THE FEASIBILITY OF SBR/EVA AND TPU/PCL COMPOSITE MATERIAL FOR FUSED DEPOSITION MODELLING

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"மாதா, பிதா, குரு, தெய்வம்..."

"To my mother, father, teacher and mighty god..."

To my beloved parents,

Mr. Mrs. Periyasamy & Padmarani

For their supports in whole of my life

To my supervisor *"sensei",*

Dr. Mustaffa Bin Haji Ibrahim

For his advice, support and patience during the completion of this project

moreover, to all my friends,

For their encouragement, cooperation and motivation in completing this thesis.

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ABSTRACT

In this research study, characterization and improvement of SBR/EVA and TPU/PCL polymer matrix composites for the Fabrication of Fused Deposition Modelling (FDM) filament wire was investigated. The limitation of feedstock materials in the FDM process, there are very limited polymer composites mixtures which can produce a flexible filament with a good mechanical properties, the very low amount of research done on flexible filament which can used in footwear and orthotic production, many problems faced by researchers in extruding or utilising flexible filaments in FDM machine are the four main problems highlighted in this research study. The main purpose of this study carried out was to mix several types of mixtures that could produce a flexible filament that will help the AM, medical and footwear industries. Styrene-butadiene rubber (SBR) and ethylene vinyl acetate (EVA) polymers were selected to be tested because it is closely related to elastic behaviour. The thermoplastic polyurethane (TPU) and polycaprolactone (PCL) are selected for their ability to be used as medical grade material and TPU has elastic behaviour which also has potential to be made as flexible filament. PCL is used widely in FDM processes all over the world and it is FDM compatible too. The EVA filled SBR, PCL and filled TPU polymer composites were compounded, injection moulded. The mechanical properties were evaluated by tensile, flexural and hardness tests while the thermal properties were observed and analysed via differential thermal analysis (DTA) and thermogravimetry analysis (TGA). The FDM filament wire with the standard diameter of 1.75mm+0.05 and 3.0mm +0.05 was extruded and tested using FDM machine. The flexural strength and tensile strength of SBR/EVA and TPU/PCL blends showed increment after the blend.TPU/PCL filament successfully used in FDM machine meanwhile SBR/EVA composite failed. The TPU/PCL composites were working in the FDM machine which had achieved the main goals of the research and showed high potential to be studied further in the future.

ABSTRAK

Dalam kajian ini, pencirian dan pembaikan komposisi matriks polimer SBR/EVA dan TPU/PCL untuk filamen “Fused Deposition Modelling (FDM)” telah disiasat. Empat masalah dinyatakan dalam kajian ini adalah, keterbatasan bahan mentah dalam proses FDM, terdapat campuran komposit polimer yang sangat terhad yang boleh menghasilkan filamen fleksibel dengan sifat mekanik yang baik, jumlah penyelidikan yang sangat rendah yang dilakukan pada filamen fleksibel yang boleh digunakan dalam pengeluaran kasut dan ortotik, dan asalah yang ketara dihadapi oleh para penyelidik dalam proses penyemperitan atau menggunakan filamen fleksibel dalam mesin FDM. Tujuan utama kajian ini adalah untuk mencampurkan beberapa jenis campuran yang boleh menghasilkan filamen yang fleksibel yang boleh membantu industri AM, perubatan dan kasut. Polimer getah Styrene-butadiena (SBR) dan ethylene vinyl acetate (EVA) telah dipilih untuk diuji kerana berkait rapat ciri-ciri elastik. Poliuretana termoplastik (TPU) dan polycaprolactone (PCL) dipilih kerana keupayaan mereka untuk digunakan sebagai bahan gred perubatan dan TPU mempunyai kelakuan elastik yang juga berpotensi dibuat sebagai filamen fleksibel. PCL digunakan secara meluas dalam proses FDM di seluruh dunia dan ia juga bersesuaian dengan FDM. EVA dicampur dalam SBR, PCL dan TPU dicampur menggunakan pengadun dan dibentuk menggunakan pengacuan suntikan . Ciri-ciri mekanikal dinilai dengan ujian tegangan, lenturan dan kekerasan manakala sifat terma diperhatikan dan dianalisis melalui analisis terma taksiran (DTA) dan analisis thermogravimetri (TGA). Filamen FDM dengan diameter yang ditetapkan 1.75mm + 0.05 dan 3.0mm +0.05 telah diekstrusi dan diuji menggunakan mesin FDM. Kekuatan lenturan dan kekuatan tegangan campuran SBR/EVA dan TPU/PCL menunjukkan kenaikan selepas campuran. Campuran filament TPU/PCL dapat digunakan dalam mesin FDM manakala filament SBR/EVA gagal. Komposit TPU/PCL telah mencapai matlamat kajian ini dan boleh dikaji pada masa yang akan datang.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	-	Area
b	-	Mean width of the specimens
°C	-	Degree Celsius
E	-	Elastic Modulus
d_1	-	Density
d_2	-	Mean thickness of the specimens
Fn	-	Norml component force
Hz	-	Hertz
HS	-	Shore Hardness
N	-	Newton
M	-	Mass
m	-	Meter
mm	-	Millimeter
mm/s	-	Millimeter per second
MPa	-	Mega Pascal
S	-	Increment in deflection
t	-	Time
v%	-	Volume Percentage
wt%	-	Weight Percentage
ρ_w	-	Density of water
σ	-	Tensile Stress
ε	-	Strain
μm	-	Micrometre
ASTM	-	American Standard of Testing Method
AM-	-	Additive Manufacturing
BR	-	Polybutadiene Rubber
CAD	-	Computer-aided Design

DCP	-	Dicumyl Peroxide
DTA	-	Differential Thermal Analysis
DTGA	-	Derivative Thermogravimetric
DSC	-	Differential Scanning Calorimetry
EVA	-	Ethylene Vinyl Acetate
EPDM	-	Ethylene Propylene Diene Monomer
FDM	-	Fused Deposition Modelling
FTIR	-	Fourier Transform Infra-Red
HAF	-	High Abrasion Furnace
HDPE	-	High-density polyethylene
HS	-	Hard Segments
ISAF	-	Intermediate Super Abrasion Furnace
ISO	-	International Organization of Standardization
MFI	-	Melt Flow Index
MMT	-	Montmorillonites
NBR	-	Nitrile Butadiene Rubber
NBS	-	Nitrile Butadiene Stryene
NR	-	Natural Rubber
ODA-MMT	-	Octadecylamine Modified montmorillonites
PCL	-	Polycaprolactone
PMMA	-	Polymethyl methacrylate
PP	-	Polypropylene
PS	-	Polystyrene
PU	-	Polyurethane
RHP	-	Rice Husk Powder
RPM	-	Revolution Per Minute
SEBS	-	Styrene-Ethylene/Butylene-Styrene
SEM	-	Scanning Electron Microscope
SBR-	-	Styrene Butadiene Rubber
SBS	-	Styrene-Butadiene-Styrene
SGF	-	Short Glass Fibre
SIS	-	Styrene-Isoprene-Styrene
SLA	-	Stereolithography
SLS	-	Selective Laser sintering

