FUSED DEPOSITION MODELLING OF KENAF FIBRE/THERMOPLASTIC POLYURETHANE/EPOXIDIZED NATURAL RUBBER COMPOSITES

MOHAMAD SYAFIQ BIN MOHAMAD RAFI

UNIVERSITI SAINS MALAYSIA
2019
FUSED DEPOSITION MODELLING OF KENAF FIBRE/ THERMOPLASTIC POLYURETHANE/EPOXIDIZED NATURAL RUBBER COMPOSITES

By:

MOHAMAD SYAFIQ BIN MOHAMAD RAFI

Supervisor: Dr. Raa Khimi bin Shuib

Dissertation submitted in partial fulfillment of the requirement for the degree of Bachelor of Engineering with Honours (Polymer Engineering)

Universiti Sains Malaysia

JULY 2019
DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Fused Deposition Modelling of Kenaf Fibre/Thermoplastic Polyurethane/Epoxidized Natural Rubber Composites”. I also declare that it has not been previously submitted for the award or any degree or diploma or other similar title of this for any examining body or University.

Name of Student: Mohamad Syafiq bin Mohamad Rafi    Signature:
Date:

Witness by:
Supervisor: Dr Raa Khimi bin Shuib    Signature:
Date:
ACKNOWLEDGEMENT

First and foremost, I would like to express my heartfelt to Engineering School of Materials and Mineral Universiti Sains Malaysia for providing me with the machine and equipment to carry out this research successfully as well as prepared me a suitable and convenient place to proceed my experimental work.

My deepest appreciation and sincere thanks is dedicated to my supervisor Dr Raa Khimi bin Shuib who has helped me improves my thesis provides constructive advice during completing my final year project. This project would not have been possible without his knowledge and moral support.

I owe my sincere gratitude to polymer technician, Encik Norshahrizol bin Nordin, Encik Mohammad bin Hassan and postgraduate students Nuur Laila Najwa binti Thajudin for their valuable advice and helped me along my research. I also wish to thanks all the other technician of Polymer Engineering Laboratory at University Science Malaysia for providing the necessary technical support.

Moreover, my warm thanks to Dr. Arjulizan binti Rusli and all Polymer Engineering lecturers for providing valuable knowledge during my degree in University Science Malaysia. My special gratitude to my family and friends for their loving support and to those directly or indirectly helped me to complete my final year project.

My ultimate thanks to the Almighty ALLAH for his endless pleasure bestowed upon me. Thank you

Mohamad Syafiq bin Mohamad Rafi

July 2019
# TABLE OF CONTENT

DECLARATION ........................................................................................................ ii

ACKNOWLEDGEMENT ........................................................................................ iii

TABLE OF CONTENT ............................................................................................ iv

LIST OF TABLES .................................................................................................. ix

LIST OF FIGURES ................................................................................................ x

LIST OF EQUATION ............................................................................................ xiii

ABBREVIATION .................................................................................................... xiv

ABSTRAK .......................................................................................................... xvii

ABSTRACT ............................................................................................................. xviii

CHAPTER 1  INTRODUCTION ................................................................................ 1

1.1 Background .................................................................................................... 1

1.2 Problem Statement ...................................................................................... 4

1.3 Research aim and direction ........................................................................ 5

CHAPTER 2  LITERATURE REVIEW .................................................................... 6

2.1 Introduction to 3D printing ........................................................................... 6

2.1.1 Advantages of 3D printing ...................................................................... 9

2.1.2 Applications of 3D printing .................................................................... 9

2.1.3 Fused Deposition Modelling ................................................................. 11

2.1.4 Parameters of FDM 3D printing ............................................................. 13

2.1.4.1 Effect of bed temperature ................................................................. 13
2.1.4.2 Air gap

2.1.4.3 Orientation of printing

2.1.4.4 Raster angle

2.2 Filament Materials used in Fused Deposition Modelling

2.2.1 Thermoplastic Polyurethane

2.2.2 Epoxidized Natural Rubber

2.3 Blend used in Fused Deposition Modelling

2.4 Thermoplastic Polyurethane/Epoxidized Natural Rubber Blend

2.5 Reinforcement filler for FDM filament

2.5.1 Kenaf fibre

2.6 Environmental Awareness

2.7 Sustainable Composites

CHAPTER 3 METHODOLOGY

3.1 Research Flowchart

3.2 Material and chemicals

3.2.1 Raw materials

3.2.1.1 Thermoplastic polyurethane (TPU) filament

3.2.1.2 Epoxidized Natural Rubber (ENR-25)

3.2.1.3 Kenaf fibre

3.3 Equipment

3.4 Sample preparation

3.4.1 Reduction of fibre size
3.4.2 Treatment of the fibre ................................................................. 32
3.4.3 Fused Deposition Modelling (FDM) 3D printing......................... 33
  3.4.3.1 Filament preparation................................................................. 33
  3.4.3.2 CAD Model .............................................................................. 35
  3.4.3.3 FDM 3D printing parameter ...................................................... 37
  3.4.3.4 Printing process ....................................................................... 38
3.5 Characterisation................................................................................ 39
  3.5.1 Tensile Test.................................................................................. 39
  3.5.2 Water Absorption Test................................................................. 40
  3.5.3 Scanning Electron Microscopy (SEM) ......................................... 40
  3.5.4 Tolerance Test.............................................................................. 41
  3.5.5 Hardness Test............................................................................... 42
  3.5.6 Density Test.................................................................................. 43
  3.5.7 Parallel Plate Rheological test ...................................................... 44

CHAPTER 4 RESULTS AND DISCUSSION ............................................ 45

  4.1 Stage 1: Effect of Kenaf fibre loading in thermoplastic polyurethane filament

    4.1.1 Scanning Electron Microscope Analysis ...................................... 45
    4.1.2 Mechanical Strength ................................................................. 47
      4.1.2.1 Tensile strength ................................................................. 47
      4.1.2.2 Young Modulus ................................................................. 49
      4.1.2.3 Elongation at Break .......................................................... 50
4.1.3 Water Absorption Test ................................................................. 51
4.1.4 Tolerance Test ............................................................................. 53
4.1.5 Hardness Test ................................................................................ 54
4.1.6 Density Test .................................................................................. 55
4.1.7 Rheology Analysis ........................................................................ 56
   4.1.7.1 Shear Stress vs Shear Rate ..................................................... 56
4.2 Stage 2: Effect of epoxidized natural rubber loading in kenaf fibre/thermoplastic polyurethane composite filament ................................................. 58
   4.2.1 Scanning Electron Microscope Analysis ...................................... 58
   4.2.2 Mechanical Strength ................................................................... 61
      4.2.2.1 Tensile Strength ................................................................. 61
      4.2.2.2 Young Modulus .................................................................. 63
      4.2.2.3 Elongation at Break ............................................................ 64
   4.2.3 Water Absorption Test ................................................................. 66
   4.2.4 Tolerance Test ............................................................................ 67
   4.2.5 Hardness Test ............................................................................. 68
   4.2.6 Density Test ................................................................................ 69
   4.2.7 Rheology Analysis ...................................................................... 70
      4.2.7.1 Shear Stress vs Shear Rate .................................................. 70
CHAPTER 5  CONCLUSION AND FURTHER RECOMMENDATION .............. 73
   5.1 CONCLUSION .................................................................................. 73
   5.2 FURTHER RECOMMENDATION .................................................... 75
LIST OF TABLES

Table 2.1: The types of current 3D printing available in the manufacturing of plastic products (Lee et al., 2017a) .......................................................... 8
Table 2.2 Current applications using 3D printing........................................ 10
Table 2.3 A summary of materials used in FDM 3D printing technique (Lee et al., 2017b) .............................................................................. 15
Table 2.4 A summary of reinforcement filler used in FDM 3D printing technique...... 22
Table 3.1 Material and chemical used in sample preparation for this research studies.. 29
Table 3.2 Mechanical properties and chemical composition of Kenaf ..................... 30
Table 3.3 Equipment............................................................................................ 31
Table 3.4 Formulation of the composites ............................................................. 33
Table 3.5 Constant parameters for FDM process in MeCreator ............................. 37
Table 4.1 Tolerance of printed sample ................................................................. 53
Table 4.2 Tolerance of printed sample. ................................................................. 68
LIST OF FIGURES

Figure 2.1: Overview of different rapid-prototyping (RP) technologies using the layer-by-layer build up process (Pfister et al., 2004) .......................................................... 8
Figure 2.2 Section printed specimens. Characteristic area. (Fernandez-Vicente et al., 2016) .................................................................................................................. 11
Figure 2.3 Schematic of FDM process (Ning et al., 2015) ........................................ 12
Figure 2.4 Orientation of printing line (Quan et al., 2018) ........................................... 14
Figure 2.5 Raster angle of FDM printing (Mohamed et al., 2017) ............................. 15
Figure 2.6 Chemical structure of Thermoplastic Polyurethane (TPU) ....................... 16
Figure 2.7 Illustration for synthesis of polyurethane (Xu et al., 2008) ....................... 17
Figure 2.8 Chemical structure of ENR-25 ............................................................. 18
Figure 2.9 Reaction of ENR ..................................................................................... 18
Figure 2.10 Kenaf plant (Akil et al., 2011) ................................................................ 24
Figure 2.11 Physical appearance of Kenaf (Aji et al., 2009) ..................................... 24
Figure 3.1 Overall flowchart .................................................................................... 28
Figure 3.2 Thermoplastic polyurethane (TPU) filament .......................................... 29
Figure 3.3 Grinder Machine ..................................................................................... 32
Figure 3.4 Treated Kenaf fibre powder ................................................................. 33
Figure 3.5 Haake internal mixer .............................................................................. 34
Figure 3.6 Single screw extruder ............................................................................ 34
Figure 3.7 Surface finish of extruded composite filament ....................................... 35
Figure 3.8 ASTM D412 Type C model for tensile specimen ................................. 35
Figure 3.9 ASTM D4812 model for impact specimen ............................................ 36
Figure 3.10 Model for tolerance test ...................................................................... 36
Figure 3.11 MeCreator 3D printer ......................................................................... 38
Figure 3.12 Surface finish of composite according to ASTM D412 (c) tensile specimens .......................................................................................................................................................................................... 38

Figure 3.13 Surface finish of composite for water absorption test ................................................. 39

Figure 3.14 Surface finish of composite for tolerance test .......................................................... 39

Figure 3.15 Instron 3366 machine ........................................................................................................... 40

Figure 3.16 Sample Holder .................................................................................................................... 41

Figure 3.17 Table top for scanning images .......................................................................................... 41

Figure 3.18 Dimension of tolerance test samples .................................................................................. 42

Figure 3.19 Shore D ................................................................................................................................. 42

Figure 3.20 Density balance .................................................................................................................... 43

Figure 3.21 Parallel plate rheometer ..................................................................................................... 44

Figure 4.1 SEM of cross-section of filament composites fracture surface of (a) Neat TPU (b) KF/TPU- 5/95 (c) KF/TPU- 10/90 at 50x magnification ................................................................. 45

Figure 4.2 SEM of fractured surface of (a) Neat TPU, (b) KF/TPU- 5/95 and (c) KF/TPU 10/90 at 100x magnification. ........................................................................................................... 47

Figure 4.3 Tensile strength (MPa) of printed sample with different Kenaf fibre loading. .............................................................................................................................................................. 49

Figure 4.4 Young Modulus (MPa) of printed sample with different Kenaf fibre loading. .............................................................................................................................................................. 50

Figure 4.5 Elongation at break (%) of printed sample with different Kenaf fibre loading. .............................................................................................................................................................. 51

Figure 4.6 Percentage of water absorption (%) of printed sample with different Kenaf fibre loading. ............................................................................................................................................................ 52

Figure 4.7 Layer-layer blend of printed sample ....................................................................................... 54

Figure 4.8 Hardness results of printed sample with different Kenaf fibre loading. .............................. 55
Figure 4.9 Density (g/cm³) of printed sample with different Kenaf fibre loading. .......................... 56

Figure 4.10 Shear stress vs shear rate of printed sample with different Kenaf fibre loading. ........................................................................................................................................ 57

Figure 4.11 SEM micrographs taken from the cross-section of the filaments of (a) KF/TPU/ENR- 10/90/10 (b) KF/TPU/ENR-10/80/20 (c) KF/TPU/ENR- 10/70/30 (d) KF/TPU/ENR- 20/90/10 (e) KF/TPU/ENR- 20/80/20 composites. ........................................ 59

Figure 4.12 SEM micrographs taken from the fracture surface of tensile specimen of (a) KF/TPU- 10/90 (b) KF/TPU/ENR- 10/90/10 (c) KF/TPU/ENR-10/90/20 (d) KF/TPU/ENR- 10/70/30 (e) KF/TPU/ENR- 20/90/10 (f) KF/TPU/ENR- 20/80/20 composites. ........................................................................................................................................ 60

Figure 4.13 Sample that unable to print............................................................................................................ 61

