The Use of Cellulose Nanofibers in Polymer Matrix Composites via 3D Printing

Ju Dong
Louisiana State University and Agricultural and Mechanical College, jdong8@lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Recommended Citation

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
THE USE OF CELLULOSE NANOFIBERS IN POLYMER MATRIX COMPOSITES VIA 3D PRINTING

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The School of Renewable Natural Resources

by

Ju Dong
B.Eng., Jiangnan University, 2012
M.S., North Carolina State University, 2014
May 2019
To my beloved family
ACKNOWLEDGEMENTS

I wish to express my appreciation to all professors, colleagues, and friends who gave me tremendous help and made great contributions to this dissertation.

I would like to thank Dr. Qinglin Wu, who recruited me, assigned me this amazing project, and gave me freedom in exploring different ideas. I would like to thank Korea Forest Research Institute for financial support to this work. I would like to thank my committee members: Dr. Li for agreeing to serve as my minor representative; Dr. Pojman for teaching me polymer physics; Dr. de Hoop for kindly introducing me to Dr. Boldor; and Dr. Mahmoud for his service as Dean’s representative.

I would like to thank Drs. Tiersch, Gutierrez-Wing, Liu, and Mr. Childress from Aquatic Germplasm & Genetic Resources Center (AGGRC), for their generous help with 3D printing. I would like to thank Dr. Zhao, and Kuo from Southern University (SUBR) for their help with characterizing EMI shielding properties. I would like to thank Dr. Boldor, Pranjali, and Arman for their help with the microwave heating.

I would like to thank my great labmates for leaving me a wonderful memory of conducting experiments and discussing results together with them. I would like to thank Jay and his crew for their help whenever I faced technical difficulties.

Last but not least, my deepest thanks go to my family, for their forever support and encouragement. Without them, I would not be here today. In particular, I would like to thank my parents for trusting and inspiring me all the time, with whom I can always share my ups and downs. I would also like to thank my longtime girlfriend, Xiuzhu, for driving me to a better person with her continuous love.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ iii

LIST OF TABLES .................................................................................................................. vi

LIST OF FIGURES ............................................................................................................... vii

ABSTRACT .............................................................................................................................. ix

CHAPTER 1. INTRODUCTION .............................................................................................. 1
  1.1 Background .................................................................................................................. 1
  1.2 Objectives .................................................................................................................. 5
  1.3 Organization of Dissertation ...................................................................................... 5
  1.4 References .................................................................................................................. 6

CHAPTER 2. POLY(LACTIC ACID) GRAFTED CELLULOSE NANOPIBERS ..................... 8
  2.1 Introduction ................................................................................................................ 8
  2.2 Experimental ............................................................................................................. 9
  2.3 Results and Discussion ............................................................................................. 13
  2.4 Conclusions .............................................................................................................. 23
  2.5 References ................................................................................................................ 23

CHAPTER 3. EFFECT OF NANOPIBER AND POST-FABRICATION ANNEALING TREATMENT ON COMPOSITE FLEXURAL PROPERTIES .............................................. 27
  3.1 Introduction .............................................................................................................. 27
  3.2 Experimental ............................................................................................................ 28
  3.3 Results and Discussion ............................................................................................ 32
  3.5 References ................................................................................................................ 41

CHAPTER 4. CARBONIZED CELLULOSE NANOPIBERS FOR 3D PRINTED CONDUCTIVE POLYCAPROLACTONE COMPOSITES ......................................................... 44
  4.1 Introduction .............................................................................................................. 44
  4.2 Experimental ............................................................................................................ 46
  4.3 Results and Discussion ............................................................................................ 49
  4.4 Conclusions ............................................................................................................. 61
  4.5 References ................................................................................................................ 61

CHAPTER 5. ACCELERATED ANNEALING FOR 3D PRINTED POLYLACTIC ACID VIA MICROWAVE HEATING ................................................................. 66
  5.1 Introduction .............................................................................................................. 66
  5.2 Experimental ............................................................................................................ 68
  5.3 Results and Discussion ............................................................................................ 72
  5.4. Conclusions ............................................................................................................ 85
  5.5 References ................................................................................................................ 85
CHAPTER 6. OVERALL CONCLUSIONS

6.1 Main Conclusions

6.2 Future Work

VITA
LIST OF TABLES

Table 2.1. DSC results for CNFs, PLA and PLA-g-CNFs; and composite filaments with various PLA-g-CNF content before and after annealing. .................................................................19