SRF	-	Semi Reinforcing Furnace
SS	-	Soft Segments
STA	-	Simultaneous Thermal Analysis
TGA	-	Thermogravimetric Analysis
TPU	-	Thermoplastic Polyurethane
TPU-ER	-	Ether Type Thermoplastic Polyurethane
TPU-EX	-	Ester Type Thermoplastic Polyurethane
TPR	-	Thermoplastic Rubber
TPV	-	Thermoplastic Vulcanisates
UTHM	-	Universiti Tun Hussein Onn Malaysia
UV	-	Ultraviolet
L_1	-	Length
$T_{10\%}$	-	Temperature of initial decomposition
T_g	-	Glass Transition Temperature
T_P	-	Temperature corresponding to x% mass loss
W_1	-	Increment in load
W_2	-	Ultimate failure load
W_d	-	Dry Sample
W_s	-	Wet Sample
W_T	-	Mass loss at a given temperature T, in wt%

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CHAPTER 1

INTRODUCTION

1.1 Research background

Additive manufacturing (AM) is a manufacturing technique which uses layered manufacturing to produce a solid physical model of a part using three-dimensional computer-aided-design (CAD) file (ASTM International, 2013). The standard AM manufacturing techniques are stereolithography (SLA), selective laser sintering (SLS), laminated object manufacturing (LOM), three-dimensional printing advancement of new materials and enabling technology, these AM techniques emerged out and had been practiced in rapid tooling and moulding, direct formed usable part, and bio-manufacturing (Chua *et al*., 2003).

A decade ago, fused deposition modelling (FDM) had started to develop a vastly used additive manufacturing technology for various applications in engineering such as design verification, medical applications, functional testing, and patterns for casting processes (Masood, 1996; Nikzad *et al.*, 2011).

The FDM technique is considered unique where it is more cost-efficient for fabricating small to medium size parts in the shortest lead time (Tyberg & Bohn, 1999); this is due to the delay in SLA and SLS techniques to build models where both techniques use resin and laser which deteriorates over time that causes difficulty in ensuring repeatability. FDM technique is popular among user because it is user-friendly compared to another type of AM process. Despite its easy usage, the part produced is not durable enough, of few other material properties is not suitable for the application.

As the research on the material development advances by time, new composites study are continuously done by researchers to improvise the materials. The efforts to enhance the mechanical properties of FDM products has been associated with the additives mixed to produce new polymer matrix composite which used to produce a new FDM feedstock. Much effort is carried out to improve and develop high-performance, materials used for additive manufacturing process especially FDM-related materials for engineering applications where it includes improved mechanical properties by polymer matrix composites (PMCs) (Wang *et al.*, 2005 ; Koo *et al.*, 2006).

Therefore, this research introduces a study on SBR, EVA, TPU and PCL characterization to produce a new FDM flexible filament feedstock with the reinforcement of PCL, as an additive for the enhancement of the mechanical properties on TPU flexible filament which create a fine poly composite and with the addition of EVA, SBR also be a stronger polymer composite. Thus, this research study fully focusing on the preparation of TPU/PCL and SBR/EVA flexible filament wire polymer composite for FDM with the excellent mechanical and thermal properties.

1.2 Problem Statements

Machining and Injection moulding are the vastly used conventional method to produce footwear and orthotics till today. It has been evidenced that the cost of production for these footwear and orthotics by conventional fabricating methods are high which is clearly a disadvantage to the manufacturers and the users. Secondly, the consumption of time to produce these orthotics are longer which delays the whole production flow. There is a need for the different type of customised moulds for a specific patient, where the mould needed to fabricate always according to the patients.

From time to time, additive manufacturing has become an importance alternative in manufacturing industries. It has many advantages such as large product customization, allow complexity, tool-less, and also sustainable (environmentally friendly) compare to others way of production process. The orthotic fabrication process is fabricated manually using the traditional method where the quality of production fully depends on worker skills. The productions of the insole are difficult to control due to the difference of patients and workers. However, the time consumption and material waste are high, and until now the manufacturer is still unable to resolve the problem.

Manufacturing the orthotic support devices in this way provides a very limited scope for the incorporation of innovative features, and it requires alterations to the form the device. Researchers are currently investigating the fabrication of flexible filament wires which can be adapted to the human body which can be used to produce this orthotic supports.

Thus, the method fabrication of insoles nowadays was replaced to FDM process to overcome the problems. The problems can be resolved by using the AM technique where there is no need of mould to fabricate customised orthotics for patients anymore. Figure 1.1 shows the basic idea of the foot insole scanning and 3D printing which could replace the traditional fabrication method.

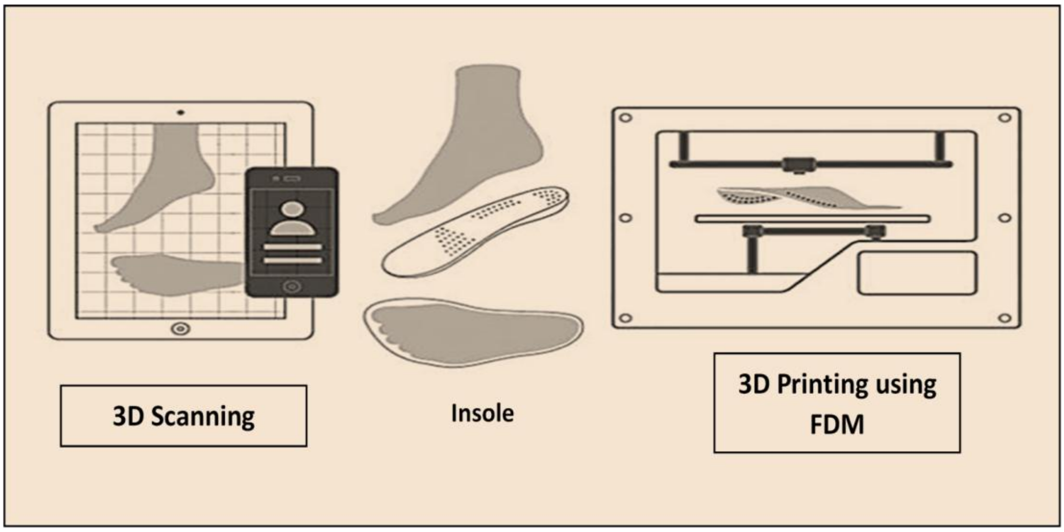


Figure 1.1: The 3D scanning and printing process for a foot insole (Millsaps, 2016)

There are four main problems highlighted in this research study which are the limitation of feedstock materials in the FDM process, there are very limited polymer composites mixtures which can produce a flexible filament with a good mechanical properties, the very low amount of research done on flexible filament which can used in footwear and orthotic production, many problems faced by researchers in extruding or utilising flexible filaments in FDM machine.

