build materials for FDM are acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET), nylon, polycarbonate (PC) and high impact polystyrene

(HIPS). Acrylonitrile butadiene styrene (ABS) is also a thermoplastic polymer that commonly used in fused deposition modeling (FDM) technology (Choi et al., 2016). According to Hylova and Manas (2017), ABS is an engineering thermoplastic and an important terpolymer, which has the butadiene part homogeneously dispersed into the acrylonitrile-styrene matrix. This material usually used in many industries because it is a flexible, strong and durable thermoplastic (Singh & Singh, 2016). Other than that, ABS can stay strong at higher temperatures compared to polylactic acid (PLA). It is a good plastic that used to produce various toys such as Lego pieces (Horvath, 2014). The utilization of ABS in the FDM technique as build material serves the ability to build a 3D object from digital model files in a variety of standard and custom colours (Singh & Singh, 2016). ABS is a great selection of build material for printing a 3D object that needs many support structures because support structure usually will detach more easily in ABS compared to other common build materials. The disadvantages of using ABS for printing, when cooling it tends to warp and resulting in defect 3D object dimensions. It is also difficult to 3D print by using this material with no heated platform. The print temperature for ABS is around 240°C and its quite high compared to PLA and the bed temperature at 115°C (Horvath, 2014).

Polyethylene terephthalate (PET) polyester is the most common thermoplastic polyester and is frequently called just “polyester”. PET exists both as a semi-crystalline (opaque and white) and as an amorphous (transparent) and thermoplastic material. The semi-crystalline PET has good ductility, strength, hardness and stiffness while the amorphous PET has better ductility however less hardness and stiffness. This material is quite a resistance to humidity (McKeen, 2012; Callister & Rethwisch, 2014). PET is a clear plastic that usually used in the production of water bottles (Horvath, 2014), container and food packaging

(Messimer et al., 2018). According to Horvath (2014), PET is a very transparent material and the 3D printed object will not be perfectly clear in all directions because of the layer lines, but then it will be translucent, particularly in the thin-walled object. Usually, these build materials were extruded via FDM at 212-224°C printing temperature and platform temperature at 80°C (Horvath, 2014).

Nylon is the common name for high molecular weight polyamides, which is a linear polymer chain (McKeen, 2012; Messimer et al., 2018). Nylons are categorized by a numbering system designating the number of carbon atoms in the repeating unit (Messimer et al., 2018). Nylons are crystalline polymers typically produced by the condensation of a diacid and a diamine. There are some types of nylon and each type is frequently described by a number, such as a Polyamide 66 or (PA66 Nylon 66). The numeric suffixes refer to the number of carbon atoms present in the molecular structures of the amine and acid respectively (or a single suffix if the amine and acid groups are part of the same molecule) (McKeen, 2012). Nylon is commonly used in engineering applications because of its appealing blend of noble mechanical properties and processability. It is established that anionically-polymerized nylon has a wide range of properties such as heat stability, high melting temperatures, mechanical strength and lightness. However, the major disadvantages of nylon are high water absorption and absorb some other liquids (Callister & Rethwisch, 2014; Messimer et al., 2018), it has low impact strength below its glass-transition temperature and in the dry state, unsatisfactory heat deflection temperatures and poor dimensional stability (Messimer et al., 2018). The printing temperature for nylon is 240°C and it is not required a heated platform (Horvath, 2014).

Polycarbonate (PC) is formed from the reaction of bis-phenol A and carbonic acid (McKeen, 2012). PC is one of the engineering polymers that widely used across all fields, particularly in electronic, medical, optical and aerospace applications. The characteristics of PC such as low water absorption, high impact resistant and ductility (McKeen, 2012; Callister & Rethwisch, 2014) and virtually unbreakable, high tensile strength, remains tough at low temperatures, transparent, high heat resistance, dimensional stability, resistant to ultraviolet light and allowing exterior use and flame-retardant properties (Novakova-Marcincinova & Kuric, 2012; McKeen, 2012). Due to these characteristics, PC is suitable for harsh application for example in aerospace applications (Messimer et al., 2018). Polycarbonate is a very strong material but is still somewhat experimental for users of 3D printing. It is very problematic to print by using this material because it is difficult to adhere to the build platform (Horvath, 2014). According to Horvath (2014), printing temperature for PC is more than 270°C and required very high temperatures for the heated bed.

Meesimer et al. (2018) stated that, high impact polystyrene (HIPS) thermoplastic that also known as rubber-toughened polystyrene that was developed as a ductile alternative to the general-purpose polystyrene. This is a polystyrene matrix that is imbedded with an impact modifier, which is basically a rubber-like polymer such as polybutadiene (McKeen, 2012). The preparation of HIPS by the thermal polymerization of styrene monomer with polybutadiene rubber. Its structure is composed of an amorphous polystyrene matrix comprising a uniform dispersion of composite spherical domains (Messimer et al., 2018). High-impact grades of HIPS typically contain in the range of 6 to 12% elastomers while medium-impact HIPS grades contain around 2 to 5% (McKeen, 2012). HIPS polymer has some benefits over other inflexible plastics, particularly in the areas of flexibility, cracking

resistance, and cost. HIPS also has a quite similar problem with PC because HIPS can adhere to build platform, but it forms weak bonds without the high temperature of build platform or with a long processing time (Messimer et al., 2018). The printing temperature for this material at 240°C and 115°C for heated bed temperature (Horvath, 2014).

Before printing a 3D object by using a different build material, there are three important settings that need to be considered which are the extruder temperature (also known as print temperature), the printing speed and the heated bed temperature (with or without heated platform) (Horvath, 2014). Table 2.1 shows the printing parameters of common filament materials for FDM.

Table 2.1: Printing parameters of common filament materials for FDM (Horvath, 2014)

Material	Print temperature, °C	Bed/platform temperature, °C	Speed
PLA	210	60	Normal
		Unheated/blue tape	Normal
ABS	240	115	Normal
HIPS	240	115	Normal
Nylon 618	240	Unheated/Garolite	Normal
PET	Nominally 212-224; some users suggest 250	80	Slow
Elastomer	210-225	Unheated/blue tape, bare glass	Very slow
Polycarbonate	> 270	Very high	Varies

2.4 Previous researches on composite filaments that utilize wax as constituent materials

Sa'ude et al. (2014) have done a study to develop a new composite filament for fused deposition modeling (FDM) process by incorporation of ABS matrix and iron powder as a filler. The viscosity of the composite material was a vital aspect that needs to consider in the production of filament (extrusion). The increase of iron powder loading in the ABS matrix formulation causes an increase in the viscosity of the composites. Therefore, surfactant material such as paraffin wax and palm stearin are required to control the melt flow behaviour during filament production. In this research, paraffin wax and palm stearin were used as surfactant materials. This two-surfactant material was reported to help in reduced the viscosity of ABS/iron composites (Sa'ude et al., 2014).

Onagoruwa et al. (2001) have done a study to develop a binder system for the fused deposition of ceramic (FDC) filament. The developed polypropylene binder system was incorporated with ceramic powders (mullite, fused silica, titanium dioxide) and then extruded in the filament form. The constituent materials of the binder system are polypropylene base polymer, plasticizer, wax, tackifier and elastomer. Onagoruwa et al. (2001) reported that the introduction of wax in the formulation can reduce the viscosity of the filament during the extrusion and printing process. Then, FDC filament of 1.78 mm in diameter was successfully extruded and was used as a build material for the Stratasys FDM 1650 3D printer to print a 3D object with high quality (Onagoruwa et al., 2001). Table 2.2 showed the functions of each compositions material in the binder system for FDC filament.

Table 2.2: The role of the binder system constituent for FDC filament (Onagoruwa et al., 2001)

Binder constituent/s	Function
Base polymer (Polypropylene)	Act as the backbone of the filament and provides strength
Tackifier	Provides flexibility and enables tackiness
Elastomer	Provide elasticity and flexibility
Plasticizer	Gives plasticity to filament for spooling
Wax	Help to reduces viscosity

2.5 Previous researches on polylactic acid (PLA) composites with the addition of polyethylene glycol (PEG) as a plasticizer

An improvement in flexibility of PLA can broaden its application as a biodegradable material especially in FDM 3D printing. A plasticizer is very important to provide plasticity to filament spooling (Onagoruwa et al., 2001). Plasticizer acts as an internal lubricant for the polymer. Recently, the addition of plasticizers has been studied to overcome the brittleness and increase the PLA elongation of break or elasticity. Previous researchers have revealed that the introduction of polyethylene glycol (PEG) as a plasticizer into PLA had successfully overcome the brittleness and as well as broaden the application of PLA (Hassan et al., 2012). Hassan et al. (2012) reported that researchers had investigated the addition of PEG into PLA and they discovered that the PLA's elongation at break significantly increased with the addition of 10 wt.% PEG. PLA showed high elastic modulus and tensile strength however it was quite brittle material. The addition of plasticizer tends to change the tensile properties of PLA. Increment in plasticizer loading, the common trend was reported that the elastic moduli and tensile strength decreased but showed an increased in elongation at break (Hassan et al., 2012).

Based on the study by Sungsanit et al. (2012), the addition of PEG might develop a more flexible material. It was reported that the PLA composites obtained miscibility of the components with the addition of 5 wt% and 10 wt% PEG. Tensile properties of PLA/PEG composites showed a reduction in tensile strength and elastic moduli, while increased in elongation at break. According to Bijarimi et al. (2016), the incorporation of PEG into PLA has significantly changed the transition glass, T_g of neat PLA indicated the flexibility of the blend was achieved. The increment of PEG content gradually decreased the melting point, T_m of PLA/PEG composite (Bijarimi et al., 2016).

2.6 Filler and plasticizer in polymer composites

Polymer composites are mixtures of polymers with inorganic or organic additives having certain geometries (fibers, flakes, spheres, particulates). Therefore, the polymer composites consist of two or more components and two or more phases (Xanthos, 2005). Additives are known as foreign substances that are intentionally introduced in polymer composites to improve or alter any of these properties and therefore, render a polymer more useable. There three primary reasons for using additives which are to property modification or enhancement, to reduce the cost and improving and controlling of processing characteristics of the polymer (Xanthos, 2005). Typical additives include filler materials, plasticizers, stabilizers, colorants, and flame retardants (Callister & Rethwisch, 2014). In this section, only fillers and plasticizers will be further discussed.

Filler materials are an additive that is most often incorporate in polymers to improve tensile and compressive strengths, abrasion resistance, toughness, dimensional and thermal

stability, and other properties (Xanthos, 2005). The example of particulate fillers used such as wood flour (finely powdered sawdust), talc, silica flour and sand, clay, limestone glass, and even some synthetic polymers. Particle sizes of filler range from 10 nm to macroscopic dimensions. Usually, the fillers material are low-cost materials that can replace some volume of the more high-cost polymer, therefore, reducing the final product cost (Callister & Rethwisch, 2014). These common fillers that were added into PLA matrix composites such as paraffin wax (Chen et al., 2018), talc (Saravana et al., 2018), starch (Li & Huneault, 2011; Kamthai and Magaraphan, 2015), rice starch (Yew et al., 2005) and wood flour (Xie et al., 2017).

A plasticizer is an additive that is added to another material usually plastic or an elastomer to make that material softer or more pliable (Godwin, 2017), more flexible and durable (Renecke et al., 2011). According to Callister & Rethwisch (2014); Hassan et al. (2012), the incorporation of plasticizer into a polymer may help to improve the flexibility, ductility, and toughness of polymers. The addition of plasticizer also causes reductions in stiffness and hardness. Plasticizers are generally low molecular weight and low vapor pressures resins or liquids, which form secondary bonds to polymer chains and spread them apart increasing the “free volume” (Renecke et al., 2011; Callister & Rethwisch, 2014). Therefore, plasticizers decrease the polymer-polymer chain secondary bonding and offer more mobility for the macromolecules, resulting in a softer, more easily deformable mass. Plasticizers are commonly used in polymers that are brittle at room temperature, for example like poly(vinyl chloride) and some of the acetate copolymers. The plasticizer lowers the glass transition temperature (Renecke et al., 2011; Callister & Rethwisch, 2014), so that at ambient conditions the polymers might be used in applications requiring some degree of ductility and

pliability. The example of these applications includes thin sheets or films, tubing, raincoats, and curtains (Callister & Rethwisch, 2014).

The addition of plasticizers in the polymer are expected to decrease in elastic moduli, tensile strength, hardness (Mansor et al., 2011), density, melt viscosity, glass transition temperature, electrostatic charge ability, and volume resistivity of a polymer (Renecke et al., 2011), while at the same time increasing its flexibility, elongation at break (ductility) (Mansor et al., 2011), toughness, dielectric constant, and power factor (Renecke et al., 2011). Good plasticizers should be highly compatible with the polymer, stable in both high and low-temperature environments, sufficiently lubricating over a varied temperature range, insensitive to solar ultraviolet (UV) radiation, migration and leaching resistant, low-cost (Renecke et al., 2011).

A study conducted by Mansor et al. (2011) on the effect of triacetin as a plasticizer on mechanical properties and morphology of polylactic acid (PLA)/starch composites. The addition of triacetin improved the dispersion and compatibility of starch on to PLA matrix phase. Then, the elongation at break (ductility) is improved remarkably that makes the PLA/starch composites less brittle. Based on Mansor et al. (2011), the addition of 5 wt.% of triacetin into PLA/starch (70/30) composite gives the best value for tensile strength and enhanced the compatibility between PLA matrix and starch filler. Several plasticizers that were added into the PLA matrix composite such as sorbitol and glycerol (PLA/starch composites) (Li & Huneault, 2011), triacetin (PLA/starch composites) (Mansor et al., 2011),

polyethylene glycol, PEG (PLA/talc composite) (Saravana et al., 2018) and isosorbide diester (PLA/baggase carboxymethyl cellulose composite) (Kamthai & Magaraphan, 2015).

2.7 Parameters for fused deposition modeling (FDM) filament

2.7.1 Tensile testing

The mechanical properties, among all the properties of plastic materials, are often the most important because virtually all service conditions and most of the end-use applications involve some degree of mechanical loading. Nevertheless, these properties are the least understood by most engineers (Shah, 2007). The material selection for a wide range of applications is quite often on mechanical properties such as tensile strength, modulus, elongation and impact strength (Davis, 2004; Shah, 2007).

Tensile testing is conducted to determine these mechanical properties such as tensile strength, elastic moduli and elongation at break. Then, the results of tensile testing are used in selecting materials for engineering applications. Tensile properties frequently are included in material specifications to ensure quality. Tensile properties usually are measured during the development of new materials and processes, therefore that different materials and processes can be compared. Other than that, tensile properties often are used to predict the material behaviour under forms of loading other than uniaxial tensile (Davis, 2004). The typical tensile test specimen as shown in Figure 2.4. The tensile specimen has enlarged ends or shoulders for gripping. The gage section is an important part of the specimen. The cross-sectional area of the gage section is reduced relative to that of the remainder of the specimen so that deformation and failure will be localized in this region. Tensile testing is performed by elongating a specimen and measuring the load carried by the specimen. This is done using

a test machine known as an Instron Universal Materials Testing Machine as shown in Figure 2.5 (McKeen, 2012). There are several standard tests of tensile testing as depicted in Table 2.3.

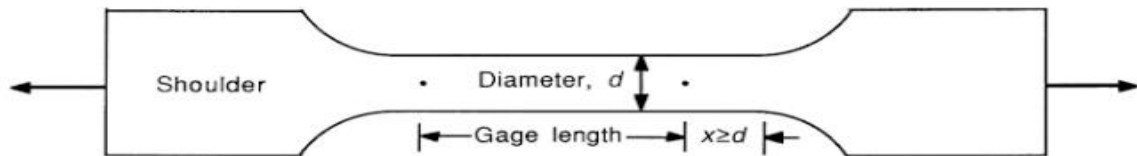


Figure 2.4: The typical tensile test specimen, showing a reduced gage section and enlarged shoulders (Davis, 2004)

Table 2.3: Standard tests of tensile testing (McKeen, 2012)

Sample	Standard
Molded plastic	ASTM D638-03 - Standard Test Method for Tensile Properties of Plastics.
	ISO 527-1:1993 Plastics - Determination of tensile properties - Part 1: General principles.
	ISO 527-2:1993 Plastics - Determination of tensile properties - Part 2: Test conditions for molding and extrusion plastics.
	ISO 37 Rubber vulcanized or thermoplastic - Determination of tensile stress-strain properties.
Films and sheets plastic	ASTM D412-98a (2002) e1 - Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers - Tension.
	ASTM D88-10 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting)
	ISO 527-3 (Plastics - Determination of tensile properties - Part 3: Test conditions for films and sheets)
	JIS K7127:1999 (Plastics - Determination of tensile properties - Part 3: Test conditions for films and sheets)

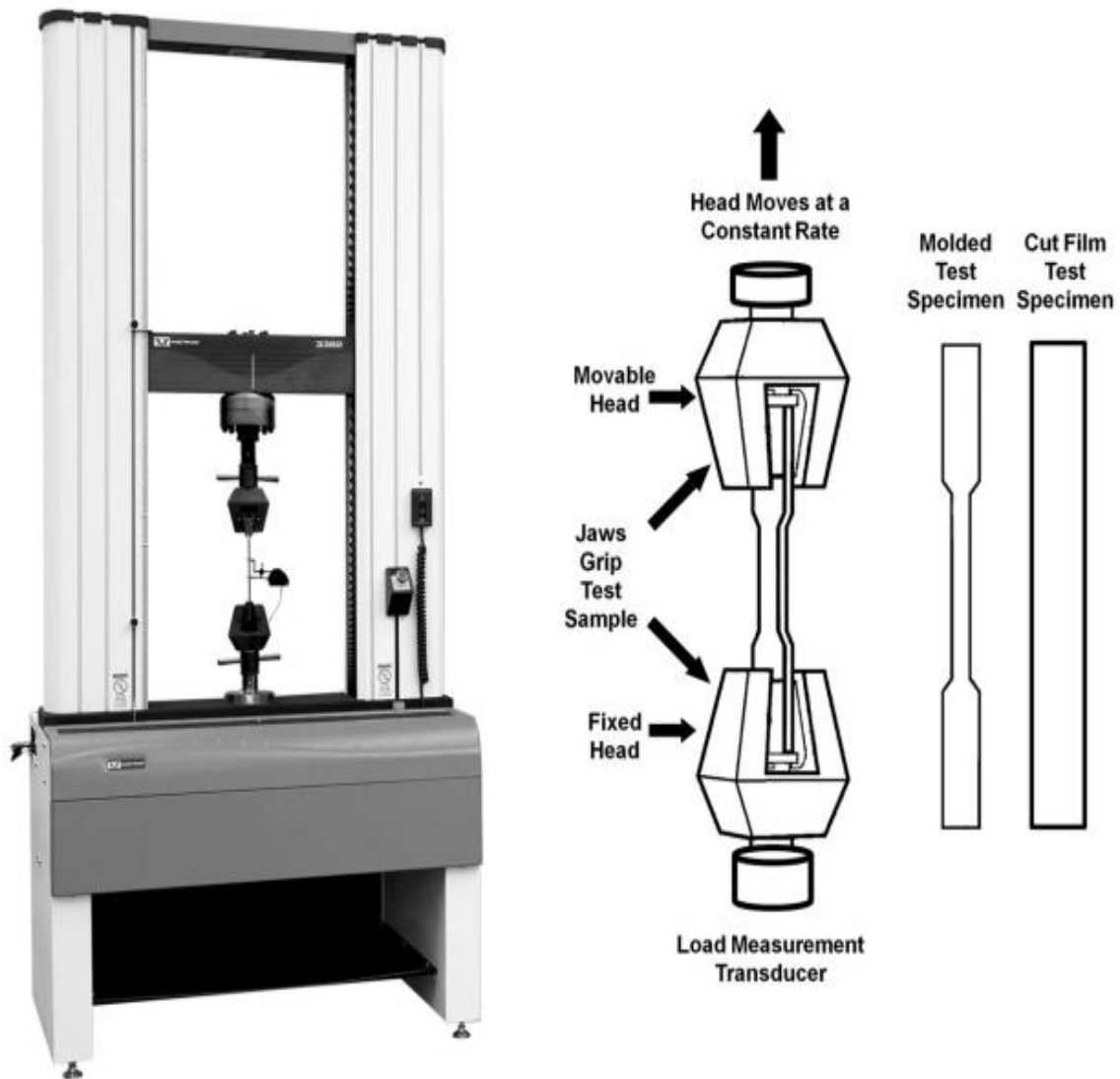


Figure 2.5: Instron Universal Materials Testing Machine and example of molded and cut film test specimen (McKeen, 2012)

2.7.2 Scanning Electron Microscopy (SEM) Analysis (Morphology)

Scanning Electron Microscopy is an important analysis to study the microstructure and chemical composition of material via the Scanning Electron Microscope (SEM). The very higher magnification of SEM is one of its advantages. The SEM image provides detailed information about the topography, composition and crystallography of the study

materials where the electrons interact with the sample atoms and producing a signal that contains about this information (Zhou & Wang, 2007; Liu et al, 2010). In the SEM, an electron beam is generated in a high vacuum by the electron gun. Then, this beam is accelerated towards the sample with the help of a positive electric field and then focused on the sample with the help of magnetic lenses (Zhou & Wang, 2007). This focused electron beam interacts with the sample surface, and then the interaction is transformed into a sample image. The resolution of the SEM image varies depending upon the function of the electron spot generated by the magnetic lenses. The electron beam interacts with a certain volume of the sample study, and the depth of this interaction is a function of the composition of the sample, energy and angle of the incident electron beam (Zhou & Wang, 2007). To investigate the morphology of material via SEM, the sample is prepared and mounted on the aluminium stub and coated with gold particles by a coater prior to the observation (Mansor et al., 2011) to avoid electrostatic charging during electron irradiation (Silverajah et al., 2012).

2.7.3 Water absorption

Water absorption was an important aspect to estimate the application of a composite. (Mansor et al., 2011). Water absorption is usually measured according to Standard Test Method for Water Absorption of Plastic ASTM D 570. This test method covers the determination of water absorption by plastics when the test sample is immersed in water. This test method is intended to apply to the testing of all plastics type, including cast, hot-molded, and cold-molded resinous products, and both homogeneous and laminated plastics in rod and tube form and sheets form. The water absorption of polymer is expressed in percentage (Mansor et al., 2011).

Water absorption in certain polymer could change the mechanical (strength, ductility and hardness) and physical properties of the material significantly. The higher water absorption after a long time would probably lead to enhanced biodegradability. Water may act as a hydrolysis agent for the PLA matrix and subsequently deteriorate the mechanical properties of PLA/rice starch composites (Leu & Chow, 2011). In the FDM application, the build material FDM the standard range of water absorption is 5% (Farbman & McCoy, 2016).