Table 2.2. A comparison of DMA data and static tensile data of composite filaments before and after annealing .................................................................21

Table 3.1. Configuration data of FFF technique used in this study.........................................................30
Table 3.2. Power law modeling parameters of the frequency sweep results for the printed composites before and after annealing.................................................................35

Table 3.3. A comparison of storage modulus (E'), flexural modulus (E), and flexural strain (ε max) at the maximum applied load (i.e., 18N) for the printed composites before and after annealing ..........................................................................................40

Table 3.4. Calculated average crystal size and FWHM corresponding to different crystal plane....40

Table 5.1. 3D printing parameters........................................................................................................71

Table 5.2. Microwave absorption and reflection at different levels of forward microwave power.74

Table 5.3. Specimen crystallinity and tensile strength as a function of annealing time for different annealing temperatures using oven or microwave annealing.................................................................78

Table 5.4. Annealing time to the maximum crystallinity and tensile strength for different annealing temperatures using oven or microwave annealing.................................................................82

Table 5.5. Average crystal size of microwave annealed 3D printed CCNFs-PLA at different annealing temperature and time.......................................................................................83
LIST OF FIGURES

Figure 2.1. Spectra of FTIR (a) for CNFs and PLA-g-CNFs; and high resolution XPS carbon spectra for (b) PLA, (c) CNFs, and (d) PLA-g-CNFs. .......................................................... 14

Figure 2.2. DSC and TG curves for PLA, CNFs, and PLA-g-CNFs: (a) first cooling; (b) second heating; (c) TGA; and (d) DTGA. ................................................................. 15

Figure 2.3. TEM images of CNFs and cross-sections of composite filaments after annealing: (a) CNFs; (b) PLA-g-CNFs; and (c–f) composite filaments with PLA-g-CN content at 0, 1, 3, and 5 wt%, respectively. .......................................................... 16

Figure 2.4. DSC thermograms for composite filaments with various PLA-g-CN content (0, 1, 3, and 5 wt%): (a) before and (b) after annealing. ......................................................... 18

Figure 2.5. Storage modulus, tan delta and reinforcement efficiency for composite filaments with various PLA-g-CN content (0, 1, 3, and 5 wt%): (a, c, and e) before and (b, d, and f) after annealing. .......................................................... 20

Figure 2.6. Composite filaments (before vs. after annealing) tensile properties as a function of PLA-g-CN content: (a) tensile modulus; and (b) tensile strength. ..................................................... 22

Figure 3.1. Storage modulus vs. temperature for the composites: (a) unannealed (unann.) and (b) annealed (ann.). .......................................................... 32

Figure 3.2. XRD patterns for the composites. Inset shows higher magnification image for unannealed and 0 wt% annealed. .......................................................... 33

Figure 3.3. Storage modulus vs. frequency for the composites: (a) unannealed at 35 °C, (b) annealed at 35 °C, and (c) annealed at 70 °C. .......................................................... 33

Figure 3.4. Stress-strain curves for the composites: (a) at 35 °C, and (b) at 70 °C. .......................................................... 37

Figure 3.5. SEM images of the edges for the composites after static bending test: (a-c) unannealed with 0, 1, and 3 wt% PLA-g-CN contents, respectively; and (d-f) annealed with 0, 1, and 3 wt% PLA-g-CN contents, respectively. Insets show higher magnification images. .......................................................... 37

Figure 3.6. Bending angles (i.e., angles between composite deflection and original position) of the composites after static bending test. .......................................................... 38

Figure 3.7. Creep and recovery strain vs. time for the composites at 70 °C: (a-b) unannealed, and (c-d) annealed. .......................................................... 39

Figure 3.8. Creep and recovery strain vs. time for the composites at 30 °C: (a-b) unannealed, and (c-d) annealed. .......................................................... 39
Figure 4.1. Fundamentals of CCNFs ................................................................. 50
Figure 4.2. Tensile properties of CCNF-PCL films ............................................. 53
Figure 4.3. Conductive PVP@CCNF-CB-PCL 3D printing filaments ...................... 55
Figure 4.4. EMI shielding properties of PVP@CCNF-CB-PCL composites ............... 58
Figure 4.5. Sensing properties of CCNF-CB-PCL composites .......................... 60

Figure 5.1. Schematic of microwave annealing method. Photograph CCNFs-PLA specimen in dumbbell shape, with two wide ends covered by a thin layer of copper tapes. Specimen narrow section reached a high temperature after annealed by microwave heating at 120 °C for 3 min. .... 69