The limitations of materials that can be used in FDM process have become an obstacle to the growth of this process to be used widely by the manufacturing industries especially medical industries. FDM process is being processed with the same polymers for years, and there is very limited filament feedstock for FDM process where there is a need for new materials. The present materials widely used in FDM processes are ABS and PLA. There are more research studies are been conducted to develop these materials by the addition of metals and fibres in the materials and used in FDM machine.

Most of the studies done before, it is known that there are very limited polymer combination of excellent mechanical, thermal and morphological ease to be processed and very high elasticity without any dangerous toxic presence is vital to produce a flexible FDM filament feedstock. The mechanical properties of the flexible FDM filament wire produced must acquire high modulus (flexural modulus and elastic modulus) and excellent strength which can be used. The blending of a polymer and another might change the properties of the main polymer. The output normally do not achieve the desired properties which has been aimed which caused by the unsuitable additive polymers.

The research studies are narrowed on the FDM compatible materials combinations only related with ABS and PLA. This polymer do not acquire the properties which is suitable to be used as flexible filament. Most of the researchers are focussed on the development on enhancing the properties of this materials and there are less research study on other polymers. There are different types of polymers which could be used as flexible filament which are not focussed by the researchers. The research studied on flexible filaments has a potential to create 3D printed objects which is flexible. It also has the potential to contribute in the manufacturing of footwear and orthotics insoles.

The current FDM machine has the compatibility to be used with ABS and PLA based polymers and composites. The problems faced by some of the flexible filaments is the extrusion where most of the current FDM machines could not extrude flexible filaments. It is a setback to researchers to extrude or use the flexible filaments. The most flexible filaments done are incompatible with the FDM machine.

The introduction of TPU/PCL and SBR/EVA polymer composites for the fabrication of the FDM flexible filament could be the newest option to resolve the problem. Currently, there are no such polymer composites FDM flexible filament wire associating TPU with PCL and SBR with EVA where this study seems to provide interesting and reliable findings.

At present, FDM has been given a higher priority to be studied, and more research are done on the development of new material which will be helpful in various fields. Currently, there is no research work been done on flexible polymer composite FDM filament feedstock with materials such as SBR, EVA, TPU and PCL which can adapt with humans body for external uses.

1.3 Objectives of Study

The main aim of this research is to investigate, and validate a suitable new flexible polymer composite by blending TPU with PCL and SBR with EVA a new FDM Feedstock. To achieve this tenacity several objectives have been defined as follows:

a. To evaluate several mixtures of polymer matrix composites which has different grades of hardness, elasticity and mechanical strength and potential to be used as FDM feedstock.
b. To investigate the effects of additive via PCL and EVA on the morphological, mechanical and thermal properties of the new polymer composite blends.
c. To determine the suitable filament's diameter, mechanical and thermal properties.
d. To assess the compatibility of the newly developed flexible filaments with FDM machine

1.4 Scope of Study

This study will concentrate on:

a. Characterization using various materials of:
    i. Thermoplastic Poly-Urethane (Pellethane 2363-80A)
    ii. Polycaprolactone (BGH600C)
    iii. Styrene Butadiene Rubber (PB-575)
    iv. Ethylene Vinyl Acetate (H2181)

b. The polymers are compounded and tested in several different compositions.
    i. (SBR: EVA) composite mix are following (100:0), (90:10), (80:20), (70:30), (60:40) where SBR is the main matrix and EVA is the additive.
    ii. (TPU: PCL) the composite mix is following (100:0), (90:10), (80:20) where TPU is the main matrix and PCL is the additive.
c. Sample Preparation through:
    i. Heat compounding using Brabender Plastograph two roll mill.
    ii. Injection Moulding using a horizontal NP7-1F moulding machine.
    iii. Extrusion of flexible filament using customised single screw extrusion machine.
d. Mechanical properties study using several mechanical testing such as:
    i. Tensile test
    ii. Flexural test
    iii. Shore Hardness test
e. Morphological and thermal studies are also carried out on all the samples.
    i. Scanning Electron Microscope (SEM)
    ii. Fourier Transform Infra-Red Spectroscopy (FTIR)
    iii. Thermogravimetric Analysis (TGA)
    iv. Differential Thermal Analysis (DTA)
    v. Melt Flow Index (MFI)
f. Characteristic studies on flexible filament are carried out using FDM machine to identify:
    i. The modification needs to be done to print the flexible filament.
    ii. Extrusion temperature ranges of the filament in FDM machine.
    iii. Extrusion speed of the FDM extruder when filament extrusion.
    iv. Time for FDM machine to extrude a constant filament diameter.
    v. Cooling time taken for the filament to cool after extrusion.

1.5 Significance of Study

This study proposes a new flexible polymer material composite which has elastic behaviour for FDM process which will help in the growth of 3D printed orthotics and flexible products manufacturing.

This material study could be used to produce alternative filament wire for FDM where it will give benefits especially to those industries which involve the usage of flexible rubber-like materials, especially footwear and medical industries in their daily manufacturing.

Vast range optional materials for fused deposition composition will enlarge the usage of FDM in the industries and lead future research of this study. It also drives to a possible product to be producing using this fabrication method.

The result of data in this research also can be used to guide the fabrication on new flexible FDM feedstock materials that have better characterized and mechanical properties to produce high-quality products in future.

1.6 Thesis Outline

This report explains the detailed study on the characterization of TPU, PCL, SBR and EVA materials. It also studies the compatibility of composites from these polymeric materials with FDM. The research study is organised into five chapters.

Chapter one is an introduction to the study which includes the background of study and also the problem statement of the study. There are also basic knowledge of the study such as objectives, scopes, purpose and expected a result from the study include in this chapter.

Chapter two is discussing the review of the literature and the case study of any former research that can help to support this research. The important theory that can be related to this study also stated in this chapter.

Chapter three is discussing on the method and the procedures used in conducting the study in a well develop research report.

As an addition to complete a report, chapter four which stated the result and discussion upon the data collected is a necessary. Analysis of the result of all the testing method was presenting in this chapter in tables and graph form.

Lastly is chapter five which contain conclusions that summarise the entire thesis and some recommendations for improvement for the overall study. Some recommendation for further research that can be accomplished upon this study also suggested in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this Chapter, the project literature review is discussed and explained. The project literature review will start by a detailed explanation on the Additive Manufacturing (AM) process. All the AM types are discussed in the classification of AM. Then, followed by Fused Deposition Modelling (FDM) process and its existing feedstock materials. After that, there are explanations on the previous FDM feedstock fabrication, SBR and TPU composite research studies.

