



**Faculty of Mechanical and Manufacturing Engineering
Technology**

**CHARACTERIZATION OF ACRYLONITRILE BUTADIENE
STYRENE – HEXAGONAL BORON NITRIDE COMPOSITE
FOR 3D PRINTING**

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**Bachelor of Manufacturing Engineering
Technology (Product Design) with Honours**

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**CHARACTERIZATION OF ACRLONITRILE BUTADIENE STYRENE –
HEXAGONAL BORON NITRIDE COMPOSITE FOR 3D PRINTING**

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TAJUK: Characterization of Acrlonitrile Butadiene Styrene – Hexagonal Boron Nitride Composite for 3d Printing

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DEDICATION

~ To my beloved mother and father ~

ABSTRACT

This thesis presents the characterizations of acrylonitrile butadiene styrene (ABS) - hexagonal boron nitride (hBN) composite for 3D printing. Filament plays an important role in the creation of a 3D object. Therefore, ABS was chosen for this thesis. ABS is a common thermoplastic polymer which is extruded from the machine nozzle tends to shrink and warp at the printing bed platform. Warping and non-uniform shrinkage of ABS is one of the problems in 3D printing for this project. Besides, hBN has a crystal structure that offers excellent lubricating properties and excellent thermal conductive filler that is becoming increasingly attractive. This is the beneficial properties to ABS. Therefore, the main goal of this thesis is to fabricate ABS – hBN composite by ABS dissolves in organic liquid process using ultrasonic agitator for sonication of small and medium size sample preparation. Moreover, this project are also to characterize the differential scanning calorimetry (DSC) and rheological properties of ABS-hBN composite fabricated. To achieve that, there are phases conducted which will be started by identifying the problem that needs to be overcome. The second stage is a literature review which is to ensure that the project is on track and can be implemented to achieve the project's objective. The material was chosen based on certain requirements and criteria. The ABS dissolves in the organic liquid process where the first process to be completed. Then, the solution mixtures will undergo a crushing process. Finally, both ABS and mixing composite will then undergo Differential Calorimetric Scanning (DSC) testing to get the result of melting point and glass transition temperature and Rheological testing to get the result of viscosity, shear rate, and pressure. By adding hBN with ABS, the degree of freedom for polymer chain motion during heating is reduced due to the reason of the free volume increased in the material in DSC testing which is 218.08°C (melting point) and 104.96°C (glass transition temperature) compared with ABS 227.99°C (melting point) and 96.31°C (glass transition temperature). Moreover, the range of melting temperatures for filament extrusion is 200°C - 245°C. Therefore, no issue and will be not effected to fabricate filament. While rheological testing results are taken into concern are the flow resistance and the pressure effect on the shear rate. The shear rate increased from about 100 to 700 Pa, while the shear viscosity decreased. In a simple term, the material is viscous at decreasing of shear rate. Due to high flow resistance, ABS has a higher viscosity than mixing composite. Thus the pressure is increased when the shear rate increases. This is caused by an increase in stress pressure (solid-state). 230°C temperature is not suitable to use for this testing due to the lower melting temperature that caused fractured filament produced by the rheometer.