Figure 4.14 Tensile Strength (MPa) of FDM printed dumbbell specimens. ......................... 63

Figure 4.15 Young Modulus (MPa) of FDM printed dumbbell specimens......................... 64

Figure 4.16 Elongation at break (%) of FDM printed dumbbell specimens....................... 66

Figure 4.17 Percentage of Water Absorption of FDM printed specimens. ......................... 67

Figure 4.18 Hardness of FDM printed specimen............................................................................... 69

Figure 4.19 Density (g/cm³) of FDM printed sample.............................................................. 70

Figure 4.20 Illustration of formation gross separation .......................................................... 71

Figure 4.21 Shear stress vs shear rate of FDM printed sample............................................ 72
LIST OF EQUATION

Equation 1 .................................................................................................................. 40

Equation 2 .................................................................................................................. 42
### Abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Acrylonitrile Butadiene Styrene</td>
</tr>
<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>DLP</td>
<td>Digital Light Processing</td>
</tr>
<tr>
<td>DV</td>
<td>Dynamic Vulcanization</td>
</tr>
<tr>
<td>ENR</td>
<td>Epoxidized Natural Rubber</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene-vinyl acetate</td>
</tr>
<tr>
<td>FDM</td>
<td>Fused Deposition Modelling</td>
</tr>
<tr>
<td>FFF</td>
<td>Fused Filament Fabrication</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density Polyethylene</td>
</tr>
<tr>
<td>LOM</td>
<td>Laminating Object Manufacturing</td>
</tr>
<tr>
<td>NR</td>
<td>Natural Rubber</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly-Lactic Acid</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl Alcohol</td>
</tr>
<tr>
<td>RP</td>
<td>Rapid Prototyping</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SLA</td>
<td>Stereolithography</td>
</tr>
<tr>
<td>SLS</td>
<td>Selective Laser Sintering</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>TPE</td>
<td>Thermoplastic Elastomer</td>
</tr>
<tr>
<td>TPNRs</td>
<td>Thermoplastic Natural Rubber</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>TPO</td>
<td>Thermoplastic Polyolefin</td>
</tr>
<tr>
<td>TPU</td>
<td>Thermoplastic Polyurethane</td>
</tr>
<tr>
<td>TPV</td>
<td>Thermoplastic Vulcanize</td>
</tr>
<tr>
<td>Wt</td>
<td>Weightage</td>
</tr>
</tbody>
</table>
PEMODELAN PEMENDAPAN LENTURAN KOMPOSIT GENTIAN KENAF/TERMOPLASTIK POLIURETANA/GETAH ASLI TEREPOKSIDA

ABSTRAK

Pemodelan pemendapan yang digunakan adalah teknologi pembuatan tambahan yang mudah dan berpatutan dengan menggunakan pengekstrudan filamen bahan polimer bagi menghasilkan produk lapisan 3D berdasarkan lapisan demi lapisan. Kajian ini meneroka kemungkinan menggunakan pemodelan pemendapan untuk menghasilkan komposit elastomerik diperkuatkan gentian semulajadi. Gentian kenaf dan poliuretana termoplastik (TPU) filamen komposit telah disediakan dengan menggunakan pencampur dalaman untuk tujuan penyebatian dan telah diekstrud untuk membentuk filamen bagi stok umpan percetakan 3D dengan kandungan pembebanan yang berbeza bagi gentian kenaf (0-20wt%). Filamen TPU dengan gentian kenaf 0-10wt% telah berjaya diekstrud untuk menghasilkan sampel ujian. Filamen komposit dengan 20wt% gentian kenaf telah patah sebelum diestrud semasa percetakan 3D. Keputusan menunjukkan kekuatan tegangan, pemanjangan takat putus, ketumpatan dan tegasan ricih adalah menurun, modulus Young, kekerasan, penyerapan air sampel dicetak meningkat dengan peningkatan pembebanan gentian kenaf. Ujian toleransi menunjukkan pengecutan produk bercetak dapat dikawal dengan peningkatan pembebanan gentian kenaf. Seterusnya, untuk meningkatkan fleksibiliti bahan matrik bagi komposit pencetakan dengan kandungan gentian yang lebih tinggi, penilaian selanjutnya dilakukan dengan mencampurkan TPU dengan kandungan getah asli terepoksida (GAT) yang berlainan (10-30 wt%). Gaulan TPU / GAT telah disebatikan dengan 10wt% dan 20wt% gentian kenaf dimana filamen tersebut berjaya diekstrud. Hasil penemuan telah menunjukkan bahawa kekuatan tegangan, pemanjangan takat putus, modulus Young dan kekerasan sampel bercetak menurun manakala penyerapan air dan ketumpatan sampel dicetak meningkat dengan peningkatan
pembebanan GAT. Ujian toleransi menunjukkan kehadiran GAT meningkatkan kestabilan dimensi sampel dicetak. Tegasan ricih menunjukkan variasi dengan peningkatan nisbah pembebanan GAT. Kesimpulannya, dengan peningkatan pembebanan gentian kenaf dan pembebanan getah asli terepoksida akan mempengaruhi sifat mekanikal dan fizikal bahan yang dicetak.
FUSED DEPOSITION MODELLING OF KENAF FIBRE/THERMOPLASTIC POLYURETHANE/EPOXIDIZED NATURAL RUBBER COMPOSITES

ABSTRACT

Fused deposition modelling is a simple and affordable additive manufacturing technology utilising filament extrusion of polymeric materials to manufacture 3D products layer by layer. This work explored the feasibility of using fused deposition modelling to produce natural fibre reinforced elastomeric composite. Kenaf fibre and thermoplastic polyurethane (TPU) composite filament were prepared by using internal mixer for compounding and extruded to form filament for feed stock of 3D printing with different kenaf fibre loading (0-20wt%). The TPU filament with 0-10wt% of kenaf fibre were successfully extruded to fabricate test samples. The composites filament with 20wt% of kenaf fibre fracture prior to extrusion in 3D printing. The results showed that tensile strength, elongation at break, density and shear stress decreased, Young modulus, hardness, water absorption of printed samples increased with increasing kenaf fibre loading. Tolerance test showed shrinkage of printed products can be controlled with increasing of kenaf fibre. Next, in order to improve the matrix flexibility of the composite with higher fibre content for printing purposes, further assessment was carried out by blending TPU with different loading of epoxidized natural rubber (ENR) (10-30wt%). TPU/ENR blends were compounded with 10wt% and 20wt% kenaf fibre and their filament were successfully extruded. Results obtained shows that tensile strength, elongation at break, Young modulus and hardness of the printed samples decreased while water absorption and density of printed sample increased with increasing ENR loading. Tolerance test showed inclusion of ENR increase dimensional stability of printed sample. Shear stress showed the variation in trend with increasing ENR loading. As conclusion, with increasing Kenaf fibre and epoxidized natural rubber loading would affect the mechanical and physical properties of the printed samples.
CHAPTER 1 INTRODUCTION

1.1 Background

3D printing or well known as additive manufacturing is a fast prototyping and fabrication technology where the products are made layer-by-layer through digital model such as Computer Aided Design (CAD) (Hung et al., 2014, Lukić et al., 2016, Mirón et al., 2017, Wang et al., 2017). 3D CAD model can be separated into 2D layered section which allowing each layer of the geometry can be analysed digitally (Milosevic et al., 2017). 3D printing offer a new and unique technique to fabricate mechanical and functional parts that unable to produce by using conventional method such as injection moulding and extrusion (Christ et al., 2017).

There are several technique used in 3D printing method such as Fused Deposition Modelling (FDM), Stereolithography Apparatus (SLA) and Selective Laser Sintering (SLS). SLA is a process, which convert the hardened liquid plastic to form of 3D solid object. The plastic liquid is solidified using UV laser beam and been solidified simultaneously layer by layer. The SLS process is complex; the properties of parts obtained are directly dependent on initial material properties, such as particle size and shape as well as machine parameters such as bed temperature, laser scanning speed, laser power, layer thickness, and laser spot size. Any change in machine or material parameters will ultimately affect the sintering process, material molecular structure, and subsequently the mechanical properties of the obtained parts (Beard et al., 2011).

FDM 3D printing has seen significant publicity over the last decade. Due to the relatively simplistic mechanical design, affordability, and the capabilities of FDM machines, it has garnered significant interest in both industry and academia and the design of FDM printers has seen a rapid growth, the field of printable materials has also
experienced a rapid influx of unique and novel thermoplastic materials; conductive, magnetic, flexible, and dissolvable filaments (Christ et al., 2017).

In this study, FDM technique was used since thermoplastic polymer are preferred as a feedstock material and commonly used to date for FDM. This is because the polymer consist more amorphous region with limited crystallinity which exhibit low degree of shrinkage such that increase the accuracy of parts produced by 3D printer (Pickering and Stoof, 2017). FDM 3D printing getting significant over last decade due to simplistic mechanical design, low cost and its capabilities which garnered significant interest in industry and academia (Christ et al., 2017, Milosevic et al., 2017, Stoof et al., 2017). There are various types of material available for FDM 3D printing such as polymer, ceramic, gypsum, metal and concrete (Milosevic et al., 2017).

Since FDM method was introduced in the market, there are less exposure in producing flexible products compared to brittle products. Therefore, thermoplastic polyurethane (TPU) was introduced in this study to produce flexible product by using FDM method. TPU is type of polymer that cover variety of different semi-crystalline polymer with excellent mechanical properties and flexibility. TPU are a class of polymers usually made by the addition of poly-isocyanates and macro-polyols. Flexible polyurethane is widely used in packages and building for fabricating furniture cushions, mattresses, moulded foam seats in cars, and others (Wang et al., 2019).

To date there is no available 3D printing technology develop for gum rubber material. Therefore, in order to utilize current available equipment design of FDM thermoplastic elastomer offers a huge potential to fabricate more soft and flexible products. Thermoplastic elastomer (TPE) is material that exhibits functional performance of conventional elastomeric material at room and service temperature. Recently, TPE getting more demand due to its wide range of application such as in automotive, electrical
equipment, medical application and etc. (Kalkornsurapanee et al., 2012). TPE also having the ability to be reprocessed and usually been process by using thermoplastic processing equipment. However, most of TPE were manufactured as non-renewable synthetic polymer. Under increasing awareness of environmental issue, renewable and sustainable material should be used. Natural rubber (NR) one of sustainable material can be used to prepare TPE material and typical known as thermoplastic natural rubber (TPNRs).

Although NR consist saturated structure that cause the structure sensitive to heat, oxygen and ozone, it can be improved by thermoplastic polyurethane (TPU) since its properties are excellent ozone, aging and weather resistance and provide superior mechanical properties. By blending these two types of polymer, it can provide higher elasticity and better damping properties. According to Al Minnath et al. (2011), blending of TPU and NR improved mechanical properties of the material. Although that, the final product performance also depends on printing ability. For NR cured compound, it is known that the material forms irreversible chemical crosslinks upon heating at evaluated temperature which prevent reprocessing and re-melting of the material. For TPU/ENR blends, this sets a challenge. Premature crosslinking of NR during 3D printing would blocked the nozzle due to the material cannot be melted. Therefore, a substitutional studies need to be carried out to process the TPU/NR blend using FDM. Since TPE have the ability to reprocess, this research is used to access the ability of TPE composite to form flexible product by using 3D printer in order to enhance the flexibility of 3D printing product.

Another concern is the rising popularity of 3D printing has coincided with increasing environmental awareness. This promoted the development of natural fibre-reinforced composite to replace synthetic fibre. The advantages of natural fibre are its
potential biodegrade, low-cost and having specific strength which possess excellent tensile properties. Besides, natural fibre is more preferred due to high energy processing required to manufacture synthetic fibre (Milosevic et al., 2017). However, there are less literature can be found related to natural fibre composite products fabricated by using FDM method since the application of natural fibre composite in 3D printing technology is quite new in the field (Stoof et al., 2017). This work focuses on development kenaf fibre/thermoplastic polyurethane/epoxidized natural rubber based novel FDM filament feedstock that demonstrate high elasticity, sustainability as well as good mechanical properties. Particular attention is paid towards the flexibility to fabricate the filament and extrusion process by 3D printing. The mechanical, morphology, water absorption, tolerance, hardness, density and rheological were investigated to assess the performance of the final product.

1.2 Problem Statement

Acrylonitrile-Butadiene-Styrene (ABS) and Poly-Lactic Acid (PLA) are commonly materials for FDM method to produce 3D printing product (Pickering and Stoof, 2017). However, these materials are in lack of the elasticity or flexibility. The elasticity and flexibility are important to certain product such as gasket and seal. Thus, the use of Thermoplastic Polyurethane (TPU) in this research as the matrix could increase the flexibility of the product.