2.7.4 Melting point

The thermal properties of plastic materials are equally as important as mechanical properties. Unlike metals, plastics are extremely sensitive to changes in temperature. The mechanical, electrical, or chemical properties of plastics cannot be examined without looking at which the value was derived (Shah, 2017). The melting temperature, T_m of a polymer also be contingent on molecular weight. At relatively low molecular weights, increasing chain length raises T_m . Furthermore, the melting of a polymer takes place over a range of temperatures; so, there is a range of melting temperatures rather than a single melting temperature. This is because every polymer is composed of molecules having a variety of molecular weights and because T_m depends on molecular weight. For most polymers, this melting temperature range is normally on the order of several degrees Celsius (Callister & Rethwisch, 2014).

In ISO 3146, Method A (capillary method), a sample of polymer is heated at a defined rate in capillary and its physical behaviour is observed. This method is based on the changes in the shape of the polymer. It is applicable to all semi-crystalline polymers and

their compounds. The melting temperature range is observed on heating, from the first change of shape of the solid particles to the transformation into a highly viscous or viscoelastic liquid, with accompanying vanishing of the crystalline phase. There are several parameters such as molecular mass, molecular mass distribution, thermodynamic properties and percent crystallinity are highly affected by the melting temperature of the material (Gardziella et al., 2013).

2.7.5 Melt flow index

Melt flow index (MFI) analysis one of the important aspects in the development of 3D printing build material. When formulating novel composites, the melt flow index characteristics may change significantly to a point where it is no longer possible for an off-the-shelf 3D printer to extrude. A typical FDM type 3D printer depends on small stepper motor as a mechanism to extrude 3D print build material and it may not able to provide sufficient force and heating power to extrude a composite material with high viscosity. Melt flow index (MFI) is a measure of the flow rate of the melt thermoplastic polymer (McKeen, 2012; Santhoskumar & Ramkumar, 2014). It is very important to know the MFI value for new polymer composites in order to control and anticipating its processing (Santhoskumar & Ramkumar, 2014). It is defined as the weight of the polymer in grams flowing in 10 minutes via a die of specific diameter and length by a pressure applied by a given weight at a given temperature. The standard method of MFI analysis is conducted according to ASTM D1238 and ISO 1133 (McKeen, 2012). The higher the MFI value, the higher the fluidity rate of the material passing via the 3D printer nozzle, allowing for higher printing speeds. A high MFI value indicates an easier flow material via the dies and known as low viscosity fluid,

while a low MFI indicates a high viscosity fluid and difficult to flow via the dies (Isa et al., 2015; Sa'ude et al., 2016).

2.8 Filament extrusion

The extrusion process is a common method for melting thermoplastics and it is the first step for extrusion coating, blown film extrusion, filament extrusion line, cast film extrusion and other processes method for polymers. The extrusion process is the molding of a viscous thermoplastic under pressure through an open-ended die, similar to the extrusion of metals. Single screw extruder as shown in Figure 2.6 is usually used in the extrusion of polymer (Jamshidian et al., 2010). The major components in the screw extruder are electrically heated metal barrel, a hopper for feeding the plastic pellets, a motor for rotating a screw and die where the melted plastic exits. Therefore, both thermal energy produced by the heater and frictional heat by the friction between the plastic pellets and the barrel and screw is combined and give adequate heat to melt the plastic pellets (Jamshidian et al., 2010).

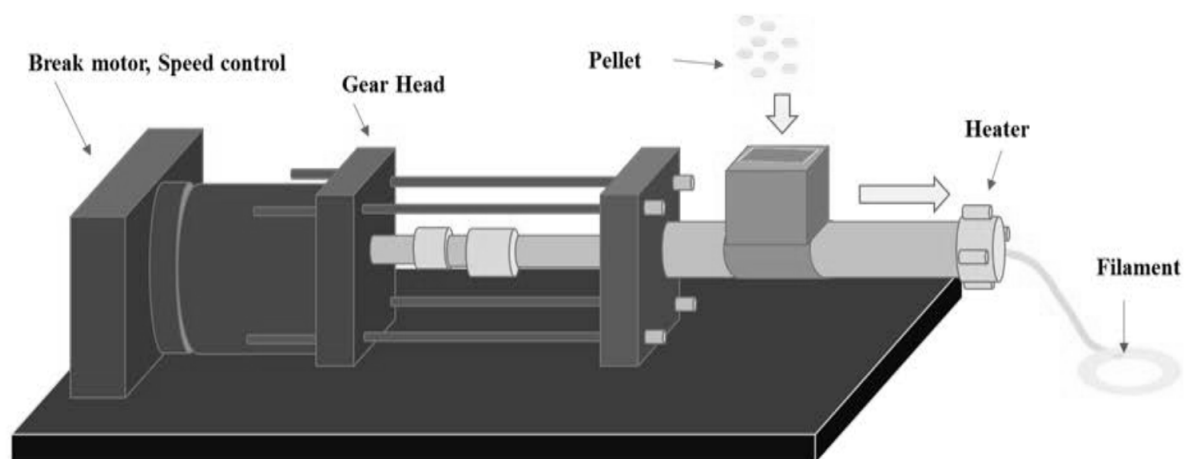


Figure 2.6: Schematic diagram of the filament extruder used for filament production (Nájera et al., 2018)

Eldridge and Whitton (2012) mentioned that the basic mechanism of the extrusion process involves a screw that transports raw plastic pellets from a hopper through a heating zone in a metal pipe where the plastic is melted. The raw plastic granules or pellets are gravity-fed from the hopper then transfer to the screw (Eldridge & Whitton, 2012). A mechanical screw or auger propels the pelletized material through a chamber, where it is successively compacted, melted, and formed into a continuous charge of viscous fluid (Eldridge & Whitton, 2012; Callister & Rethwisch, 2014). Extrusion takes place as this molten mass is forced via a die orifice. Then, the solidification or cooling process of the extruded length is expedited by blowers, a water spray, or a bath. The method is adapted to producing continuous lengths having constant cross-sectional geometries, for example rods, tubes, hose channels, sheets (Callister & Rethwisch, 2014). In the 3D printing field, the extrusion process is the process of filament production for the 3D printer (FDM). Figure 2.5 shows the filament extrusion line process.

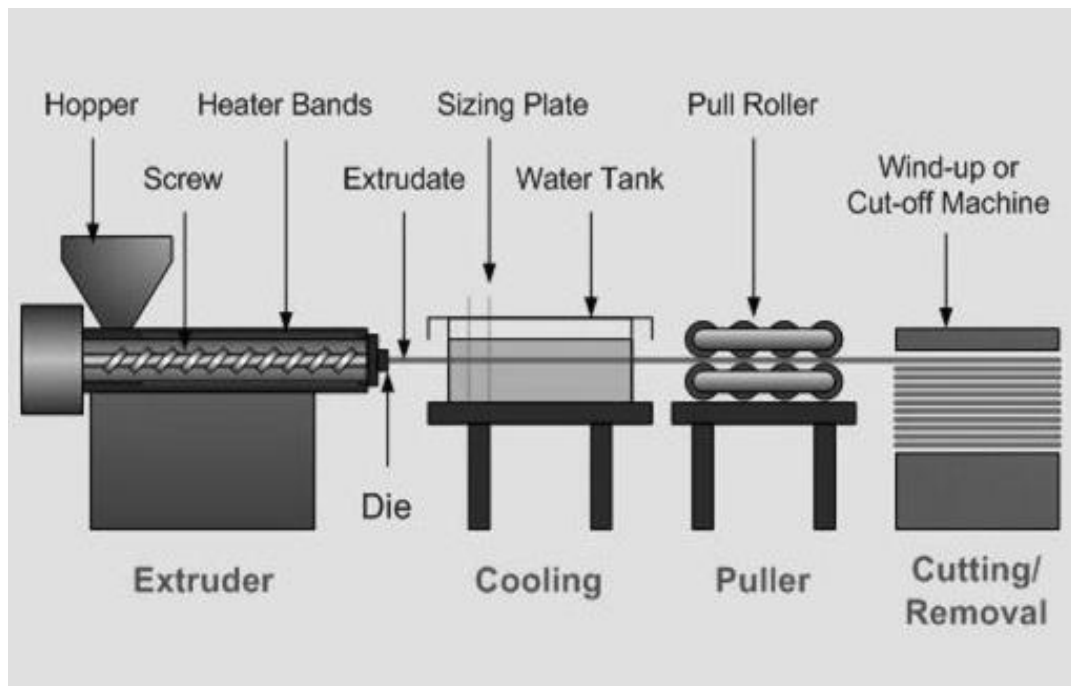


Figure 2.7: Filament extrusion line process

Generally, a temperature-controlled water cooling is employed for consistent rounded filament production. However, for a prototype production run, the air cooling was adequate and satisfactory roundness of the filament was achieved. The consistency of the filament diameter is very important for its applications in fused deposition modeling (FDM) (Liu et al., 2017). This to make sure the extrusion flow rate during the printing process is consistent.

According to Cardona et al. (2016), inconsistent filament diameter will affect the flow rate during the filament extrusion. Then, it will cause bad surface quality, uneven gaps in-between individual extrusions and/or excessive overlap and extruder jams, which eventually cause failure in the 3D printing process. If the filament diameter is bigger than the standard diameter (1.75 mm), the filament will not be able to fit in the opening of the temperature-controlled nozzle and not melt properly, so the FDM printing is unsuccessful. While, the small diameter will cause the mechanism of FDM not able to grip the filament due to the lack of tension, causing failure of the extruder since no filament will melt for the extrusion (Cardona et al. (2016). Cardona et al. (2016) stated that the gold standard across the industry for filament diameter is 1.75 mm with tolerance $\pm 0.05\text{mm}$.

2.8 Tensile properties and characteristics of common commercial filament for fused deposition modeling (FDM)

The development of new build materials for FDM technology needs to consider several important characteristics of filament as shown in Table 2.4. The range of tensile properties

of FDM filament also depicted in Table 2.4. These parameters were used in the selection of suitable new composite material for FDM technology.

Table 2.4: Standard tensile strength and characteristics of common FDM filament

Parameters	Standards	Range
Tensile strength	29.54 -60.10 MPa (Svensson, 2017). 22.00 – 72.40 MPa (Messimer et al., 2018).	22.00 -72.40 MPa
Elastic moduli	800 – 3500 MPa (Messimer et al., 2018). 890 – 3410 MPa (Svensson, 2017).	800 – 3500 MPa
Elongation at break	3.5 – 186 % (Messimer et al., 2018). 2.46 – 42.96% (Svensson, 2017)	2.46 – 186.00 %
Water absorption	Up to 5% (Farbman & McCoy, 2016).	$\geq 5\%$
Melting point (Printing temperature)	180 -240°C (Bates-Green & Howie, 2017).	180 - 240°C
Melt flow index	5.0 – 100.0 g/mins (Misumi Corporation, 2012). 11.1 to 74.7 g/10 mins (Wang et al., 2018).	5 to 100 g/10 mins
Filament diameter	1.75 ± 0.05 (Cardona et al., 2016).	1.75 ± 0.05 mm

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction of the methodology

The aim of this chapter is to explain the materials and methods used to achieve the objective of the current research. The main materials used in this study were polylactic acid as a matrix, wax as a filler and polyethylene glycol as a plasticizer to compose PLA/wax/PEG composites for fused deposition modeling (FDM) technology.

In this study, there are two main sections, first to investigate the tensile properties (ASTM D638) and characteristics of PLA/wax/PEG composite. The characteristics of PLA/wax/PEG composites were determined based on morphological (Scanning Electron Microscopy Analysis), water absorption (ASTM D570), melting point (Malaysian Standard ISO 3146:2004, Method A: Capillary tube) and melt flow index, MFI (ASTM D1238).

Then, the two composite designations that met the standard tensile properties and characteristics of filament for FDM technology was used to fabricate the filament. The filaments were used to 3D print a cube via FDM and the printing qualities were validated according to three aspects; dimensional accuracy, quality of the outer surface 3D printed cube and the layer height accuracy. The flowchart summary of the methodology for the study was shown in Figure 3.1.

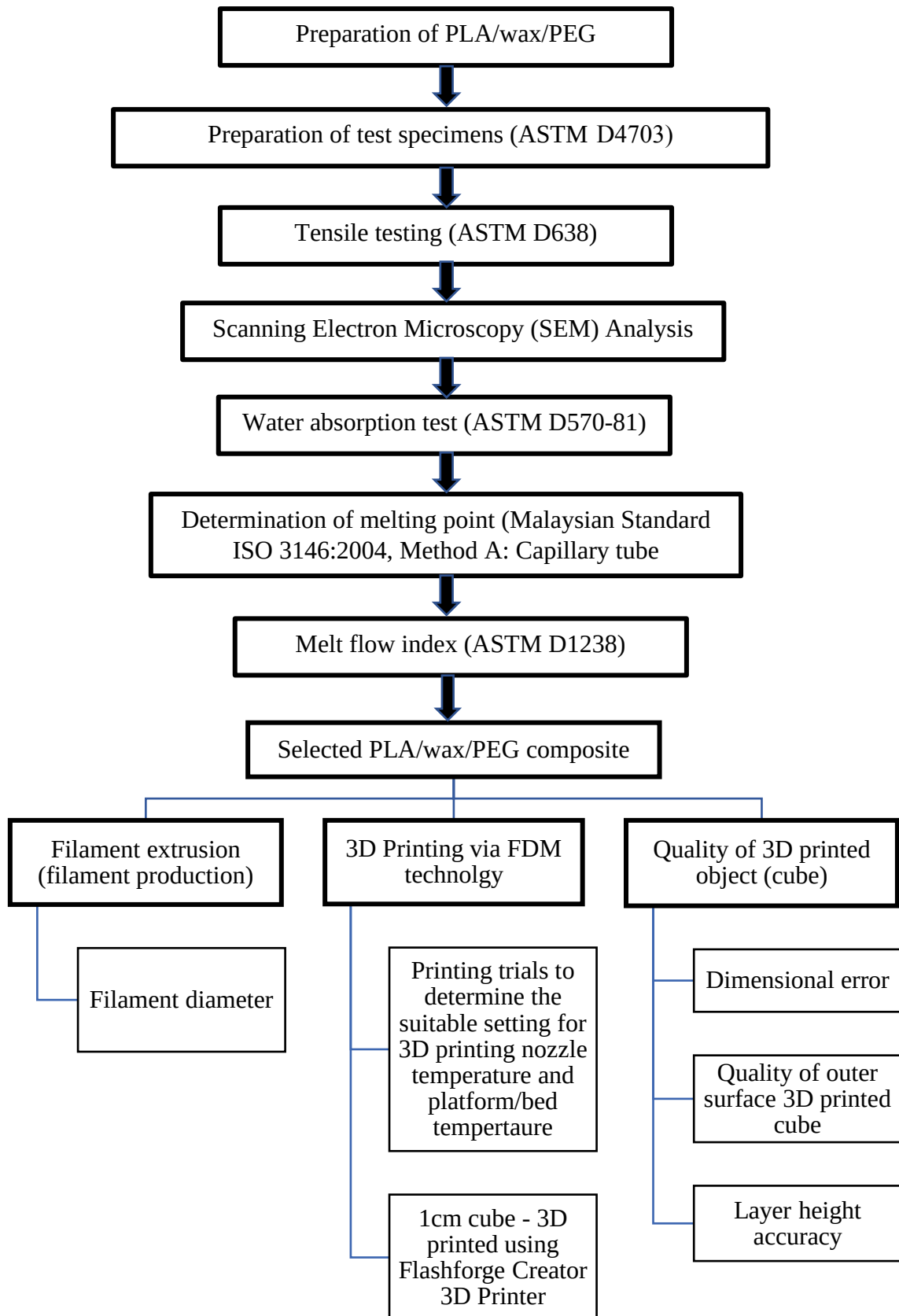


Figure 3.1: Flowchart summary of the methodology for the study

3.2 Materials

Polylactic acid (pellet form) (melting point 180°C), wax (congealing point: 102-106°C, flash point: > 250°C) was supplied by Shell MDS, Sarawak Malaysia. The plasticizer used in this study, polyethylene glycol (melting point 60-63°C) was purchased from Sigma-Aldrich, Germany. The materials as shown in Appendix A.

3.3 Composites preparation

Polylactic acid (PLA) was dried in the oven for 24 hours at 60°C before used to prevent hydrolysis caused by residual moisture during melt processing (Chieng et al., 2013; Kang et al., 2016). Two sets of compositions were used to determine the plasticizing effect of polyethylene glycol (first set) and wax loading (second set) on the composites designation. The composite composed of (95/5); 95 wt.% PLA and 5 wt.% wax was selected to study the effect of polyethylene glycol loading. Only 5 wt.% of wax was added into the composite because if the addition of wax greater than that, it was difficult to reach homogeneous mixture during the mixing process. Therefore, the composition of the composite designations was proposed as shown in Table 3.1. The composition of PLA/wax composites with the addition of PEG was prepared with the addition of 3, 5, 8, 10, 13 and 15 wt.% PEG based on a weight ratio. The mixing process starts by melting the corresponding amount of PLA in a glass petri dish since it has a higher melting point and heated for 15 minutes at 180°C in the oven. Then, wax and polyethylene glycol were added into the hot PLA and stirred the mixture. After that, it was heated again for 10 minutes and then, stirred the mixture until it reached a homogenous mixture. After the mixture (feedstock) had solidified, it was crushed by using an industrial blender to form granules with approximately similar size (Nájera et al., 2018). The fabrication process of PLA/wax/PEG composite was shown in Figure 3.2.

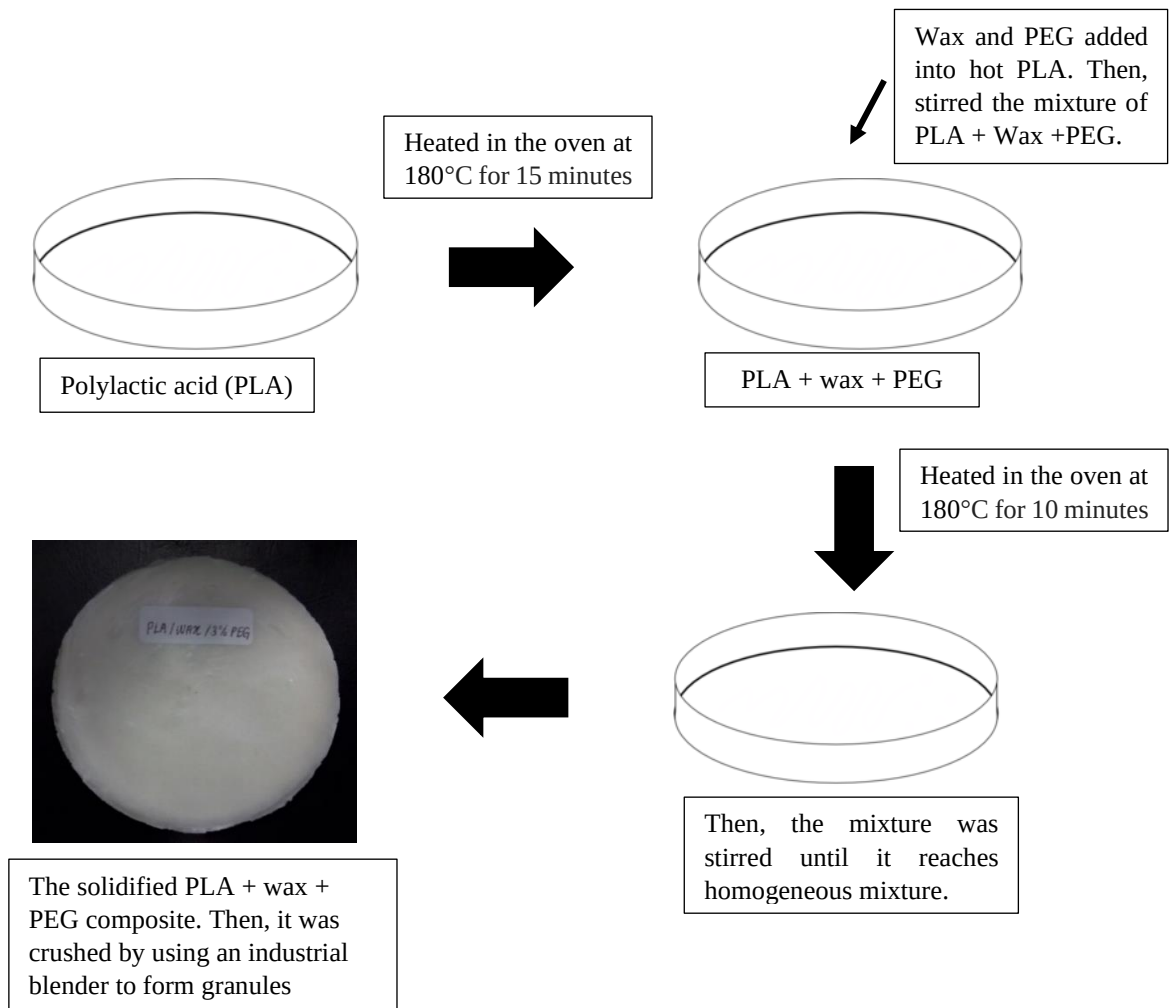


Figure 3.2: The fabrication process of PLA/wax/PEG composite

Neat PLA, PLA/wax (95/5/0) and PLA/PEG (100/0/5) were also prepared for comparison. The feedstock granules were used in compression molding for the tensile test specimen preparation. After testing tensile properties of PLA/wax/PEG composites, a mixture of PLA/wax/5wt.% PEG was selected with different compositions of wax (5, 10 and 15 wt.%) were blended to study the effect of wax loading as shown in Table 3.2.

Table 3.1: Composition of composite designation to study the effect of polyethylene glycol (PEG) loading

Blend designation	Polylactic acid (PLA) (wt. %)	Wax (wt. %)	Polyethylene glycol, PEG (wt. %)
Control (neat PLA)	100	0	0
100/0/5	100	0	5
95/5/0	95	5	0
95/5/3	95	5	3
95/5/5	95	5	5
95/5/8	95	5	8
95/5/10	95	5	10
95/5/13	95	5	13
95/5/15	95	5	15

Table 3.2: Composition of composite designation to study the effect of wax loading

Blend designations	Polylactic acid (PLA) (wt. %)	Wax (wt. %)	Polyethylene glycol, PEG (wt. %)
95/5/5	95	5	5
90/10/5	90	10	5
85/15/5	85	15	5

3.4 Preparation of test specimens

Compression molding was carried out using the Hydraulic Hot Press Machine with a cooling device, (GOTECH Model GT – 7014 - A50C) (GOTECH Testing Machines Inc., Taiwan) (Appendix B) according to the Standard Practice for Compression Molding Thermoplastic

Materials ASTM D 4703. The mold that follows the standard ASTM D638 Type IV was used in tensile test specimen preparation as shown in Appendix A. The feedstock granules were dried in the oven for 24 hours at 60°C. A feedstock was placed on each mold and evenly spread over the mold surface. After that, the mold was placed in the hot press machine, preheating the feedstock in the mold was done at 180°C by applying a contact pressure (2 bars) for 5 minutes. Then, it was pressed with full pressure (20 bars) for 3 minutes at 180°C. The hot mold was transferred to the cooling device (below the hot press) for rapid cooling and pressed with full pressure (20 bars) for 3 minutes at 10°C. After that, the mold in the cooling device was removed, molded tensile test samples were removed from the mold and stored in a desiccator until tested. Figure 3.3 shown the dimensions (dog-bone shape) for specimens of the tensile test.