ABSTRAK

Tesis ini menerangkan pencirian mengenai filamen komposit diantara 'hexagonal boron nitride' (hBN) untuk pencetakan 3D serta 'acrylonitrile buterena styrene' (ABS). Filament memainkan peranan penting dalam penciptaan objek 3D. Oleh itu, ABS dipilih untuk tesis ini. ABS adalah polimer termoplastik biasa yang diekstrak daripada muncung mesin cenderung mengecil dan meledingkan di platform katil percetakan. 'Warping' dan 'non-uniform shrinkage' adalah salah satu masalah dalam percetakan 3D untuk projek ini. Masalah 'warping' terjadi kerana lapisan pertama tidak berfungsi dengan baik dan dikupas dari platform percetakan. Selain itu, hBN mempunyai struktur kristal yang menawarkan sifat pelincir yang sangat baik dan pengisi konduktif haba yang sangat baik yang menjadi semakin menarik. Ini adalah ciri-ciri bermanfaat kepada ABS. Oleh itu, matlamat utama tesis ini adalah untuk menghasilkan komposit ABS - hBN dengan menggunakan kaedah manual yang larut dalam proses cecair organik oleh agitator ultrasonik untuk penyempurnaan penyediaan sampel saiz kecil dan sederhana. Selain itu, projek ini juga dapat mengenal pasti calorimetri pengimbasan pembezaan (DSC) dan sifat rheologi komposit ABS-hBN. Untuk mencapai itu, terdapat fasa yang dijalankan yang akan bermula dengan mengenal pasti masalah yang perlu diatasi. Tahap kedua ialah kajian literatur yang bertujuan untuk memastikan projek itu berjalan lancar dan dapat dilaksanakan untuk mencapai objektif projek. Bahan dipilih berdasarkan keperluan dan kriteria tertentu. ABS larut dalam proses cecair organik di mana proses pertama selesai. Kemudian, campuran larutan akan mengalami proses penghancuran. Akhirnya, kedua-dua ABS dan campuran komposit kemudian akan menjalani ujian Berbeza Calorimetrik Pengimbasan (DSC) untuk mendapatkan hasil titik lebur dan suhu peralihan kaca dan ujian Rheologi untuk mendapatkan hasil kelikatan, kadar ricih dan tekanan. Dengan menambah hBN dengan ABS, tahap kebebasan untuk pergerakan rantaian polimer semasa pemanasan berkurangan disebabkan oleh sebab volum bebas meningkat dalam bahan dalam ujian DSC iaitu 218.08°C (titik lebur) dan 104.96°C (suhu peralihan kaca) berbanding dengan ABS 227.99°C (titik lebur) dan 96.31°C (suhu peralihan kaca). Selain itu, pelbagai suhu lebur untuk penyemperitan filamen adalah 200°C - 245°C . Oleh itu, tiada masalah dan tidak akan dilaksanakan untuk membuat filamen. Walaupun keputusan ujian rheologi diambil kira adalah rintangan aliran dan kesan tekanan pada kadar ricih. Kadar ricih meningkat dari kira-kira 100 hingga 700 Pa, manakala kelikatan ricih berkurangan. Dalam jangka sederhana, bahan itu likat pada penurunan kadar ricih. Oleh kerana rintangan aliran tinggi, ABS mempunyai kelikatan yang lebih tinggi daripada campuran komposit. Oleh itu tekanan meningkat apabila kadar ricih meningkat. Ini disebabkan oleh peningkatan tekanan tekanan (keadaan pepejal). Suhu 230°C tidak sesuai digunakan untuk ujian ini kerana suhu lebur yang lebih rendah yang menyebabkan filamen patah yang dihasilkan oleh rheometer.

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LIST OF ABBREVIATIONS

3D	-	Three-dimensional
STL	-	Surface Tessellation Language
ABS	-	Acrylonitrile Butadiene Styrene
hBN	-	Hexagonal Boron Nitride
W	-	Watt
mK	-	Meter.Kelvin
TGA	-	Thermal gravimetric analysis
CAD	-	Computer-Aided Design
FDM	-	Fused Deposition Modeling
2D	-	Two-dimensional
PLA	-	Polylactic Acid
PVA	-	Polyvinyl Alcohol
SSap	-	Solid state
Srap	-	Shear rate
Viscap	-	Viscosity
Pa*s	-	Pascal*second

CHAPTER 1

INTRODUCTION

1.1 Project background

3D printing or so-called additive manufacturing is a rapidly arise technology that allows for physical parts to be created from a computer model by building the part in a layer by layer approach. Since its invention in the 1980s, three-dimensional (3D) printing has gained great status in the manufacturing process. In manufacturing industries, the use of 3D printing technology for fabricating of certain products is not new. Moreover, it is becoming popular for the recognition of physical models by using several materials. By converting the design into Computer Aided Data (CAD) into STL, this technology can manufacture nearly any designed product, and then be printed with the 3D printer. Therefore, this 3D printing process can reduce production time and also decrease the manufacturing cost. Various 3D printing type have been produced, however. They all involve layer by layer computer-controlled material deposition in accurate geometries. This system makes it impossible by other manufacturing methods to produce complex geometries. Therefore, ABS material plays an important role in 3D printing filament, which has been classified as thermoplastic polymers (Coakley and Hurt, 2016).