Thermoplastic polymer elastomeric (TPE) was been explore since several years ago. By blending process, this can improved the properties of the polymer blend by combining the properties of two type of material. TPE are usually processed by using thermoplastic processing equipment with a capability of reprocessing and thermal welding. However, there are lack of literature review regarding the use of TPE composite as filament to produce 3D printing product. Due to lack of this exploration, the research
is used to discover the ability of kenaf fibre/thermoplastic polyurethane/epoxidized natural rubber composite to enhance the flexibility of 3D printing product.

Due to increase environmental awareness situation, the development of natural fibre-reinforced polymer has been prompted to replace synthetic petrol chemical (Stoof et al., 2017). Since 3D printing was patented, the product produced are from non-renewable resources that leads to increasing in number of polymer that sent to landfill which can cause environmental problem. Thus, this research will explore the effect of kenaf fibre as a filler loading for composite filament.

1.3 Research aim and direction

The objective of this research was to fabricate flexible kenaf fibre/thermoplastic polyurethane/epoxidized natural rubber composite by using FDM method. The specific research objective are as follows:

i. To investigate the feasibility to 3D printing kenaf fibre and thermoplastic polyurethane.

ii. To evaluate the effect of epoxidized natural rubber loading in kenaf fibre/thermoplastic polyurethane composite.
CHAPTER 2 LITERATURE REVIEW

2.1 Introduction to 3D printing

Additive manufacturing (AM) is a process of joining material to produce object from 3D model data layer by layer as opposed to subtractive manufacturing methodologies. AM technologies enable the industry to build a wide range of prototype or functional components with complex geometry shape that having difficulties to be manufactured by using conventional methods (Ning et al., 2015). However, Lukić et al. (2016) state that additive manufacturing is fabrication process of an object by progressive addition of layers of materials. Additive manufacturing machines is been process by depositing or solidifying material by means of extrusion in X, Y and Z direction in order to control manufactured 3D products..

Christ et al. (2017) claims that AM field employs various manufacturing technologies. These technologies all function similarly as they produce physical parts from a computer aided design (CAD) program. AM have ability to shorten the design-manufacturing cycles which will reduce the production cost. Due to the ability of AM, AM technologies have been involved in various application in several past decades. The largest application of AM fall into area of medical, aerospace and automotive. Besides, AM also are getting more popular in area of education, architecture, fashion, etc. (Ning et al., 2015).

The great advantages of 3D printing technologies are high accuracy for complex structure and the waste produce by manufacturing process of 3D printing is very little. Currently, various material are available for Fused Deposition Modelling (FDM) 3D printing specifically from polymer such as polyamide, polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polyvinyl alcohol (PVA) etc. Besides polymer, ceramic, gypsum, metal and event concrete are also type of material that available for FDM 3D
printing method (Wang et al., 2017). However, among the materials PLA is the most popular within 3D printing field since PLA is biodegradable polymer. Due to the biodegradability properties, PLA is a material that widely been used in medical industry and this material has been approved by FDA in order to produce biomedical application products.

There are several different additive manufacturing technique been used in 3D printing technologies. These technique are mainly based on three types of construction such as solidification of liquid, sintering and deposition of the material. Based on these techniques, several different system has been patented which are stereolithographic (SLA), selective laser sintering (SLS) and fused deposition modelling (FDM). The first technique has been patents are FDM technology followed by SLA and SLS. Fused filament fabrication (FFF) is types of technique which share similar technique with FDM however to avoid legal problems it was named as FFF technology (Fernandez-Vicente et al., 2016).

Figure 2.1 shows the overview of Rapid prototyping technologies of 3D printing from CAD until the object has been printed by 3D printer. In FDM, to form a printed object, the heated nozzle head moves across the cross-sectional area and the thin materials are deposited layer by layer. However, SLA works as the polymerisation of liquid resin polymer by exposure to ultraviolet (UV) light laser to build products layer by layer at one time (Chu et al., 1998). Besides, SLS process use high power laser fuses the resin material by scanning the cross section of the products through the 3D model. The cross-section is examined and the powder bed is lowered by a layer thickness. A new layer of material is applied on top and the process is repeated until desirable products obtained (Ahlbrandt, 2014).
Figure 2.1: Overview of different rapid-prototyping (RP) technologies using the layer-by-layer build up process (Pfister et al., 2004).

The material selection advantages and disadvantage of different types of 3D printing is presented in Table 2.1

Table 2.1: The types of current 3D printing available in the manufacturing of plastic products (Lee et al., 2017a)

<table>
<thead>
<tr>
<th>Technique</th>
<th>State of starting material</th>
<th>Materials</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>FDM</td>
<td>Filament</td>
<td>Thermoplastics such as PC, ABS, PLA and nylon</td>
<td>Low cost, good strength and multi-material capability</td>
<td>Anisotropy and nozzle clogging, required a support structure, grainy appearance</td>
</tr>
<tr>
<td>SLA</td>
<td>Liquid photopolymer</td>
<td>Photo-curable resin</td>
<td>High printing resolution</td>
<td>Materials limit, high cost</td>
</tr>
<tr>
<td>SLS</td>
<td>Powder</td>
<td>PCL and polyamide powder</td>
<td>Good strength and ease removal of support powder</td>
<td>High cost</td>
</tr>
<tr>
<td>DLP</td>
<td>Liquid photo-polymer</td>
<td>Photo-sensitive polymer</td>
<td>Faster than SLA</td>
<td>Small build size, Materials limit</td>
</tr>
<tr>
<td>LOM</td>
<td>Plastic film</td>
<td>Thermoplastic</td>
<td>Fast build-up, relatively cheap</td>
<td>Poor strength, newly printed parts required post-processing</td>
</tr>
</tbody>
</table>
2.1.1 Advantages of 3D printing

Since past decades, 3D printing technology is expanding due to several advantages such as zero specialization of tooling or mould, enable for changing the design followed desired design rapidly, waste reduction due to the printed design followed exact dimension with high accuracy, able to customize products and equipment, short processing times for low inventories and good quality (Malik, 2017). Excellent quality of products can be predicted at the designation stage. During designation stage, the finite element analysis (FEA) can be carried out before printing to help in evaluating the manufacturability of the design in term of motion, mechanical stress, force, vibration, heat flow and physical effect (Lipson and Kurman, 2013). Increased cost efficiency is one of the main benefit offered by 3D printing. Conventional traditional methods truly less expensive in large mass production but for small size production, 3D printing becomes more competitive as it can give large benefits through it (Ventola, 2014). Moreover, 3D printing can minimize the processing cost by reducing the non-essential resources. 3D printing also can increase the productivity of products that required milling, forging and long delivery time (Ventola, 2014). Several arrays of materials can be used in printing technology which allows the user to design their imaginary products and reduce the manufacturing cost. Evolution of 3D printing gives significantly to the price and technical specification which in future benefits the society, economy and environment.

2.1.2 Applications of 3D printing

Automotive, aerospace, medical and consumer goods are main industries that capitalize the 3D printing technology (Bogue, 2013). Medical sector has aimed the 3D printing in producing medical parts and human implants as 3D printers provide custom-made medical products and equipment which are fast and cost-efficient (Ventola, 2014).
But in the medical sector, it has some limitations as only a few 3D printing materials are not harmful to be placed inside human body (Sons, 2016). Aerospace and automotive sectors also focus on 3D printing technology in producing products as it improved functionality and maximise performance (Bogue, 2013). Furthermore, 3D printing technology is also broadly used in food sector due to many benefits such as customized food design, reduce the complexity of food chain, personalized nutrition and expanding of available food material (Liu et al., 2017). Sectors for the military, outer space food and sweet food including ocean world mostly used products made of 3D printing (Liu et al., 2017). 3D printed component has been used quite a lot in underwater such as 3D printed coral reef is used to replace the existence of damaged coral reef (Mohammed, 2016). Table 2.2 shows current applications developing through 3D printing.

Table 2.2 Current applications using 3D printing

<table>
<thead>
<tr>
<th>Application</th>
<th>Materials</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradable scaffold and</td>
<td>PLA</td>
<td>(Kutikov et al., 2014, Senatov et al., 2016,</td>
</tr>
<tr>
<td>other medical device</td>
<td></td>
<td>Malik, 2017, Ngo et al., 2018, Economidou et</td>
</tr>
<tr>
<td>Electronic device</td>
<td>Carbon black/PCL</td>
<td>(Leigh et al., 2012, Flowers et al., 2017, Lee et al., 2017a, Sochol et al., 2018, Zarek et al., 2016)</td>
</tr>
<tr>
<td>Engine exhaust and turbine</td>
<td>Metal</td>
<td>(Appleyard, 2015, Watkins et al., 2013, Murr,</td>
</tr>
<tr>
<td>blade</td>
<td></td>
<td>Lee et al., 2017b)</td>
</tr>
</tbody>
</table>
2.1.3 Fused Deposition Modelling

FDM is a one of technique of 3D printing that invented by Scott Crump, Stratasys Ltd. founder, in 1980 (2014, Ferreira et al., 2017). Besides, Scott Crump introduced another technique which is Fused filament fabrication (FFF) right after FDM (Balletti et al., 2017). Both of these techniques involves lamination of liquid plastic materials. In FDM, to produce a printed object, the heated nozzle head will moves across the cross-sectional area and the thin polymeric materials are deposited layer by layer.

3D printing process with FFF technology consists of pushing thermoplastic filament using an extruder element into a fusion chamber or known as hotend. This material that had been pushed through the hotend will be deposited in control way which normally at certain distance from the diameter of the tip hole. In the structure of FDM parts, four characteristic zones can be differentiate as shown in Figure 2.2. The first layer comprises several solid layers that form the outmost layer of the piece. Second is the main body which a set of parameter filament are deposited built the body parts. The interior of the object is built according to infill of a density and mesostructured that can be varied. Although the infill percentage can be control, value of air gap cannot be specified. This leads to the real density values varies among the printer and the 3D printing software.

*Figure 2.2 Section printed specimens. Characteristic area. (Fernandez-Vicente et al., 2016)*
According to Ning et al. (2015), FDM is the most widely used method compared to all AM technique for fabricate the plastic parts. This is because FDM technique can produce the product with low cost, minimal wastage and ease to change the material compared to conventional manufacturing. Before FDM fabricating process, the file need to convert to STL file by using CAD software before it be sliced into horizontal layers and the thickness of the layer can be set up depending on the requirement. In FDM process, the filament is fed into the liquefier head with aid of feeding pressure that generate by driver gear. Plastic parts can be built layer by layer through depositing the filament which be heated to glass transition temperature (Tg) state and extruded through the nozzle at constant temperature and pressure. The schematic FDM process is shown in Figure 2.3.

*Figure 2.3 Schematic of FDM process (Ning et al., 2015)*
2.1.4 Parameters of FDM 3D printing

There are certain parameters that affect the properties of printed FDM parts such as air gap, a layer of thickness, raster angle, raster width, the speed of deposition and orientation of printing (Brock et al., 2000, Anitha et al., 2001) in improving dimensional accuracy and increase strength of the parts. Taguchi method is used to study the relationship between the mentioned parameter and design optimization for products properties (EQUBAL et al., Basavaraj and Vishwas, 2016). The result showed that layer of thickness and orientation of give huge impact in increasing mechanical properties of FDM 3D printed products.

2.1.4.1 Effect of bed temperature

In the journal, Choi et al. (2016) state that shape error has occur in the product by manufacturing hexahedral ABS plastic component using FDM method due to heat shrinkage. As the experiment done, As a result, the higher the bed temperature, the lower the deformed shape errors of the specimens were. However, if the bed temperature had exceeded 120˚C, laminating adhesion became poor. That seems to occur because of the material phase change and can make 3D printing work very hard as a consequence. Results of this study can be helpful to set optimum bed temperature condition in FDM additive manufacturing.

According to Spoerk et al. (2018), the adhesion between first printed layer and printing bed for parts that produce by FFF is crucial since it provides the foundation to the subsequent layers. This can be prove when inadequate adhesion the results in printing can be poor or it will destroy the bed surface. Through their study, the result shows a significant increase in adhesion forces, when printing parts at a bed temperature slightly above the glass transition temperature of the printing material.
2.1.4.2 Air gap

The air gap is between adjacent raster on the same layer which can be either positive or negative gap. As for the positive gap, the beads of material do touch and through this, a loose structure can be built faster. A negative gap of beads requires a long period of build time as it takes times for two beads occupy same space. Based on (EQUBAL et al.), it is shown that air gap does not give significant impact on dimension and accuracy but give affects the strength of printed products.

2.1.4.3 Orientation of printing

Orientation is the main critical concern during printing as it leads to good mechanical strength of the printed parts (Brock et al., 2000). Figure 2.4 explained about the orientation of printing which consists of 0°, 45° and z-direction. 0° and 45° direction create more pores compared to the z-direction. Thus, z-direction is believed to exhibit good mechanical strength compared to other orientation (Quan et al., 2018).

Figure 2.4 Orientation of printing line (Quan et al., 2018).
2.1.4.4 Raster angle

Raster angle is known as a direction of raster relative to the x-axis of the platform plate as shown in Figure 2.5 (Mohamed et al., 2017). This causes the alignment of the polymer molecules along the direction of deposition during printing which affects the tensile and impact strength of the printed sample (Sood et al., 2010).