2.2 Additive Manufacturing

The term Additive manufacturing (AM) was standardised and approved by the International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM) (ASTM International, 2013) that refers to a manufacturing technique which uses layered manufacturing to produce a solid physical model of a part using three-dimensional computer-aided-design (CAD) file. Earlier in the 80's the technique of Rapid Prototyping was developed for producing prototypes parts in three dimension by utilising the layer by layer manufacturing and Computer Aided Design (CAD) started replacing injection moulding and other conventional techniques (Hopkinson & Dicknes, 2003; Hague *et al.*, 2004; Wong & Hernandez, 2012). The RP technology was created and developed to for designer to ensure that 3D visualisation of their conceptual design. The part is modelled with actual measurements then it is built directly from a digital 3D model designed through

Computer Aided Design (CAD) software. Historically, the AM technology was used for the conceptual prototypes construction and was referred as RP, a synonym term which had been used for a long time before the term AM was standardised in the year 2013 and still often been used. The purpose of building those prototypes is to accelerate the development phase of a product to enter the market and under zero circumstances of comparison to the final output of the product regarding the quality, material and durability (Thymianidis *et al.*, 2012). The scientific research played a major role in the development of AM technology which enhanced the printer capabilities towards the functional prototype manufacturing which lead to Rapid Manufacturing (RM). Furthermore, RM has progressed through AM due to technological growth defined by as the production of end-use products utilising AM techniques (Pal & Ravi, 2007). As the effect on the development of the AM technology in the past decade, RM distinguished from AM technology due to the usage of improvised printing techniques which enabled by various sophisticated materials which promote the manufacture of products with long-term consistency for the product life (Levy *et al.*, 2003).Initially, the AM built prototypes offered benefits such as the new design concept analysis and discovery with the performance accomplishments to initiate the production (Das, 2004). The AM technology benefits the designers to create and produce 3D models of their virtual models from CAD drawings due to the shorter lead time for production. Also, the intricacy of new design concept can be constructed using this AM technique.

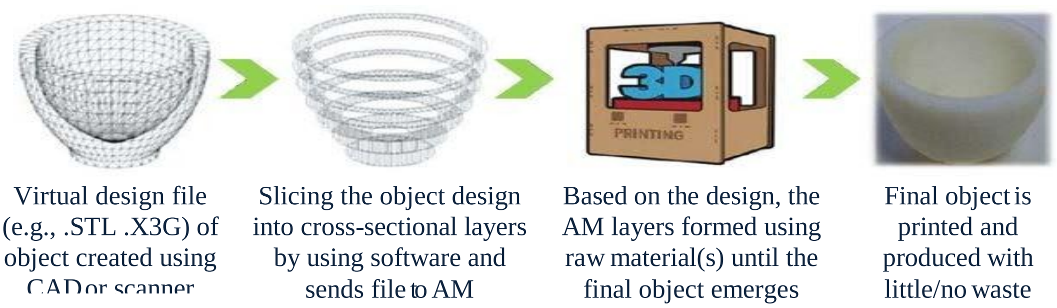


Figure 2.1: The detailed AM process (Niaki & Nonino, 2017)

Many of the AM techniques depends on the core concept of the draft model of CAD Drawing. The 3D CAD model is converted to a Stereolithography (STL) file and been sliced into many 2D thin layers, and the manufacturing equipment uses this geometric data to build each layer sequentially until the part is completed. The final step is diverse between AM machines and it depends on the fundamental deposition principle utilised in AM machines (Sokovic & Kopac, 2006). The available technology for additive manufacturing of prototype models is rapidly changing, as new materials and processes are introduced to the market. Some other benefits of AM technology are studied and identified.

The benefits of AM are manufacturing of objects with a high geometrical complexity without the need for any other tooling and the possibility of the fabrication of objects from a different mixture of materials or any composites. Apart from that, the ability to even various feed materials in a highly controlled way at various position of an object. Finally, AM technology has an advantage of improvising the scope of product development with minimised cost and time. There are some most widely available additive creation of RP processes which is Selective Laser Sintering (SLS), Stereolithography (SLA), Laminated Object Manufacturing (LOM), and Fused Deposition Modelling (FDM).

The term AM has a variety of names based on its capability in manufacturing the prototypes such as Free Form Fabrication (FFF), 3D Printing, Layer Manufacturing (LM) and Rapid Prototyping. In recent times, the AM technology has created a huge impact and attracted more researchers and manufacturers to collaborate to explore more in AM for the future.

2.2.1 Classification of Additive Manufacturing

The AM is the unique approach to resolving the problems faced by the manufacturing industry for the increment in demand where AM could reduce fabrication cost and lead time in the production process. The AM technology has triggered the third industrial revolution in manufacturing products due to the cost-effectiveness and time consumption. Particularly, after the increment of accessibility and capability of AM in mass customisation on a vast range of products in industries such as medical, automotive and metals. In recent days, 3D printing known as AM is used only in 28 percent of the whole manufacturing sector, but the market is assumed to explode (Wohlers, 2013).

Meanwhile, it is identified that the consumer market is the main driver of the manufacturing sector growth, with space for innovations in the market. These different methods of additive manufacturing can be classified by the type of material and process that is employed. There are seven types of AM processes as defined by ASTM International. The mass production allows the consumer demands to be fulfilled due to the early of the 20th century and the amount of the goods produced in short time have increased. While the production time is lower than before, they did so at expenses customization. The AM technology makes it possible for customers to customise the goods that they are buying. Table 2.1 comprises the summary of the seven process classifications and the technologies that contain in the 3D printer in the market.

Table 2.1: Classification of AM process (ASTM International, 2013)

Classification	Technology	Materials	Developers
Direct Energy Deposition	-Direct Metal Deposition -Electron Beam Direct	Polymer, Metal, Wire	Irepa Laser Sciaky DM3D Triumpf
Binder Jetting	-Ink Jetting -3D Printing	Polymer, Metal, Ceramic	Voxejet ExOne 3D Systems
Material Extrusion	-Fused Deposition Modelling	Polymer	Delta Micro Factory Stratasys 3D Systems
Material Jetting	-Thermojet -Polyjet -Ink-Jetting	Photopolymer, wax	Stratasys 3D Systems LuXeXcel
Sheet Lamination	-Ultrasonic Consolidation -Laminate Object Manufacturing	Ceramic, Hybrids, Metallic	CAM-LEM Fabrisonic
Powder Bed Extrusion	-Direct Metal Laser Sintering -Selective Laser Sintering	Metal, Polymer, Ceramics,	3D Systems EOS Matsuura Machinery Phenix Systems
Vat Polymerisation	-Stereolithography -Digital Light Processing	Photopolymer, Ceramic	DWS Srl Lithoz 3D Systems Envision TEC

2.3 Fused Deposition Modelling (FDM)

After the year 2010, fused deposition modelling (FDM) has been a leading rapid prototyping process where fabricated parts are mainly used for additive manufacturing technology for various applications in engineering such as design verification, medical applications, functional testing, and patterns for casting processes (Nikzad *et al*., 2011). This FDM technology was developed by Scott Crump and trademarked by Stratasys Inc (Crump, 1992). Besides FDM it can also be called as Fused Filament Fabrication (FFF) which is an extrusion-based system. This extrusion based 3D printer is widely popular among users and researchers. For FDM process, the filament material is extruded in a fragile layer onto the previously constructed model layer on a build platform to form the object (Sun *et al*., 2009).