ABS is oil based plastic and is a sturdy, solid material that companies commonly use for the manufacture of products like plastic car parts, musical instruments and the ever-popular Lego building blocks. ABS has a high melting point and may experience warping when cooled

while printing. Because of this, ABS objects must be printed on a heated surface as well as requires ventilation when in use, as the fumes can be unpleasant. However, hexagonal boron nitride (hBN), or so-called “white graphene” is an electrically insulating yet thermally conductive analog to graphene. It is an excellent thermal conductive and also its exceptional thermal conductivity ($\sim 300\text{W} / \text{mK}$) has attracted increasing attention. It’s important to reduce the thermal contact resistance for the better thermal conductivity (Qi et al., 2014). Therefore, process parameters utilized is also considered one of the important factor that can change the characteristics and the properties of the composites. Because of that, any necessary process parameters and techniques must be carefully chosen to obtain the excellent properties of the processing composite.

Other than that, warping also takes place due to material shrinkage during 3D printing. 3D printing filament is normally made up of ABS material which changes its characteristics by certain temperature ranges and it lifts and removes the corners from the printing tray. When plastics are printed, they firstly expand slightly but contract as they cool down. If material contracts too much, this causes the print to bend up from the build plate (Lamin, 2019).

1.2 Problem statement

For this project, warping and non-uniform shrinkage is one of the problems in 3D printing. ABS filament is a common thermoplastic polymer which is extruded from the machine nozzle tends to shrink and warp at the printing bed platform. And also several researchers have highlighted this as requiring an adhesive layer between the first layer and the printing platform to counter the problem. This problem can be reduced by applying heat to the bed where the higher the bed temperature, the less the deformed shape. While the problem of

warping occurs because the first layer does not stick well and is peeled away from the platform of printing. This is due to the first layer's adhesion to the printing platform (Nazan, et al, 2017). As for that, hexagonal boron nitride (hBN) is considered to have high thermal conductivity and non-toxic characteristic (Zhang et al, 2017). It is a challenging candidate to mix up with ABS to fabricate the 3D printing filament.

Other than that, although ABS and hBN are the challenging composites for fabricate 3D printing filament, there is a bonding issue occurred between them. Due to partial reasons for mixing, the bonding between ABS and hBN is not so attached to one another. Therefore, acetone should be added in ABS-hBN composite to achieve the objects. This paper will describe the input data from Differential Scanning Calorimetry (DSC) and rheology, mixing of ABS and hBN methods, experimental procedure.

1.3 Objective

Two objectives will be achieved at the end of this study. These are as follows:

- i. To fabricate ABS-hBN composite by ABS dissolves in organic liquid process using ultrasonic agitator for the sonication of small and medium size sample preparation.
- ii. To characterize the differential scanning calorimetry (DSC) and rheological properties of ABS-hBN composite fabricated by manual mixing process.

1.4 Scope

There will be two scopes carry out in this experiment and below are the scopes:

- i. This project will deal with a process of ABS dissolves in organic liquid method to characterization of ABS – hBN composite.

- ii. Differential scanning calorimetry (DSC) is to measure a number of characteristic properties of sample and rheometer is used for measuring the rheological characteristics of the material.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

3D printing is a process of building a digital file with 3D objects. A digital 3D object is designed using computer-aided design (CAD) software in this process. The popular CAD software used in commercial industries is such as SolidWorks, AutoCAD, and ZBrush. Furthermore, in 3D printing, the material is laid in the required shape in a layer by layer fashion until the object is formed. There are several types of 3D printing processes involved in this technology. However, fused deposition modeling (FDM) is one of the most widely used techniques in fabricating of Acrylonitrile Butadiene Styrene (ABS) thermoplastic material. Because the filament is liquid based (molten) and it is material extrusion printing categories, as well as Acrylonitrile Butadiene Styrene (ABS), has a low melting temperature which makes it especially suitable for 3D printing processing on an FDM machine. One of the promising composite used in these applications is hexagonal boron nitride also called as hBN. In addition, 3D printing technology today has wide-ranging applications in several fields and is expanding rapidly.