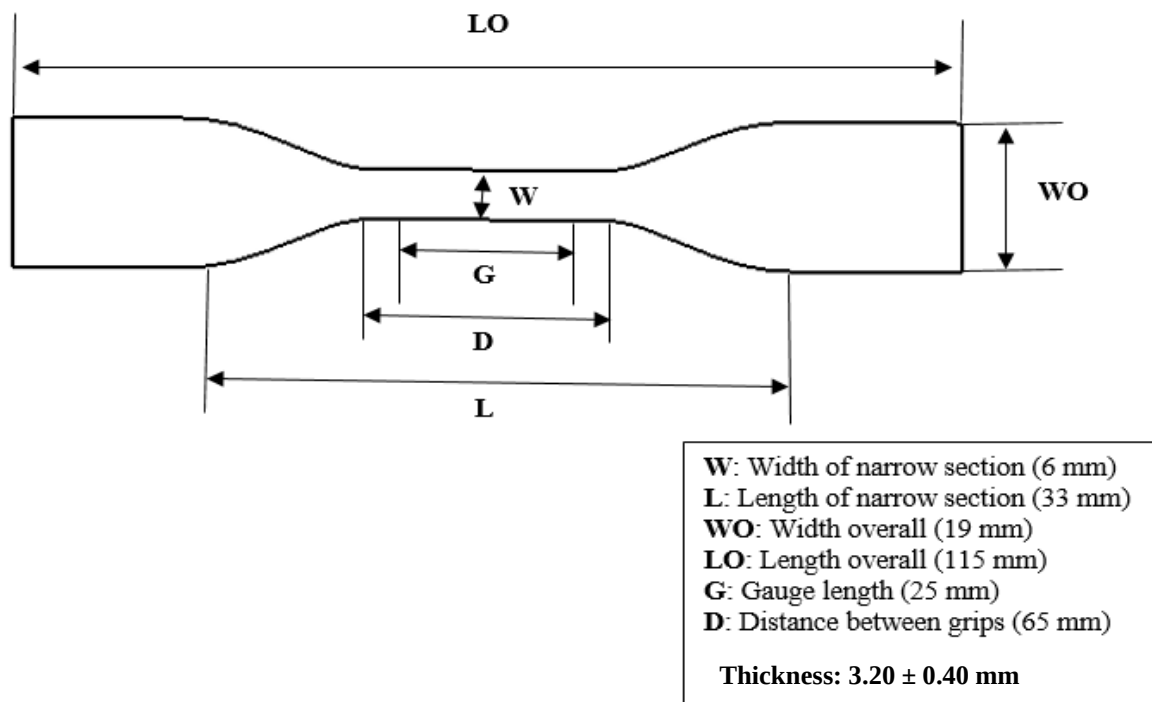


Figure 3.3: Dimensions of tensile test specimens (ASTM D638 Type IV)

3.5 Tensile testing

All specimen samples were dried in the oven for 24 hours at 60°C before testing (Xue et al., 2013). The tensile test was performed using a mechanical testing machine (mod. AG-1/250 kN) (Appendix B) following the standards of ASTM D638 Type IV (Tsou et al., 2014). Tests were conducted carried out at room temperature with a constant crosshead speed 5mm/minute, load cell of 3 kN and a gauge length 25 mm. The elastic moduli, elongation at break and tensile strength were determined using Trapezium2 Version 2.37. Five specimens were tested for each composite sample.

3.6 Scanning Electron Microscopy (Morphology)

The scanning electron microscope, JEOL JSM – 6390LA Analytical Scanning Electron Microscope used to examine the morphology of the composite designations. The tensile fractured surfaces for all samples were mounted on an aluminium stub and coated with gold particles by coater (JEOL JFC – 1600 Auto Fine Coater) before the observation (Mansor et al., 2011).

3.7 Water absorption test

The water absorption test was performed according to the ASTM test method D570. The tensile specimens from all the composites were oven-dried for 24 hours at 60°C to eliminate the moisture in the samples before used it for the water absorption test. The dried samples test was weighed for the initial value and immersed in distilled water at room temperature for specific intervals. Then, at days 1, 7, 14, 21 and 30 the specimens were weighed to record the water uptake. The water on the specimens was removed, blotted by using tissue paper to eliminate the excess water on the surfaces and then weighed using Mettler Toledo weighing

scale, d = 0.001g (Mettler Toledo Group, Switzerland). For each sample, three replicates were tested. The water uptake was determined based on the dried weight as shown in the formula below (Mansor et al., 2011).

$$\text{Water absorption} = \frac{\text{Wet weight} - \text{dry weight}}{\text{dry weight}} \times 100\% \quad (3.1)$$

3.7 Determination of melting temperature

The method used to determine the melting points was Malaysian Standard ISO 3146:2004, Method A: Capillary tube. The melting point of PLA and PLA/wax composites were determined by using Stuart SMP10 Melting Point Apparatus (Stuart, UK). Capillary tube (open one end) was filled with the composite samples about 3 mm high and then it was placed in a heated block of Melting Point Apparatus. Then, the process of melting was observed via the magnifying lens and the melting point (range) was recorded.

3.8 Melt flow index test

The melt flow index (MFI) value of composites designation was determined following the standard of American Society for Testing and Materials, ASTM D1238 by using Dynisco Melt Indexer Model LMI D4004HV (Dynisco, US). Melt flow index MFI is the rate of mass flow expressed in gram per 10 minutes (g/10 minutes). The sample as a pellet or a powder was pre-heated for 6 minutes in the barrel and extruded via the die under a constant load of 2.16 kg. The MFI value of neat PLA, PLA/wax, PLA/PEG and all PLA/wax/PEG composite were measured at a temperature of 180°C (Pivsa-Art et al., 2013). All samples were sent to Universiti Sains Malaysia (USM), Penang, Malaysia for MFI analysis that followed the above standard.

3.9 Filament extrusion

Based on the results of tensile testing, two composites designation were chosen for filament production which is 95/5/5 wt.% PEG and 95/5/8 wt.% PEG. Neat PLA was also extruded as a comparison. The composites feedstocks were crushed into powder form to reduce the formation of air sacks in the filament. The prepared composites were dried at 60°C in a laboratory oven prior to extrusion (Slapnik et al., 2016). The prepared composites were dried prior to extrusion in the oven at 60°C to remove any moisture to avoid hydrolysis because PLA tends to absorb moisture (Finnis et al., 2016; Kang et al., 2016). Filament for 3D printing was prepared by a single screw extruder (Filastruder, US). The extrusion of the filament was conducted at a set temperature of 230-240°C. The air cooling was used as the cooling method (to solidification process) while the filament was pulled and spooled manually. The low-speed extrusion was used in the filament extrusion to produce a consistent filament diameter. The setup of filament extrusion as shown in Figure 3.4. The diameter of the filament was measured by using vernier calipers. The diameter of the selected composites designations filament and neat PLA filament was measured, and 5 measurements were performed for each filament. The measurement was performed every 0.4 m along the filament and the average values were taken as the resultant value (Liu et al., 2017).

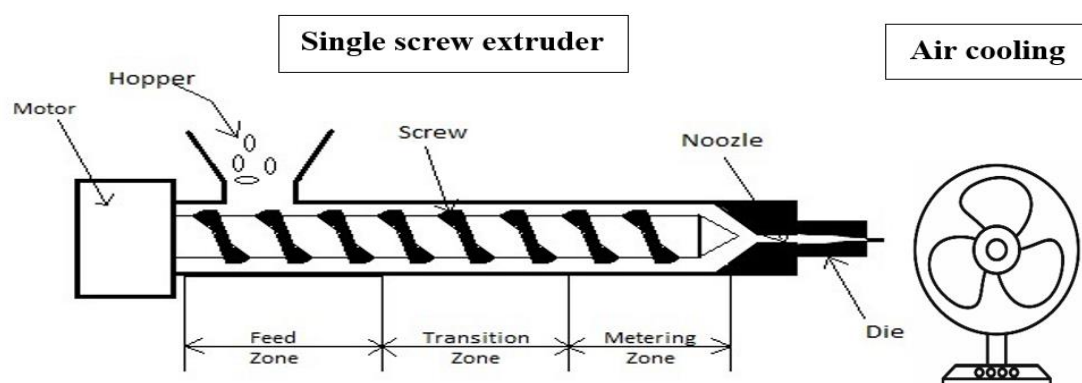


Figure 3.4: Setup for extrusion of filament

3.10 3D Printing via FDM by using PLA/Sarawax composites

A cube $1\text{cm} \times 1\text{cm} \times 1\text{cm}$ was created by using SketchUp Make software (version 17.2.2555 64-bit) and exported in stereolithography (STL) file format. Then, the STL file format was imported into slicer software (MakerBot software version 3.9.1.1143) to generate the G-code used to print each specimen (Abbas et al., 2017). Then, the cube was 3D printed using a Flashforge Creator 3D Printer. Several trial prints were run in order to determine the suitable setting for 3D printing nozzle temperature and also printing platform/bed temperature. 3D printing parameters such as the number of shells (2), layer height (0.20 mm), infill pattern (hexagonal) and percentage (25%) travel speed (150 mm/s) and print speed (90 mm/s) were kept constant.

3.11 Quality of 3D printed object by using PLA/wax composites (dimensional accuracy and layer height consistency)

To evaluate the dimensional accuracy, all the printed specimens were measured and compared to the designed CAD model. The dimensions ($L1 \times L2 \times H$) were measured using a Vernier calliper. Three printed specimen (cube) were measured for each sample and the average value was used as the resultant value. The dimensional errors were determined by using the equation below (Alafaghani et al., 2017):

$$\text{Dimensional error} = \text{Measured value} - \text{design value} \quad (3.2)$$

Then, to determine the quality of the outer surface of the 3D printed cube, the outer surface (layer by layer) was observed via Scanning Electron Microscope (SEM). The layer height of each layer was measured by using Smile View Version 2.26. 10 as shown in Appendix C.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Preparation of PLA/wax/PEG composite

This section presented the effect of wax as filler and polyethylene glycol (PEG) as a plasticizer on the preparation of feedstock PLA/wax /PEG composites.

4.1.1 Effect of polyethylene glycol loading on the feedstock of PLA/wax composites

In the composite designation, 5 wt.% composition in PLA/wax composite was chosen since the addition of more than 5 wt.% wax causes a more phase separation between PLA and wax during feedstock preparation. Thus, the composition of PLA/wax composite used was 95 wt.% PLA and 5 wt.% of wax. In this study, polyethylene glycol (PEG) was used as a plasticizer to overcome the brittleness of PLA matrix materials and enhanced the compatibility between the PLA matrix and wax filler. Pivsa-Art et al. (2015) were conducted a study to modify PLA properties through the plasticization process. Therefore, in this study, PEG was added into the PLA/wax composites to investigate the plasticizing effect of PEG.

Based on observation, all PLA/wax composites with the addition of PEG showed a good homogeneity between PLA and wax as depicted in Figure 4.1. PLA/wax composites with no addition of PEG was showed non-homogeneous feedstock as shown in Figure 4.1c. According to Saravana et al. (2018), the addition of plasticizers like PEG acts as a lubricant for the PLA and filler, so it improved the dispersion of filler in the PLA matrix and could improve brittle feature changes to ductile one. Based on the observation, the addition of

PEG and wax into the PLA matrix made the colour change from transparent (as shown in Figure 4.1a) to white cream (as shown in Figure 4.1b-i) and all the composites designation with the addition of PEG showed a homogenous mixture. This indicates that the wax and PEG were successfully incorporate in the PLA matrix via the melt blending technique.

Melt blending wax and PLA without polyethylene glycol (PEG) was very difficult to obtained homogeneous mixture and this may be due to the high viscosity of PLA at the beginning of the mixing process. This situation was reflecting the result of the melt flow index (MFI) of neat PLA where MFI value increased significantly when added with PEG and this indicates PEG was helped to reduces the viscosity of PLA. The higher the MFI value the lower the viscosity of the materials. The addition of PEG into the PLA/wax composites decreased the viscosity of the mixture thus, easier to obtained homogenous mixture. The increment of PEG contents in PLA/wax composites causes the mixture to become softer and helps to increase the homogeneity in the mixture. Sau'de (2016) stated that plasticizer act as a lubricant agent that increases the homogeneous dispersion and reduces the intermolecular friction between each particles distribution in the composites material. According to Pivsa-Art et al. (2015), to avoid phase separation the percentage of PEG added into PLA should be equal or less than to 20 wt %.

Therefore, in this study the addition of PEG into the composite only up to 15 wt.% cause if greater than that the more phase separation can be observed on the tensile fractured surface as shown in results of Scanning Electron Microscopy Analysis (Figure 4.11). Based on the results shown in Figure 4.1 it concluded that the addition of PEG helps to increase the homogeneity of the PLA matrix and wax.

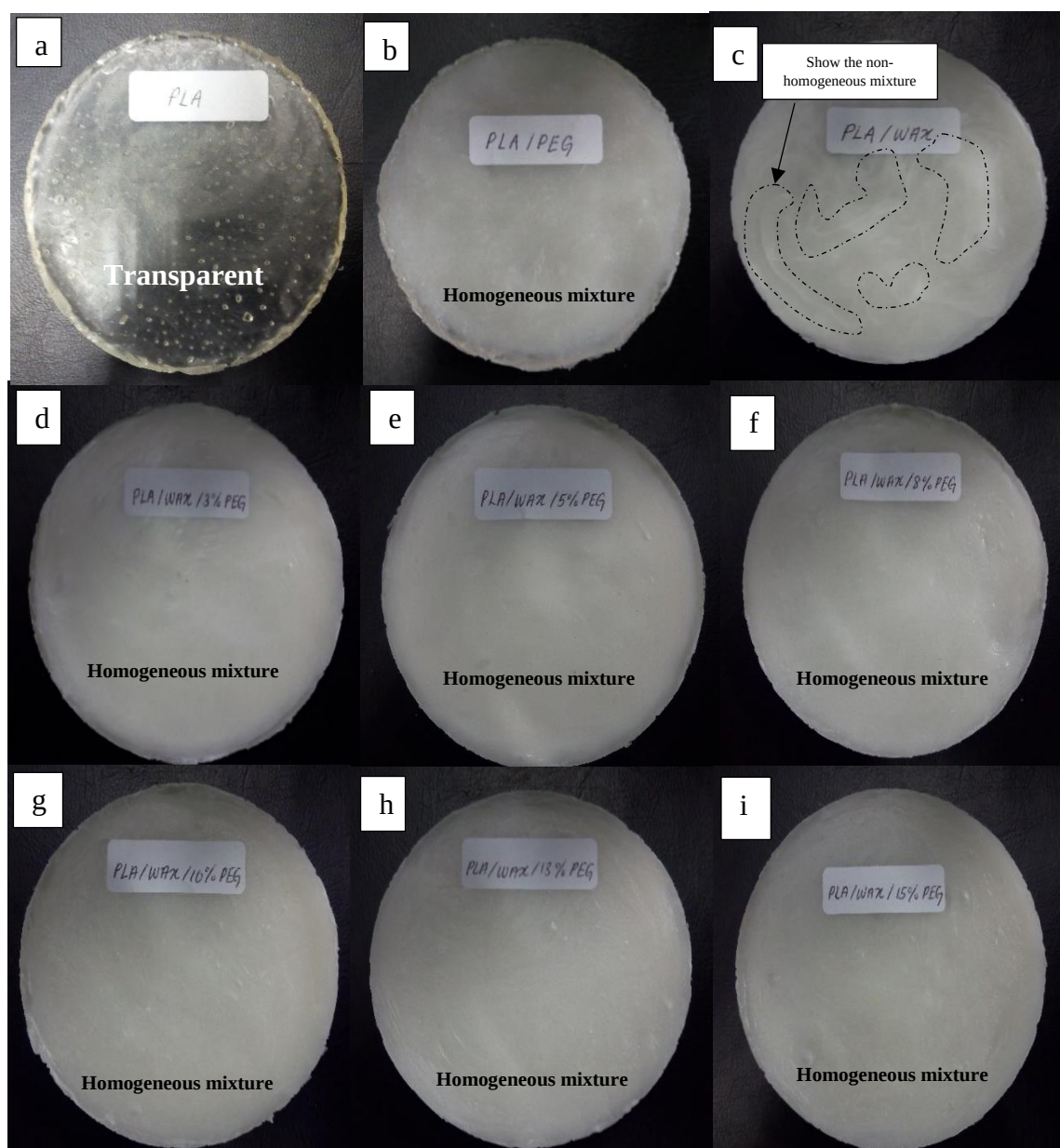


Figure 4.1: PLA/wax composites prepared by melt blending method with different percentage of plasticizer. (a) neat PLA (control), (b) PLA/PEG composites (100/0/5), (c) PLA/wax (95/5/0), (d) PLA/wax/PEG (95/5/3), (e) PLA/wax/PEG (95/5/5), (f) PLA/wax/PEG (95/5/8), (g) PLA/wax/PEG (95/5/10), (h) PLA/wax/PEG (95/5/13), (i) PLA/wax/PEG (95/5/15)

4.1.2 Effect of wax loading on the feedstock of PLA/wax composites

Three percentage of wax (5, 10 and 15wt.%) was used to determine the effect of wax in the composites. 5 wt.% plasticizer (polyethylene glycol) was fixed for all composites except PLA/wax composite (Control). Based on the results obtained in tensile testing (Table 4.1) and scanning electron microscopy analysis of tensile fractured surface (Figure 4.11), the addition of 5 wt.% of PEG was selected because at this concentration it helps to increase the compatibility between PLA matrix and wax. Based on the results of Scanning Electron Microscopy Analysis (SEM), it was shown that addition 5 wt.% PEG enhanced the compatibility between PLA and wax and no clear phase separation was observed (Figure 4.11 c).

Based on observation, the higher percentage of wax made the blends designation whiter as depicted in Figure 4.2. This indicated that the good dispersion of wax in the PLA matrix. In the blending process, the addition of 5 wt.% of wax was easier compared to the addition of 10 and 15 wt.% of wax into the composites, this is due to the addition of a high amount of wax cause the PLA and wax difficult to reach homogenous mixture. The addition of 5 wt.% of PEG into the composites helps to improve the homogeneity of PLA and wax. The composites designation with addition 5 wt.% of polyethylene glycol (PEG) (Figure 4.2b) shows more homogeneous composites as compared with no addition of polyethylene glycol (Figure 4.2a).

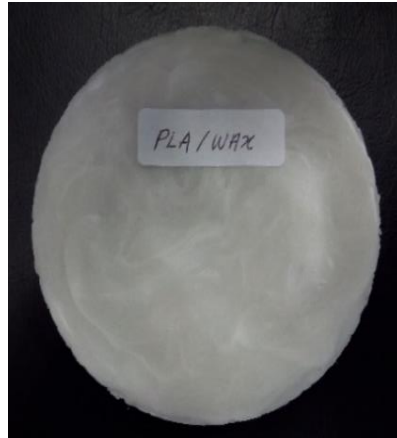


Figure 4.2: PLA/wax composites prepared by melt blending method with different wax loading. (a) PLA/wax composite (95/5/0) with no addition of polyethylene glycol (PEG), (b) PLA/wax composite (95/5/5) with the addition of 5 wt.% PEG, (c) PLA/wax composite (90/10/5) with the addition of 5 wt.% PEG, (d) PLA/wax composite (85/15/5) with the addition of 5 wt.% PEG

4.2 Tensile properties of PLA/wax composites

The tensile test specimens were prepared by using a compression molding method that was carried out using the Hydraulic Hot Press Machine. Figure 4.3 shows the example of tensile test specimens of PLA/wax composites that were prepared by using the compression molding method. In this study, the drying of feedstock composites was a very important aspect prior to the compression molding to eliminate moisture content present in the composites. It is very important to eliminate the moisture as the presence of water in the

composites may enhance the presence of air bubbles in the tensile specimens (Sungsanit, 2011).

This section presents the tensile properties of the composites as determined by the tensile test that followed ASTM D 638. The tensile strength, elastic moduli and elongation at break of the composites were reported in Chapter 4.2.1 and Chapter 4.2.2. The effect of wax loading and plasticizer, polyethylene glycol (PEG) on PLA matrix composite was determined. Then, the results for the composites were compared to the results of neat PLA to study the effects of blending wax and PEG with PLA. According to Liu et al. (2017), tensile strength is significant for the applications of the 3D printer filaments. If the filament is too fragile, it will break during the 3D printing process, which is very undesirable to the continuity of printing. The standard tensile strength for FDM filament is 22.00 MPa to 72.40 MPa, elastic moduli range (800 MPa to 3500 MPa) and the elongation at break from 2.6% to 186% (Svensson, 2012; Messimer et al., 2018).

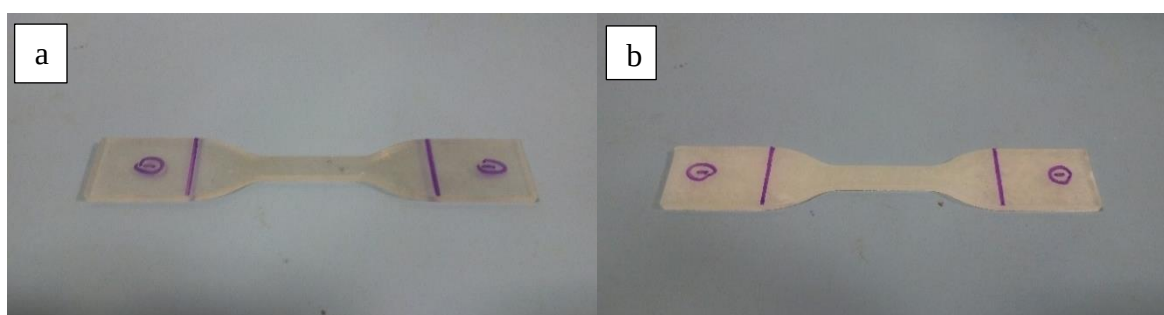


Figure 4.3: Example of a tensile test specimens. (a) neat PLA and (b) PLA/wax composites with addition 5 wt.% of PEG (95/5/5)

4.2.1 Effect of polyethylene glycol (PEG) loading on the tensile properties

The effect of adding polyethylene glycol (PEG) up to 15 wt.% on the tensile properties of PLA/wax composites was shown in Table 4.1.