The rapid growth of AM technology has vastly spread all over the world, hence offering a compact, personal and affordable desktop 3D printer. Most of the desktop 3Dprinters available in the market for the present time is based on filament extrusion process. FDM process is a very common and visible process compared with other AM processes. Acrylonitrile butadiene styrene (ABS) and Polylactic Acid (PLA) are the most common material for beginner level FDM users. Apart from that, there are other materials available in the market such as conductive and flex in which sold in a variety of colours.

The FDM process initially starts with a direct feed of the polymers filament material into the extruder which uses a torque and pinch system to feed in FDM filaments. After that, the filament moves through the extruder and flows directly into the heater block. The heater block heats the filament according to the required temperature. The semi-molten material is pressured out through the heated nozzle at a minuscule diameter.The thread-like material is deposited onto the built platform forming a layer on layer in XYZ axis (Chua *et al.*, 2003; Bellini *et al*., 2004). Figure 2.1 shows the schematic of FDM process.

Most of the present FDM filament in the market are focussed on very rigid and stiff polymers that produce products which tend to break easily. However, there are rarely found elastically or rubbery materials that used as a feedstock. There are studies done to produce flexible filaments which can be used for various manufacturing. The continuous development of new materials with modifications on its characteristics actually could widen up the possible outcome of the FDM product. In today's world, many industries are on this additive manufacturing technology especially FDM technique to produce their prototype or fully functional new products. The development of flexible FDM filaments could help in many industries such as footwear and medical industries by helping them to produce footwear and medical products.

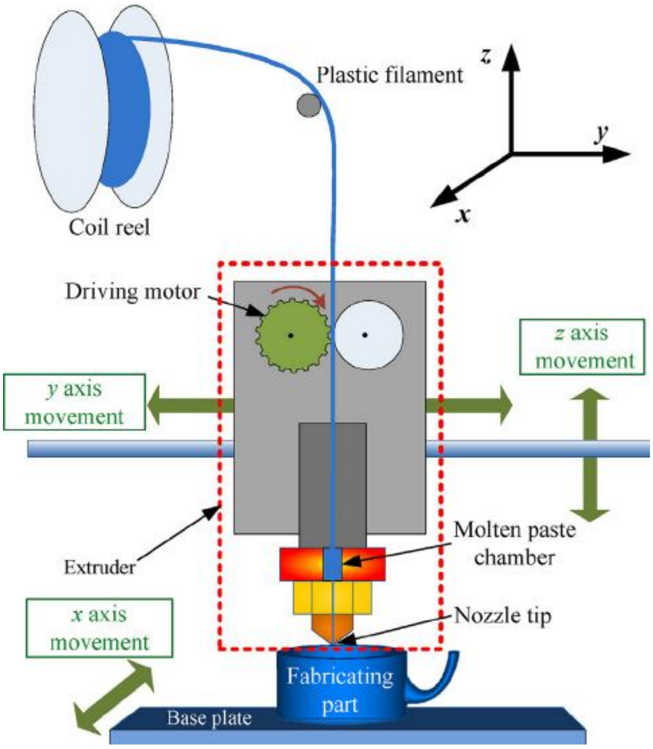


Figure 2.2: Schematic of Fused Deposition Modelling Process (Jin, 2015)

2.4 Fabrication of FDM Feedstock

The filament that used in the FDM process requires a specific diameter, strength, and certain other properties. A filament that fabricated from a composite mixture, a single screw extruder which uses the basic extrusion principle is used. However, due to the die swell phenomenon that occurs during extrusion of a polymer, there is a slight difference in diameter between the die and the produced filament. In order to achieve a consistent diameter and minimise this difference, the machine has an adjustable screw for the speed, pressure, and also temperature.

All these parameters are adjusted, examined and selected until an optimum diameter for the filament is reached (1.75 mm). For an elastic and soft filament such as rubber-like filaments, water bath cooling process is used. The developed extruder consists of one heat zone with controlled temperature. The temperature must be precisely controlled due to overheating of the composition may cause swelling and rapid degradation of filament material properties (Dudek, 2013). After the extrusion process succeeds with the ideal diameter of the filament, then it can be used in FDM process. Figure 2.3 shows the schematic of the filament extrusion process.

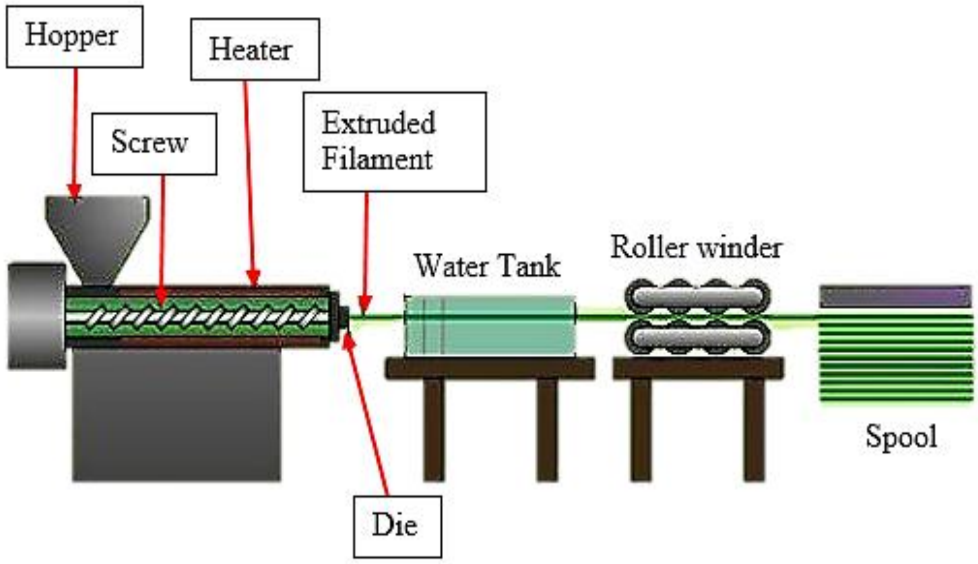


Figure 2.3: Schematic of FDM Filament Fabrication Process (Mostafa *et al.*, 2009)

2.4.1 Existing of Thermoplastic Feedstock Materials

The FDM process is a filament-based process which feeds in the filament material into the heated extruder, and the nozzle extrudes molten polymer material that hardens layer-by-layer to form a solid part. FDM produces highest-quality parts which are a common end-use engineering material that allows performing functional tests on sample parts. Because thermoplastics materials are environmentally stable, part accuracy or tolerance does not change with ambient conditions or time which advantages in enables FDM parts to be among the most dimensionally accurate. That was the reason why it is chosen to be used as feedstock material alternative.