2.2 3D printing

3D printing also branded as additive manufacturing; is a popular manufacturing technique for making difficult parts or small quantity batches. It is a manufacturing process

class in which material is deposited in a layer by layer fashion to manufacture a three-dimensional part directly from a computer-aided model (CAD) (Hull et al., 2015). It also begins with a meshed 3D computer model, which can be built by obtaining picture data or structures in the software of computerized design (CAD). The surface tessellation (STL) file is frequently created. Then, before sent to the 3D printing machine, the solid mesh model is sliced into 2D layers. The data flow in a typical 3D printing process can be seen below in Figure 2.1. In almost every industry, it has transformed manufacturing, leading to incredible advances in research and medicine. Unlike traditional manufacturing methods such as cutting, joining, molding, casting, and milling. 3D printing carries out a maximum limit of difficulties in the geometry of the element. It also agrees that the rapid prototyping and the fabrication of custom parts in low volumes (Coakley and Hurt, 2016)

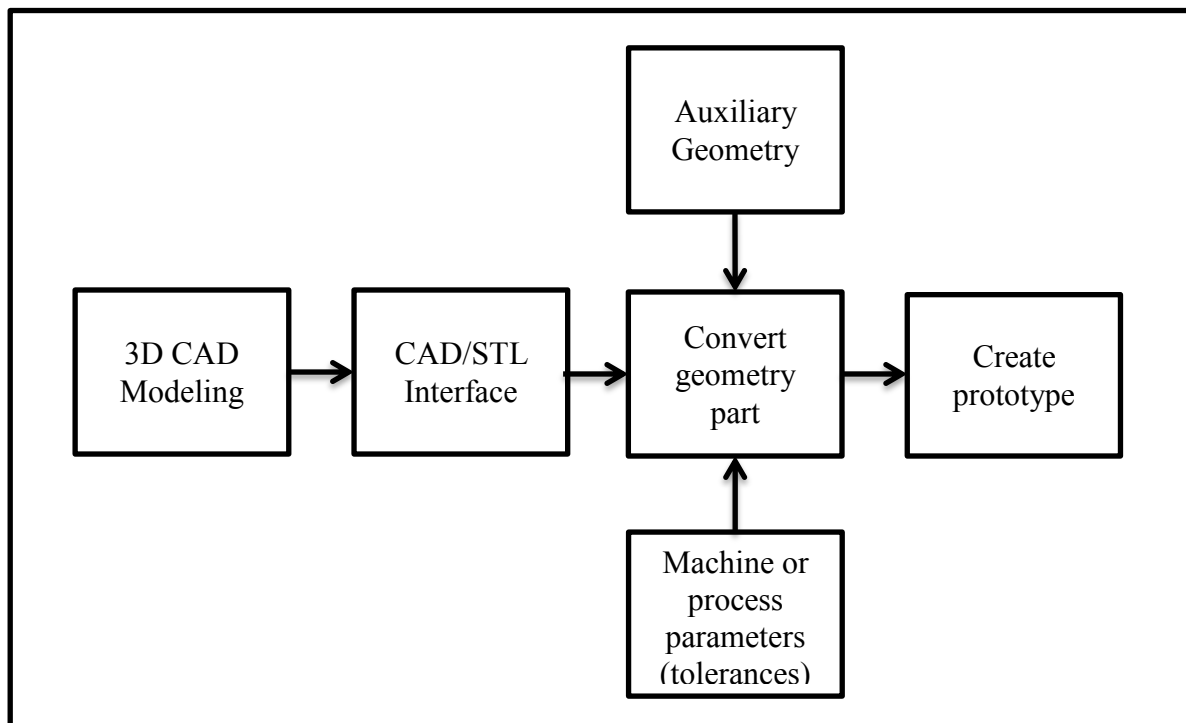


Figure 2.1: The Flow of data in the 3D printing process

2.2.1 Technique of 3D printing

These processes can be classified according to the nature of the 3D printing material, which can be used in the form of liquid, solid or powder. It also can be categorized according to the method of deposition, solidification or collected to form the desired geometry, layer by layer. Fused Deposition Modeling (FDM), Stereolithography (SLA), Laminated Object Manufacturing (LOM), and Selective Laser Sintering (SLS) are the most used in 3D process techniques (Patel, et al., 2017). Figure 2.2 below shows the technique of 3D printing and Table 2.1 shows the comparison of 3D Printing Technologies of various types.