Table 4.1: Tensile properties of PLA/wax composites with different content of polyethylene glycol (PEG)

Composites designation (wt.%)			Tensile strength (MPa)	Elastic moduli (MPa)	Elongation at break (%)
Polylactic acid	Wax	Polyethylene glycol (PEG)			
100	0	0	55.75 ± 3.17	1506.78 ± 36.81	5.89 ± 0.22
100	0	5	50.77 ± 1.58	1345.08 ± 46.25	6.51 ± 0.85
95	5	0	41.59 ± 0.84	1326.88 ± 11.99	5.73 ± 0.28
95	5	3	39.43 ± 2.05	1305.27 ± 41.41	6.13 ± 0.49
95	5	5	41.98 ± 1.50	1350.00 ± 29.56	6.35 ± 0.49
95	5	8	33.43 ± 0.10	1052.32 ± 36.94	7.38 ± 0.15
95	5	10	25.37 ± 1.97	801.76 ± 60.81	18.06 ± 2.76
95	5	13	19.52 ± 0.28	725.09 ± 27.90	19.71 ± 0.60
95	5	15	16.62 ± 0.70	597.20 ± 32.67	21.05 ± 1.90

The addition of plasticizer causes a substantial decrease in both tensile strength and elastic moduli of PLA/wax composites while an increase in the percentage of elongation at break. This trend was similar as reported in the study by Mohapatra et al. (2013); Noori and Ali (2014). Interestingly, PLA/wax composites with addition of 5 wt.% PEG was recorded higher value of tensile strength and elastic moduli compared to composite PLA/wax with no addition of PEG (41.59 MPa). It infers that the distribution of filler granules in the PLA matrix was good (Kamthai & Magaraphan (2015). The tensile strength of plasticized composites showed an increment for addition 3 wt.% PEG (39.43 MPa) to 5 wt.% PEG (41.98 MPa) contents and decreased thereafter as shown in Figure 4.4. The highest value of tensile strength was recorded at 41.98 MPa 95/5/5 wt.% PEG composites designation before dropped at 33.43 MPa (8 wt.% PEG), 25.37 MPa (10 wt.% PEG), 19.52 MPa (13 wt.% PEG) and 16.62 MPa (15 wt.% PEG). Increment in tensile strength was due to the increase in

dispersion of matrix and filler and the compatibility between the composite and the plasticizer. The decreased in tensile strength at above 5 wt.% PEG contents was may be explained by the accumulation of PEG at the interface when it exceeded in saturation concentration (Mansor et al., 2011). According to Messimer et al. (2018), the standard range of tensile strength for FDM filament is 22.00 to 72.40 MPa. When compared the elastic moduli results with the standard range, PLA/wax/PEG with addition 13 wt.% and 15 wt.% are not suitable since it also lower than the standard range.

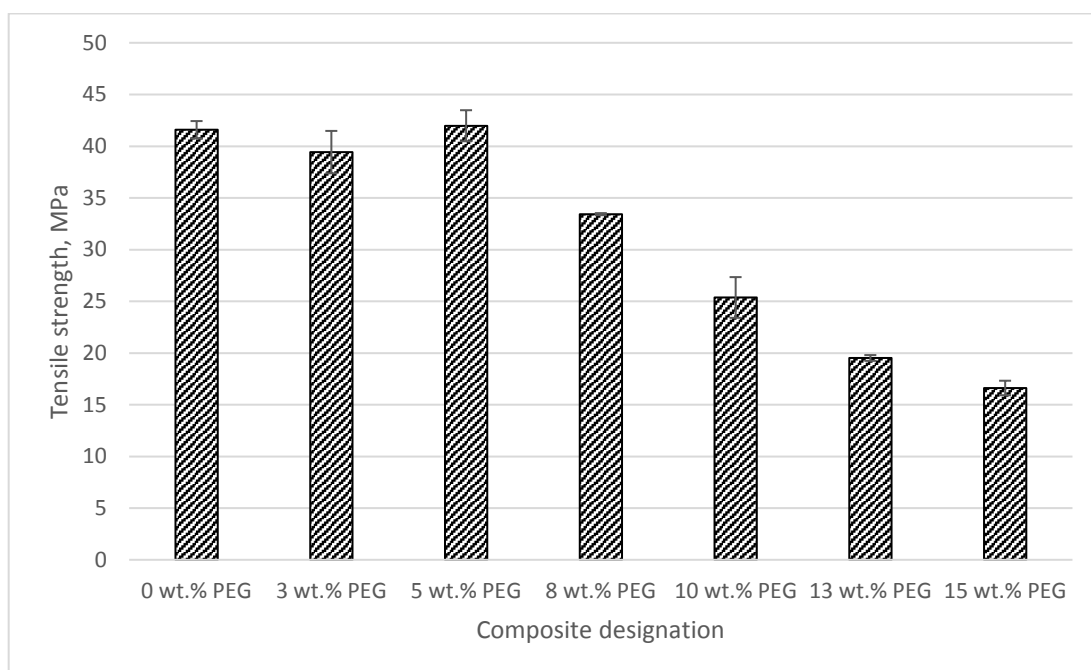


Figure 4.4: Effect of polyethylene glycol (PEG) loading on the tensile strength of PLA/wax composites (95/5)

In Figure 4.5 depicted the effect of PEG loading on elastic moduli of PLA/wax composites. The highest elastic moduli were recorded at 1350.00 MPa for PLA/wax composites with addition 5 wt.% PEG among the rest of PLA/wax composites; 1326.88 MPa (0 wt.% PEG), 1305.27 MPa (3 wt.% PEG), 1052.32 MPa (8 wt.% PEG), 801.76 MPa (10 wt.% PEG), 725.09 MPa (13 wt.% PEG), and 597.20 MPa (15 wt.% PEG). Results

obtained for elastic moduli of these composites also exhibited a similar trend with tensile strength results. The elastic moduli representing the stiffness of the composites dropped as the addition of PEG exceeded 5wt.%. This demonstrated that the addition of plasticizer decreased the stiffness of the composites. The addition of plasticizer typically leads to a decrease in stiffness, brittleness and hardness of composites. This was due to the plasticizer acts like a solvent when mixed with polymer then, the macromolecule chains cohesion was decreased, and tensile strength and elastic moduli properties thus reduced (Mansor et al., 2011). The standard range of elastic moduli for FDM filament is 800 to 3500 MPa. Based on this standard range, only two composite designations not suitable as FDM build material which is PLA/wax/PEG with addition 13 wt.% and 15 wt.% since its lower than the standard range (Svensson, 2017; Messimer et al., 2018).

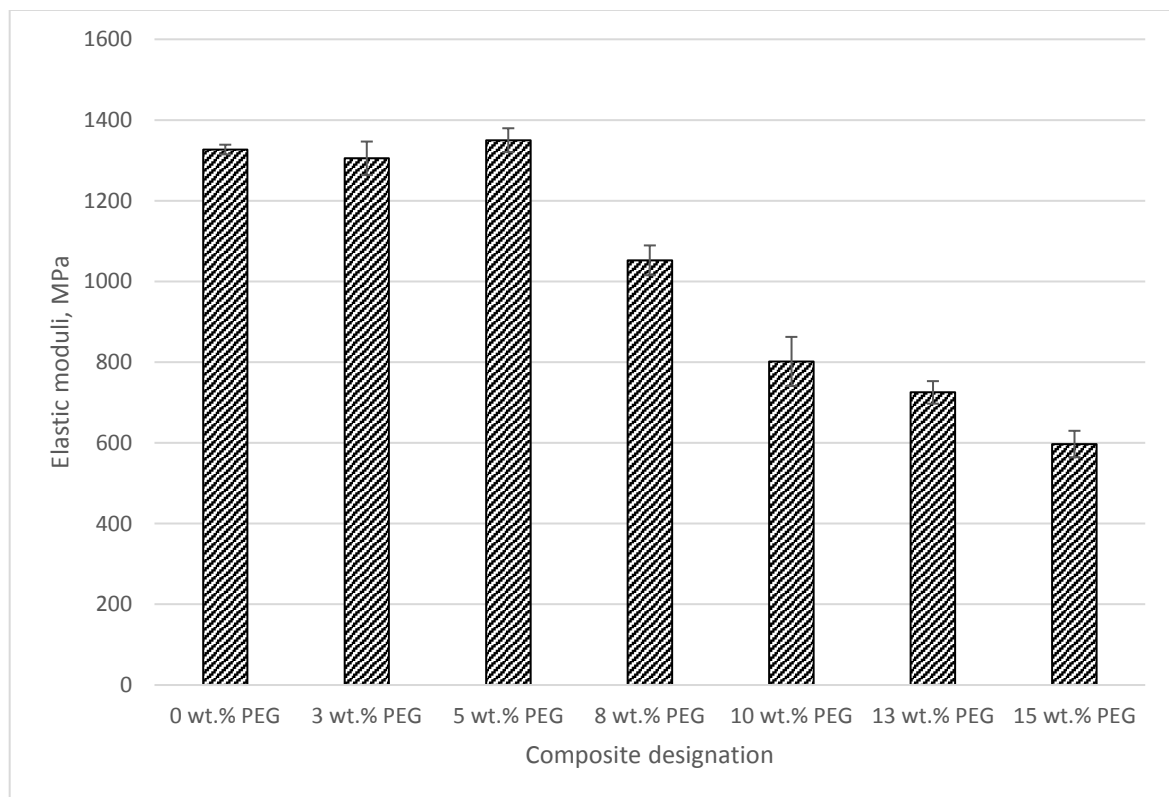


Figure 4.5: Effect of polyethylene glycol (PEG) loading on the elastic moduli of PLA/wax composites (95/5)

In contrast, an increase in elongation at break was observed. As can be seen in Figure 4.6, the elongation at break of PLA/wax composites showed an increase with the increment of PEG contents. The highest elongation at break was recorded at 21.05% for PLA/wax/15 wt.% PEG and the lowest was recorded at 5.73% for unplasticized PLA/wax. Based on this result, it shows that the PLA/wax/PEG composites were increased in ductility as the amount of PEG increased and this trend was similar with the findings by Mansor et al. (2011) and Pivsa-Art et al. (2015) on the plasticizer on elongation at break of PLA composites. Mansor et al. (2011); Pivsa-Art et al. (2015), stated that the addition of PEG showed the positive effect (increased) on the elongation at break and it is improved the ductility and overcome the brittleness of the composites. As a plasticizer, PEG molecules could penetrate the composites and disrupt the binding force between the macromolecules of PLA and wax that makes it easy for molecular chains to slide and move, thus increasing in elongation at break (Mansor et al., 2011). The plasticizer is a substance added to materials to improved flexibility, elongation and workability. This is an important aspect in the production of build material (filament) for FDM since the filament needs to be spooled during the production process.

In this research, the addition of PEG enhanced remarkably the elongation at break of PLA/wax composites that make it less brittle while maintaining the good values of tensile properties. Svensson (2017); Messimer et al. (2018) reported that the standard range of elongation at break for FDM filament is 2.46 to 186.00%. Based on this standard range it can be concluded that all the elongation at break composite designation suitable as FDM filament.

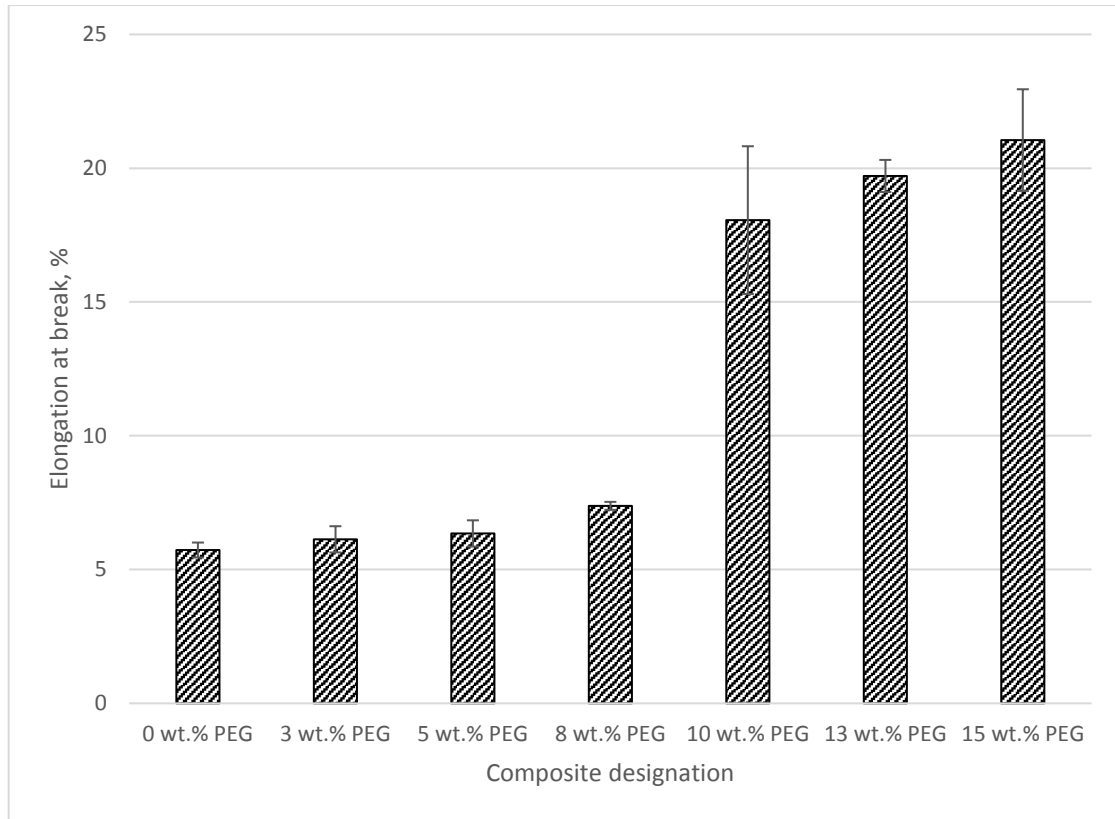


Figure 4.6: Effect of polyethylene glycol (PEG) loading on the elongation at break of PLA/wax composites (95/5)

4.2.2 Effect of wax loading on tensile properties

The effect of wax loading on tensile strength of PLA/wax composited was depicted in Table 4.2. The highest tensile strength for PLA/wax composite as shown in Figure 4.7 was recorded at 41.98 MPa for addition 5 wt.% wax and the lowest was recorded at 27.36 MPa (15 wt.% of wax). Tensile strength for the addition of 10 wt% of wax was recorded at 33.08 MPa. The tensile strength decreased with increasing wax content up to 15 wt.% and this trend may be explained as the wax is weaker (low strength and stiffness) material compared to PLA matrix (Pu et al., 2007).

Table 4.2: Tensile properties of PLA/wax composites with increasing of wax loading up to 15 wt.%

Composites designation (wt.%)			Tensile strength (MPa)	Elastic moduli (MPa)	Elongation at break (%)
Polylactic acid	Wax	Polyethylene glycol (PEG)			
95	5	0	41.59 ± 0.84	1326.88 ± 11.99	5.73 ± 0.28
95	5	5	41.98 ± 1.50	1350.00 ± 29.56	6.35 ± 0.49
90	10	5	33.08 ± 1.79	1236.97 ± 25.98	5.66 ± 0.32
85	15	5	27.36 ± 0.95	1119.86 ± 20.76	5.34 ± 0.37

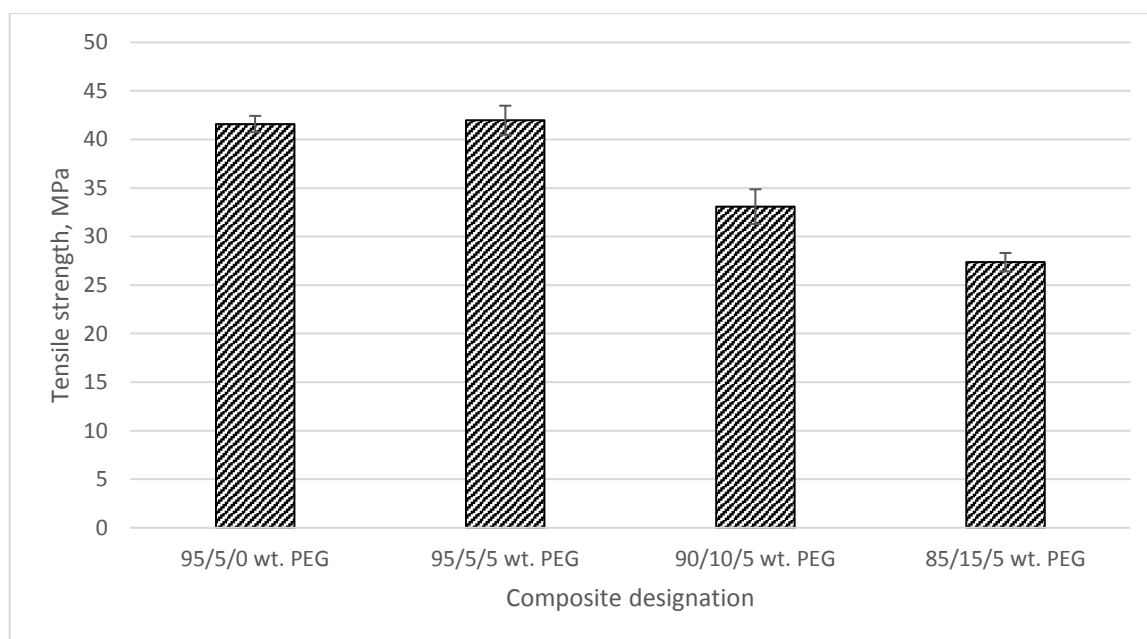


Figure 4.7: Effect of the wax loading on the tensile strength of the PLA/wax composites

The highest elastic moduli as depicted in Figure 4.8 was recorded at 1350.00 MPa for 5 wt.% wax before dropped at 1236.97 (10 wt.% wax) and 1119.86 MPa (15 wt.% wax). A similar trend was reported in a previous study by Mu et al. (2016). This indicates that the stiffness of the composites reduced with an increment of wax content. Even though the

composites reduced in stiffness, but it increased in flexibility because low elastic moduli are indicated flexible material, and this will provide flexibility to filament for spooling.

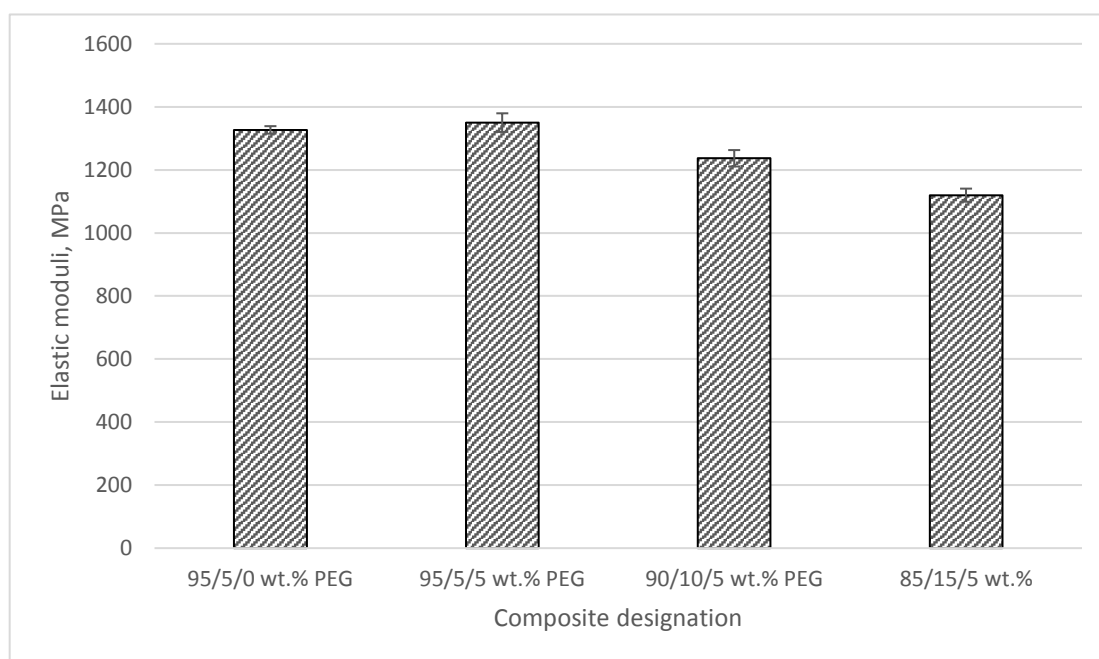


Figure 4.8: Effect of the wax loading on the elastic moduli of the PLA/wax composites

Composite designation with the addition of 5 wt.% wax (6.35%) also showed the highest elongation at break (ductility) as shown in Figure 4.9. A material that experiences very little or no plastic deformation upon fracture is termed brittle while the material that undergoes significant plastic deformation before rupture is term as ductile. The addition 15 wt.% of wax (5.34%) also recorded the lowest value for elongation at break. While addition 10 wt.% wax was recorded at 5.66%. The increment of wax content decreased the elongation of PLA/wax composites. It showed a similar trend as tensile strength and elastic moduli, where increment in wax loading leads to a decrease in tensile properties of PLA/wax composites. It can be concluded that the addition of more wax reduced the ductility of the composites this is due to the PLA matrix reduced in polymer chain mobility (Mu et al.,

2016). The decrease in ductility of composite also due to the wax is a brittle material with low strength and stiffness (Pu et al., 2007).