Generally, the most common FDM filament materials which can easily be acquired is ABS and PLA. For years these two materials were the main materials for fabrication of FDM objects. In recent years the research study on possible new materials for FDM process was vastly done by researchers all over the world. The consequences of the research opened doors for many new materials to enter the filament market with different types of properties. Most of the materials are composite mixes which enhance the mechanical and thermal properties of the end products. The Table 2.2 below shows the existing FDM materials which used to fabricate filaments and used for FDM process.

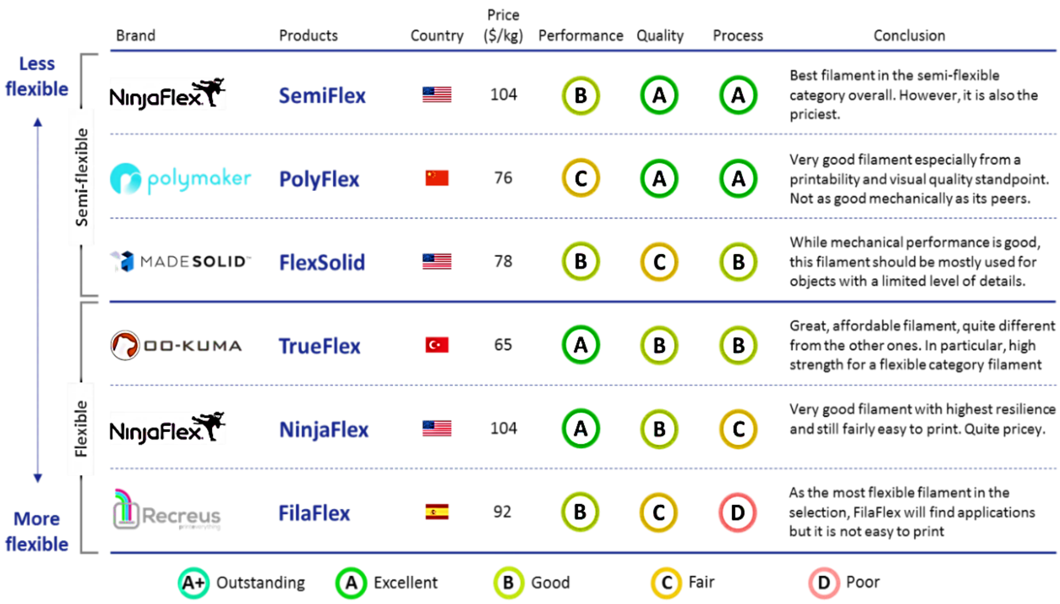
Table 2.2: Existing FDM materials (Marcincinova & Kuric, 2012)

Materials	**Characteristics / Behaviours**
ABSplus thermoplastic (Acrylonitrile Butadiene Styrene)	- Environmentally stable - no appreciable warpage, shrinkage or moisture absorption - 40 percent stronger than standard ABS material
ABS-M30 thermoplastic	- 25-70 percent stronger than standard ABS material - Greater tensile, impact, and flexural strength - Layer bonding significantly stronger for more durable part - Versatile Material: Good for form, fit and moderate functional applications
ABS-M30i thermoplastic	- Biocompatible (ISO 10993 certified) material - Ideal material for pharmaceutical, medical and food packaging industries - Sterilize-able using gamma radiation or ethylene oxide (EtO) sterilisation methods.
ABSi thermoplastic	- Translucent material - Ideal for automotive tail lens applications - Ideal blend of mechanical and aesthetic properties - Available in, amber and translucent natural red colours
PC-ABS thermoplastic (Polycarbonate Acrylonitrile Butadiene Styrene)	- Highly desired properties of both PC and ABS materials - Better mechanical properties and heat resistance of PC - Excellent specification definition and surface appeal of ABS - Highest impact strength
PC thermoplastic (Polycarbonate)	- Most widely used industrial thermoplastic - Accurate, durable, and stable for strong parts - Superior mechanical properties and heat resistant - Able to handle high temperatures and has high tensile strength

PC-ISO thermoplastic	- Biocompatible (ISO 10993 certified) material - Ideal material for pharmaceutical, medical and food packaging industries - Sterilize-able using gamma radiation or ethylene oxide (EtO) sterilisation methods - Best fit applications with high strength and sterilisation
PPSF/PPSU thermoplastic (poly-phenyl-sulfonic)	- Highest heat and chemical resistance of all FDM materials - Mechanically superior material, greatest strength - Sterilize-able via steam autoclave, EtO, plasma, chemical, and radiation sterilisation - Ideal for applications in high heat environments (Please refer next page for Table 2.2 continuation)
FDM Thermoplastic Material ULTEM 9085	(Table 2.2 continued) - Highly durable, lightweight, flame-retardant thermoplastic widely used in aircraft interiors - V-Zero rating for flame, smoke & toxicity (FST) - High strength to weight ratio - Higher heat deflection temperature (320° F / 160° C) - Flight & other certifications in aerospace industry

2.5 Development of Flexible FDM Filament

Over the past two decades, fused deposition modelling been a vital process in the development of new prototypes in the manufacturing industries. FDM is what many people thinks and understands as 3D printing as this FDM process is the most common and simplest technology of all other possible AM processes (Griffey, 2014). Most of the current FDM filaments available in the market are focussed on very rigid and stiff polymers that produce products which tend to break easily. However, there are rarely found elastically or rubbery materials that used as a feedstock. The flexible filaments acquire important characteristic which is high elastic modulus and low hardness value. There are few products in the market which are flexible, but all the flexible filaments have a range of shore hardness above 85A and are considered hard to apply in footwear industries. The flexible FDM filament products are listed in Figure 2.4 which shows their quality, performance, price and processability.



