MECHANICAL AND THERMOELECTRIC PROPERTIES OF FUSED DEPOSITION MODELING (FDM) FABRICATED ABS AND CABS – ZnO COMPOSITE

by

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
AM	Additive Manufacturing
ASTM	American Society for Testing and Materials
CB	Carbon Black
CABS	Conductive Acrylonitrile Butadiene Styrene
DMA	Dynamic Mechanical Analysis
FDM	Fused Deposition Modeling
PLA	Polylactic Acid
SEM	Scanning Electron Microscope
SLA	Selective Laser Melting
SLM	Selective Laser Sintering
SLS	Spark Plasma Sintering
SPS	Stereolithography Apparatus
TE	Thermoelectric
TGA	Thermogravimetric Analysis

SIFAT MEKANIKAL DAN TERMOELEKTRIK KOMPOSIT CABS/ZNO YANG DIHASILKAN MELALUI KAEDAH FDM

ABSTRAK

Dalam tesis ini, sifat mekanik dan termoelektrik komposit ABS/ZnO dan CABS/ZnO yang dihasilkan melalui kaedah FDM telah dikaji. Mudah diproses, berkos rendah dan mempunyai fleksibiliti yang tinggi adalah kelebihan Teknik FDM berbanding dengan teknik-teknik lain dalam bidang pemprosesan komposit polimer termoelektrik. Kajian ini fokus kepada kesan jarak percetakan (0 mm, 0.25 mm, 0.5 mm), corak percetakan (line dan rectilinear) dan peratus pengisi ZnO pada sifat tegangan, mekanik dinamik dan termoelektrik komposit CABS/ZnO yang dihasilkan melalui teknik FDM. Model Monte Carlo direka untuk meramal modulus tegangan dan kekonduksian di bawah parameter percetakan yang berbeza. Matlamatnya adalah untuk mengurangkan tempoh masa eksperimen dan mengoptimumkan parameter FDM untuk mendapatkan sifat komposit yang dikehendaki. Penggabungan pengisi dalam matriks ABS meningkatkan kekuatan tegangan dan modulus Young komposit sebanyak 90% dan 13% masing-masing. Keputusan ketumpatan dan keliangan membuktikan bahawa proses salutan mengurangkan lompang dalam komposit. Pemanjangan pada putus juga bertambah baik pada sampel yang digabung dengan pengisi yang bersalut berbanding dengan pengisi yang tidak bersalut. Pengurangan jarak percetakan menambah baik sifat-sifat komposit. Kekuatan tegangan maksimum iaitu 28.24 MPa diperolehi oleh sampel ABS/ZnO yang dicetak dengan gabungan corak line dan jarak percetakan 0 mm. Pencetakan corak garis diperhatikan mempunyai pergerakan penyemperitan yang lebih konsisten menyebabkan lekatan yang lebih baik di antara lapisan komposit, justeru mempunyai sifat tegangan yang lebih baik. Pengurangan kesan kekakuan pengisi pada sampel yang mempunyai jarak percetakan 5 mm menghasilkan modulus storage yang lebih rendah tetapi modulus loss dan faktor redaman yang lebih tinggi. Perubahan jarak percetakan 5 mm kepada 0 mm menambah baik kekonduksian elektrik dan pekali Seebeck sebanyak 90% dan 13% untuk komposit CABS/ZnO yang dicetak dengan corak line. Kekonduksian haba meningkat 6% hasil daripada kekurangan jarak percetakan yang menyebabkan pemindahan haba yang lebih baik apabila jurang antara filamen-filamen percetakan semakin berkurang. Perubahan yang kecil dalam kekonduksian haba berbanding kekonduksian elektrik dan pekali Seebeck menghasilkan nilai ZT yang tinggi, iaitu 5.7×10^{-5}. Kekuatan tegangan dan modulus Young komposit ABS meningkat 22% dan 18% masing-masing dengan penambahan 2.8 vol.% pengisi. Walau bagaimanapun, lekatan yang lemah antara karbon hitam, ABS dan ZnO menghasilkan kekuatan tegangan dan modulus komposit CABS yang rendah. Peningkatan modulus kehilangan disebabkan oleh penambah baikan kekakuan melalui penambahan pengisi. Modulus kehilangan dan faktor redaman yang lebih rendah diperolehi oleh komposit yang mempunyai pengisi yang lebih tinggi. Dengan penambahan 2.8 vol.% ZnO, sifat semikonduktor CABS telah meningkat 100% dan nilai ZT meningkat kepada 3.55×10^{-6}, > 500 kali melebihi CABS tanpa pengisi (5.57×10^{-9}). Perbezaan kecil (± 11%) diperhatikan dalam ramalan kekonduksian haba, kekonduksian elektrik dan modulus Young menunjukkan bahawa model ramalan setanding dengan data eksperimen. Daripada keputusan yang diperolehi, CABS/ZnO amat berpotensi dalam aplikasi termoelektrik dan model yang direka dicadangkan untuk digunakan dalam pelarasan parameter FDM.