![Figure 2.5 Raster angle of FDM printing (Mohamed et al., 2017)](image)

2.2 Filament Materials used in Fused Deposition Modelling

Thermoplastics with proper melt properties and thermoplastic elastomers are common types of materials that can be extruded to prepare the filament for FDM printing. Table 2.3 shows the summary of common material used in FDM process.

*Table 2.3 A summary of materials used in FDM 3D printing technique (Lee et al., 2017b)*

<table>
<thead>
<tr>
<th>Materials</th>
<th>Properties</th>
<th>Application/ industries</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Tough and strong</td>
<td>Automotive, aerospace and medical</td>
</tr>
<tr>
<td>Nylon 12</td>
<td>Good chemical resistance, high fatigue resistance and high impact strength</td>
<td>Ideal for impact protective component (automotive and aerospace)</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>high tensile and flexural strength</td>
<td>Functional prototype, tooling and features (aerospace and automotive)</td>
</tr>
<tr>
<td>Poly-Lactic Acid</td>
<td>Good tensile strength and surface quality</td>
<td>Medical parts</td>
</tr>
<tr>
<td>Thermoplastic polyurethane</td>
<td>Excellent wear and tear resistance, high impact strength and hardness</td>
<td>Industrial chemical and oil, sealant and gasket</td>
</tr>
</tbody>
</table>
2.2.1 Thermoplastic Polyurethane

Thermoplastic polyurethane (TPU) is a type of polymer with properties covering from high performance elastomer to tough thermoplastic that has been extensively used due to its superior physical and mechanical properties such as high tensile strength, abrasion, tear resistance, solvent resistance, low temperature flexibility etc. and versatile chemical structures (Lu and Macosko, 2004). TPU have widely being used in application such as coatings, adhesive, foams, rubbers and thermoplastic elastomers (Pattanayak and Jana, 2005).

TPU is a linear segmented block copolymer composed of alternating hard (adduct of di-isocyanate and small glycols) and soft (e.g. polyester, polyether, hydrocarbon, silicone, etc.) segments. Hard domain is for physical crosslinks and acts as a high modulus filler however the soft segment provide extensibility properties for TPU (Xu et al., 2008). The morphology of TPU is depending on the structure and amount of soft and hard segment and their ordering. Meanwhile, urethane linkages (carbamate, –NHCOO–) in the hard segments become unstable and reversibly decompose into free isocyanate and alcohol. The equilibrium between the urethane linkages and free functional (isocyanate and hydroxyl) groups can be rapidly established (Lu and Macosko, 2004). The chemical structure of polyurethane is shown in Figure 2.6.

![Chemical structure of Thermoplastic Polyurethane (TPU)](image)

*Figure 2.6 Chemical structure of Thermoplastic Polyurethane (TPU)*

Thermoplastic polyurethane (TPU) were synthesized by a one-pot two-step polymerization process. Figure.2.7 shows the synthetic pathway of polymerization process of TPU.
2.2.2 Epoxidized Natural Rubber

Epoxidation of NR was first conducted in 1922 by Pummerer and Bukhard but potential applications of ENR were only realized in the 1980s. There are only two grades of ENR available commercially: ENR 25 (25 mole % epoxide) and ENR 50 (50 mole % epoxide). The two grades are significantly different from each other and have properties that are distinct from NR. As the mole % of epoxide increases, the properties shift from those of a general purpose elastomer to those of a specialty elastomer (Wan et al., 2010).

Epoxidized natural rubber is a modified natural rubber with epoxide and alkene group randomly distributed in its backbone. This make the rubber possess low glass transition temperature (Tg) with high polarity, more flexible and good elastomeric and adhesion properties (Tan and Abu Bakar, 2013). The chemical structure of ENR is shown in Figure 2.8.
Epoxidized natural rubber (ENR) is a modified molecule of natural rubber with the chemical name cis-1,4polyisoprene. There structuring using chemicals such as peroxy acid will react with double bonds of the natural rubber molecules to form ring oxygen that is replaced; the epoxidation reaction of natural rubber is shown in Figure 2.9. In the beginning, formic acid reacts with hydrogen peroxide to form peroxy formic acid. Then, the peroxo formic acid reacts with double bond of natural rubber is arranged as a ring epoxide and formic acid is a by-product.
2.3 Blend used in Fused Deposition Modelling

The development of blends has become major research in FDM area since it can improved the properties of the end products. For example, the PLA materials has low crystallization rates and with brittle properties. Nowadays, there are been very limited amount of research conducted over the years to develop new materials for the FDM process. Thus, ability of blends with other polymer is a good success as it will contribute to the new development of blends in FDM. The filament used in fabrication of 3D printing is usually in the pure state which is not been mixed with other materials. Only some additives has been added such as colorant for the good finishing product and good appearance. Some research has start to develop the blends materials for the FDM process since past decades. The research of Nikzad et al. (2011) which developed the metal-filled FDM-grade ABS composite materials. The mixed of metal-ABS and copper-ABS which aim to produce the ABS filament with desired properties of the composite material with desirable thermo-mechanical properties to be used in FDM process.

Similar studies has been report by Zhong et al. (2001) which involve the improvement of ABS in FDM process. Even though ABS have good stiffness properties, but in filament it has low strength and hardness. Thus, ABS is been modifier with compatibilizer and short glass fibre in order improve the strength of the ABS filament. In tissue engineering field, the production of scaffold has become major interest due to the implantation of the scaffold inside the human body and the site for cell to growth. So, the fabrication of scaffold using the fused deposition modelling has been investigate by many researcher to find the good scaffold with better properties.

The studies of Kalita et al. (2003) which used polypropylene (PP) polymer blend with tricalcium phosphate (TCP) ceramic to get the porous scaffold with improve plasticity and processibility to the composites by adding processing aids. Result shows
that 36 vol. % porosity showed the best compressive strength and non-toxic. The PLA also been improved to suitable used in tissue engineering as PLA is biodegradable and suitable with human body. The research of Drummer et al. (2012) where the PLA is blend with tricalcium phosphate (TCP) for filament produce used in FDM. Result shows the increase of tensile strength and elongation at break that meet the requirement of scaffold which need to be strong enough to hold up inside human body.

2.4 Thermoplastic Polyurethane/Epoxidized Natural Rubber Blend

The improvement properties of polymer blend than individual polymer component have made it widely used in several industry such as transportation, aerospace, food industry etc. (Al Minnath et al., 2011). Polymer blend are prepared by blending two type of polymer material in order to obtain combination of properties that could not achieve by single type of polymer. The properties of polymer blend (TPE) is depending on the blend constituent, their morphology and the interaction between two polymer (Pichaiyut et al., 2012).

According to KalkornsuraPranee et al. (2012), most of commercial TPE products are manufactured as non-renewable petrochemical polymer. Under increasing of awareness of environmental issue and fuel shortage, there are several step need to be consider before produce the new products. Natural rubber (NR) is types of renewable polymer which is known as alternative environmental friendly polymer material. NR can be blend with thermoplastic polymer which known as thermoplastic natural rubber (TPNRs). However, NR is unsaturated polymer which cause it be more sensitive towards oxygen, ozone and heat but this advantages can be covered by thermoplastic polyurethane (TPU) which know as excellent ozone resistance which can prevent the product to degrade faster.
Thermoplastic elastomer (TPEs) plays the important role in polymer industry due to good process ability and its elastomeric properties. Thermoplastic elastomer form based on natural rubber blend with thermoplastic and was classified as thermoplastic natural rubber (TPNR). There are two type of TPNRs which are the NR blend with thermoplastic in order to get co-continuous phase morphology which classified as thermoplastic polyolefin (TPO) and the another types is thermoplastic vulcanize (TPV) which been prepared by blending NR with polyolefin. This rubber phase is vulcanized during mixing and it was process at high temperature which known as dynamic vulcanization (DV) (Nakason et al., 2006).

Pichaiyut et al. (2012) claims that epoxidized natural rubber (ENR) can be blended with many types of thermoplastic includes polypropylene (PP) and high density polyethylene (HDPE). This type of elastomer are frequently be used and it can improve its compatibility by blending with polar thermoplastics product such as poly-(methyl methacrylate) (PMMA) and ethylene vinyl acetate (EVA). Besides, thermoplastic polyurethane (TPU) blending has been considered since past 7 years ago due its advantages which can form product with outstanding performance especially with low hardness.

Thermoplastic polyurethane (TPU) properties is related to service temperature and its hardness. Hardness of TPU determine the strength of its mechanical properties where low hardness will exhibit poor mechanical properties. Damping properties of TPU also are slightly higher than other conventional elastomers such as natural rubber (NR). NR having excellent mechanical properties even the hardness of the material is low and also unattainable low damping properties under dynamic load condition. Thus, the bending of TPU and NR could results outstanding performance. ENR was used instead of natural rubber is due to compatibility reason (Pichaiyut et al., 2012).

21
2.5 Reinforcement filler for FDM filament

Fibre-reinforced plastic composites was introduced in 1908. The first reinforced fibre is cellulose fibre in phenolic, followed by urea and melamine. In 1940s, reaching commodity status with glass fibre in unsaturated polyesters was explored (Mohanty et al., 2000). The main function of reinforcement filler is to increase mechanical properties of the composites by transferring the stress from matrix to the fibre. Usually, this type of fibre can withstand with high force applied. Table 2.4 shows the summary of reinforcement filler used in FDM 3D printing.

Table 2.4 A summary of reinforcement filler used in FDM 3D printing technique

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reinforcement filler</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>Short glass fibre</td>
<td>(Sodeifian et al., 2019)</td>
</tr>
<tr>
<td>Recycle Polypropylene</td>
<td>Hemp and Harakeke</td>
<td>(Pickering and Stoof, 2017)</td>
</tr>
<tr>
<td>Poly-Lactic Acid</td>
<td>Hemp and Harakeke, Nano-clay, Glass fibre, Cellulose melamine polyphosphate (MPP) and Cloisite, Natural jute and flax fiber Strands,</td>
<td>(Cataldi et al., 2018, Coppola et al., 2018, Guo et al., 2017, Hinchcliffe et al., 2016, Li et al., 2018, Pitt et al., 2017, Stoof et al., 2017)</td>
</tr>
<tr>
<td>Acrylonitrile Blend</td>
<td>MWCNTs, SiO$_2$, ZrB$_2$, Al, Graphene oxide</td>
<td>(Aumnate et al., 2018, Çantı, 2017)</td>
</tr>
<tr>
<td>Butadiene Styrene</td>
<td>Carbon nanotube, multi-wall carbon nanotube (MWCNT), conductive carbon black (CCB), and graphite</td>
<td>(Christ et al., 2017)</td>
</tr>
<tr>
<td>Thermoplastic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyeurthane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.5.1 Kenaf fibre

Hibiscus cannabinus L. or well known as kenaf is a warm season annual fibre crop which closely related to cotton and jute. Historically, kenaf has been used cordage crop in order to produce twine, rope and sackcloth. Nowadays the application of kenaf has been varied such as in paper product, building material, absorbent and as animal feeds. Kenaf stalk are made up of an inner woody core and outer fibrous bark surrounding the core. This type of fibre has superior flexural strength and tensile strength which make the material been chosen of wide range extruded, moulded and non-woven product. This kenaf fibre can be utilised as reinforcement material for polymeric composite as replace material of glass fibre. Kenaf is type of natural fibre which have the advantage over glass fibre due to its low cost, renewability, recyclability, abrasiveness and biodegradability. The effectiveness of fibre reinforced composites is depending on the fibre-matrix interface and the ability of stress to transfer from matrix to the fibre (Edeerozey et al., 2007).

El-Shekeil et al. (2012) state that kenaf are getting famous due to its good mechanical properties. Kenaf is type of natural fibre play the important role in substitution of wood that was harvested once in 20 to 25 years while Kenaf plant can be harvested two to three times a year. This plant can grow and reach three to four meter within five months. Figure 2.10 shows picture of Kenaf plant. This kenaf fibre consists of three layers which are bast, core and pith as shown in Figure 2.11. Kenaf bast represent one third of the plant and the rest was represent by core and pith. This kenaf bast has been reported that it have superior mechanical properties that other type of plant. Thus, this make Kenaf fibre well known as reinforce material in the composite.
According to Aji et al. (2009), kenaf bast fibre have superior flexural strength with combination of excellent tensile strength which makes it chosen material for a wide range of extruded, moulded and non-woven products as widely discussed by other authors. However, it is well known that the performance of the composites are depending on the properties of materials itself and their interfacial compatibility. There are much work has been done on virgin thermoplastic and natural fibre composites with positive results that prove their application to various fields of technical applicability, especially for loadbearing application.
2.6 Environmental Awareness

Renewable polymer and composites are being engineered in targeting application of automotive, construction and packaging industry as rate of environmental concern are getting attention globally (Hinchcliffe et al., 2016). Kargarzadeh et al. (2017) claims that renewable and biodegradable material are receiving extra attention form scientific and industrial communities recently. This is due to use of conventional petroleum-based polymer has created ecological threats.

