FTIR AND POROSITY ANALYSIS OF THE HUMIDITY-EXPOSED PLA-TPU FILAMENTS IN ADDITIVE MANUFACTURING

Submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

by

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Tajuk: **FTIR AND POROSITY ANALYSIS OF THE MOISTURE-EXPOSED PLA-TPU FILAMENTS IN ADDITIVE MANUFACTURING**

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Hons.). The member of the supervisory committee are as follow:

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ABSTRAK

Bahagian pencetakan 3D yang biasa digunakan seperti polimer, seperti asid polilaktik (PLA) dan poliuretana termoplastik (TPU), mempunyai kemerosotan bahan yang ketara apabila terdedah kepada kelembapan dan suhu tinggi untuk tempoh yang lama. Berdasarkan itu, penemuan ini menunjukkan bahawa degradasi filamen adalah salah satu kesan utama lembapan dalam filamen disebabkan oleh interaksi antara molekul yang dihasilkan oleh molekul air dengan molekul polimer, dan filamen higroskopik biasanya sensitif untuk menyerap air. Gambaran keseluruhan kajian ini dimulakan dengan perbincangan tentang prinsip percetakan 3D sebelum masuk ke ciri-ciri kritikal percetakan berasaskan polimer dan zarah. Tujuannya adalah untuk mengenal pasti pengaruh air (H_20) pada ikatan rantai kimia polimer filamen PLA-TPU bercetak 3D terdedah kelembapan. Konsep densimeter kemudiannya digunakan untuk menentukan keliangan filamen cetakan 3D (PLA-TPU) terdedah kelembapan di bawah pelbagai keadaan kelembapan dengan menggunakan Prinsip Archimedes. Seterusnya, untuk melihat perubahan struktur filamen cetakan 3D (PLA-TPU) terdedah kelembapan. Analisis spektroskopi inframerah transformasi Fourier (FTIR) bagi percetakan 3D digunakan untuk mencirikan komposisi kimia zarah yang mengandungi zarah mikro dan nano. Selain itu, struktur mikro objek bercetak 3D telah diperiksa menggunakan Mikroskop Elektron Pengimbasan (SEM) dengan salutan sputter yang digunakan supaya imej SEM boleh menjadi kualiti yang diingini. Kajian itu menyimpulkan bahawa kelembapan mengubah rantai kimia ikatan polimer (kumpulan kimia O-H). Selain itu, TPU lebih berliang daripada PLA dan mempunyai ketumpatan yang lebih rendah daripada PLA. Ketumpatan tertinggi dikesan pada PLA, dan ketumpatan terendah ialah TPU, kerana pelbagai keadaan mempengaruhi ketumpatan filamen. Seterusnya, struktur TPU lebih berliang dan lompang di bawah imej SEM daripada struktur PLA. Kajian ini boleh menjadi lebih baik jika tahap kelembapan dikawal oleh peranti seperti kotak kabinet kering dengan kelembapan boleh laras.

ABSTRACT

Commonly used 3D printing parts like polymers, such as polylactic acid (PLA) and thermoplastic polyurethane (TPU), have significant material degradation when exposed to humidity and high temperatures for extended periods. Based on that, these findings show that degradation of the filament is one of the main effects of moisture in a filament due to the intermolecular interactions that the water molecules create with the polymer molecules, and the hygroscopic filaments are usually sensitive to absorbing water. The overview of this study began with a discussion of the principles of 3D printing before going into the critical features of polymer and particle-based printing. The purpose is to identify the influence of water (H_20) on the polymeric chemical chain bonding of the humidity-exposed 3D printed PLA-TPU filaments. The densimeter concepts were then used to determine the porosity of the humidity-exposed 3D printed (PLA-TPU) filaments under various humidity conditions by using the Archimedes Principle. Next, to observe the structural change of humidity-exposed 3D printed (PLA-TPU) filaments. The Fourier transform infrared spectroscopy (FTIR) analysis of 3D printing was used to characterize the chemical composition of particles containing micro and nanoscale particles. Additionally, the microstructure of the 3D printed objects was examined using a Scanning Electron Microscope (SEM) with a used sputter coating so that the SEM images could be of the desired quality. The study concluded that humidity alters the chemical chain of the polymeric bonding (O-H chemical group). Other than that, TPU is more porous than PLA and has a lower density than PLA. The highest density was spotted on PLA, and the lowest density was TPU, because the various conditions were affecting the density of the filament. Next, TPU structural is more porous and void under the SEM image than PLA structural. This study could be better if the humidity level was controlled by a device like a dry cabinet box with adjustable humidity.