MECHANICAL AND THERMOELECTRIC PROPERTIES OF FDM FABRICATED CABS/ZNO COMPOSITE

ABSTRACT

In this thesis, the mechanical and thermoelectric properties of fused deposition modeling (FDM) fabricated acrylonitrile butadiene styrene (ABS)/ zinc oxide (ZnO) and conductive acrylonitrile butadiene styrene (CABS)/ZnO were studied. The ease of processing, low cost and high flexibility of FDM technique are strong advantages compared to other techniques for thermoelectric polymer composite fabrication. This work focuses the effect of printing spacing (0 mm, 0.25 mm, 0.5 mm), printing pattern (line and rectilinear) and ZnO filler loading on the tensile, dynamic mechanical and thermoelectric properties of CABS/ZnO composites fabricated via FDM technique. A Monte Carlo prediction model was developed to predict the materials' tensile modulus and conductivity under different printing parameters. The aim was to reduce the experimental period and optimize the parameters for desired properties. The incorporation of precoated fillers in ABS matrix improved the tensile strength and Young's modulus of the composites by 90 % and 13 % respectively. Density and porosity results proved that the precoating process reduced the voids within the composites. Elongation at break was also improved in FDM fabricated samples with precoated fillers compared with non-precoated fillers. Reduce the printing spacing improved the properties of the composites. Maximum tensile strength of 28.24 MPa was observed for ABS/ZnO sample printed with the combination of line pattern and 0 mm printing spacing. Line pattern which exhibited a more consistent extruder motion allowed for more consistent adhesion between layers, and thus better tensile properties. The reduction of the stiffening effect of fillers at 5 mm printing spacing resulted in lower storage modulus but higher loss modulus and damping factor. Change from 5 mm to 0 mm printing spacing brought 90 % and 13 % improvement on electrical conductivity and Seebeck coefficient for CABS/ZnO composite printed with line pattern. The thermal conductivity improved 6 % with decreasing printing spacing, resulted from better heat transfer when the air gap between filament strands was getting smaller. A relatively small change in thermal conductivity when compared with their electrical conductivity and Seebeck coefficient resulted in high figure of merit (ZT), 5.7 x 10^{-5}. Tensile strength and Young's modulus of ABS composites increased 22 % and 18 % respectively with 2.8 vol.% filler loading. However, the poor adhesion between carbon black, ABS and ZnO resulted in low tensile strength and modulus of the CABS composites. Increase of storage modulus was associated to the stiffness improvement incorporation with the filler addition. The loss modulus and damping factor were lower for composites with higher filler loading. With the addition of 2.8 vol.% ZnO fillers, the semiconducting behavior of CABS has tremendously improved by 100 % and the ZT value increased to 3.55 x 10^{-6}, which was > 500 times greater than CABS without filler (5.57x10^{-9}). Minor discrepancy (± 10 %) was observed in predicting the thermal conductivity, electrical conductivity and Young's modulus with different printing spacing and pattern indicated that the prediction models were well fitted to the experimental data. From the results obtained, FDM fabricated CABS/ZnO showed much potential as a promising candidate for thermoelectric application and the developed model was recommended for use in optimizing FDM parameter for desired properties.

CHAPTER 1 : INTRODUCTION

1.1 Introduction

Global warming and climate change issue has led to the rapid development of thermoelectric (TE) materials as they are green options which can turn waste heat into electricity without pollution (Dubey & Leclerc, 2011). Conventional methods such as hot pressing, injection molding and spark plasma sintering (SPS) to fabricate TE materials are expensive, has low flexibility and are more time consuming (He et al., 2015). This thesis attempts to address this issue by fabricating TE materials using a desktop fused deposition modeling (FDM) 3D printer. Materials used are ABS and conductive ABS (CABS) as matrix with zinc oxide (ZnO) as reinforcement fillers. CABS is electrically conductive, less costly and ease of processing while ZnO has high electrical conductivity and Seebeck coefficient, and also is thermally stable making it a promising TE material (Jood et al., 2011). Testing was carried out to study the TE and mechanical properties of the composites. A Monte Carlo model was also developed to predict the Young's modulus, electrical and thermal conductivity of the composites with the objective to reduce the cycle of data collection in the future.

1.2 Background

Global warming has become a serious issue around the world due to human activities such as fuel combustion, waste heat and gases emission, etc. (Dubey & Leclerc, 2011). These man-made disruptive action and limitations of energy resources have motivated scientists to actively look for other renewable energy. One of the simplest methods is to recover the heat wastes through converting them into electricity from temperature gradient using thermoelectric material. Thermoelectric device possesses various unique advantages over other new energy resources, for example functioning without sound pollutions, no moving segments and long operating period, thus it has become one of the best renewable energy technology to substitute conventional energy material (Gao & Chen, 2016).