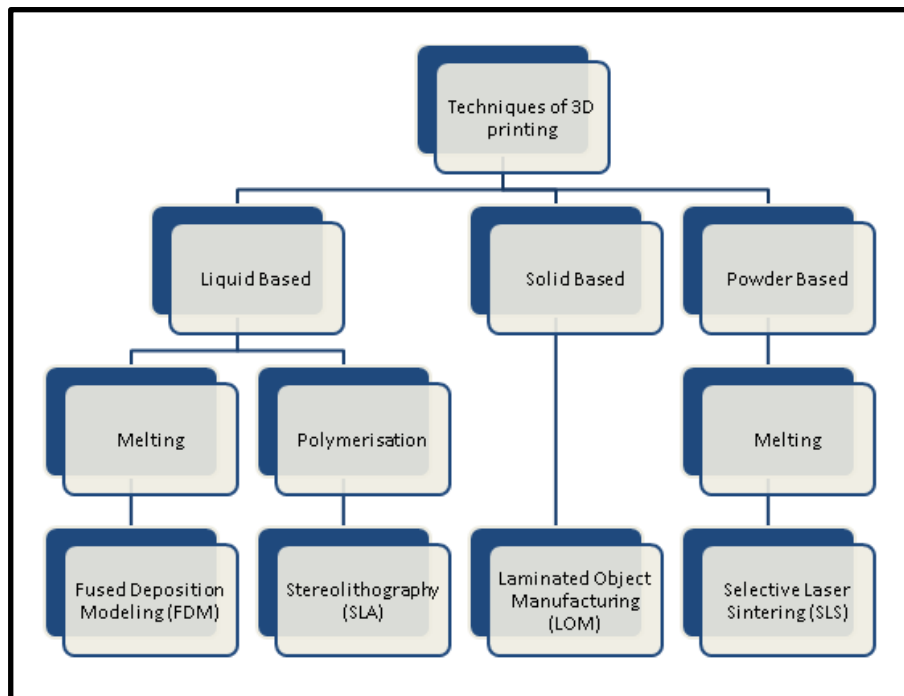


Figure 2.2: 3D printing techniques (Jasveer and Xue, 2015).

Table 2.1: Comparison of 3D Printing Technologies of various types (Jasveer and Xue, 2018).

	FDM	SLA	LOM	SLS
Application	<ul style="list-style-type: none"> • Suitable for prototype • Home use application 	<ul style="list-style-type: none"> • Excellent for form testing • The best process for water-resistant material 	<ul style="list-style-type: none"> • Ideal for non-functional prototypes 	<ul style="list-style-type: none"> • Ideal for functional parts with various application • Suitable for a complex shape object • Heat and chemical resistant
Overall Accuracy	Accuracy and reliable process	The most accurate printing process	Slightly less dimensional accuracy	Not very accurate
Material Options	Thermoplastic material	<ul style="list-style-type: none"> • ABS • Semi-flexible materials • High-temperature Abs 	<ul style="list-style-type: none"> • Paper • Plastic • Metal 	<ul style="list-style-type: none"> • Nylon • Glass-filled Nylon
Finish Option	Standard finish	Excellent surface finish	Wood like characteristics and can be treated similarly	Standard finish
Post-processing requirement	Requires post processing to remove support structure	Requires post processing to remove support structure	<ul style="list-style-type: none"> • Polishing • Painting 	Does not require support structure, less post processing requires

2.2.1.1 Fused Deposition Modelling (FDM) Technique

As long as the material can be fabricated in filament wire, fused deposition modeling (FDM) has been able to deposit only thermoplastic filament in a layer through a layering process. Filaments from the spool will flow through the heated liquefied head and nozzle, depositing the melt material on the heated platform of the FDM. Crump developed this technology since the 1980s and was launched in early 1990 (Sa'ude et al., 2014). Initially, the fused deposition modeling (FDM) technology was used to produce prototypes, but in recent years, the application has been extended to rapid tooling where parts digitally manufacture (Guo and Leu, 2013).

2.2.1.2 Stereolithography (SLA) Technique

SLA is one of the main techniques to be commercialized. By using CAD or CAM software, the UV laser is used to draw on the surface of the liquid UV-curable polymer so-called photopolymer, vat a pre-programmed design. The resin is photochemically solidified and forms a single layer of the desired 3D object due to the photopolymers being sensitive to ultraviolet light. A laser light beam is used to trace the first slice of an object on the liquid surface, hardening a very thin layer. Then, one layer is lowered by the build platform and a blade recoats resin from the top of the tank. This process is repeated until the entire object 2 has been printed (Patel et al., 2017).

2.2.1.3 Laminated Object Manufacturing (LOM) Technique

In terms of dimensional accurateness, speed and cost-effectiveness, Laminated Object Manufacturing (LOM) is one of the greatest promising 3D printing techniques. A commonly