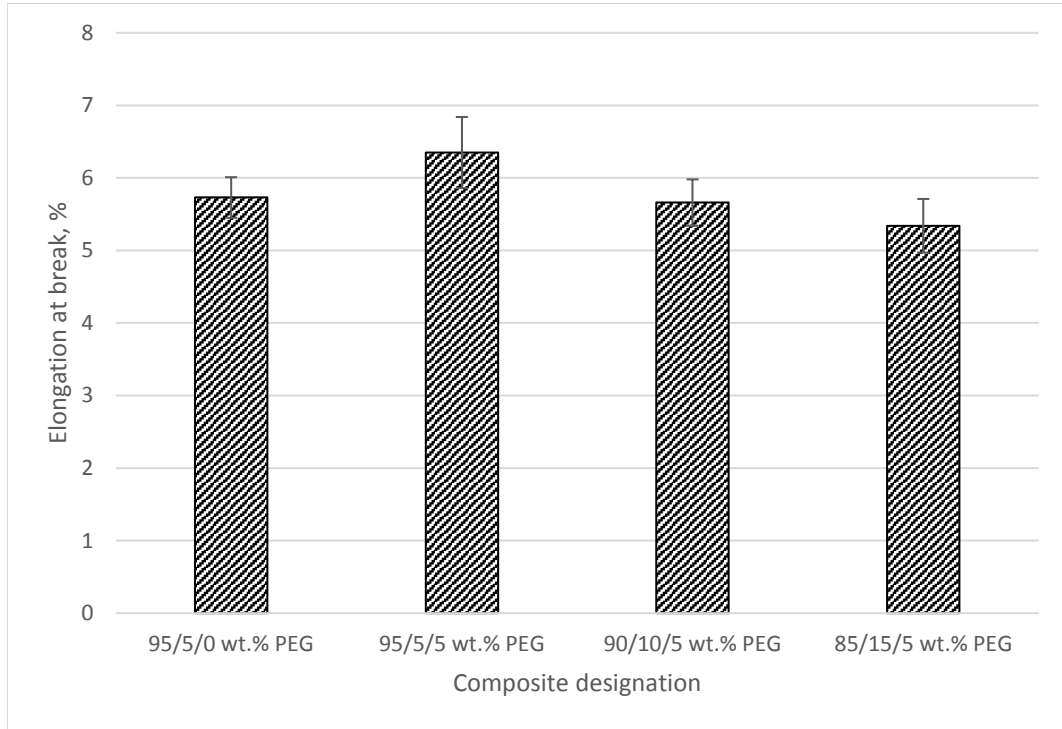


Figure 4.9: Effect of the wax loading on the elongation at break of the PLA/wax composites

4.3 Scanning Electron Microscopy (SEM) analysis (morphological properties)

4.3.1 Effect of polyethylene glycol (PEG) loading on the fractured surfaces of composites

The fractured surfaces of the tensile failed specimens of the composites were examined via Scanning Electron Microscope (SEM). The tensile fractured surfaces micrographs of neat PLA and PLA/PEG (100/0/5) were depicted in Figure 4.10. In Figure 4.10a, it can be observed that neat PLA showed a brittle failure, while the fractured surfaces of PLA/PEG (100/0/5) were homogenous and a smooth microstructure can be observed. This indicated that no clear phase separation has occurred between the PLA and PEG phase. Based on Figure 4.10b, no agglomerates or brittle crack behaviour were observed, which evidences

good interfacial adhesion between the two phases of the PLA matrix and PEG. (Silverajah et al., 2012).

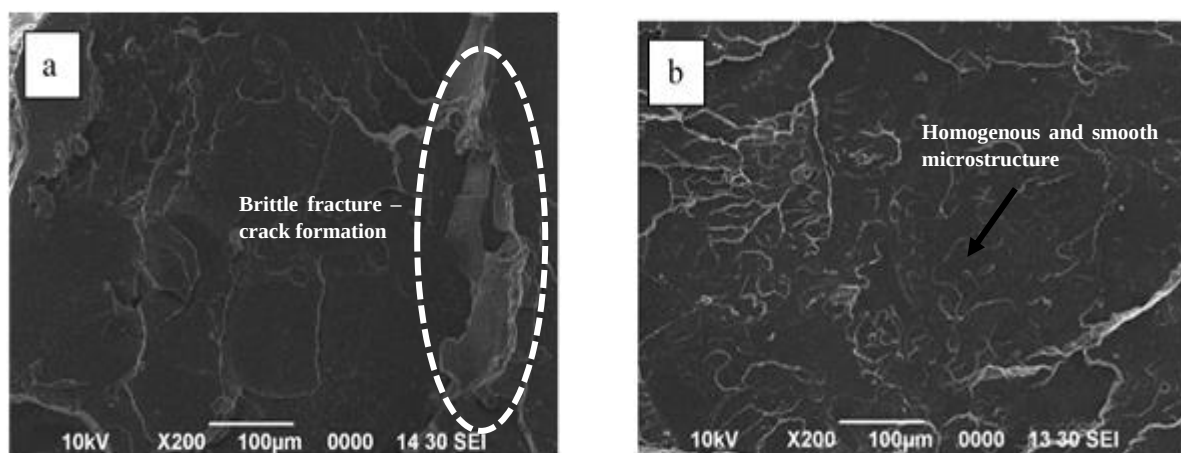


Figure 4.10: SEM micrographs of (a) neat PLA and (b) PLA/PEG (100/05)

SEM micrographs of tensile fractured specimens of PLA/wax and PLA/wax/PEG composites were also depicted in Figure 4.11. To investigate the effect of polyethylene glycol (PEG) on fractured surface of PLA/wax composites, 6 different percentage of PEG were used (3, 5, 8, 10, 13, 15 wt.%). The fractured surface of PLA/wax composites (95/5/0) was more roughness when compared with neat PLA (Figure 4.10a). The fractured surface of PLA/wax composite without the addition of plasticizer which is PEG (Figure 4.11a) clearly exhibited a two-phase separation of PLA matrix phase and the wax phase. Based on the SEM micrographs, the phase of wax dispersed as spherical domains were observed in the PLA matrix. The addition of 3 wt.% PEG slightly improved the compatibility between wax and PLA matrix and less phase separation was observed. While the addition of 5 wt.% of PEG showed an improvement in the dispersion of wax in the PLA matrix and no clear phase separation was observed. However, further addition of PEG above 5 wt.% decreased the compatibility between wax and PLA matrix. This indicated that the right amount of PEG into PLA/wax composites played an important role in enhancing the compatibility between

PLA and wax. Therefore, it can be concluded that the compatibility between wax and PLA matrix might be improved by the introduction of 5 wt.% PEG.

Based on the results obtained in tensile testing, it was shown that the addition of 8 wt.%, 10 wt.%, 13 wt.% and 15 wt.% PEG was significantly increased the elongation at break of PLA/wax composites. As can be seen in Figure 4.11, SEM micrographs of the tensile fractured surfaces show longer fibrils were produced when PEG introduced at 8 wt.% (Figure 4.11d), 10 wt.% (Figure 4.11e), 13 wt.% (Figure 4.11f) and 15 wt.% (Figure 4.12g) and according to Thomas et al. (2013), this indicated that PLA composites changed from brittle fracture to a ductile fracture. However, when the PEG loading at 10 wt.% and above, the formation of big voids and more phase separation of wax and PLA matrix was observed especially at 15 wt.% addition of wax. The formation of voids due to the poor interfacial interaction between matrix (PLA) and filler (wax) resulting in poor mechanical properties (Kamthai & Magaraphan, 2015).

When compared to the tensile fractured surface of PLA/PEG 100/0/5 (Figure 4.10 b) with PLA/wax/PEG composites (Figure 4.11), the PLA/PEG showed a smooth fractured surface while the composites showed rough surface. This exhibited that the addition of wax in the composites make the fractured surface rough due to the incompatibility of PLA matrix and wax. Among the PLA/wax/PEG composites 95/5/5 was showed a smooth tensile fractured surface and no significant difference in microstructure when compared to PLA/PEG. This showed that even though, the wax was added into the composition, the addition of 5 wt.% can help to make the PLA matrix and wax compatible. It can be concluded that the addition of 5 wt.% of PEG as the optimum PEG loading for PLA/wax composites.

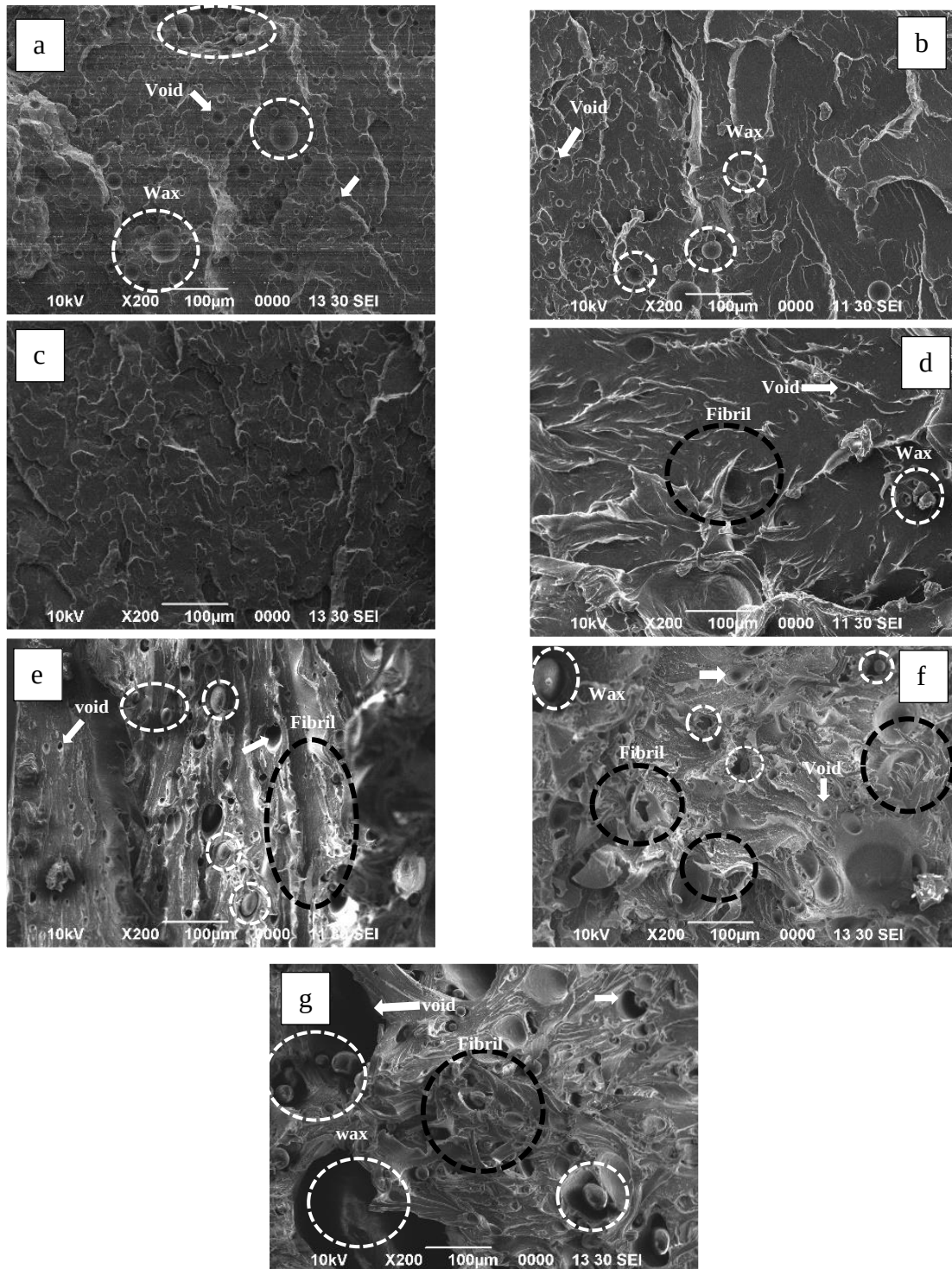


Figure 4.11: SEM micrographs of (a) PLA/wax composite (95/5/0), (b) PLA/wax/PEG composite (95/5/3), (c) PLA/wax/PEG composite (95/5/5), (d) PLA/wax/PEG composite (95/5/8), (e) PLA/wax/PEG composite (95/5/10), (f) PLA/wax/PEG composite (95/5/13) and (g) PLA/wax/PEG composite (95/5/15)

4.3.2 Effect of wax loading on the fractured surface of composites (morphological properties)

In this study, to investigate the effect of wax loading on fractured surfaces of PLA/wax composite, 3 different percentages were used (5, 10 and 15 wt.% wax). As can be seen in Figure 4.12, at the lowest content of wax (5 wt.%), a homogeneous fractured surface and good dispersion of the wax was observed. However, the miscibility of the wax within the PLA matrix become poor and accumulation of wax was observed at a higher percentage; 10 wt.% and 15 wt.%. In Figure 4.12c and Figure 4.13d, a heterogeneous surface was observed on the fractured surface of 90/10/5 (10 wt.% wax) and 85/15/5 (15 wt.% wax). This indicated that the immiscibility of the wax within the PLA matrix. AlMaadeed et al. (2015) also reported a similar trend on the effect of wax loading on the fractured surface of polymer matrix composites. Increment in wax content causes an increase of phase separation in polymer matrix composite (AlMaadeed et al., 2015).

Other than that, more voids were observed on the fractured surface of PLA/wax composites with the addition of 10 wt.% and 15 wt.% wax compared to 5 wt.% wax. Then, the wax phase surrounded by voids was observed and Wacharawichanant et al. (2017) stated that this indicated a poor interfacial adhesion in the composites. A study conducted by Chen et al. (2018) on the morphology of PLA/paraffin wax composites showed that increased concentration of paraffin wax, bigger paraffin wax particles and voids can be seen on the tensile fracture. Chen et al. (2018) reported that the voids were produced by large paraffin wax particles falling out during the tensile testing experiment. Therefore, it can be concluded that the addition of a high amount of wax into the composites causes an increased in immiscibility between the matrix and filler.

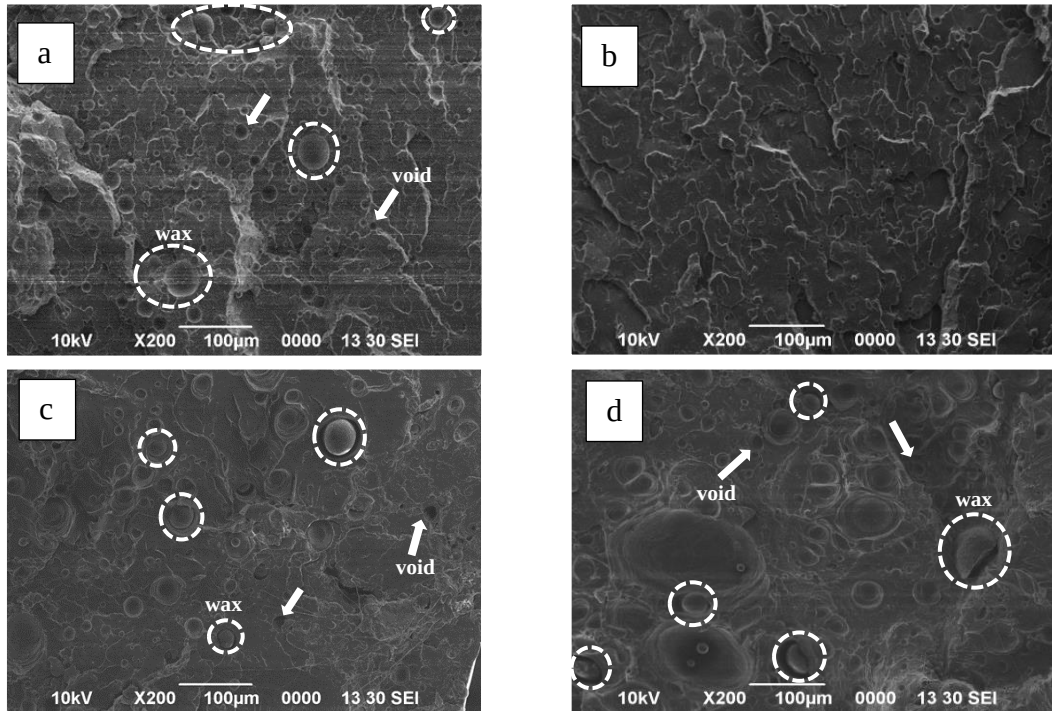


Figure 4.12: SEM micrographs of (a) PLA/wax composite (95/5/0) with no addition of PEG, (b) PLA/wax/PEG composite (95/5/5), (c) PLA/wax/PEG composite (90/10/5) and (d) PLA/wax/PEG composite (85/15/5)

4.4 Water absorption test

4.4.1 Effect of polyethylene glycol loading on the water absorption

In this research, the effect of wax and plasticizer loading on water absorption was determined. Table 4.3 and Figure 4.13 show the maximum water absorption for 30 days, the composites were immersed in distilled water at room temperature. While Figure 4.14 shows the water absorption on day 1,7,14,21 and 30. As can be seen in Figure 4.13 the water absorption of composites was gradually increased as the PEG (plasticizer) loading increased and dropped for 15 wt %. PEG loading. Leu and Chow (2011) reported that the water uptake of PLA composites increased with the increment of PEG concentration. The results obtained in this study, the water absorption of PLA with the addition of 5 wt.% PEG (100/05) was high compare to neat PLA; where the water absorption was recorded at 1.78% while for neat

PLA was 0.55%. This indicated the addition of PEG in the PLA matrix increased its hygroscopy (water absorption). 100/0/5 was used as a control to investigate the effect of PEG on water absorption of the PLA matrix only not for the PLA/wax composites. The highest water absorption was 95/5/13% PEG (3.83%) and reached the maximum water uptake on day 14 (Figure 4.14). Then, after day 14 the water absorption decreased. 95/5/15 wt % PEG was the second-highest maximum water absorption at 3.83%. However, it reached the maximum water uptake on day 7 and decreased (1.04%) in water absorption after that. While for the rest of the composites their reached maximum water absorption at day 30 and no decreased in water uptake was observed.

The decrease of water uptake showed in Figure 4.13 for 95/5/13 wt.% (started at day 14) PEG and 95/5/15 wt.% PEG (started at day 7) may be due to the characteristics of polyethylene glycol that easily dissolve in water. This situation showed that 13 wt% PEG and 15 wt% PEG was too high amount of plasticizer for the composites formulation and may exceed the saturation concentration. Water uptake might decline slightly as immersion time was increased (Yew et al., 2005), due to the fact that some PEG was dissolved in water. Meints et al. (2018) stated that polyethylene glycol is highly hydrophilic and easily dissolved in water.

Water absorption is one of the important aspects to estimate the application of a composite (Mansor et al., 2011). As the criteria of 3D printer filament need a material with high water resistance because low water resistance will influence the strength of the material over time. According to Chow et al. (2014), water absorption in polymer composites could change the mechanical and physical properties of the material significantly. Even though the

addition of PEG was increased the water absorption of PLA/wax composite, but it is not exceeded the standard water absorption for common build material for FDM which is up to 5 % (Farbman and McCoy, 2016).

Table 4.3: Water absorption of PLA/wax composites with different polyethylene glycol (PEG) content for 30 days

Composite designation	Maximum Water Absorption
Neat PLA (control)	0.55 ± 0.02
100/0/5	1.78 ± 0.12
95/5/0	0.60 ± 0.05
95/5/3	1.45 ± 0.03
95/5/5	1.94 ± 0.09
95/5/8	2.85 ± 0.30
95/5/10	3.47 ± 0.32
95/5/13	3.83 ± 0.13
95/5/15	3.77 ± 0.02

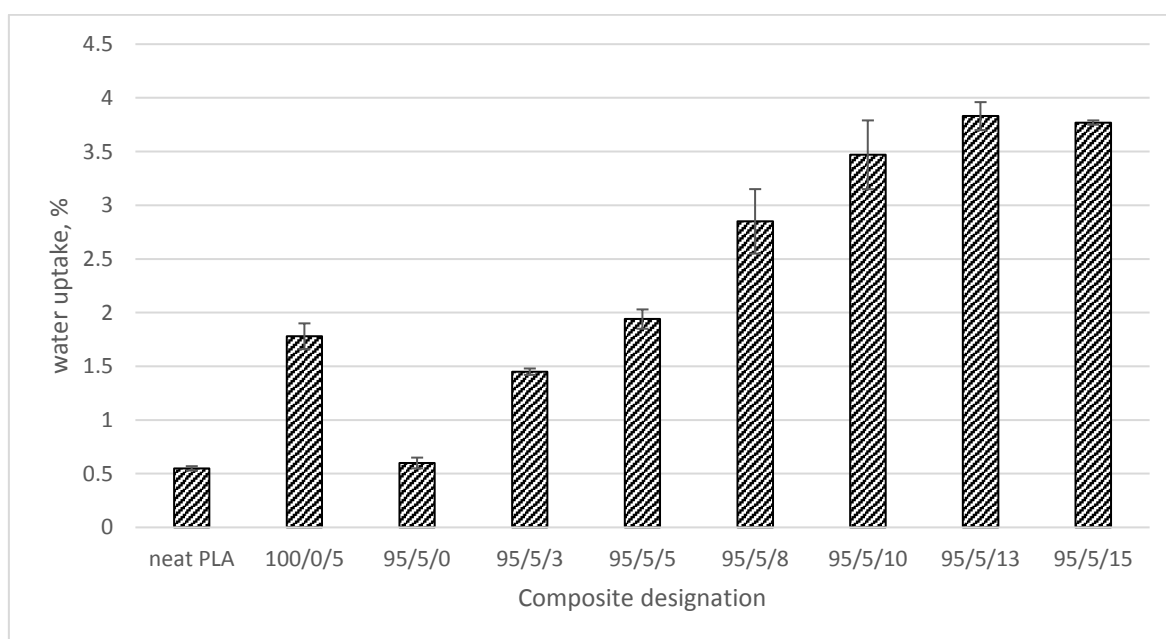


Figure 4.13: The effect of polyethylene glycol (PEG) loading on the water absorption of PLA/wax composite for 30 days

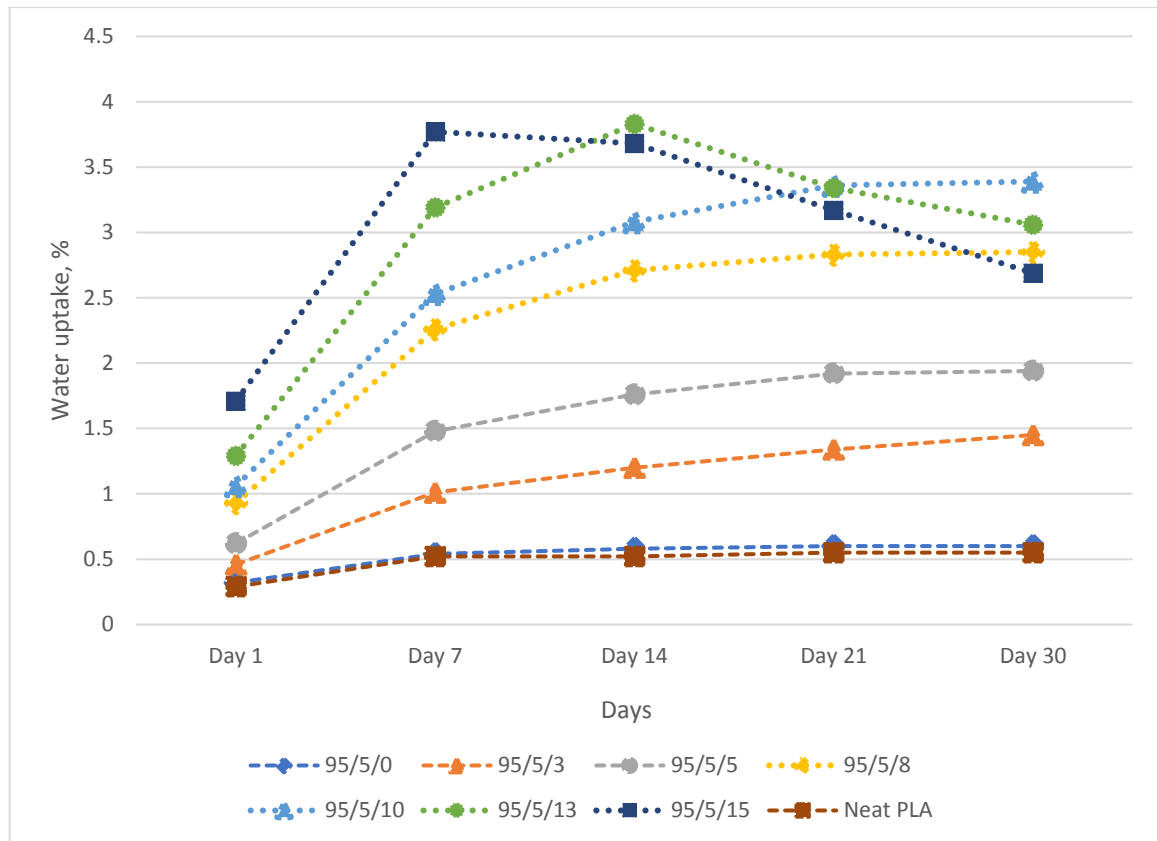


Figure 4.14: Water absorption from day 1 until day 30 of PLA/wax composites at different polyethylene (PEG) loading

4.4.2 Effect of wax loading on the water absorption

The effect of wax loading on the water absorption of the composites designation for 30 days as depicted in Table 4.4 and Figure 4.15. While Figure 4.16 shows the water absorption on day 1,7,14,21 and 30. Based on the results of water absorption, 95/5/0 wt.% PEG composite has a slight increase in water absorption which 0.60% as compared to control 0.55% (neat PLA). The increment of water absorption for 95/5/0 may be contributed by some factors such as the presence of voids inside the composites. Based on the results of the SEM micrograph, there were a formation of the void was observed on the fractured surface of PLA/wax composites (95/5/0). Leu and Chow (2011) stated that water molecules could

penetrate composites via voids due to incompatibility of matrix and filler, and subsequently, higher water absorption. All PLA/wax composites show higher water absorption when compare to neat PLA and 95/5/0. 95/5/5 wt.% PEG composite was the highest water absorption at 1.94% and gradually decreased for 90/10/5 and 85/15/5 which are 1.84% and 1.71% respectively. Based on these results shown in Figure 4.14 and Figure 4.15, the addition of wax may increase the water-resistance of the composites designation.