DEDICATION

This humble work is dedicated to
my beloved father, Sindam Galakin
my true loved mother, Sianim Ransoi
my adored siblings, and
my appreciated friends
for giving me moral support, cooperation, encouragement,
and understandings. Thank you so much.

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LIST OF ABBREVIATIONS

3D	-	Three dimensional
ABS	-	Acrylonitrile butadiene styrene
AM	-	Additive manufacturing
ASTM	-	American society for testing and materials
CAM	-	Computer Aided-Design
DMA	-	Dynamic mechanical analysis
FDM	-	Fused Deposition Modelling
FTIR	-	Fourier transform infrared
HIPS	-	High-intensity polystyrene
ISO	-	International Organization for Standardization
Mw	-	Molecular weight
N-H	-	Nitrogen-Hydrogen
PDLA	-	Poly (D-lactic acid)
PDLLA	-	Amorphous poly (D, L-lactic acid)
PE	-	Percentage of error
PEEK	-	Polyether ether ketone
PEI	-	Polyetherimide
PET	-	Polyethylene terephthalate
PETG	-	Polyethylene terephthalate glycol
PLA	-	Polylactic acid
PLLA	-	Poly (L-lactic acid)
Pt	-	Platinum
ROP	-	Ring opening polymerization RP - Rapid prototyping
SEM	-	Scanning electron microscope
SOP	-	Standard operation procedure

SLA	-	Stereolithography
STL	-	Standard triangle language
Tg	-	Glass transition temperature
THF	-	Tetrahydrofuran
Tm	-	Melting temperature
TPU	-	Thermoplastic polyurethane

LIST OF EQUATIONS

LIST OF SYMBOLS

Cm	-	Centimetre
m	-	Metre
%	-	Percent
g/cm^3	-	Grams per centimetre cube
g/m3	-	Gram per metre cube
g/ml	-	Gram per millilitre
g/mol	-	Gram per molecule
J/g	-	Joule per gram
mm	-	Millimetre
MPa	-	Mega Pascal
GPa	-	Giga Pascal
°C	-	Degree Celsius
TPa	-	Tera Pascal
W/mK	-	Watt per metre per Kelvin
K	-	Kelvin
nm	-	Nanometre
kg.cm3	-	Kilogram centimetre cube
phr	-	Part per hundred resin
τ_{ISS}	-	Interfacial shear strength
P	-	Peak force
kg	-	Kilograms

mm/min.	-	Millimetre per minute
mm/s	-	Millimetre per second
N	-	Newton
N/mm2	-	Newton per millimetre square
nm	-	Nano metre
kN	-	Kilo newton
W	-	Sample width
B	-	Sample thickness
K_{IC}	-	Fracture toughness
W_m	-	Matrix mass
W_f	-	Fibre mass
m	-	Mass
v	-	Volume
p_f	-	Kenaf density
p_m	-	Matrix density
°C/min	-	Degree celsius per minute
µm	-	Micron metre

CHAPTER 1

INTRODUCTION

This chapter describes the introduction of this research work, including the background, problem statement, objective, scope, and significance of the study. In this work, the analysis of the Fourier-transform infrared spectroscopy (FTIR) and porosity of the moisture-exposed PLA and TPU filaments are carried out.

1.1 Background of Study

3D Printing, often known as Additive Manufacturing (AM), is a contemporary manufacturing process that has grown in popularity. Physical models and complicated geometric constructions may be generated with great precision and at a reasonable cost using 3D printing. The military and other businesses have widely used customizable and uncomplicated 3D printing because of its ability to produce working models and conceptual models and prototypes in a short period (Liao et al., 2019).