Furthermore, Kopczyńska et al. (2016) state that plastic production are keep increasing yearly by level of 9.9%. This is due to their diversity of production and its ability to replace conventional material such as metal, glass etc. However, the increasing in usage of polymer leads to huge amount of waste which need to be managed and not spread on the landfill. According to arising of this problem, international regulation were introduce to prevent this problem becoming worst. In accordance to European Directive 2008/98/EC, the waste management should be manage in order as according to step as follow:

1. Prevention
2. Reuse
3. Recycle
4. Other recovery as energy recovery
5. Disposal

Sustainable life style are getting more important since this world have limited resources and facing serious metal impacts. During the last century, environmental problems were often seen as local problems due to the impact from a certain product. However, it becomes more obvious that the problems are much more complex and related
to all the phases in a product’s life cycle from extraction of material to waste or deposition of the used product (Ljungberg, 2007).

According to Singh et al. (2017), scenario of recycling/recovery/management of the plastic solid waste are getting attention. As industries are getting more interested in plastic manufacturing field, thus plastic production are increase gradually during past 50 years since plastic product become crucial part of the lifestyle. Traditional plastic are not easy to be degraded in ambient surrounding in fact its need hundreds of years in order to degrade at environmental surrounding. Besides, this plastic waste is harmful as the pigment of the plastic product is highly toxic. This results environmental pollutant from synthetic plastic and has been identified as a huge hassle.

2.7 Sustainable Composites

Additive manufacturing of wood waste presents an opportunity in order to create 3D products from cheap and sustain sources with limited material losses during processing. Wood-thermoplastic composite are getting more popular in commercial products such as in construction, furniture and other application. Wood plastic composite might be produce via variety technique such as injection moulding, extrusion and compression moulding. There are several patents claiming to manufacture wood product via additive manufacturing. However, there are no properties of printed product has been reported (Pitt et al., 2017).

The popularity of additive manufacturing technology has coincided with increasing environmental awareness. This situation urge to develop innovative and sustainable composites by using natural fibre as alternative to reinforced polymer composites. This is due to the advantages of natural fibre itself which have the ability to biodegrade, renewable and it possess excellent mechanical properties (Milosevic et al., 2017).
CHAPTER 3 METHODOLOGY

3.1 Research Flowchart

Figure 3.1 shows the overall procedure of experimental flowchart in this studies. This research starts with literature review before start with sample preparation. Next for sample preparation, there are 6 different compound of kenaf fibre/polyurethane/natural rubber composites with different compound ratio that manufactured as composite product by fused deposition modelling (FDM) of 3D printing. The filament were set up before proceeding with FDM process by compound it using internal mixer and extruded the filament by using extrusion with diameter 1.75mm. This experiment was carried out to investigate the mechanical, physical properties of the composite and tolerance of 3D printer using composite filament.
Stage 1
Objective:
To investigate the effect of Kenaf fibre loading in thermoplastic polyurethane filament

Testing conduct
• Tensile test
• Hardness test
• Density test
• Water absorption test
• SEM
• Rheological test
• Tolerance test

Stage 2
Objective:
To evaluate the effect of epoxidized natural rubber loading in Kenaf fibre/thermoplastic filament.

Testing conduct
• Tensile test
• Hardness test
• Density test
• Water absorption test
• SEM
• Rheological test
• Tolerance test

Figure 3.1 Overall flowchart
3.2 Material and chemicals

Materials and chemicals used in this experiment are listed in Table 3.1

Table 3.1 Material and chemical used in sample preparation for this research studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoplastic Polyurethane (TPU) filament</td>
<td>Cytron Technologies Sdn. Bhd.</td>
<td>Sample preparation</td>
</tr>
<tr>
<td>Epoxidized Natural Rubber (ENR-25)</td>
<td>Muang Mai Guthrie Public Company</td>
<td></td>
</tr>
<tr>
<td>Kenaf fibre</td>
<td>Lembaga Kenaf Malaysia</td>
<td></td>
</tr>
</tbody>
</table>

3.2.1 Raw materials

3.2.1.1 Thermoplastic polyurethane (TPU) filament

Thermoplastic polyurethane (TPU) filament was purchased from Cytron Technologies Sdn. Bhd. The diameter of this filament is 1.75±0.5 mm and the total weight of this filament is about 1 kg. The suggested melting temperature of this filament is in range of 190°C to 240°C. The suggest bed temperature for this filament is about 30°C to 50°C. This material was supplied in white solid form with high flexibility properties filament. Figure 3.2 below illustrated the physical appearance of TPU filament used in this study.

Figure 3.2 Thermoplastic polyurethane (TPU) filament
3.2.1.2 Epoxidized Natural Rubber (ENR-25)

Epoxidized natural rubber (ENR-25) was purchased from manufactures Muang Mai Guthrie Public Company Limited of Thailand. Epoxidation results in systematic increase in the polarity and glass transition temperature. The increase epoxidized will increase damping properties, reduce selling when contact with hydrocarbon oil, decrease permeability and reduced rolling resistance. The ash content in ENR-25 is about 0.50 wt%. The Mooney viscosity of this rubber is in range 70-100 ML (1’ + 4’) 100°C.

3.2.1.3 Kenaf fibre

Kenaf fibre was obtained from Lembaga Kenaf Negara, Terengganu, Malaysia. The properties of the kenaf fibre as shown in Table 3.2

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>930</td>
</tr>
<tr>
<td>Tensile Modulus (GPA)</td>
<td>53</td>
</tr>
<tr>
<td>Tensile elongation (%)</td>
<td>1.6</td>
</tr>
<tr>
<td>Extractive (%)</td>
<td>5.5</td>
</tr>
<tr>
<td>Holo-cellulose (%)</td>
<td>86.8</td>
</tr>
<tr>
<td>Cellulose (%)</td>
<td>55</td>
</tr>
<tr>
<td>Lignin (%)</td>
<td>14.7</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>5.4</td>
</tr>
</tbody>
</table>
3.3 Equipment

The equipment used in sample preparation of this research are listed in Table 3.3.

*Table 3.3 Equipment*

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Brand / Model</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Screw Extruder</td>
<td>Brabender</td>
<td>Melchers techexport GmbH</td>
</tr>
<tr>
<td>3D printing (FDM)</td>
<td>McCreator</td>
<td></td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>FESEM Supra 35 VP</td>
<td>Carl Zeiss, Germany</td>
</tr>
<tr>
<td>Universal testing machine</td>
<td>Instron 3366</td>
<td>MecombMalaysia Sdn. Bhd.</td>
</tr>
<tr>
<td>Internal Mixer</td>
<td>Haake</td>
<td>Thermo Electron Corporation</td>
</tr>
<tr>
<td>Grinder machine</td>
<td>-</td>
<td>Chyun Tseh Industrial Co. Ltd</td>
</tr>
<tr>
<td>Density balance</td>
<td>XB220A</td>
<td>Precisa</td>
</tr>
<tr>
<td>TableTop Scanning Electron Microscopy (SEM)</td>
<td>TM3000</td>
<td>Hitachi</td>
</tr>
<tr>
<td>Thermal Gravimetric Analysis (TGA)</td>
<td>Pyris 6</td>
<td>PerkinElmer</td>
</tr>
<tr>
<td>Plate-plate rheometer</td>
<td>MCR301</td>
<td>Aston Paar Malaysia Sdn Bhd</td>
</tr>
<tr>
<td>Hardness tester</td>
<td>Wallace dead load hardness tester</td>
<td>H W Wallance &amp; Co Ltd Croydon</td>
</tr>
</tbody>
</table>
3.4 Sample preparation

3.4.1 Reduction of fibre size

Kenaf fibre was received with 2mm in length. The size of the fibre been reduced by using grinding machine as shown in Figure 3.3 in order to get the smallest size (targeted 25μm) of the fibre. Next, the fibre undergoes mechanical sieving to remove fibre that big in size before the fibre undergoes alkali treatment.

![Grinder Machine](image)

*Figure 3.3 Grinder Machine*

3.4.2 Treatment of the fibre

Kenaf fibre been treated by using alkalisations process or well known as alkali treatment. Alkali treatment was used to reduce the average fibre diameter and remove impurities from the fibre which might affect the properties of end product. Besides, alkali treatment also can increase the compatibility of non-polar polymer interface with natural fibre. The dried kenaf fibre were immersed in NaOH solution with concentration 4% wt for 3 hours at room temperature. Then, the fibre were washed six times by using distilled water to remove excessive NaOH. Kenaf fibre then been dried at 80°C for 24 hours. The treated kenaf fibre shown in Figure 3.4
3.4.3 Fused Deposition Modelling (FDM) 3D printing

3.4.3.1 Filament preparation

Figure 3.5 shows Haake internal mixer which been use in initial mixing for the composite compound. Composite with different ratio of thermoplastic polyurethane, kenaf fibre and epoxidized natural rubber were mixed in small batched (45g) at temperature 180°C and 50rpm rotor speed for 10 minutes. The formulations are shown in Table 3.4

Table 3.4 Formulation of the composites

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kenaf fibre</th>
<th>Thermoplastic polyurethane</th>
<th>Epoxidized Natural Rubber (ENR-25)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat TPU</td>
<td>-</td>
<td>100%</td>
<td>-</td>
</tr>
<tr>
<td>KF/TPU- 5/95</td>
<td>5%</td>
<td>95%</td>
<td>-</td>
</tr>
<tr>
<td>KF/TPU- 10/90</td>
<td>10%</td>
<td>90%</td>
<td>-</td>
</tr>
<tr>
<td>KF/TPU/- 20/80</td>
<td>20%</td>
<td>80%</td>
<td>-</td>
</tr>
<tr>
<td>KF/TPU/ENR- 10/90/10</td>
<td>10%</td>
<td>90%</td>
<td>10%</td>
</tr>
<tr>
<td>KF/TPU/ENR- 10/80/20</td>
<td>10%</td>
<td>80%</td>
<td>20%</td>
</tr>
<tr>
<td>KF/TPU/ENR- 10/70/30</td>
<td>10%</td>
<td>70%</td>
<td>30%</td>
</tr>
<tr>
<td>KF/TPU/ENR- 20/90/10</td>
<td>20%</td>
<td>90%</td>
<td>10%</td>
</tr>
<tr>
<td>KF/TPU/ENR- 20/80/20</td>
<td>20%</td>
<td>80%</td>
<td>20%</td>
</tr>
<tr>
<td>KF/TPU/ENR- 20/70/30</td>
<td>20%</td>
<td>70%</td>
<td>30%</td>
</tr>
</tbody>
</table>
Subsequently, the all the mixtures were dried in the oven at 80°C 24 hours in order to remove the surface moisture. Figure 3.6 shows single screw extruder which is used to drawn the filament through circular fabricated die with 1.75mm diameter. The diameter of the produced filament are between ranges 1.20mm – 1.90mm was winded as it was extruded. The range of processing temperature used is 210°C with screw speed of 50rpm for the all composite formulation. The surface finish of composite filament is shown in Figure 3.7. The obtained filament were used as feedstock to MeCreator 3D printer.

Figure 3.5 Haake internal mixer

Figure 3.6 Single screw extruder
3.4.3.2 CAD Model

Before 3D specimen printed using FDM technique, the specimen was design using SolidWork software according to desired mechanical and physical test. In this research, the dumbbell shape was moulded according to ASTM D412. The water absorption test the specimen was design according to ASTM D4812 with dimension 55mm x 10mm x 2.5mm respectively. Next for the tolerance test, the specimen was design in pyramid shape. The drawing models are shown in Figure 3.8, Figure 3.9 and Figure 3.10. The design file was exported into STL file format before reopen it by using Repetier-Host software.