Hot pressing, SPS and melt spinnings are common ways to manufacture thermoelectric material. But, these approaches are expensive, less flexible, require high temperatures and more time (He et al., 2015). Hot pressing is one of the simplest methods to produce polymer based TE materials. Ball milling is usually required if hot pressing is used to reduce the grain size of the materials to achieve better TE efficiency. But, uncontrolled grain growth during hot pressing was reported (Nielsch et al., 2011). Furthermore, the ball milling process involves high energy input while hot pressing needs to be done at high temperature (Luo, 2014). SPS is another common method to fabricate TE materials. Cost is one of the main drawbacks for SPS method although particle size may be retained at ball-milled size after sintering. In melt spinning, the polymer material is melted and extruded through the spinneret and then directly solidified by cooling. However, high cost is needed for proper maintenance of the machine.

FDM has been extensively applied in medical devices, aircraft and aerospace, home-based appliance, toy, automobiles, and so on (Weng, Wang, Senthil, & Wu, 2016; Gao et al., 2015; Farahani, Dubé, & Therriault, 2016). The ease of manufacturing, low cost and good flexibilities of FDM method are great benefits compared to other fabrication methods (Christ, Schnabel, Vorndran, Groll, & Gbureck, 2015). Many scholars have presented their works in producing composites material via FDM technique (He et al., 2015; Dawoud, Taha, & Ebeid, 2015). However, there is limited literature focusing on TE behaviour of the FDM processed composite material. This thesis aims to provide a better understanding on it.

TE materials convert waste heat into electricity and is a green option for energy harvesting applications. Common TE materials like bismuth tellurium (BiTe) alloys, bismuth antimony tellurium (BiSbTe) alloys and rhenium tellurium (ReTe) alloys are costly and Te which is a rare earth element is toxic (Kamarudin et al., 2013). Therefore, substitute material such as polymer composite which is cheaper and easier to handle have been considered by researchers for thermoelectric application (Hamid et al., 2014; Deng et al., 2014; Dey, Bajpai, Sikder, Chattopadhyay, & Shafeeuulla, 2016). Various type of fillers such as carbon black, silica, and metal oxides have been added in the polymer to obtain better TE and mechanical properties (Harishanand et al., 2013; Du, Shen, Cai, & Casey, 2012). Oxide fillers have attracted high attention due to its low cost, ease of processing and more importantly its high thermal stability (Harishanand et al., 2013; Han, Li, & Dou., 2014). The efficiency of thermoelectric materials is represented by thermoelectric figure of merit (ZT). $ZT = (S^2\sigma) T/ \kappa$ where S denotes Seebeck coefficient, σ denotes electrical conductivity, T denotes absolute temperature, and κ denotes thermal conductivity. An effective thermoelectric material is required to have high electrical conductivity and Seebeck coefficient, but low thermal conductivity. CABS is a mixture of ABS and carbon black residue. It is electrically conductive, low cost and easy to process. To date, not many research have been published on this material. ZnO has high electrical conductivity and Seebeck coefficient, and also high thermal stability therefore could be a promising TE material (Jood et al., 2011). In view of the above-stated requirement, CABS/ ZnO composites have high potential as thermoelectric materials.

Monte Carlo simulation is a statistical method to predict the probability of certain outcomes which depends on repeated random sampling. It provides a quick method for assessing risk and helps researchers to make a quick decision without the need of repeated experiments and data collection cycle. This study also includes a Monte Carlo statistical model which could be used to predict Young's modulus, electrical and thermal conductivity of the composites. Crucial FDM printing parameters such as printing pattern and printing spacing can be modelled and Young's modulus, electrical and thermal conductivity values can be estimated. By having the prediction model, cycle of data collection is expected to be reduced in the future.

1.3 Problem statement

Conductive polymer such as CABS, is electrically conductive, therefore has been extensively studied for TE application. But the main drawback of the pure conductive polymer materials are their low strength and stiffness which restrict their extensive application. Reinforcement fillers are required so that the composite material could combine the merits of conductive polymer matrix and fillers within a single material for TE applications. Thus, there is a critical need to improve the properties of pure polymer parts by incorporating reinforcement filler to overcome their limitations (Kondawar et al., 2010).

When fillers are added into pure polymer, poor interfacial bonding between fillers and matrix could deteriorate the mechanical properties of composites. The debonding of fillers from the surrounding matrix is the indicative of inhomogeneous filler dispersion within matrix resulted from the poor interfacial adhesion bonding between fillers and matrix (Bikiaris et al., 2006). Therefore, surface treatment or modification is required to improve the interfacial adhesion between matrix and fillers.