According to Amza et al. (2021), Fused Deposition Modelling (FDM) is one of the most often utilized AM techniques because of its ease of use, flexibility, and low-cost technology that employs thermoplastic polymers with hot melt adhesive properties. The FDM technology creates three-dimensional (3D) structures by layering the primary material through the heated nozzle of the FDM 3D printer.

One of the most common raw materials for Polylactic Acid (PLA) plastic is maize starch, and it is commonly used in the production of the product. Typically, the monomer is produced from fermented plant starch. It is a thermoplastic aliphatic polyester utilized as the principal natural raw material in 3D printing.

PLA is an entirely biodegradable thermoplastic polymer made from renewable essential ingredients and is one of the most common 3D printing materials in the market today. TPU, or thermoplastic polyurethane, is the thermoplastic elastomer, a mix of rubber and plastic. PLA is a popular feedstock for desktop Fused Filament Fabrication (FFF) 3D printers. According to Wang et al. (2018), PLA is popular for 3D printing because it is easy to sand, paint, or post-process. As a result, the FDM 3D printer may create a solid product after the semi-liquid extrusion of the source material. TPU is a robust, flexible, durable polymer resistant to abrasions such as oils and lubricants. Because of its unique rubber-plastic blend, it is appropriate for a wide range of applications, including automotive, sports, and textile coatings, as well as breathable films. There are numerous other uses for thermoplastic polyurethane (TPU), including instrument panels for vehicles, wheels for sporting goods, medical equipment, drive belts, shoes for inflatable rafts, and a wide range of extruded film, sheet, and profile applications. TPU is also used in a wide range of other products. TPU is a highly recyclable and biodegradable material (Li and Huneault, 2011).

Humidity is one of the key factors influencing the filament's properties. If the PLA and TPU filaments are subjected to heavy moisture for an extended period, the filament has lost tensile strength at printing, allowing bubbles to emerge on the product's surface (Valerga et al., 2018). Furthermore, PLA and TPU are humidity sensitive, and exposure to excessive moisture causes changes in their characteristics. According to Mitchell et al. (2015), the elongation ratio, degradation rate, and average molecular weight increase when humidity increases. As a result, the mechanical properties of the 3D printed parts will decrease due to the changes in the chemical structure of the polymer with the exposure to water (H_2O). Therefore, in this study, the influence of humidity on the chemical bonding of two different thermoplastic polymers (PLA, TPU) was investigated through Fourier-transform infrared spectroscopy (FTIR) analysis. In addition, the porosity of the 3D printed parts exposed to various humidity conditions was examined through the densimeter by using the Archimedes Principle. Finally, the microstructure was analyzed using a Scanning Electron Microscope (SEM) machine.

1.2 Problem Statements

Humidity refers to the amount of moisture or water in the air, which has become a nemesis for 3D printing users who have embraced the FDM technology due to thermoplastic polymers. When stored in a humid environment, the polymeric filament absorbs moisture or humidity. Moisture saturation occurs after prolonged exposure to even mildly damp indoor air. PLA is an organic substance that quickly absorbs moisture and is particularly sensitive to trace water levels (Zaldivar et al., 2018). As a result, humidity and ultraviolet (UV) radiation can increase the breakdown of the filament, weakening it and causing prints to be inconsistent or of low quality. When the filament absorbs water, and the 3D printer heats it for extrusion, the water and heat combine to form steam, which causes the filament to bubble as it exits the hot end, resulting in an uneven surface on the print. When there is a large concentration of water vapor in the air, the humidity level will be elevated. According to Hossain et al. (2014), water altered the polymeric chain bonding of the printed material while also affecting the mechanical properties. Manufacturing effective 3D printed goods necessitate a thorough grasp of the mechanical characteristics of 3D printed components. Mechanical qualities of 3D printed objects typically differ from conventionally manufactured parts. Excessive humidity can cause the PLA and TPU filaments to degrade (Elmrabet and Siegkas, 2020).