Figure 3.7 Surface finish of extruded composite filament

Figure 3.8 ASTM D412 Type C model for tensile specimen
Figure 3.9 ASTM D4812 model for impact specimen

Figure 3.10 Model for tolerance test
### 3.4.3.3 FDM 3D printing parameter

The FDM machine parameter were fixed for all composite formulation. The parameter set up for specimen fabrication are shown in Table 3.5

*Table 3.5 Constant parameters for FDM process in MeCreator*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
<th>Value or state</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Layers and perimeter</strong></td>
<td>Layer height</td>
<td>0.2mm</td>
</tr>
<tr>
<td></td>
<td>First layer height</td>
<td>0.35mm or %</td>
</tr>
<tr>
<td></td>
<td>Vertical shells perimeter</td>
<td>3 minimum</td>
</tr>
<tr>
<td><strong>Infill</strong></td>
<td>Fill density</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Fill pattern</td>
<td>Rectilinear</td>
</tr>
<tr>
<td></td>
<td>Fill angle</td>
<td>45°</td>
</tr>
<tr>
<td></td>
<td>Solid infill threshold area</td>
<td>70mm²</td>
</tr>
<tr>
<td><strong>Speed</strong></td>
<td>Perimeter</td>
<td>45mm/s</td>
</tr>
<tr>
<td></td>
<td>Small perimeters</td>
<td>45mm/s</td>
</tr>
<tr>
<td></td>
<td>External perimeters</td>
<td>45mm/s</td>
</tr>
<tr>
<td></td>
<td>Infill</td>
<td>45mm/s</td>
</tr>
<tr>
<td></td>
<td>Solid Infill</td>
<td>40mm/s</td>
</tr>
<tr>
<td></td>
<td>Top solid infill</td>
<td>40mm/s</td>
</tr>
<tr>
<td></td>
<td>Support material</td>
<td>45mm/s</td>
</tr>
<tr>
<td></td>
<td>Bridges</td>
<td>40mm/s</td>
</tr>
<tr>
<td></td>
<td>Gap fill</td>
<td>20mm/s</td>
</tr>
<tr>
<td></td>
<td>Travel</td>
<td>110mm/s</td>
</tr>
<tr>
<td></td>
<td>First layer speed</td>
<td>25mm/s</td>
</tr>
<tr>
<td></td>
<td>Max print speed</td>
<td>80mm/s</td>
</tr>
<tr>
<td><strong>Extruder</strong></td>
<td>Nozzle diameter</td>
<td>0.8mm</td>
</tr>
</tbody>
</table>
3.4.3.4 Printing process

After the printing parameter was set, the digital model was sliced and layer of extrusion road paths were generated. Digital model was sliced by using Repetier-Host software and click print after the slicer done. The nozzle then will start to preheat at the set temperature which is 240°C with bed temperature at 80°C prior to filament feeding. The printing process was performed as the temperature achieved as set temperature. Five tensile dumbbell specimens, five impact specimen and three pyramid model for tolerance test were fabricated for each compound. The total specimen have been fabricated are 39 specimen with 10 to 20 minutes duration for each of the specimen that were fabricated. This process was perform by using MeCreator 3D printer as shown in Figure 3.11. Figure 3.12 until Figure 3.14 show the surface finish of printed samples.

![MeCreator 3D printer](image1)

*Figure 3.11 MeCreator 3D printer*

![Composite surface finish](image2)

*Figure 3.12 Surface finish of composite according to ASTM D412 (c) tensile specimens*
3.5 Characterisation

3.5.1 Tensile Test

Tensile test were performed using Instron 3366 at room temperature according to ASTM D412. The span length was set at 750mm with test speed of 500 ± 50 mm/min. Every specimen was placed in the grip of the universal tester at a specified grip distance and pulled until it failed. Five specimen were tested and tensile strength, elongation at break and Young’s modulus were obtained and analysed. Figure 3.15 shows the Instron machine that been used for tensile test purpose.
3.5.2 Water Absorption Test

Water absorption test was performed according to ASTM D570. Firstly, the specimens were dried in an oven for 24 hours at a temperature of 80°C. After dried, the specimens were weighed immediately and emerged in distilled water at room temperature for 24 hours. After 24 hours, the specimens were removed, patted dry with a clean cloth, and again weighed. The water absorption is expressed as an increase in weight percent and the weight loss was calculated using following equation 1.

\[ \text{Percent weight loss} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100\% \quad \text{Equation 1} \]

3.5.3 Scanning Electron Microscopy (SEM)

SEM micrograph of fracture surfaces of dumbbell specimen were taken using TableTop Scanning Electron Microscopy (SEM) model Hitachi TM3000. Next, the surface of the filament composite has been observed by using SEM machine (FESEM, Supra 35 VP, Carl Zeiss, Germany). As the sample are not conductive, the fracture surface sample were sputtered with gold-paladium first for 30-120 secs prior to scanning. Each of the sample was placed on the sample holder. Figure 3.16 shows the sample holder used to hold the sample and Figure 3.17 shows the TableTop machines used for scanning images.
3.5.4 Tolerance Test

Tolerance test was conducted by measuring the tolerance test model using Vernier calliper. Each of side and layers of the model were measured including the thickness for each layer as shown in Figure 3.18. This test was performed to investigate the effect of kenaf fibre and ENR loading on tolerance of the model. Tolerance of the specimens were measured by minus the dimension of measured value with dimension of design value as shown in equation 2.
3.5.5 Hardness Test

Hardness is defined as the resistance of the surface to penetration by an indenter of specified dimensions under specified load. Hardness is dependent on ductility, elastic stiffness, plasticity, strain, strength, toughness, viscoelasticity, and viscosity. The sample for hardness was tested with shore D. The reading was taken three times for determined the average value. The result obtained was recorded. The equipment for this test is shown in Figure 3.19.

Figure 3.18 Dimension of tolerance test samples

\[
\text{Tolerance value} = \text{Measured Value} - \text{Design Value} \quad \text{Equation 2}
\]
3.5.6 Density Test

The density of the specimens were measured using density balance (XB220, Precisa). Each specimen was weighed in the air before weighed again after the specimen was immersed in distilled water at room temperature. Each sample submerged into the distilled water using sinker and wire as required. The density and specific gravity are calculated automatically by the density balance as shown in Figure 3.20.

![Density balance](image)

*Figure 3.20 Density balance*
3.5.7 Parallel Plate Rheological test

The rheological behaviour of all samples were measured using Antoon Paar MCR 301 rheometer as shown in Figure 3.21. The measuring system used to evaluate shear stress and viscosity against shear rate was CP 25-2. The rheometer was used to evaluate the shear stress and viscosity against shear rate of the samples. The test was conducted within the temperature range of 220°C.

Figure 3.21 Parallel plate rheometer
CHAPTER 4 RESULTS AND DISCUSSION

4.1 Stage 1: Effect of Kenaf fibre loading in thermoplastic polyurethane filament

4.1.1 Scanning Electron Microscope Analysis

Figure 4.1 shows the cross-section of the filament composites. It can be seen that, the quantity and the size of voids increased within the filament with increasing kenaf fibre content. This could affect the infill density of printed product which might cause more voids in printed samples. Besides, Figure 4.1(b)-(c) show poor fibre distribution which leads to agglomeration of fibre. This might be due to insufficient and inconsistence temperature supply within the material during filament extrusion which could possibly cause inconsistence melting of the composites during 3D printing.

![SEM images](image)

*Figure 4.1 SEM of cross-section of filament composites fracture surface of (a) Neat TPU (b) KF/TPU- 5/95 (c) KF/TPU- 10/90 at 50x magnification*
Figure 4.2 shows SEM micrograph of surface fractured of TPU and kenaf fibre composite. Smooth fractured surface with little voids were observed on fracture surface of neat TPU. Furthermore, Figure 4.2(b) shows that kenaf fibre does not seem to have good interaction with matrix although the applied surface treatment would be expected to produce kenaf fibre and interaction between TPU by formation of hydrogen bond due to removing the impurities inside the kenaf fibre and present of hydroxyl group at the surface of kenaf fibre. This might be due to poor wettability of kenaf fibre with the TPU matrix which minimize the probability to form interaction between fibre and matrix. TPU sample at 5% fibre loading shows some agglomeration of fibre and present of big voids. The present of voids might due to poor adhesion between layers in 3D printing process (Rahim et al., 2016). It also shows inter-diffusion between layers which could be due to high printing speed. High printing speed might cause the first layers do not have sufficient time to solidify before the next layers been printed.

Next, Figure 4.2(c) shows rougher fractured surface with more obstructed structure owing to irregular morphology of kenaf fibre which resulted in deterioration of elongation of the composites. The figure also shows that there are gaps between the kenaf fibre and the matrix which proved that there are poor fibre and matrix interaction. Besides, it also shows the localised bunch of fibres which indicated poor dispersion of fibre in TPU matrix.

El-Shekeil et al. (2012) reported that as the fibre loading increase, filler-filler interaction increase and this could result the fibre not sufficiently wetted by the matrix and leads to increase the population of the fibre thus this would affect mechanical properties since the stress get blocked to transfer from matrix to the fibre. Hence, the higher fibre loading in the matrix, the higher possibility of Kenaf fibre to agglomerate.
4.1.2 Mechanical Strength

4.1.2.1 Tensile strength

The TPU filament with 0-10 wt% of kenaf fibre were successfully extruded to fabricate test samples, however the composite filament with 20 wt% of kenaf fibre fracture prior to extrusion in 3D printing process. Mechanical testing was conduct to determine the strength of composite.

Figure 4.3 shows the effect of increasing kenaf fibre content on tensile strength in comparison with neat TPU printed samples. The general trend shows tensile strength decreased with increasing kenaf fibre content. The decrease of tensile strength for FDM printed samples might be due to low infill density. Voids within filament increased as fibre loading increased which resulting lower final infill density. This might be explained
due to remaining gaps between the printed filaments become larger thus reduced the bonding between each layer (Aw et al., 2018). The molten filament does not attach to the surface of the solid layer which creates poor structure of sample containing large gaps between the strands. Another factor that causes reduction of tensile strength of FDM printed samples for all materials is randomness in printing orientation and printing delays. During printing, the process is paused for inserting new filaments which might affect the bonding between each layer of strands. The results obtained agreed with previous work carried out by (Weng et al., 2016, Rahim et al., 2016).

Moreover, decreasing in tensile strength could also be explained due to poor wettability which leads to poor interfacial bonding between kenaf fibre and TPU matrix. As fibre loading increased the fibres were not sufficiently wetted by the matrix such that leads to agglomeration of the fibre which will blocked the stress to transfer from matrix to fibre (El-Shekeil et al., 2012). Besides, this may due to high fibre-fibre loading interaction and agglomeration of the fibre in TPU matrix. Furthermore, constant drop of tensile strength also could be due to the present of void content within filament in printed sample and void content in the filament itself. The results is in agreement with other researcher (Stoof et al., 2017).
Figure 4.3 Tensile strength (MPa) of printed sample with different Kenaf fibre loading.

4.1.2.2 Young Modulus

Figure 4.4 shows the effect of different kenaf loading on Young modulus of printed KF/TPU composites. Young modulus increased with increasing kenaf fibre loading. The results showed evidence that addition of kenaf fibre increased the material stiffness. This suggest that kenaf fibres contribute to the overall stiffness to the composite by efficiently hinder the chain movement during deformation. Theoretically, fibre is stiffer than the polymer matrix and it deform less which leads to reduction in matrix strain and elongation at break of the composites. Furthermore, stiffening effect occurs when large amount of fibre in matrix which will restricting the flexibility and continuality of TPU matrix. According to Tawakkal et al. (2014) stiffness of the composites is dependent on filler content and homogeneity of the filler dispersion which will affect the flexibility and toughness of the composites. The results is in agreement with past research work (El-Shekeil et al., 2012, Milosevic et al., 2017))
4.1.2.3 Elongation at Break

Figure 4.5 shows elongation at break of printed sample with different loading of kenaf fibre. Elongation at break of printed sample decreased when kenaf fibre loading increased. It can be seen that the fracture of FDM 3D printing samples were mainly due to the raster orientation (Wu et al., 2015). When the stress reaching a constant value, the sample that already undergoes necking will further propagate. Crazing occurs for the printed samples rapidly due to the presence of voids and when both end of the sample craze, the sample failed due to a non-oriented layer of the filaments. Extensive pores inside FDM printed samples also lead the sample to break at a shorter time before further elongate.

Furthermore, decreasing in elongation at break could be explained due to the fact that deformation of the fibre is generally much less than polymer matrix and this may leads the fibre forces the matrix to deform more than the overall deformation of the composites. Incorporation of fibre into polymer matrix would increase the stiffness and hardness of the composite and leads to decrease in ductility Therefore, less strain are required to cause the sample to fail. The poor interaction of kenaf fibre and TPU matrix
permits easier crack propagation. Thus the composite fail at lower elongation at break with increased kenaf fibre loading. Besides, increasing fibre loading will create a possibility of fibre bundle which results further decrease in elongation at break. Tawakkal et al. (2014) state that poor fibre-matrix bonding decreases the strength, stiffness, interfacial adhesion and increase the flexibility of the composite due to capability of the filler particles to split and fall apart.