Different printing parameters could bring significant effect on the properties of composites. Printing pattern and printing spacing are among the important parameters determining the performance of the composites. Experimental works to optimize the best and desired parameters will involve long duration of testing time and high cost of prototyping and testing. The more complex the part, the more expensive it is to manufacture. Therefore, it is essential to simplify these complex experimental work in alternative way including through simulation and modeling.

1.4 Research objectives

The research objectives of this thesis are:

1. To evaluate the effect of ZnO filler precoating on mechanical properties of ABS/ZnO composite

2. To study the effect of printing parameter (printing spacing and printing pattern) on physical, mechanical and thermoelectric properties of ABS/ZnO and CABS/ ZnO composite.

3. To investigate the effect of ZnO filler loading on physical, mechanical and thermoelectric properties of ABS/ZnO and CABS/ ZnO composite.

4. To develop Monte Carlo model and compare prediction result against experimental conductivity and modulus results.

1.5 Research scope

The scope of this thesis is divided into 3 stages which covered the fabrication of the composites, mechanical and thermoelectric properties characterization and Monte Carlo model development. ABS, CABS and precoated ZnO powder were used as raw materials. Pure ABS, pure CABS and composite samples were fabricated using desktop FDM 3D printer. Then, physical, mechanical and thermoelectric properties of the fabricated samples were characterized. Monte carlo model was developed and prediction results were compared against experimental and theoretical data.

1.5.1 Raw materials

ABS and Polylactic Acid (PLA) are the two most common thermoplastics used for FDM. In this thesis, ABS and CABS were used as the polymer matrix while zinc oxide (ZnO) powder was added as filler reinforcement by varying the filler loading to form composites. Comparing between ABS and PLA, ABS is less brittle and has higher glass transition and melting temperature, thus ABS is more suitable for applications which are subjected to heat and mechanical stress. ABS is the most widely used plastic in industry due to its rigidity and processability, heat stability and chemical resistance (Kumar et al., 2009; Ou, Gerhardt, Marrett, Moulart, & Colton., 2003). CABS which consists of an insulating matrix and conductive carbon black fillers is used to achieve the desired conductivity for TE purposes (Ou et al., 2003). Zinc oxide was chosen as the fillers due to its high thermal stability, high electron mobility and wide band gap which are the important properties required in a TE material (Batool, Kanwal, Imran, Jamil, & Siddiqi, 2012).

1.5.2 Fabrication method and printing parameter

The composites were manufactured in two dissimilar pattern (line and rectilinear pattern) and three printing spacing (0, 0.25, 0.5 mm) using RepRap Mendelmax 1.5 (Kludgineer, 2012) desktop FDM 3D printer. It is using FDM technology which has several advantages over other conventional methods like hot pressing, melt spinning and SPS. This method is cost effective, waste free and easy to process. The printing parameter tested were printing pattern and spacing because these are the two factors which strongly affected the mechanical properties of the composites based on several literature studies (Wang, Jiang, Zhou, Gou, & Hui, 2016; Wu et al., 2015; Fernandez, Calle, Ferrandiz, & Conejero, 2016; Mahmod, Qureshi, Goh, & Talamona, 2017; Torres, Cotelo, Karl, & Gordon, 2015).

1.5.3 Mechanical and thermoelectric properties characterization

The mechanical properties of fabricated composites were characterized through density measurement, tensile testing, dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The ZnO filler content based on different dispenser speed and the carbon content in CABS were characterized from thermogravimetric analysis (TGA). Density measurements were carried out to study the effect of filler loading and printing parameters. Tensile testing determined the maximum stress that the composites can take before breaking. Dynamic storage modulus, loss modulus and damping factor were obtained from DMA result. SEM were used to inspect the fracture surface of tensile samples in order to understand the failure mode of the composite.

TE properties including thermal conductivity, electrical conductivity, Seebeck coefficient and the thermoelectric figure of merit were studied to determine the thermoelectric efficiency of the composites. Thermal conductivity was measured via temperature differential method at room temperatures and electrical conductivity was characterized by using two-probe method. Seebeck coefficient and thermoelectric figure of merit were calculated based on respective equations.

1.5.4 Simulation method

In this thesis, a statistical prediction model was developed using R language (R Core Team, 2014). The objective is to simulate the real distribution of fillers under different filler loading and printing parameters and to calculate the Young's modulus, electrical and thermal conductivity of the FDM fabricated composite materials. Particle distribution in both line and rectilinear pattern with different filler content and printing spacing were simulated. Young's modulus, electrical and thermal conductivity of the composites were predicted and compared against experimental results and theoretical data. Model was run for numerous iterations to study the convergence rate. The advantages of developing this prediction model is to cut down the complexity and