Table 4.4: Water absorption of PLA/wax composites with different wax content for 30 days

Composite designation	Maximum Water Absorption (for 30 days)
95/5/0	0.60 ± 0.05
95/5/5	1.94 ± 0.09
90/10/5	1.84 ± 0.13
85/15/5	1.71 ± 0.13

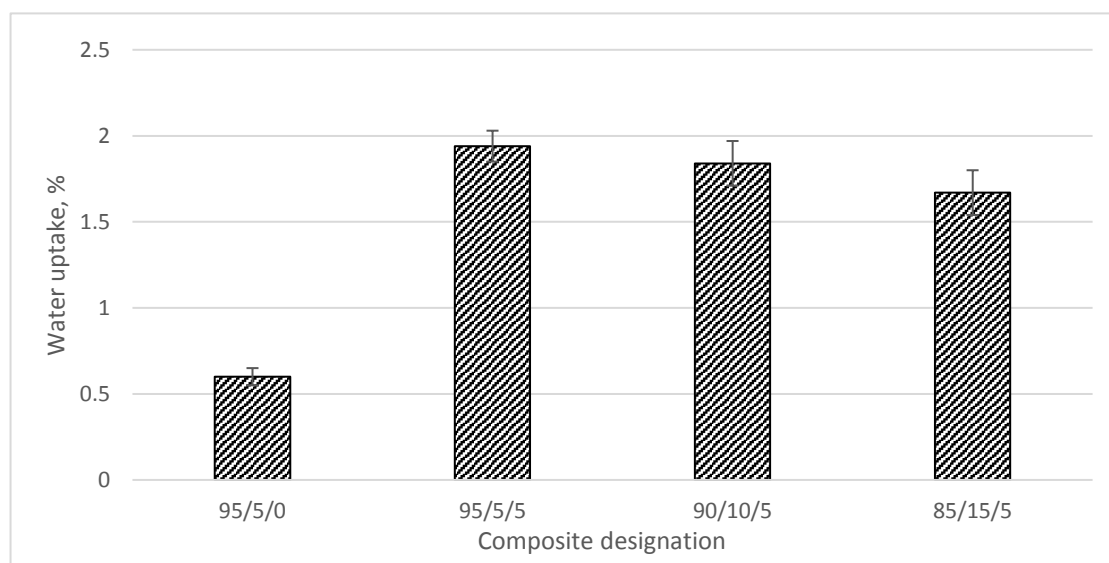


Figure 4.15: The effect of wax loading on the water absorption of PLA/wax composite for 30 days

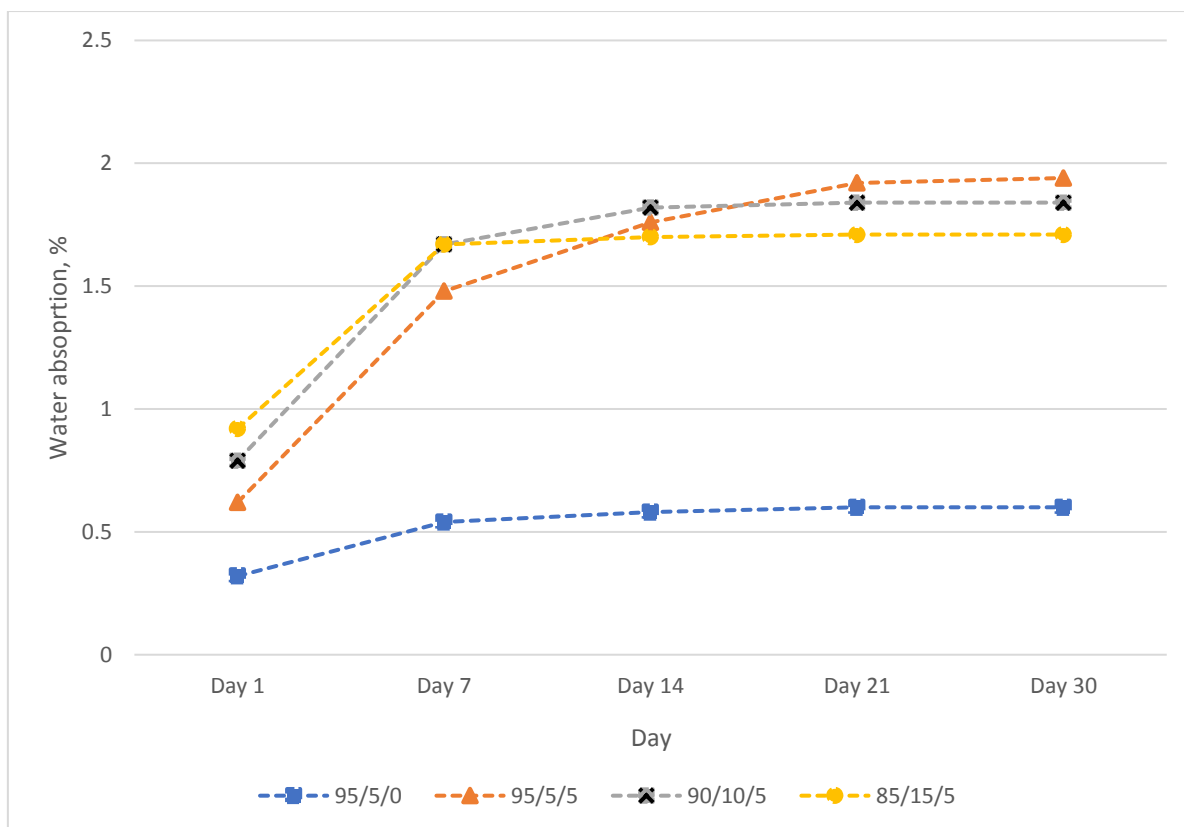


Figure 4.16: Water absorption from day 1 until day 30 of PLA/wax composites at different wax loading

4.5 Determination of melting point

The melting point of designated composites was depicted in Table 4.5 and Table 4.6. The effect of polyethylene glycol (PEG) loading on the melting point as depicted in Figure 4.17. When neat PLA was introduced with 5 wt.% PEG (100/0/5), the melting point significantly decreased. It was shown very clearly evident in Figure 4.17, that the melting temperature of PLA decreased from (180-181°C) to (171-173°C). Chiulan et al. (2017), also reported that the melting point of PLA decreased with the addition of PEG. According to Mohapatra et al. (2013), the melting temperature was influenced by the incorporation of PEG into the PLA matrix.

PLA/wax composites also decreased in the melting point as the PEG content increased as shown in Figure 4.17. The melting point of PLA/wax composites without PEG (95/5/0) was the highest at 175-177°C and gradually decreased as the amount of PEG increased. Sungsanit et al. (2012); Bijarimi et al. (2016) reported that the incorporation of PEG into PLA composites reduced the melting point and gradually dropped as the PEG concentration was increased. According to Mohapatra et al. (2013); Saravana et al. (2018), this trend showed good miscibility between the polymer composites and the plasticizer. The decreased in melting points was a desirable effect as this will allow 3D printing using these composites to be possible at a lower temperature.

Table 4.5: Melting point (range) of PLA/wax composites with the addition of different polyethylene glycol (PEG) content

Composite designation	Melting point (°C)
Control (neat PLA)	180 - 181
100/0/5	171 - 173
95/5/0	175 - 177
95/5/3	171 - 175
95/5/5	169 - 173
95/5/8	168 - 172
95/5/10	167 - 171
95/5/13	166 - 171
95/5/15	165 - 170

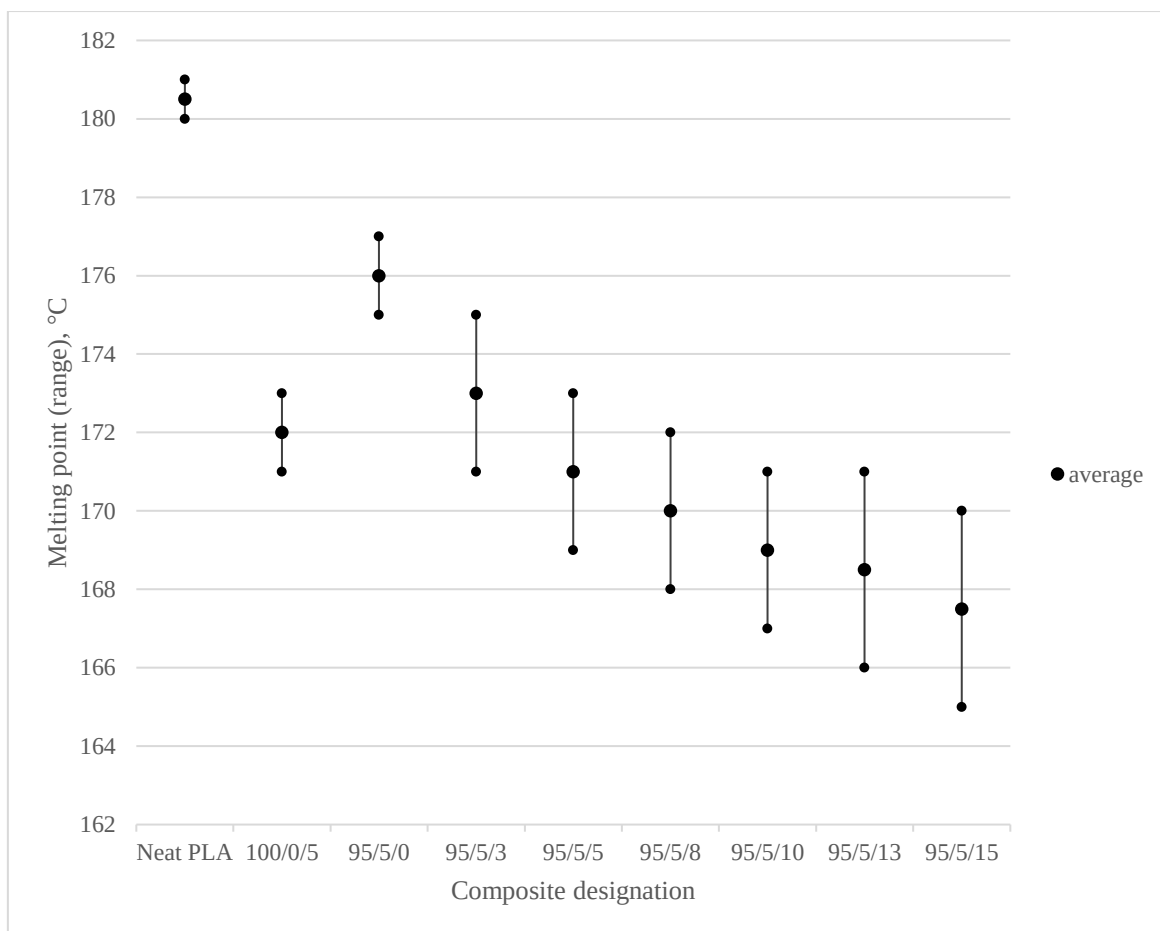
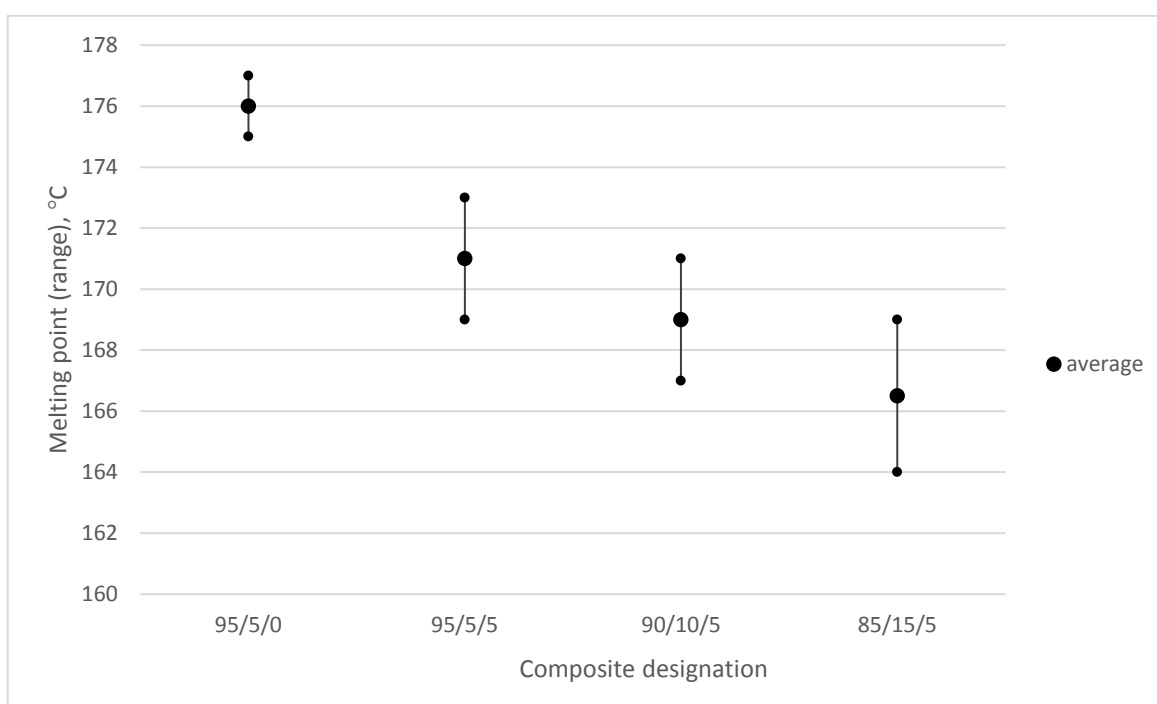


Figure 4.17: Effect of PEG loading on the melting point (range) of PLA/wax composites

Melting point (range) of PLA/wax composites with different wax content as depicted in Table 4.6 and Figure 4.18 show the effect of wax loading on the melting point of these composites. As shown in Figure 4.18, increment in the amount of wax was reduced the melting point. The highest melting point of PLA/wax composites was recorded at 169 -173°C for PLA/wax composites with 5 wt.% wax contents and then, dropped at 167-171°C (10 wt.%) and 164-169°C (15 wt.%). In the study conducted by AlMaaded et al. (2015), increment in wax content was reduced the melting point of the polymer matrix.

Table 4.6: Melting point (range) of PLA/wax composites with different wax content

Composite designation	Melting point (°C)
95/5/0	175- 177
95/5/5	169 - 173
90/10/5	167 - 171
85/15/5	164 - 169

**Figure 4.18:** Effect of wax loading on the melting point (range) of PLA/wax composites

4.6 Melt flow index (MFI) test

Six different percentages of plasticizer (3, 5, 8, 10, 13 and 15 wt.% PEG) were used to investigate the effect of plasticizer loading on the MFI of PLA/wax composites. The effect of polyethylene glycol loading on the MFI of PLA/wax composites shown in Figure 4.19 and Table 4.7. Based on the results obtained in the MFI test, the melt flow of PLA/wax composites was increased as the PEG content was increased. The highest MFI value for

PLA/wax composite with the addition of PEG was 95/5/15 wt.% PEG (364.49 g/10 min) while the lowest was 95/5/3 wt.% PEG (72.11 g/10 min) as shown in Figure 4.19. The MFI value of the composites was significantly increased after the addition of PEG that more than 3 wt.%. The results obtained showed that PEG reduced the viscosity of PLA composites very effectively by increased the MFI value.

Xue et al. (2013) stated that this indicated that the addition of PEG effectively improves the plasticization of the composites and subsequently decreased the melt viscosity. According to Xie et al. (2017), the addition of plasticizer in the composites was enhanced the flowability of the composites. Too high or too low melt index is not a desirable characteristic as this may place the composites designation not suitable to be used in the FDM 3D printers.

The standard melt flow index for common materials for FDM is 5 to 100 g/minutes (Masumi Corporation, 2012; Wang et al., 2017). Based on the results obtained, the MFI value of the material is higher than the standard MFI of common materials for FDM and this one of the desirable characteristics in this study. This will allow the composites filament were printed at high speed because it increased in flowability via the nozzle of the FDM machine. However, the addition of equal and more than 10 wt.% PEG showed a very high MFI value and is considered too high and not suitable for the FDM 3D printer. Based on the results in Section 4.7 filament extrusion addition of 5 and 8 wt.% PEG in the composition were suitable for filament production and it was successfully extruded even though the MFI of these composites exceeded the standard MFI value as mention before.

Table 4.7: Melt flow index (MFI) of PLA, PLA/wax composite and PLA/wax composites with different PEG content

Composite designation	Melt Flow Index (g/10 minutes)
Control (PLA only)	47.45 $\pm$ 0.49
100/0/5	72.11 $\pm$ 0.38
95/5/0	55.45 $\pm$ 0.07
95/5/3	96.82 $\pm$ 0.45
95/5/5	159.77 $\pm$ 0.36
95/5/8	282.09 $\pm$ 0.41
95/5/10	307.75 $\pm$ 0.46
95/5/13	348.18 $\pm$ 0.32
95/5/15	364.49 $\pm$ 1.82

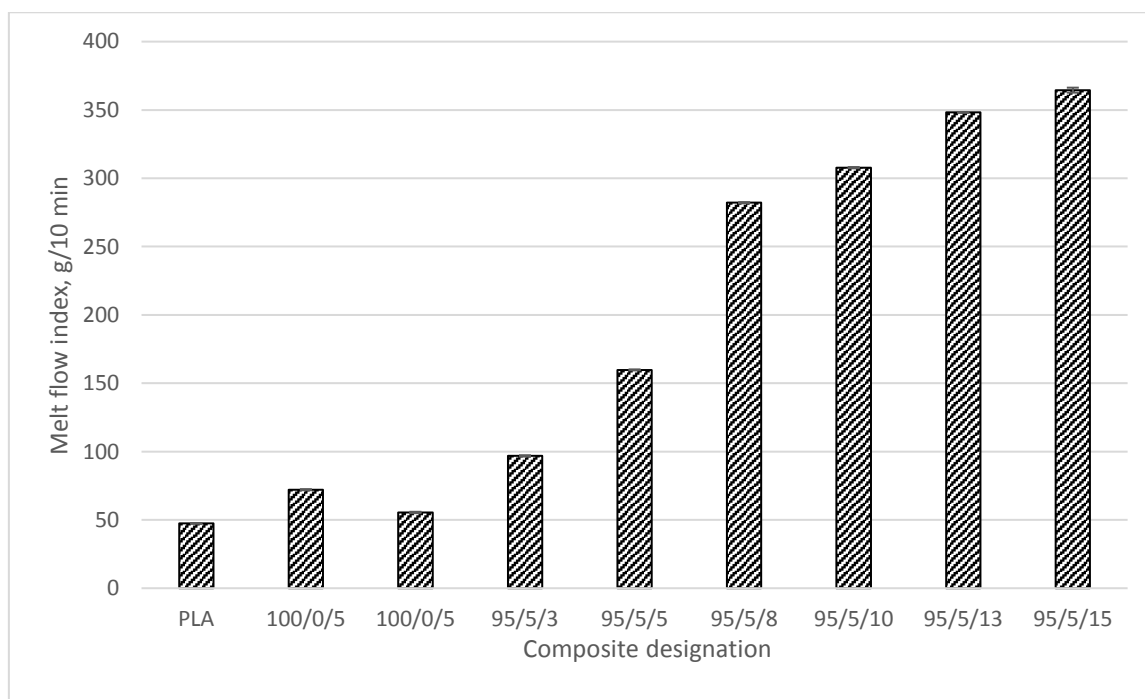


Figure 4.19: Effect of polyethylene glycol (PEG) loading on the MFI values of PLA/wax composites

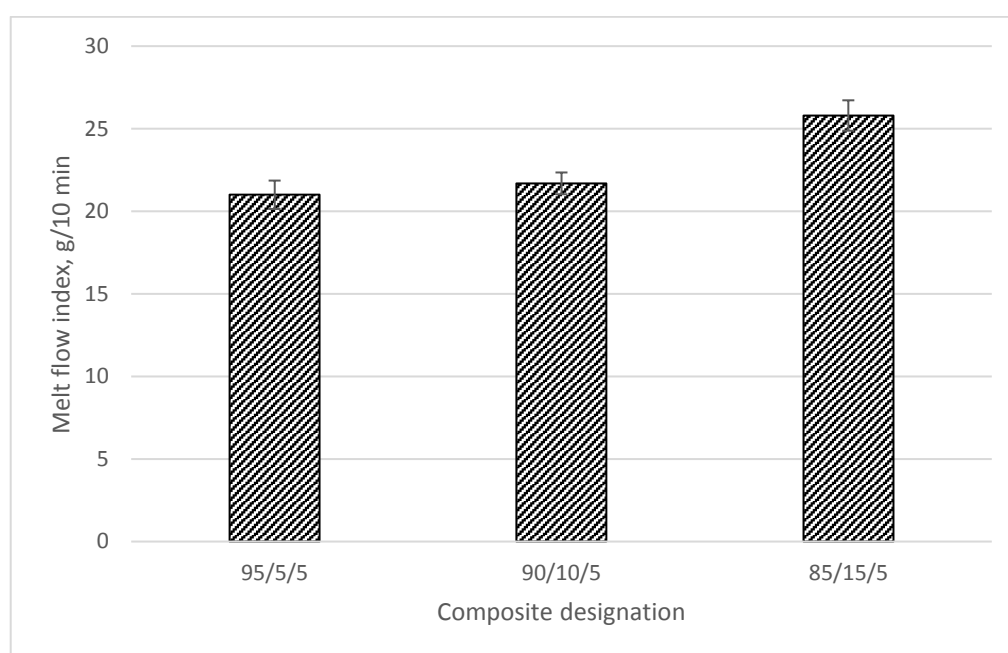
In this study, to investigate the effect of incorporation of wax with PLA; 5,10 and 15 wt.% of wax was blended with PLA and addition of 5wt.% of PEG. Among these three formulations, the highest MFI value was 85/5/5 (25.80 g/10 min) followed by 90/10/5 (21.69g/10 min) and 95/5/5 (21.00 g/10 min) as shown in Figure 4.20 and Table 4.8. This result showed that the addition of wax helped to reduce the viscosity of the composites. Onagoruwa et al. (2001) stated that the wax component acts to reduces the viscosity of the composites filament formulation.