![Graph showing elongation at break (%) for different Kenaf fibre loading](image)

**Figure 4.5** Elongation at break (%) of printed sample with different Kenaf fibre loading.

### 4.1.3 Water Absorption Test

Percentage of water absorption for printed sample is plotted in Figure 4.6. As can be seen, percentage of water absorption increased when fibre loading increased. The water absorption occurs due to the present of cavities and void between the layers of printed sample. Furthermore, higher and inconsistent temperature during extrusion of filament induced formation of the microcracks on the filament surface which lead to higher percentage of water absorption, in which water can be absorbed into the sample through the microcracks of polymer chain itself (Fernandes et al., 2018).
Besides, kenaf fibre is a polar molecule that contain hydroxyl group which can form hydrogen bond with water molecules, contrary to hydrophobic properties of polyurethane matrix. More formation of hydrogen bonding between hydroxyl group and water molecules with increasing fibre loading. This could be the reason of increasing in percentage of water absorption when fibre loading increase. When fibre loading increase, the filament generate more voids. The results is in agreement with other work (Datta and Kopczyńska, 2015, Husseinsyah and Ahmad, 2013)

![Figure 4.6 Percentage of water absorption (%) of printed sample with different Kenaf fibre loading.](image-url)


4.1.4 Tolerance Test

Table 4.1 shows tolerance of printed sample with different amount of kenaf fibre. It can be seen contribution of kenaf fibre reduce dimensional tolerance of the printed sample. In x-axis, it shows that neat TPU shrink the most. This might be due the soft segment of TPU forming pseudo crystalline region during cooling process. However, KF/TPU- 5/95 and KF/TPU- 10/90 shows insignificant change in x-axis. This could be due to present of kenaf fibre restrict soft segment of TPU chain to be align during cooling process. In y-axis, that printed sample with different kenaf fibre loading showed significant changed in dimension. For z-axis, KF/TPU- 10/90 shows the highest shrinkage of printed sample. This could be explained due to swerve printing, process due to the breakage of the filament while printing which cause the sample to leap several layer and affect the measurement of z-axis. Besides, this happened could due to the layer of printed sample has been blend together and fill the void between the layers. This might be due to the first layer of printed sample do not have enough time to solidify while the next layer has be printed. This can be proved as shown in Figure 4.7. Thus, this might be main reason of reducing in thickness of the printed sample.

<table>
<thead>
<tr>
<th></th>
<th>Neat TPU</th>
<th>KF/TPU- 5/95</th>
<th>KF/TPU- 10/90</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>-0.427</td>
<td>0.073</td>
<td>-0.027</td>
</tr>
<tr>
<td>y</td>
<td>-0.280</td>
<td>-0.170</td>
<td>-0.223</td>
</tr>
<tr>
<td>z</td>
<td>-0.197</td>
<td>-0.153</td>
<td>-0.230</td>
</tr>
</tbody>
</table>

Table 4.1 Tolerance of printed sample
4.1.5 Hardness Test

Figure 4.8 shows the hardness properties of printed sample with different loading of kenaf fibre. The trend shows the hardness properties increased as fibre loading increased. Hardness of the composite depends on fibre loading and dispersion of fibre in polymer matrix. The presence of kenaf fibre in TPU matrix will restrict the movement of TPU chain due to stiffening effect. This could be explain due to formation of hydrogen bond between kenaf fibre and TPU chain which could leads to increase the stiffness and hardness of printed products (Summerscales et al., 2010). The results is in agreement with previous research paper that prepared by (El-Shekeil et al., 2012, Milosevic et al., 2017).
4.1.6 Density Test

Figure 4.9 shows the density results of printed sample with different kenaf fibre loading. Density of the printed sample decreased with increasing fibre loading. This could be attributed to the present of cavities and voids between the layers of the printed sample. Furthermore, higher and inconsistent temperature during extrusion of filament induced formation of microcracks on the filament surface which decreased the density of the sample. Moreover, formation of voids within the filament could affect the infill density during printing process and the thin strands of filaments are not perfectly bonded between adjacent filaments which creates a grooved layer filled with an air gap in between the layers also might affect density of printed samples. This is in agreement with the results reported by other researchers (Abdullah et al., 2017).
4.1.7 Rheology Analysis

4.1.7.1 Shear Stress vs Shear Rate

Shear stress versus shear rate of printed sample with different kenaf fibre loading are plotted in Figure 4.10. It can be seen that, shear stress decreased with increasing kenaf fibre loading. Decrease in shear stress could be explained due to heat history of the materials during sample preparation which include compounding process in internal mixer, forming filament by extrusion and fabricate the sample by using 3D printer. These process involve application of shear forces and heat which might cause the kenaf fibre to burn out. When kenaf was burned, the size of kenaf reduced and carbon layer might form on the surface of kenaf fibre. This might leads the TPU matrix and kenaf become incompatible since the presence of carbon layer will weaken the adhesion bonding. Thus, less shear stress was recorded since energy required to break-up interaction of TPU matrix and kenaf fibre are lesser. (Arsad et al., 2013) stated that excessive heat history will burned kenaf fibre partially and will forming a carbon layer on the surface of kenaf fibre itself which act as lubricant rather than act as reinforcement agent to composite. Thus this would affect mechanical properties of the end product.
Figure 4.10 Shear stress vs shear rate of printed sample with different Kenaf fibre loading.
4.2 Stage 2: Effect of epoxidized natural rubber loading in kenaf fibre/thermoplastic polyurethane composite filament

4.2.1 Scanning Electron Microscope Analysis

Figure 4.11 show the cross-section of KF/TPU/ENR filament composites. It can be clearly seen that the formation of voids become more dominant with increase of ENR loading which could possibly fracture prior printing process. Besides, the surface of cross-section also become rougher with increasing ENR loading. Figure 4.11(d)-(e) show agglomeration of kenaf fibre. This could be due poor wettability of fibre as increasing kenaf fibre loading. Furthermore, Figure 4.11 also show the surface of filaments consists of micro-crack and fibre-pull out.

Figure 4.12 shows SEM micrograph of the surface fractured of KF/TPU/ENR composites. Figure 4.12(a) shows smooth with less agglomeration of kenaf fibre due to good dispersion of fibre within the matrix. Besides, it also shows the present of gap between matrix and filler and fibre-pull out. Figure 4.12(b)-(c) shows good dispersion of kenaf fibre with present of fibre-pull-out. Next, the figure also shows uneven surface fractured with present of big voids. In Figure 4.12(c) it shows that the fibre partially break and the remaining embedded inside the matrix. Figure 4.12(d) shows the poor interaction of rubber particles and TPU matrix. This could be due to incompatibility of TPU matrix and rubber phase which form gross separation between the phases. Figure 4.12(d)-(e) show agglomeration of kenaf fibre on the surface of fractured samples. This could be due poor dispersion and poor wettability of kenaf fibre. The present of fibre-pull out also increased with increasing kenaf fibre loading. Besides, it also shows phase separation when ENR loading increased. This might be due to incompatibility of rubber phase and TPU matrix.
Figure 4.11 SEM micrographs taken from the cross-section of the filaments of (a) KF/TPU/ENR-10/90/10 (b) KF/TPU/ENR-10/80/20 (c) KF/TPU/ENR-10/70/30 (d) KF/TPU/ENR-20/90/10 (e) KF/TPU/ENR-20/80/20 composites.
Figure 4.12 SEM micrographs taken from the fracture surface of tensile specimen of (a) KF/TPU-10/90 (b) KF/TPU/ENR-10/90/10 (c) KF/TPU/ENR-10/80/20 (d) KF/TPU/ENR-10/70/30 (e) KF/TPU/ENR-20/90/10 (f) KF/TPU/ENR-20/80/20 composites.
4.2.2 Mechanical Strength

4.2.2.1 Tensile Strength

TPU/ENR blend were compounded with 10wt% and 20wt% of kenaf fibre and their filament were successfully extruded to fabricate the samples. From the first stage, the kenaf composites with 20wt% were fracture prior extrusion in 3D printing process. Thus, this stage used to identify the ability of ENR to increase the flexibility of composites in order to print the composites with higher kenaf loading. However, KF/TPU/ENR- 20/70/30 filament cannot be extruded while printing process. This might due to poor wettability of ENR in TPU matrix. The filament hard to be extrude since the filament is quite sticky. This sticky properties leads to the blockage of nozzle since the filament cannot fully melt and blocked the nozzle. The sample that cannot be printed due to this problem is shown in Figure 4.13.

![Figure 4.13 Sample that unable to print.](image)

The effect of epoxidized natural rubber (ENR) on tensile strength of composite with 10%wt and 20%wt of kenaf fibre is shown in Figure 4.14. It can be seen the tensile strength of the printed sample decreased as the ENR loading increased. This could be due to low infill density which might affect the gap between printed filaments. This is might due to presence of voids in the filament which will affect infill density of printed samples. When the gap increased, it will reduce bonding between the layers thus leads to decrease in tensile strength. Another factor that causes reduction of tensile strength of FDM printed samples for all composites is printing speed. High print speed may cause the layers not
properly attached from previous layer and leads to formation of huge empty space that effect on reduction of tensile strength. Besides, the viscosity of the composites are not same thus this might affect the melt flow while printing process The results obtained agreed with previous work carried out by (Weng et al., 2016, Rahim et al., 2016).

Moreover, reduction of tensile strength would be due to disruption of crystalline region in TPU hard phase by the rubber phase resulting decrease in inferior strength of the printed samples. Furthermore, this may due to morphological properties of the blend which consist of co-continuous phase that will leads poor stress absorption towards the matrix. As ENR loading increase, the particle-particle interaction of the rubber phase will increase, thus it resulting in occlusion which leads to decrease in tensile strength. According to Mohamad et al. (2013), the decrease in tensile strength could be due to decrease in crystallinity of the matrix because the present rubber particles in intra and inter spherulitic region of the crystallinity phase of plastic matrix. This explained the present of rubber particles in the blend interrupt the formation of crystallite which results in lower down tensile strength. This results is in agreement with other research work (Kalkornsurapranee et al., 2012, Noor Azammi et al., 2018, Pichaiyut et al., 2012).

Based on Figure 4.11, it shows that KF/TPU/ENR- 10/80/20 have higher tensile strength compared to KF/TPU/ENR- 20/90/10. This might be due to poor dispersion or uneven orientation of kenaf fibre in KF/TPU/ENR- 20/90/10. Moreover, as the fibre loading increase, the fibre particles are not equally separated or wetted by the polymer matrix. This leads to poor interfacial adhesion between fibre and polymer matrix due to poor wettability of fibre by TPU/ENR blends which be resulted in weak interfacial regions. Agglomeration of fibre particles will form domain which be act as foreign body as well as weak interfacial region and leads to reduction of strength. This results is in agreement with (Ratnam et al., 2010).

62
Young modulus of printed sample with different ENR loading is presented in Figure 4.15. Young modulus of printed sample decreased as the ENR loading increased. This could be due to inconsistence of infill density of printed layers. Infill density strongly affects the Young modulus of FDM printed samples. This indicates that inconsistent of infill density leads to a reduction of the modulus of the samples by low adhesion of bonding between printed layers. A large raster and deposition filaments generated from low inconsistence infill density make the structure less dense and also reduce the modulus of printed parts (Aw et al., 2018).

Furthermore, the reduction in Young modulus could be explained due to decreasing rigidity in the blend with increasing ENR loading. Decreasing rigidity of the blends is due to flexibility properties of ENR and low crystallinity of TPU in the blends. As the ENR loading increased, occlusion of rubber occur due to rubber-rubber interaction and will leads to decrease in Young modulus. Besides, rubber-like properties that was introduced by ENR also might lower down Young modulus of printed samples.
However, KF/TPU/ENR-20/90/10 shows the higher Young modulus compared to KF/TPU/ENR-10/90/10. This observation indicates incorporation of kenaf fibre into TPU/ENR blend matrix which improve the stiffness of TPU/ENR blends. This is a common results with effect of filled polymer system. According to Tawakkal et al. (2014) stiffness of the composites is dependent on filler content and homogeneity of the filler dispersion which will affect the flexibility and toughness of the composites. This result is in agreement with paper that prepared by Noor Azammi et al. (2018).

Figure 4.15 Young Modulus (MPa) of FDM printed dumbbell specimens.

4.2.2.3 Elongation at Break

Elongation at break of printed samples with different ENR loading is presented in Figure 4.16. The results showed that elongation at break of the composite decreased as ENR loading increased. The parameter such as nozzle temperature and printing speed of 3D printing process might affect the elongation at break of the printed samples. The ideal nozzle temperature is important since it would affect the adhesion between the layers and it can control the presents of void in the samples. If the nozzle at higher than required temperature, the layers not able to cool properly before the next layer been printed. Thus it will leads to poor adhesion between the layers thus the sample can elongate more. High
printing speed also might cause increasing in elongation at break. This could be explained
due formation of weak interlayer which would allowed the material able to stretch thus
increase the flexibility. Thus, in order to increase flexibility of printed product it required
high nozzle temperature and printing speed.