Humidity influences the chemical bonding of the PLA and TPU polymer chains in 3D printed parts. As a result, a chemical analysis of the moisture-exposed filament is significant to ascertain the chemical bonding modifications between the humidity-exposed and original filaments (Shahmirzadi et al., 2021). Additionally, moisture may influence the porosity of the 3D-printed parts due to the inconsistent layer bonding mechanism resulted from poor material extrusion, in addition to the bubbles formation during printing. Therefore, a FTIR and porosity analysis are substanstial as FTIR spectroscopy is used to determine the amount of infrared (IR) radiation absorbed by a Micro Plastic (MP) sample, enabling the study of its molecular composition. An infrared spectrum is a material fingerprint, with absorption peaks matching the vibrational frequencies of the atoms' bonds. Since each polymer material comprises a unique combination of particles, no two compounds have the same infrared spectrum. Thus, FTIR can be used to determine the chemical composition of a polymer molecule (Nodari and Ricciardi, 2019). The filament was subjected to varying humidity levels to achieve a range of moisture concentrations.

On the other hand, moisture also influences the filament's diameter during storage. After 150 hours of operation under standard conditions, PLA filament may expand up to 40 micrometres before saturation. As a result, 3D printers rely on close tolerances and extremely thin layer heights. Additionally, the TPU elastomer is slightly hygroscopic, collecting moisture from the surrounding air. Assume that the filament becomes excessively saturated with water in an overly humid environment, like one near the seaside. In that instance, print quality difficulties such as air pockets may occur. However, no comparative study has been conducted to educate 3D printer users about the need to seal old filament in an airtight container with desiccant gels as an alternative to dry cabinets. So, it's important to do a study that looks at how humidity affects different thermoplastics.

1.3 Objectives of Study

The objectives of this study are as follows:

i. To identify the influence of water absorption (H_2O) in the polymeric chemical chain bonding of the humidity-exposed 3D printed PLA-TPU filaments using Fourier Transform Infrared Spectroscopy (FTIR).

ii. To measure the porosity of the humidity-exposed 3D printed PLA-TPU filaments restructured under different humidity conditions using a densimeter (Archimedes Principle).

iii. To observe the structural changes of the humidity-exposed 3D printed PLA-TPU filaments through microstructure analysis using a Scanning Electron Microscope (SEM) machine.

1.2 Scopes of Study

The scope of this study are as follows:

a) A red PLA and TPU filaments with a diameter of 1.75 mm, manufactured by SunLu, was used for this study. There is no specific PLA or TPU as the filaments are directly obtained from the manufacturer in a spool form.

b) Porosity analysis was conducted using a densimeter due to the lack of porosity equipment at the laboratory. The Archimedes Principle was explored in this method, where less density indicates a higher porosity level.

c) The humidity level was decided through four conditions as follows:

i. New PLA-TPU filament roll, which acts as the reference (control).
ii. PLA-TPU filament roll stored in the vacuum bag with 50g silica gels.
iii. PLA-TPU filament roll stored in the vacuum bag without silica gels.
iv. PLA-TPU filament roll stored in an open environment, exposed to a humidifier for a variant of 48, 96, and 150 hours. The printing parameters for all conditions were similar, with three replications of each conditional setting.

d) A house humidifier was employed for the humidity-exposure purpose, but the time (day/night) and ambiance temperature during the exposure for each condition was not controlled. Therefore, the study only considers the duration of exposure instead.

e) The composition of the sputter-coated material used was gold (Au) 80% and palladium (Pd) 20%.

f) Due to the FTIR chamber's size limitation, the dimension of samples was set to 10 mm to 10 mm (W x L) for both PLA-TPU filaments.

g) This study aims not to solve the humidity problems but to observe the polymer chain's structural changes when thermoplastic polymers are exposed to moisture. Therefore, it is hoped that the output of this study could create awareness among the FDM 3D printer users concerning the importance of storing their filament correctly.