However, the MFI value in this section was lowered (in Table 4.8) as compared to the MFI of PLA/wax composites with different content of PEG (Table 4.7). All samples were sent for MFI analysis in University Sains Malaysia, Penang, Malaysia since the melt indexer machine was not available in the laboratory. The first batch of samples was sent to the analyzer; that samples are to study the effect of PEG loading on the MFI value of PLA/wax composites (Table 4.7) and measured at 180°C. Then the second batch of samples were these three samples (to study on wax loading effect on MFI value of PLA/wax composite, Table 4.8) were sent separately to USM, Penang, and the analyzer reported that the samples should be measured at 165°C instead of 180°C. This is because 180°C was too high for these samples (second batch) and the data obtained was not reliable. Thus, these three samples were measured at 165°C as reported by the analyzer.

Therefore, the data obtained for wax loading effect on MFI value of PLA/wax composites were lowered compared to the data obtained for PEG loading effect on MFI value of PLA/wax composites since the different measured temperature was used for both of study.

Table 4.8: MFI of PLA/wax composite with different content of wax

Composite designation	Melt Flow Index (g/10 minutes)
95/5/5	21.00 $\pm$ 0.86
90/10/5	21.69 $\pm$ 0.66
85/15/5	25.80 $\pm$ 0.92

**Figure 4.20:** Effect of wax loading on the MFI of PLA/wax composites

4.7 Extrusion of filament

Prior to the selection, the data for PLA/wax/PEG composite was compared to the standard range of tensile properties and characteristic common FDM filament (depicted in Chapter 2, Table 2.4). Based on the results obtained, PLA/wax composites with 5 wt.% PEG and 8 wt.% PEG were selected for this test as it showed promising characteristics to be developed as build materials for 3D printer. Trial-and-error runs were needed to optimize the extrusion flow, cooling and spooling to produce consistent quality filaments ready for

3D printing. The extrusion was conducted at a set temperature of 230-240°C. However, this is the set temperature for the machine, while the actual temperature needed to extrude neat PLA and PLA/wax composites may be significantly lower than this. The set temperature was set higher usually to compensate heat energy loss to other parts of the extrusion mechanism and the environment. The neat PLA was extruded at 240°C while the selected PLA/wax composites were extruded at 230°C since both composites have a lower melting point compared to the neat PLA as reported in melting point results.

In this study, the cooling method of the extruded filaments was achieved by air cooling through the fan. During the extrusion of PLA/wax composites 95/5/5 wt.% PEG and 95/5/8 wt.% PEG, it was extruded smoothly compare to neat PLA in accordance with the results reported in melt flow index test. In melt flow index results, PLA/wax composites 95/5/5 wt.% PEG and 95/5/8 wt.% PEG were higher compared to the MFI value of neat PLA this indicates neat PLA possess a higher viscosity compared to these two composites. According to Isa et al. (2015), the addition of wax in the composition was acted as a release agent for a smoother flow of composites material in the extrusion process. PLA/wax composites 95/5/5 wt.% PEG and 95/5/8 wt.% PEG was successfully extruded as shown in Figure 4.21. The neat PLA was extruded with filament diameter 1.77 mm while, 95/5/5wt.% PEG and 95/5/8wt.% PEG was 1.73 mm and 1.71 mm respectively (as shown in Table 4.9). Cardona et al. (2016) stated that the gold standard across the industry for filament diameter is 1.75 mm with tolerance $\pm 0.05\text{mm}$. 95/5/5 wt.% PEG and 95/5/8 wt.% PEG composites wire filament were successfully extruded around 2 meters each and were used to print a 3D object.

One of the most important aspects of 3D printing filament production is the ability of the material to be extruded from the extruder to form unbreakable filament which can be wound into spools. Filament production procedures are highly dependent on the setup of the extruder. PLA/wax composite was extruded by using a single screw extruder to produce the filament. Single screw extruder is the machine that produces a continuous profile by melting thermoplastic materials (Math et al., 2018).

Table 4.9: The extrusion temperature and cooling method for the production of filament

Composites designation	Filament Production Extrusion temperature, °C	Cooling method	Filament diameter (mm)
PLA	240	Air cooling	1.77 ± 0.01
95/5/5 wt.% PEG	230	Air cooling	1.73 ± 0.02
95/5/8 wt. % PEG	230	Air cooling	1.71 ± 0.02

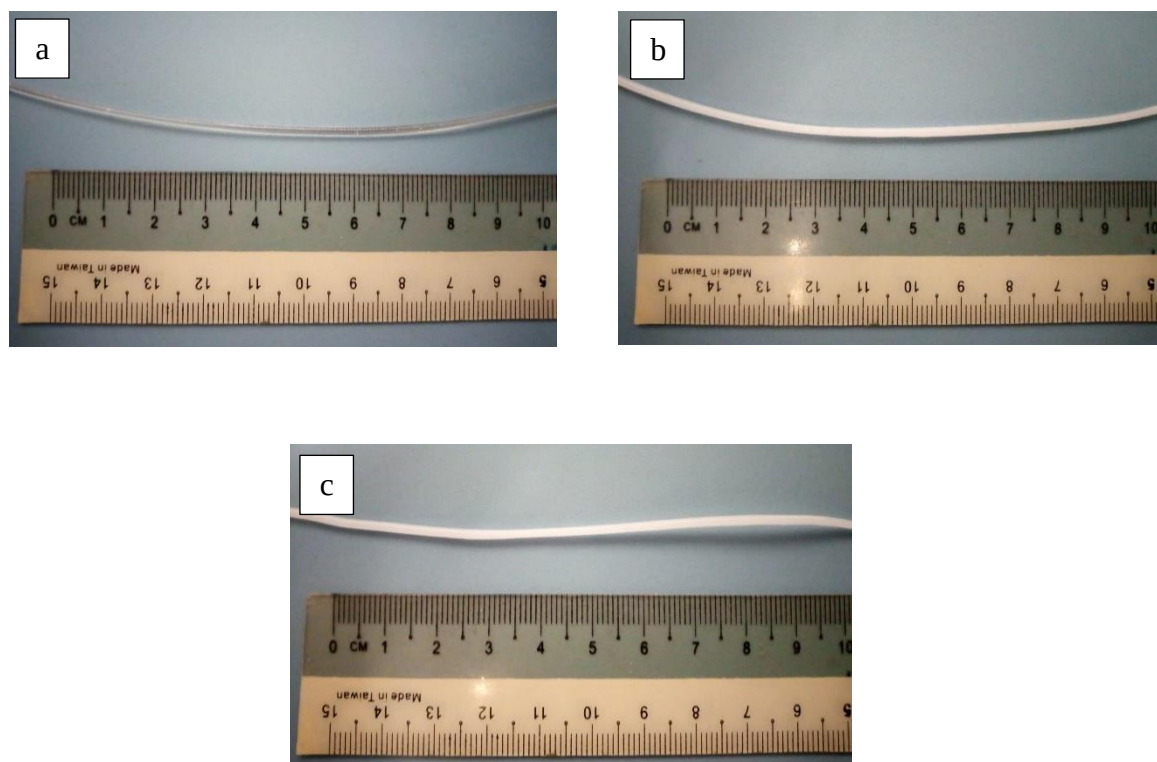


Figure 4.21: A filament of FDM technology produced via single screw extruder. (a) neat PLA filament, (b) PLA/wax/PEG (95/5/5) filament, (c) PLA/wax/PEG (95/5/8) filament

4.8 3D Printing using PLA/wax/PEG composites.

For a 3D printing test, a minimum of 2 meters long filament is needed for printing small solid three-dimensional objects. A simple cube of 1 x 1 x 1 cm was chosen to be the test object to be printed with the PLA-Sarawax composites. Several trial prints were run in order to determine the suitable setting for 3D printing nozzle temperature and also printing bed temperature. The temperature settings for the bed and 3D printer nozzle are a highly important aspect of the 3D printing process (Choi et al., 2016). The test object (cube) was successfully 3D printed via fused deposition modeling (FDM) at 180°C for nozzle temperature and 50°C for printing bed temperature. The nozzle and bed temperature, 180°C and 50°C respectively were used to print the cube by using PLA/wax composite was lower compared to neat PLA (190°C and 60°C) as shown in Table 4.10. The 3D printed cube adheres consistently onto the bed surfaces during the printing process. The adhesion between the printing bed and the extruded polymer filament must be high enough to make sure the 3D printed object in place during printing (Spoerk et al., 2018). Based on observation, the qualities of the prints were comparable to the commercial PLA filament prints as shown in Figure 4.22. Through the observation and experimentation, the PLA/wax composites filament were determined to be suitable for fused deposition modeling printing.

In this study, the diameter of nozzle used was 0.4 mm and 3D printing parameter such as a number of shells (2), layer height (0.20 mm), infill pattern (hexagonal) and percentage (25%), printing speed (90 mm/s) and travel speed (150 mm/s) were kept constant. According to Horvath (2014), infill is known as the internal support inside the solid surfaces of the 3D object to reduce the use of a filament. Infill percentage is the percentage of material inside the 3D printed object while the number of shells is the number of paths deposited to

define the outer surface in each layer (Lužani et al., 2013; Horvath, 2014). Based on the results depicted in melt flow index (MFI) analysis (Figure 4.19) it was showed that the MFI value of selected PLA/wax/PEG composites (5 wt.% PEG & 8 wt.% PEG) was higher than the neat PLA and this indicates the composite increased in fluidity. Even though the fluidity of the selected composites was increased, the printing speed was fixed at 90 mm/s since it showed a good deposition of material at that printing speed. As can be seen in Table 4.10, the infill pattern hexagonal was used to print the all 3D cube with 25% infill percentage. Horvath (2014) stated that the common use of infill patterns is a honeycomb/hexagonal structure due to a strong structure that needs less material compared to other types of infill patterns.

Table 4.10: 3D printing parameters for commercial PLA filament, neat PLA and PLA/wax composites

Composites designation	Printing/nozzle temperature °C	Heated platform/bed °C	Infill pattern	Infill percentage, %
Commercial PLA filament	190	60	Hexagonal	25
PLA	190	60	Hexagonal	25
95/5/5 wt.% PEG	180	50	Hexagonal	25
95/5/8 wt.% PEG	180	50	Hexagonal	25

4.9 Quality of 3D printed object by using PLA/wax composites (dimensional error and layer height consistency)

The dimensional errors of 3D printed cube by using selected composites designation were depicted in Table 4.11. The dimensional error for 95/5/5 wt.% PEG and 95/5/5 wt.% PEG was negative value indicates reduced in design value (ideal dimension). (10 mm × 10 mm

× 10 mm). According to Galantucci et al. (2015), the reduction of design value (ideal dimension) cause by the shrinkage phenomenon. While commercial PLA filament and neat PLA filament shows an increase in design value. This phenomenon occurred might be due to the printing temperature of commercial PLA filament and neat PLA filament were 10°C higher than the selected PLA/wax composites filament. According to Alafaghani et al. (2017), printing temperature has a significant effect on accuracy; as the extrusion temperature increases the error increases as it might be due to the increased fluidity of the extruded filament at a higher temperature. Then, it allows the extruded filament to flow out of the nozzle control thus increasing the error (increased in size). However, based on the results obtained, the dimensional errors were considered relatively small because the highest dimensional error was not exceeded 0.05mm (0.5%).

Table 4.11: Dimensional errors of 3D printed cube (10 mm × 10 mm × 10 mm). Samples measurements (averaged results), dimensions in mm

Composite designation	Dimensional errors, cube (mm)					
	Length, L1	Dimensional error	Length, L2 (width)	Dimensional error	Height, H	Dimensional error
CAD model	10.00	-	10.00	-	10.00	-
Commercial PLA filament	10.02	0.02	10.05	0.05	10.03	0.03
PLA	9.99	-0.01	10.02	0.02	10.01	0.01
95/5/5 wt.% PEG	9.97	-0.03	9.98	-0.02	9.97	-0.03
95/5/8 wt. % PEG	9.97	-0.03	9.97	-0.03	9.96	-0.04

(-) the sign indicates reduced in size

In this study, to determine the quality of the outer surface of 3D printed objects via FDM technology, the layer height of each deposited layer was observed under the Scanning Electron Microscope (SEM) and measured by using SMileView software (Appendix C). Usually, the user of FDM technology used a 0.2 mm layer height to 3D print object. Table 4.12 shows the layer height of deposited material via FDM technology that printed using commercial PLA, neat PLA, 95/5/5 wt.% PEG and 95/5/8 wt.% PEG composites. During the slicing process, the layer height of 0.2 mm/200 μm was used. Then, to determine the layer height accuracy after printing, the layer height of each layer was measured. Even though commercial PLA filament was used, the layer height was not too accurate. Commercial PLA filament and neat PLA filament were exceeded the selected layer height (0.2 mm/200 μm) while the selected PLA/wax composites were lowered than selected layer height.

According to Alabdullah (2016), layer height is the vertical height change from one layer to the next. A smaller layer height gives a higher resolution of 3D parts however, the build time is much longer. On the other hand, large layer heights require less time to build 3D parts but decrease the surface quality. It is very important to select the right layer height to print 3D parts. The layer height must not exceed the nozzle diameter because if exceed, this will lead to little or no bond between the layers (Alabdullah, 2016).

Table 4.12: The layer height of 3D printed cube (outer surface)

Composite designation	Layer height (μm)
Commercial PLA filament	205.0 $\pm$ 13.84
PLA	202.2 $\pm$ 5.98
95/5/5 wt.% PEG	197.1 $\pm$ 5.32
95/5/8 wt.% PEG	194.2 $\pm$ 15.32

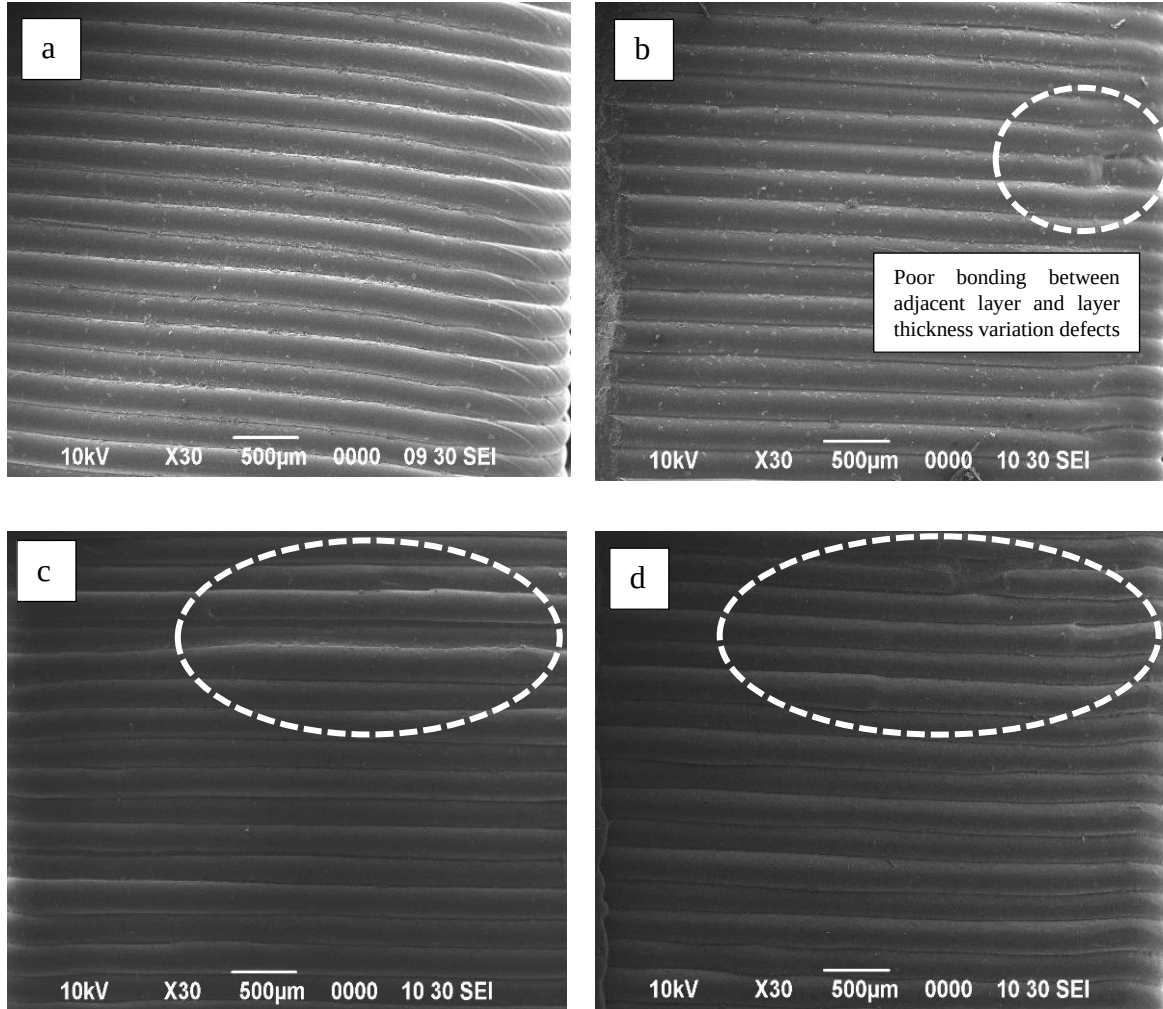


Figure 4.22: The SEM micrographs of outer surface of 3D printed cube by using (a) commercial PLA filament, (b) neat PLA, (c) PLA/wax composites (95/5/5 wt.% PEG) and (d) PLA/wax composites (95/5/5 wt.% PEG)

Figure 4.22 shows the scanning electron microscopy of layer by layer of the 3D printed cube. As can be seen, the layer by layer of 3D printed cube that printed by using commercial PLA filament shows a more consistent layer height compared to printed using neat PLA, PLA/wax composites (95/5/5) and (95/5/8) filament. As can be seen in Figure 4.24 c and d, some defect on the outer surface of the 3D printed object that printed using (95/5/5 and 95/5/8). Some layers show poor bonding between adjacent layer and layer height thickness variation defects. These defects were contributed to the inconsistent material flow

due to variations in filament diameter (inconsistent filament diameter) (Weeran et al., 1995). Therefore, the production of filament via extrusion is very important to yield a consistent filament diameter (Masood and Song, 2004). However, due to the limitation of the laboratory scale extruder used in this study, the production of high quality and the consistent filament was difficult. Based on the scanning electron microscopy analysis of outer surface 3D printed cube, it can be concluded that the quality of 3D printed cube by using selected PLA/wax/PEG composites were comparable with commercial PLA filament. Even though there were some defects on the outer surface of 3D cube printed using the selected PLA/wax composite filament but these two composites filament have great potential as build materials for the FDM machine.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The effect of wax and polyethylene glycol of PLA/wax composites on tensile properties and characteristics were determined. In this study, the addition of PEG increased the elongation at break and reduced the elastic moduli and tensile strength of PLA/wax composites. The increment of wax content in PLA/wax composited reduced the elongation at break, tensile strength and elastic moduli.

The PLA/wax composites and PLA/wax/PEG composites have successfully characterized in terms of morphological, water absorption, melting point and melt flow index (MFI). The morphological of tensile fractured surfaces were investigated and SEM micrographs of the tensile fractured surfaces of PLA/wax composites (95/5) showed longer fibrils were produced when PEG was introduced at 8 wt.% and above, this indicated the changes of PLA/wax composites from brittle fracture to a ductile fracture. However, the addition of a high concentration of PEG causes more phase separation to occur. While for the effect of wax loading at the lowest content of wax (5wt.%) it showed a homogeneous fractured surface and good dispersion of wax in the PLA matrix. However, the miscibility of the wax within the PLA matrix become poor and accumulation of wax was observed at a higher percentage. The addition of PEG increased the water uptake of PLA/wax composites since PEG is a hygroscopic material. While water absorption of PLA/wax composites could reduce with the addition of wax since it showed a decrease in water uptake with an increment of wax content.