Moreover, elongation at break decrease could be due to incorporation of rubber
phase which might cause chain restriction of the soft segment of TPU matrix hence this
will lower down elongation at break of the sample. As ENR loading increase, formation
of occluded rubber increase in inter spherulitic region due to formation of rubber-rubber
interaction thus it would restrict the TPU matrix to elongate. According to Pongtanayut
et al. (2013), addition of ENR would increase the softness and flexibility of polymer
composites in order to increase elongation at break of the blend. However, ability the
blend to elongate is depending upon dispersion and size distribution of rubber particles.
As rubber particle size increased, discontinuity of TPU matrix was intense thus it would
reduce the elongation at break of the printed samples. Furthermore, incompatibility of
TPU and ENR matrix also would affect elongation at break since will permits easier crack
propagation to form. This results is in agreement with other research paper (Pichaiyut et
al., 2012).
4.2.3 Water Absorption Test

Percentage of water absorption of FDM printed samples with different ENR loading are plotted as in Figure 4.17. Percentage of water absorption increased with increasing ENR loading. This might be due to present of void in the filament which affect the infill density of the printed samples. Decreasing infill density will increase the formation of cavities and voids in printed sample due to low adhesion interaction between the layers. Furthermore, microcracks on the filament surface that induced by inconsistence temperature during extrusion process also will increase percentage of water absorption which water molecule can penetrate the samples through the microcracks of polymer chain.

Percentage of water absorption shows drastically increase when ENR were introduced in the system might due to rubber particles of ENR restrict the TPU chain to form crystalline region. This will resulted the amorphous region in polymer blend will increase thus more water molecule can penetrate and fill the vacancy between the chain. As ENR loading increase, particle-particle interaction of rubber phase will increase thus
resulting formation of occluded rubber between the chains. This leads the chain to become far apart from each other and it will increase the vacancy between the polymer chain thus more water molecules can fill the vacancy. Besides, the figure also shows that there are drastically increase from KF/TPU/ENR- 10/70/30 to KF/TPU/ENR- 20/90/10. This could be explained due to hydrophilic properties of kenaf fibre. This could be the main reason of drastic increase in percentage of water absorption. This properties will cause kenaf fibre to absorb more water since hydrophilic structure will form hydrogen bonding with water.

![Figure 4.17 Percentage of Water Absorption of FDM printed specimens.](image)

**4.2.4 Tolerance Test**

Table 4.2 shows the results of tolerance test of printed sample with different ENR loading. From the table, it shows that effect of ENR do not shows any significant changes on dimension of printed sample since it do exceed 1mm in length. This might be due to present of ENR loading which control the dimension of printed sample by restrict the TPU chain to form crystalline region by formation of occluded rubber in TPU matrix. Besides, this could be explained due to the ENR matrix do not have sufficient energy to make the matrix to shrink while cooling process. Theoretically, rubber will shrink as the
extreme temperature applied. The shrinkage of the rubber occurs due to the rubber chain gain energy and begin to vibrate more violently, causing the chains to shorten again. Thus, it can be conclude that present of ENR as matrix of the composite will restrict the shrinkage properties of the overall composite as there are no extreme temperature apply. This proved that the present of ENR is good to control dimension of printed samples.

### Table 4.2 Tolerance of printed sample.

<table>
<thead>
<tr>
<th></th>
<th>KF/TPU/ENR-10/90/10</th>
<th>KF/TPU/ENR-10/80/20</th>
<th>KF/TPU/ENR-10/70/30</th>
<th>KF/TPU/ENR-20/90/10</th>
<th>KF/TPU/ENR-20/80/120</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>-0.027</td>
<td>-0.037</td>
<td>-0.023</td>
<td>0.013</td>
<td>-0.027</td>
</tr>
<tr>
<td>y</td>
<td>0.003</td>
<td>0.003</td>
<td>-0.003</td>
<td>0.007</td>
<td>-0.013</td>
</tr>
<tr>
<td>z</td>
<td>0.023</td>
<td>-0.013</td>
<td>-0.023</td>
<td>-0.027</td>
<td>-0.053</td>
</tr>
</tbody>
</table>

#### 4.2.5 Hardness Test

Hardness of printed samples with different ENR loading was plot in Figure 4.18. Hardness value of the printed sample decreased with increasing ENR loading. This might due to contribution of elastic properties of ENR rubber phase in the blend which reduce rigidity of printed samples. Rigidity of printed sample decrease due to low crystallinity of TPU and flexible properties of ENR in the blend. Low crystallinity of TPU is due to rubber-rubber interaction which restrict the TPU chain to align in order. The results is in agreement with tensile properties and Young modulus discussed above. However, the figure shows hardness increase with 20wt% of kenaf fibre. This could be explain due to formation of hydrogen bond between kenaf fibre and TPU matrix which could leads to
increase the stiffness and hardness of printed products. This result is in agreement with paper that prepared by Noor Azammi et al. (2018).

![Figure 4.18 Hardness of FDM printed specimen.](image)

### 4.2.6 Density Test

Figure 4.19 shows density of FDM printed sample with different ENR loading. It shows that density of the sample increased with increasing of ENR loading. This might be due to density of ENR is the higher compared to density of thermoplastic polyurethane and kenaf fibre. KF/TPU/ENR- 10/70/30 represent the highest density while KF/TPU-10/90 shows the lowest density. This is a proof that ENR affect the overall density of the printed sample although there are some void present in the filament and printed sample. However, when kenaf fibre loading increase, it shows that drastically decrease in density. This could be due to the kenaf fibre exhibit the low density thus affect overall density of printed samples. Besides, increase kenaf fibre in TPU/ENR blends leads to formation more voids in the filament as shown in Figure 4.11. Thus, this could be the reason since it would affect the infill density of printing process and leads it to form poor adhesion of the layers hence increase the voids in the samples.
4.2.7 Rheology Analysis

4.2.7.1 Shear Stress vs Shear Rate

Figure 4.21 shows shear stress versus shear rate of FDM printed sample with different ENR loading. KF/TPU/ENR- 10/70/30 shows the higher shear stress followed by KF/TPU/ENR- 10/90/10 and KF/TPU/ENR- 10/80/20 respectively. This could be due to formation of gross separation between TPU matrix and ENR matrix. Gross separation is a phenomenon when the rubber phase is incompatible with polymer matrix and leads to form formation of occluded rubber on the surface of polymer matrix. Figure 4.20 illustrate formation of gross separation. Gross separation occur could due to poor interaction between TPU matrix and ENR rubber phase. This gross separation makes the rubber phase acts as tertiary component in the system and consists extra resistance in motion that leads to increase in internal stress thus increase in shear stress and viscosity. Increase in internal stress due to surface friction of two polymer phase in blending system. KF/TPU/ENR- 10/90/10 should show lower shear stress compared to KF/TPU/ENR- 10/80/20. However, by assuming Newtonian fluid at early region only, good interaction between TPU and ENR matrix which leads to increase in friction between the surfaces.
could be the reason KF/TPU/ENR- 10/90/10 show the higher shear stress compared to KF/TPU/ENR- 10/80/20. In KF/TPU/ENR- 10/80/20, due to less compatibility of rubber phase and TPU matrix, viscosity and shear stress decrease. This could be due to weak interaction between phases which leads to less friction needed thus shear stress reduced.

The figure shows shear stress increase as the kenaf fibre loading increased. This could be explained due to agglomeration of fibre increase as kenaf fibre increase with 20 wt%. This could be proved by Figure 4.12(e) which shows fractured surface of samples with 20 wt%. When agglomeration of fibre increase, it would leads to increase in viscosity. Although 10 wt% of ENR was introduced in the composite system, the shear stress still high might due to 10 wt% ENR not effective to improve flexibility of the composites thus shear stress increased. However, shear stress of composite with 20 wt% of ENR decreased may be due to the present of ENR that capable acts as plasticizer thus reduce the shear stress.

![Illustration of formation gross separation](image)

*Figure 4.20 Illustration of formation gross separation*
Figure 4.21 Shear stress vs shear rate of FDM printed sample.
CHAPTER 5 CONCLUSION AND FUTHER RECOMMENDATION

5.1 CONCLUSION

Fused deposition modelling is a simple and affordable additive manufacturing technology that utilising filament extrusion of polymeric materials to manufactured 3D products layer by layer. This study was carried out to explore the flexibility of fused deposition modelling method to produced natural fibre reinforced elastomeric composites. This work focusses on development KF/TPU/ENR based novel FDM filament feed stock that demonstrate high elasticity, sustainability as well as good mechanical properties. Particular attention is paid towards the flexibility to fabricate the filament and extrusion process by 3D printing.

In phase 1, kenaf fibre and thermoplastic polyurethane were blend together with different kenaf fibre loading (0-20 wt%) to form composite filament as the feed stock of 3D printing. The main intention of using kenaf fibre is to reinforce properties of thermoplastic polyurethane. Throughout the experiment, TPU filament with 0-10 wt% of kenaf fibre were successfully extruded to fabricate test samples. However, composites filament with 20 wt% of kenaf fibre was fracture prior to extrusion in 3D printing process. Their mechanical, water absorption, tolerance, hardness, density and rheological behaviour were tested and compared. With the increased kenaf fibre loading, the tensile elongation at break of printed sample show decreasing trend. This could be explained due to poor wettability and poor interaction of kenaf fibre in TPU matrix. Young modulus of printed sample increased with increasing kenaf fibre loading. This could be due to stiffening effect resulted by kenaf fibre which leads the printed samples to behave in brittle manner. Through morphology study, it can be seen that the present of voids in printed samples and filament increased with increasing of kenaf fibre loading. Besides, SEM also show the fracture surface become rougher and agglomeration of kenaf fibre in
TPU matrix increased as kenaf fibre loading increased. Tolerance test show kenaf fibre give a good impact on dimensional stability. This due to shrinkage of printed decrease as kenaf fibre introduced to TPU matrix. The may be explained due to present of kenaf fibre that restrict the TPU chain to form pseudo-crystalline region that resulting less shrinkage of printed samples. Hardness of printed samples increased with increasing of kenaf fibre loading. This might be due to the present of kenaf fibre that form hydrogen bond with TPU chain that cause retraction of TPU mobility. Next, density of printed samples reduced with increasing of kenaf fibre. This may be explained due to present of voids in extruded composite filament which might affect infill density of the printed samples thus would affect the overall density. From rheological analysis, it show shear stress is decreased with increasing fibre loading. This might be due to effect of heat history that burned out kenaf fibre and leads to reduction of size of kenaf fibre and formation carbon layer on the surface of kenaf fibre. In order to improve material flexibility to print composite with higher fibre content, further assessment was carried out in phase 2 by blending thermoplastic polyurethane with different content of epoxidized natural rubber (10-30 wt%). TPU/ENR blend were compounded with 10 wt% and 20 wt% of kenaf fibre and the filament were successfully extruded. However, KF/TPU/ENR- 20/70/30 composite filament was unable to be printed due to the filament unable to melt properly thus block the nozzle prior printing process. Their mechanical, water absorption, tolerance, hardness, density and rheological behaviour were tested and compared. Tensile, Young modulus and elongation at break of printed samples decrease with increasing ENR loading. This could be explained due to due to disruption of crystalline region in TPU hard phase by the rubber phase. Decreasing in tensile strength could be due to decrease in crystallinity of the matrix because the present rubber particles in intra and inter spherulitic region of the crystallinity phase of plastic matrix. Young modulus
decrease due to rubber-like properties that was introduced by ENR which leads molecular entanglement in the rubber chain restrict mobility of TPU chain. Decreasing elongation at break could be due to incorporation of rubber phase which might cause chain restriction of the soft segment of TPU matrix hence this will lower down elongation at break of the sample. Water absorption increased when ENR loading increased. This could be explained due to rubber particles of ENR restrict the TPU chain to form crystalline region. This will resulted the amorphous region in polymer blend will increase thus more water molecule can penetrate and fill the vacancy in the between chain. The study of morphology show

Tolerance test show inclusion of ENR affect dimensional stability of printed sample. This may be due to ENR phase restrict the TPU chain to form crystalline region by formation of occluded rubber in TPU matrix thus avoid the sample to shrink. Besides, ENR matrix required extreme temperature in order to make the rubber matrix shrink. Hardness of printed sample decreased with increasing ENR loading. This might due to contribution of elastic properties of ENR rubber phase in the blend which reduce rigidity of printed samples. Next, density of printed samples increased with increasing ENR loading. This might be due to density of ENR is the higher compared to density of thermoplastic polyurethane and kenaf fibre.

5.2 FURTHER RECOMMENDATION

There are very wide scope for future scholars to explore this area of research. TPU filament with presence of kenaf fibre and epoxidized natural rubber show the significant drop in mechanical properties when fibre and ENR loading increase. Dispersion and wettability of kenaf fibre in TPU matrix play the main role of affecting mechanical properties and water absorption behaviour of KF/TPU composites. Thus, suitable coupling agent should be added in order to improve interfacial interphase between kenaf
fibre and TPU matrix. Besides, suitable compatibilizer should be introduce to the system for improving miscibility of ENR and TPU matrix. Hence, the mechanical properties can be upgraded for the future benefits especially in producing sustainable product that able to be degrade in certain interval of time. Next, the processing method also should be considered in order to produce good dispersion of filler. Thus, twin screw extruder should be used while formation of the filament in order to increase the well distribution of kenaf fibre and blending of the TPU and ENR.
REFERENCES

2014. FRONT MATTER. 3D Printing and Additive Manufacturing. 4th ed.: WORLD SCIENTIFIC.