Brand	Products	Country	Price ($/kg)	Performance	Quality	Process	Conclusion
NinjaFlex	SemiFlex	USA	104	B	A	A	Best filament in the semi-flexible category overall. However, it is also the priciest.
polymaker	PolyFlex	China	76	C	A	A	Very good filament especially from a printability and visual quality standpoint. Not as good mechanically as its peers.
MADESOLID	FlexSolid	USA	78	B	C	B	While mechanical performance is good, this filament should be mostly used for objects with a limited level of details.
OO-KUMA	TrueFlex	Turkey	65	A	B	B	Great, affordable filament, quite different from the other ones. In particular, high strength for a flexible category filament
NinjaFlex	NinjaFlex	USA	104	A	B	C	Very good filament with highest resilience and still fairly easy to print. Quite pricey.
Recreus	FilaFlex	Spain	92	B	C	D	As the most flexible filament in the selection, FilaFlex will find applications but it is not easy to print

Figure 2.4: The comparison chart for flexible filament (3D matter, 2015)

There are more studies done to produce flexible filaments which can be used for various manufacturing including medical and footwear industries. The current flexible filaments are not compatible for footwear and also medical industries. The continuous development of new flexible materials with modifications on its characteristics actually could widen up the possible outcome product of the fused deposition modelling.

2.5.1 Purpose for Flexible Filament Development

Nowadays, a wide range of industries are on this additive manufacturing technology especially FDM technique to fabricate their prototype or fully functional new products. The research and development of new flexible FDM filaments could help in various industries such as footwear and medical industries on their products. The customisation of footwear provides an advantage for many individuals, who are older adults and patients suffering from foot affecting disease or foot irregularities. There are research studies which have shown data that between 26 and 50% of older adults wear footwear that is either short or narrow (Nixon *et al*., 2006; McInnes *et al*., 2012). The footwear is considered to be an essential accessory, and the customisation on footwear helps to satisfy the individual measurements as shown in Figure 2.5, and desires regarding comfort, fit, support and injury preventive.

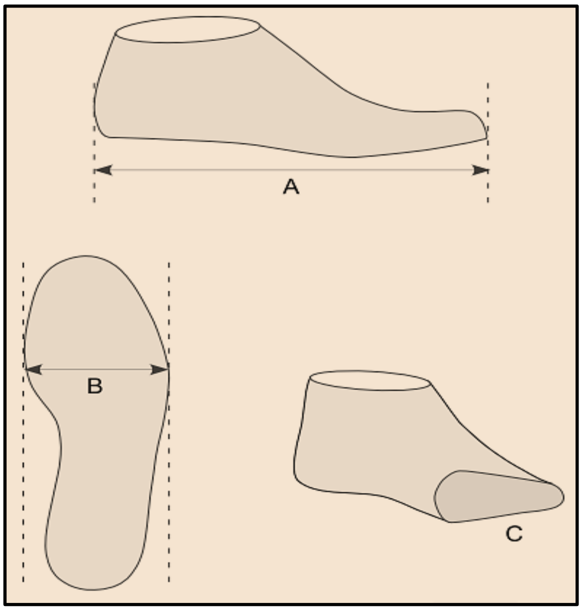


Figure 2.5: Measurements obtain for the footwear manufacture a) Length b) Ball Width c) Ball Girth (Menz *et al*., 2014)

Many researchers have recorded that fit is a vital criterion of footwear manufacturing because it is related comfort and injury prevention (Cheng & Perng, 2000; Luximon *et al*., 2003). In recent days, the design of custom and customised orthotics for ankle and foot is restricted by the methods and materials used to fabricate them. The most common method which has been used involves vacuum forming a thermoplastic sheet around a balanced, corrected positive plaster cast of the anatomy of interest, then removing away unwanted material by cutting it to form the orthotics (Mason & Vuletich, 1981; Lusardi & Nielsen, 2000). There are some manufacturers using a standardised range of moulds with different size and shape that can be chosen based on a few predefined measurements from the patient (Zifchock & Davis, 2008; Telfer *et al*., 2012).

The three-dimensional (3D), foot scanning process, is promising specifically for footwear customisation where it provides accurate measurements (Menz *et al*., 2014). The usage 3D scanning technologies to acquire and manufacture digitised models of parts of the human body anatomy has a high potential to aid and change the way a vast range of products are designed and produced (Treleaven, 2004; Telfer *et* *al*., 2012). Geometric freedom and tool-less capability are the advantages offered by FDM process.

This factor allows the manufacturing of customised parts directly from accurately designed solid models at lower cost. The possibility of combining FDM process with 3D foot scanning and solid modelling or computer aided design (CAD) is been indicated by the growth of the paper quantities reporting their use to manufacture footwear insoles and orthotics. Despite the customisation of footwear in this method shows high possibility, there is only limited research on the flexible materials to build it, but its impact on the sports profession and footwear industry is in the growth.

Past decade, the medical industry applications of rapid manufacturing are rapidly on growth and have shown higher benefits over the common conventional techniques (Saleh & Dalgarno, 2009). Medical industries have been highly impacted by this technology where there are more researches done on various medical fields such as implants and organ printing (Espalin *et al*., 2010). The ease in converting 3D medical imaging data into solid objects is the prominent reason for the usage of this technology. By utilising this technology, the objects or product can be customised to accommodate the needs of a particular patient (Menz *et al.*, 2014).

The usage of this technology had directly resulted on the decrement of the cost that charged on the patients by reducing the production cost (Pallari *et al.*, 2010). A precise and quantitative description of foot shape and size is vital for a number of various applications associated with the footwear ergonomics and design, foot orthotics and insoles, and for research study on clinical evaluation of foot irregularities such as those related to rheumatoid arthritis (Luximon & Goonetilleke, 2004; De Mits *et al*., 2010). This technology can surmount these limitations and allow healthcare professionals involved in the prescription of these type of devices the opportunity to explore truly novel orthotic design features (Leong *et al.*, 2003).

Nowadays, most of the studies conducted towards the development of new materials or processes related to FDM which focused on the enhancement of the mechanical properties of the product produced and different types of polymer composites are one of the top choices materials for researchers (Masood, 1996; Woodruff & Hutmacher, 2010). Flexible material which can be made as a flexible filament that is suitable to be in contact with the human body and with a lower value of hardness is in need to the footwear and medical industries.

2.6 Footwear Insole Fabrication

2.6.1 Existing Materials for Insole Fabrication

There are three different types of materials that were usually used in the manufacturing of shoe insole which is Ethylene Vinyl Acetate (EVA), Polyurethane (PU), and Polyethylene (PE). Ethylene vinyl acetate (EVA) is a closed-cell cellular polymer which allows it to be moldable, elastic and resilient. It also has low density makes it light weighted, and it is soft where it gives good shock absorption and cushioning properties.

It is a common material for clinical use in manufacturing diabetic insoles as top and bottom layers. However, it tends to suffer high compression set, which means these properties deteriorate rapidly after several wears (Saraswathy *et al.*, 2009). High-density materials can be used as bottom layers for supporting because it can provide sufficient support for the body weight.