The melting point of PLA/wax composites was reduced as the wax and PEG content increased. And this trend showed good miscibility between the polymer matrix and the plasticizer. The decrease in melting points is a desirable effect as this will allow 3D printing using these composites to be possible prints at a lower temperature. Melt flow index also reduced in viscosity of PLA/wax with the addition of wax and PEG and this can be allowing for the PLA/wax composites 3D prints with high printing speed. Two selected PLA/wax/PEG composites were successfully extruded in filament production. 3D printing by using PLA/wax/PEG composites filament via fused deposition modeling was successfully achieved. The printing quality of the selected composites was also determined. The quality of 3D parts printed using the selected composites was comparable with the control (PLA commercial PLA filament). However, some layers show poor bonding between adjacent layer and layer height thickness variation defects that cause by inconsistent filament diameter. Therefore, it is important to produce a consistent filament diameter to yield a good quality of printing by using a large scale of single screw extruder since the laboratory scale of single screw extruder not adequate to produce consistent filament diameter. In conclusion, the selected PLA/wax composites have great potential as a build material for FDM technology.

5.2 Recommendations

From the experiments conducted, PLA/wax/PEG composites have great potential as a build material in 3D printing (fused deposition modeling, FDM). The tensile properties and characteristics of PLA/wax/PEG composites can be improved by investigating the effect of other types of plasticizer. Since there is little data or research on polymer matrix/wax

composites with the addition of plasticizer were reported. It is also recommended to investigate the thermal properties of PLA/wax composites by using Differential Scanning Calorimeter (DSC) analysis to further exploration on the thermal properties. In this study, some layers that printed using selected PLA/wax composites show poor bonding between adjacent layer and road thickness variation defects that cause by inconsistent filament diameter. Therefore, it is important to further study on optimization of extrusion parameters during filament production to produce consistent filament diameter since inconsistent diameter will affect the printing quality.

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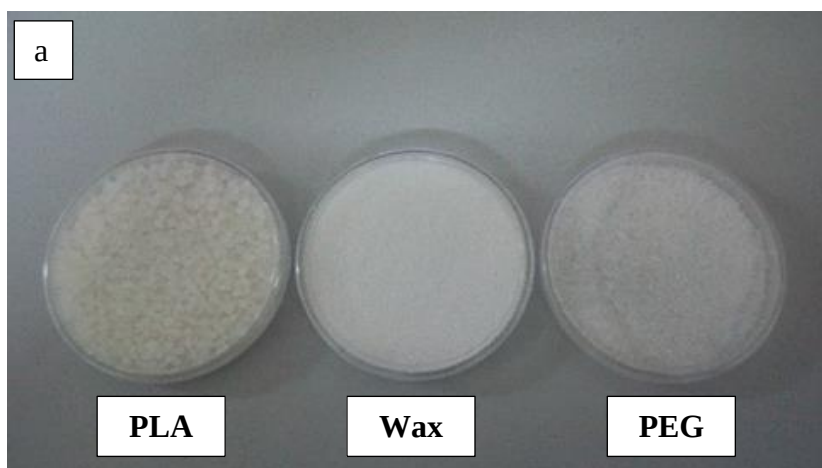
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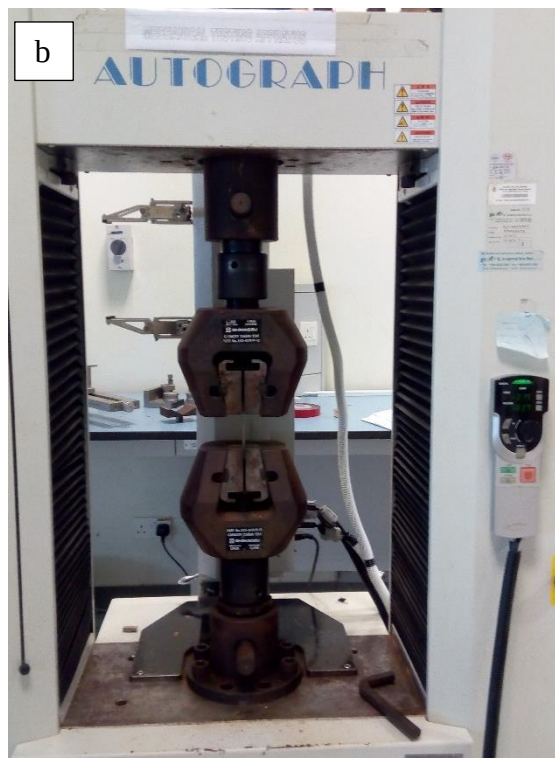
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APPENDICES

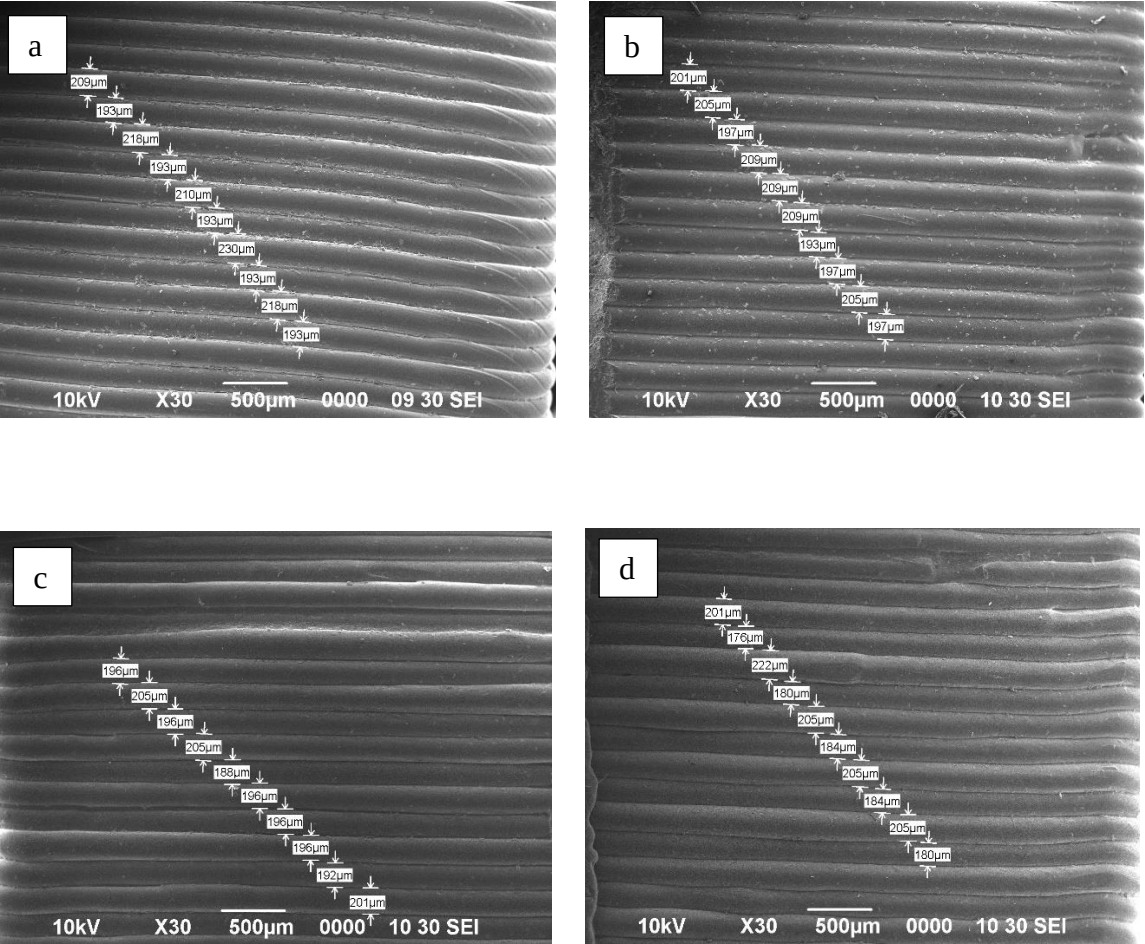
Appendix A. (a) Materials for the composites designation and (b) the mold for tensile test specimens (ASTM D638 Type IV).



Appendix B. (a) Hydraulic Hot Press Machine, GOTECH Model GT – 7014 - A50C (with a cooling device) and (b) mechanical testing machine (mod. AG-1/250kN).



Appendix C. Measurements of layer height of deposited material (outer surface) by using different build materials, (a) commercial PLA filament, (b) neat PLA filament, (c) PLA/wax composite (95/5/5) filament, (d) PLA/wax composite (95/5/8).



Appendix D. ASTM standard used for the preparation of test specimens in this study.



Designation: D 4703 – 03

Standard Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets¹

This standard is issued under the fixed designation D 4703; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice covers the compression molding of thermoplastic granules and milled stock for the preparation of test specimens.²

1.2 While conditions for certain materials are given, the primary source of specific conditions shall be the material specification standards for each type of material.

1.3 The values stated in SI units are to be regarded as the standard. The values given in brackets are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—The main body of this practice is equivalent to ISO 293-1986. Annex A1 and ISO 293-1986 differ in some details; however, specimens prepared using Annex A1, Procedure A should be equivalent to those prepared using ISO 293-1986, Cooling Method D. Specimens prepared using Annex A1, Procedure C should be equivalent to those prepared using ISO 293-1986, Cooling Method B. However, due to the greater cooling rate tolerances of the ISO standard, specimens prepared in accordance with ISO Cooling Method B may not be equivalent to Annex A1, Procedure C.

2. Referenced Documents

2.1 ASTM Standards:

D 618 Practice for Conditioning Plastics for Testing³

D 1248 Specification for Polyethylene Plastics Extrusion Materials for Wire and Cable³

D 3350 Specification for Polyethylene Plastics Pipe and Fittings Materials⁴

D 4976 Specification for Polyethylene Plastics Molding and Extrusion Materials⁵

¹ This practice is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.09 on Specimen Preparation.

Current edition approved July 10, 2003. Published September 2003. Originally approved in 1991. Last previous edition approved in 2002 as D 4703 – 02.

² This practice was created as a coalescence of and replacement for Practices D 1928, D 2292, D 3010, and D 3463.

³ Annual Book of ASTM Standards, Vol 08.01.

⁴ Annual Book of ASTM Standards, Vol 08.02.

⁵ Annual Book of ASTM Standards, Vol 08.03.

ISO 293-1986 Plastics—Compression Moulding Test Specimens of Thermoplastic Materials⁶

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *average cooling rate* (°C/min), *n*—the cooling rate calculated by dividing the difference between the molding and demolding temperatures by the time required to cool the mold to the demolding temperature.

3.1.2 *cooling rate* (°C/h), *n*—the rate of cooling obtained by controlling the flow of the cooling fluid in such a way that during each 10-min interval, the deviation from this specified cooling rate shall not exceed the specified tolerance.

3.1.3 *demolding temperature*, *n*—the temperature of the mold or the press platens at the end of the cooling time, measured in the nearest vicinity to the molded material.

3.1.3.1 *Discussion*—For positive molds, holes are normally drilled in the mold for measuring the temperatures defined in 3.1.3 and 3.1.4.

3.1.4 *molding temperature*, *n*—the temperature of the mold or the press platens during the preheating and molding time, measured in the nearest vicinity to the molded material.

3.1.5 *molding time*, *n*—the time during which full pressure is applied while maintaining the molding temperature.

3.1.6 *picture frame mold*, *n*—a flat piece of metal, usually of brass or steel, that has a center portion removed to provide the specified shape and dimensions of the final molding. The thickness of the metal is dependent on the desired thickness of the finished molding, taking into consideration the shrinkage of the material to be molded. The picture frame mold is sometimes referred to as a chase.

3.1.7 *preheating time*, *n*—the time required to heat the material in the mold up to the molding temperature while maintaining the contact pressure.

⁶ ISO/IEC Selected Standards for Testing Plastics, available from ASTM. Also available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

*A Summary of Changes section appears at the end of this standard.

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Appendix E. ASTM standard used for tensile testing.

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.



Designation: D638 – 14

Standard Test Method for Tensile Properties of Plastics¹

This standard is issued under the fixed designation D638; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of the tensile properties of unreinforced and reinforced plastics in the form of standard dumbbell-shaped test specimens when tested under defined conditions of pretreatment, temperature, humidity, and testing machine speed.

1.2 This test method is applicable for testing materials of any thickness up to 14 mm (0.55 in.). However, for testing specimens in the form of thin sheeting, including film less than 1.0 mm (0.04 in.) in thickness, ASTM standard D882 is the preferred test method. Materials with a thickness greater than 14 mm (0.55 in.) shall be reduced by machining.

1.3 This test method includes the option of determining Poisson's ratio at room temperature.

NOTE 1—This standard and ISO 527-1 address the same subject matter, but differ in technical content.

NOTE 2—This test method is not intended to cover precise physical procedures. It is recognized that the constant rate of crosshead movement type of test leaves much to be desired from a theoretical standpoint, that wide differences may exist between rate of crosshead movement and rate of strain between gage marks on the specimen, and that the testing speeds specified disguise important effects characteristic of materials in the plastic state. Further, it is realized that variations in the thicknesses of test specimens, which are permitted by these procedures, produce variations in the surface-volume ratios of such specimens, and that these variations may influence the test results. Hence, where directly comparable results are desired, all samples should be of equal thickness. Special additional tests should be used where more precise physical data are needed.

NOTE 3—This test method may be used for testing phenolic molded resin or laminated materials. However, where these materials are used as electrical insulation, such materials should be tested in accordance with Test Methods D229 and Test Method D651.

NOTE 4—For tensile properties of resin-matrix composites reinforced with oriented continuous or discontinuous high modulus >20 -GPa ($>3.0 \times 10^6$ -psi) fibers, tests shall be made in accordance with Test Method D3039/D3039M.

1.4 Test data obtained by this test method have been found to be useful in engineering design. However, it is important to

consider the precautions and limitations of this method found in Note 2 and Section 4 before considering these data for engineering design.

1.5 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

D229 Test Methods for Rigid Sheet and Plate Materials Used for Electrical Insulation

D412 Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension

D618 Practice for Conditioning Plastics for Testing

D651 Test Method for Test for Tensile Strength of Molded Electrical Insulating Materials (Withdrawn 1989)³

D882 Test Method for Tensile Properties of Thin Plastic Sheeting

D883 Terminology Relating to Plastics

D1822 Test Method for Tensile-Impact Energy to Break Plastics and Electrical Insulating Materials

D3039/D3039M Test Method for Tensile Properties of Polymer Matrix Composite Materials

D4000 Classification System for Specifying Plastic Materials

D4066 Classification System for Nylon Injection and Extrusion Materials (PA)

D5947 Test Methods for Physical Dimensions of Solid Plastics Specimens

E4 Practices for Force Verification of Testing Machines

¹ This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.10 on Mechanical Properties.

Current edition approved Dec. 15, 2014. Published March 2015. Originally approved in 1941. Last previous edition approved in 2010 as D638 - 10. DOI: 10.1520/D0638-14.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

*A Summary of Changes section appears at the end of this standard

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Appendix F. ASTM standard used for water absorption test.



Designation: D 570 – 98

Standard Test Method for Water Absorption of Plastics¹

This standard is issued under the fixed designation D 570; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the relative rate of absorption of water by plastics when immersed. This test method is intended to apply to the testing of all types of plastics, including cast, hot-molded, and cold-molded resinous products, and both homogeneous and laminated plastics in rod and tube form and in sheets 0.13 mm (0.005 in.) or greater in thickness.

1.2 The values given in SI units are to be regarded as the standard. The values stated in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—ISO 62 is technically equivalent to this test method.

2. Referenced Documents

2.1 ASTM Standards:

D 647 Practice for Design of Molds for Test Specimens of Plastic Molding Materials²

2.2 ISO Standard:

ISO 62 Plastics—Determination of Water Absorption³

3. Significance and Use

3.1 This test method for rate of water absorption has two chief functions: first, as a guide to the proportion of water absorbed by a material and consequently, in those cases where the relationships between moisture and electrical or mechanical properties, dimensions, or appearance have been determined, as a guide to the effects of exposure to water or humid conditions on such properties; and second, as a control test on the uniformity of a product. This second function is particularly applicable to sheet, rod, and tube arms when the test is made on the finished product.

3.2 Comparison of water absorption values of various plastics can be made on the basis of values obtained in accordance with 7.1 and 7.4.

3.3 Ideal diffusion of liquids⁴ into polymers is a function of the square root of immersion time. Time to saturation is strongly dependent on specimen thickness. For example, Table 1 shows the time to approximate time saturation for various thicknesses of nylon-6.

3.4 The moisture content of a plastic is very intimately related to such properties as electrical insulation resistance, dielectric losses, mechanical strength, appearance, and dimensions. The effect upon these properties of change in moisture content due to water absorption depends largely on the type of exposure (by immersion in water or by exposure to high humidity), shape of the part, and inherent properties of the plastic. With nonhomogeneous materials, such as laminated forms, the rate of water absorption may be widely different through each edge and surface. Even for otherwise homogeneous materials, it may be slightly greater through cut edges than through molded surfaces. Consequently, attempts to correlate water absorption with the surface area must generally be limited to closely related materials and to similarly shaped specimens. For materials of widely varying density, relation between water-absorption values on a volume as well as a weight basis may need to be considered.

4. Apparatus

4.1 *Balance*—An analytical balance capable of reading 0.0001 g.

4.2 *Oven*, capable of maintaining uniform temperatures of $50 \pm 3^\circ\text{C}$ ($122 \pm 5.4^\circ\text{F}$) and of 105 to 110°C (221 to 230°F).

5. Test Specimen

5.1 The test specimen for molded plastics shall be in the form of a disk 50.8 mm (2 in.) in diameter and 3.2 mm ($\frac{1}{8}$ in.) in thickness (see Note 2). Permissible variations in thickness are ± 0.18 mm (± 0.007 in.) for hot-molded and ± 0.30 mm (± 0.012 in.) for cold-molded or cast materials.

¹ This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D 20.50 on Permanence Properties. Current edition approved July 10, 1998. Published January 1999. Originally published as D 570 – 40 T. Last previous edition D 570 – 95.

² Discontinued 1994; replaced by D 1896, D 3419, D 3641, D 4703, and D 5227. See 1994 *Annual Book of ASTM Standards*, Vol 08.01.

³ Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

⁴ Additional information regarding diffusion of liquids in polymers can be found in the following references: (1) *Diffusion, Mass Transfer in Fluid Systems*, E. L. Cussler, Cambridge University Press, 1985, ISBN 0-521-29846-6, (2) *Diffusion in Polymers*, J. Crank and G. S. Park, Academic Press, 1968, and (3) "Permeation, Diffusion, and Sorption of Gases and Vapors," R. M. Felder and G. S. Huvar, in *Methods of Experimental Physics*, Vol 16C, 1980, Academic Press.

Appendix H. MS ISO 3146:2004 standard for determination of melting temperature or melting range

Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers by capillary tube and polarizing-microscope methods

1 Scope

This International Standard specifies two methods for evaluating the melting behaviour of semi-crystalline polymers.

Melting temperatures determined by the different methods usually differ by several kelvins for the reasons explained in the introduction.

Method A: Capillary tube

This method is based on the changes in shape of the polymer. It is applicable to all semi-crystalline polymers and their compounds.

NOTE 1 Method A may also be useful for the evaluation of the softening of non-crystalline solids.

Method B: Polarizing microscope

This method is based on changes in the optical properties of the polymer. It is applicable to polymers containing a birefringent crystalline phase. It may not be suitable for plastics compounds containing pigments and/or other additives which could interfere with the birefringence of the polymeric crystalline zone.

NOTE 2 Another method applicable to semi-crystalline polymers is described in ISO 11357-3:1999, *Plastics — Differential scanning calorimetry (DSC) — Part 3: Determination of temperature and enthalpy of melting and crystallization*.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 291, *Plastics — Standard atmospheres for conditioning and testing*.

3 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

3.1

semi-crystalline polymer

polymer containing both crystalline and amorphous phases which may be present in varying proportions

Appendix H. ASTM standard used for melt flow index (MFI) analysis.



Designation: D 1238 – 04

Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer¹

This standard is issued under the fixed designation D 1238; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers measurement of the rate of extrusion of molten resins through a die of a specified length and diameter under prescribed conditions of temperature, load, and piston position in the barrel as the timed measurement is being made.

1.2 Procedure A is a manual cutoff operation based on time used for materials having flow rates that fall generally between 0.15 and 50 g/10 min. Procedure B is an automatically timed flow rate measurement used for materials having flows from 0.50 to 900 g/10 min. By both procedures, the piston travel is generally the same during the timed measurement; the piston foot is about 46 and 20.6 mm above the die. Comparable flow rates have been obtained by these procedures in interlaboratory round-robin measurements of several materials described in 13.1. Provision is made for calculation of melt volume-flow rate as well as melt mass-flow rate.

NOTE 1—Round-robin testing indicates this test method may be suitable at flow rates up to 1500 g/10 min if the timing clock resolves the elapsed time to the nearest 0.01 s.

NOTE 2—This test method and ISO 1133-1991 are technically equivalent.

1.3 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in 5.7, 10.2.12, and 14.1.2.*

2. Referenced Documents

2.1 ASTM Standards:²

D 618 Practice for Conditioning Plastics for Testing

D 883 Terminology Relating to Plastics

E 691 Practice for Conducting an Interlaboratory Study to

Determine the Precision of a Test Method

2.2 ANSI Standard:

B46.1 on Surface Texture³

2.3 ISO Standard:

ISO 1133-1991 Determination of the Melt-Mass Flow Rate (MFR) and the Melt Volume-Flow Rate (MVR) of Thermoplastics³

3. Terminology

3.1 General:

3.1.1 For definition of some of the technical terms used in this test method refer to Terminology D 883.

4. Significance and Use

4.1 This test method is particularly useful for quality control tests on thermoplastics.

NOTE 3—Polymers having flow rates less than 0.15 or greater than 900 g/10 min may be tested by the procedures in this test method; however, precision data have not been developed.

4.2 This test method serves to indicate the uniformity of the flow rate of the polymer as made by an individual process and, in this case, may be indicative of uniformity of other properties. However, uniformity of flow rate among various polymers as made by various processes does not, in the absence of other tests, indicate uniformity of other properties.

4.3 The flow rate obtained with the extrusion plastometer is not a fundamental polymer property. It is an empirically defined parameter critically influenced by the physical properties and molecular structure of the polymer and the conditions of measurement. The rheological characteristics of polymer melts depend on a number of variables. Since the values of these variables occurring in this test may differ substantially from those in large-scale processes, test results may not correlate directly with processing behavior.

4.4 The flow rate of a material may be measured under any of the conditions listed for it in 8.2. Additional characterization of a material can be obtained if more than one condition is used. In case two conditions are employed, a Flow Rate Ratio (FRR) may be obtained by dividing the flow rate at one condition by the flow rate at the other condition.

¹ This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties (Section D20.30.08).

Current edition approved March 1, 2004. Published April 2004. Originally approved in 1965. Last previous edition approved in 2001 as D 1238 - 01^{ε1}.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

*A Summary of Changes section appears at the end of this standard.

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