Table 2.3: Existing Insole materials

Materials	**Description**
Thermoplastic	Soften when heated and harden when cooled
Polypropylene	Light weight and high strength
Subortholene	Wax-like, inert, flexible, and tough polymer. Easily cold-formed
Acrylic	Materials used for rigid orthotics
Composite Carbon Fibres	Hard to work with, requiring a higher softening temperature, faster Vacuuming, and complete accuracy
Cork	comes in various thickness, weights and vacuums to provide a firm however comfort orthotic, which is easily adjusted with a sanding wheel
Leather	Leather laminates are still used today when patients want good support but cannot tolerate firmer plastics
Polyethylene Foams	These are closed-cell foams identified as ideal material for total-contact, pressure-reducing orthotics although some are subject to compression with continued wear

Polyurethane (PU) foam material is commonly used in clinical practice for preventing plantar ulceration. It reduces pressure by distributing body weight forces over a larger area of the plantar surface due to its excellent cushioning properties. It is open-cell-structured, which means pores are presented, and they are connected and form an interconnected network that is relatively soft.

Polyurethane (PU) is a non-moldable material but can be combined with a moldable material to obtain a desirable shape and improve the durability of other soft materials (Birke & Foto, 1997). It is available in different density and elasticity. It is commonly used as soft insoles in non-molded orthoses, as a top layer for moulded orthoses, or as a sub-layer for multi-density moulded orthoses.

Polyethene material that is common thermoplastic material for clinical use in manufacturing orthotic insoles for protection against pressure points (Campbell *et al.*, 1982). It is a polyethylene foam material with closed-cell structure, which means interconnected pores are absented; perspiration moisture cannot be absorbed. It is lightweight, heat moldable and non-toxic. Since it has good cushioning and excellent self-molding properties, it is often used in the management of neuropathic foot. However, it has a very short life because of its high compressibility (Pratt *et al.*, 1986).

2.7 Potential Materials for Flexible FDM Filaments

FDM is a filament based technique on AM process which offers the possibility of introducing new composite material for the FDM process as long as the new material can be made in feedstock filament form (Nikzad *et al*., 2011). The use of rubber or rubber-like thermoplastics able to create a potential path for the fabrication of flexible filament.

The general purpose of rubbers such as natural rubber (NR) and styrene-butadiene rubber (SBR) are amongst the cheaper polymers, and even cheaper compounds may be made from them by using the oils and fillers. It is clearly known that compared with thermoplastic they do possess one serious disadvantage which is the requirement that after shaping, there is necessary to involve a chemical cross-linking process (vulcanization) which consumes both time and energy (Brydson *et al*., 1982 a ; Brydson, 1982 b).

Styrene Butadiene Rubber is also widely known as Styrene Butadiene Rubber that has all the same criteria as described for an elastomer except that chemical cross-linking is replaced by a network of physical cross-links. The ability to form physical cross-links is opposite to the chemical and structural requirements of an elastomer just described. The answer to this dilemma is that Styrene Butadiene Rubbers must be two-phase materials, and each molecule must consist of two opposite types of structure, one the elastomeric part and the second the restraining, physical cross-linking part (Bonart, 1979; El-sonbati, 2012). SBR requires reinforcing fillers for greater strength, where it has similar physical and chemical properties to NR. However, SBR acquires better abrasion resistance but slightly poorer fatigue resistance than NR. Widely used in car and light vehicle tyres. Also, conveyor belts, moulded rubber goods, shoe soles and roll coverings.Styrene Butadiene Rubbers are typically block copolymers where two or more different monomers unite together to polymerise. Commercially relevant copolymers are such as acrylonitrile butadiene styrene (ABS), styrene/butadiene copolymer (SBR), nitrile rubber (NR), styrene-isoprene-styrene (SIS), and also ethylene-vinyl acetate (EVA).

It is identified that ethylene vinyl acetate (EVA) copolymer seem to be a potential approach to develop rubbery material with good ozone and weathering resistance as well as excellent physical and mechanical properties. EVA copolymer is produced in powder form or insoluble white solid in pellet form. EVA is a part of the polyolefin family such as high, medium and low-density polyethylene and polypropylene. Polyolefin are tough, flexible and resistance to chemicals and abrasion EVA is suitable and comprises good flexibility, excellent heat seal strength, and advantages of having low-temperature performance which saves the manufacturing costs (Park, 1991). For example, several reported EVA-based systems that contain nitrile rubber (NBR) as unsaturated component that offer several significant advantages such as excellent oil resistance, abrasion resistance and better ageing resistance (Varghese *et al.*, 1995; Bandyopadhyay *et al.*, 1997; Soares *et al.*, 2001; Jansen & Soares, 2002). Ethylene-vinyl acetate (EVA) copolymer is in use to manufacture various consumer products such as flexible films for safe packaging of food, footwear insoles, and hot melt adhesives and tubing.

Thermoplastic polyurethane (TPU) is a linear segmented block copolymer which contains soft segments (SS) and hard segments (HS) (Gunatillake *et al.*, 2006; Tatai *et al.*, 2007; Jing *et al*., 2016). According to research studies done on TPU, both

HS and SS are incompatible with each other where they tend to form a nanoscale two phase-separated morphology (Gunatillake *et al.*, 2006; Zukiene *et al*., 2013). The SS have a lower melting point, polarity, and lower resistance to degradation and decomposition than the HS.

The properties of TPU are greatly influenced by the chemical type and ratio of components forming the HS and SS (Tatai *et al*., 2007). The key of interest in TPU for medical applications is due to their exceptional mechanical properties, excellent biocompatibility and structural versatility achievable to customise polymer structures to satisfy the needs of a vast range medical applications. TPU are currently being utilised in medical applications such as vascular grafts and cardiac pacemakers.

Most of the research studies on biomedical TPU was emphasised on the improvement of the biocompatibility and stability as well as designing new elastomers with low modulus for the medicals applications. PU associated foams and elastomers are commonly used as soft insoles in non-moulded orthotics, as a top layer for moulded orthotics, or as a sub-layer for multi-density moulded orthotics. In the Polycaprolactone (PCL) based TPU, PCL normally forms soft segments (Rutkowska *et al*., 1998; Da Silva *et al*., 2010).

PCL is semi-crystalline linear aliphatic polyester derived from ε-caprolactone comprising relatively low melting point, which is approximately 60–65^{o}C (Woodruff & Hutmacher, 2010). PCL is considered as a biodegradable polymer with adequate mechanical properties among the family of polyesters (Fukushima *et al*., 2010).

2.8 Materials

Thermoplastic is a polymer which made from polymer resins that become a homogenised liquid when heated and hard when cooled. Its typical behaviour becomes pliable or moldable above a specific temperature and solidifies upon cooling (Baeurle *et al*., 2006).When frozen, thermoplastic becomes glass-like and subject to fracture.

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