Figure 5.2. SEM images of fiber morphologies. (a) CNFs; (b) CCNFs; and (c) Ball milled CCNFs. (d) Number fraction distributions of sizes of CNFs, CCNFs, and ball milled CCNFs. (e) Photographs of fiber-water suspensions (fiber concentration = 0.05 wt%) ..................... 74

Figure 5.3. Measured dielectric properties of dry CNFs and ball milled CCNFs. (a) Dielectric constant; (b) Dielectric loss factor; and (c) Dielectric loss tangent .......................... 75

Figure 5.4. Crystallization properties of PLA pellet, PLA filament, PLA-CCNFs filament, 3D printed PLA, and 3D printed CCNFs-PLA .......................................................... 76

Figure 5.5. Response of temperature to forward microwave power for 3D printed CCNFs-PLA (not covered with copper tape). Insets show IR images of specimens at maximum temperatures ... 77

Figure 5.6. Cooling curves for 3D printed specimen via oven or microwave annealing at 120 °C .. 79

Figure 5.7. (a) Specimen crystallinity measured as a function of annealing time at 120 °C for 3D printed neat PLA and CCNFs-PLA composite via oven or microwave annealing method. (b-d) DSC thermograms of oven annealed PLA, oven annealed CCNFs-PLA, and microwave annealed CCNFs-PLA, respectively, as a function of annealing time at 120 °C .................. 80

Figure 5.8. (a) Specimen crystallinity measured as a function of annealing time at 80 °C for 3D printed CCNFs-PLA composite via oven or microwave annealing method. (b-c) DSC thermograms of oven annealed CCNFs-PLA, and microwave annealed CCNFs-PLA, respectively, as a function of annealing time at 80 °C ......................................................... 81

Figure 5.9. Specimen tensile strength measured as a function of annealing time. (a) At 120 °C; and (b) At 80 °C ................................................................. 83

Figure 5.10. XRD patterns of microwave annealed specimen as a function of annealing time. (a) At 120 °C; and (b) At 80 °C ......................................................... 84

Figure 5.11. Crystallinity-tensile strength relationship at all annealing conditions ........ 84
ABSTRACT

Filament fused fabrication (FFF) is an extrusion-based 3D printing technology for manufacturing thermoplastic polymers. A major obstacle of 3D printed thermoplastic is the limited crystallinity resulting from a fast quench while material leaving the hot nozzle and solidifying quickly at the low-temperature platform. As a result, the mechanical performances of 3D printed thermoplastic is normally inadequate in comparison with conventionally manufactured ones (e.g., from injection molding). In this work, we developed two strategies for reinforcing and functionalizing 3D printed thermoplastic composites using cellulose nanofibers (CNFs) as nanofillers. Firstly, L-lactide monomers were grafted onto CNFs via ring-opening polymerization. The synthesized poly(lactic acid) grafted cellulose nanofibers (PLA-g-CNFS) compounded with Poly(lactic acid) (PLA) pellets improved storage modulus of the composite in both glassy state (low temperature) and rubbery state (high temperature). Dynamic mechanical analysis, including temperature ramp, frequency sweep, and creep-recovery, confirmed the enhancement of annealed composites to viscoelastic factors. Secondly, we converted CNFs into carbonized CNFs (CCNFs) through pyrolysis. When integrated with carbon black (CB) and polycaprolactone (PCL) matrix, the CCNF-CB-PCL conductive composites found applications for reinforcing, conducting, electromagnetic interference shielding, and deformation sensing. CCNFs also have superior dielectric properties. When irradiating CCNF-PLA composites with microwave, high dielectric loss CCNFs selectively absorbed microwave energy and generated localized heat in the surrounding regions. Such heat transferred to the adjacent PLA, triggering PLA chains to repack and form crystallites, and as a result, enhancing crystallinity as well as mechanical.

ix
CHAPTER 1. INTRODUCTION

1.1 Background

1.1.1 Annealing of 3D Printed Thermoplastics

Three-dimensional printing (i.e., rapid prototyping, or additive manufacturing) technology was invented in 1986 [1]. It has been revolutionizing the way of manufacturing components with complicated features for decades. This new paradigm presents great benefits, including bringing concept to real product in a short period of time, reducing usage of materials and costs, and manageable at multiple stages throughout the process. 3D printing has found applications in aerospace industries for creating complex lightweight structures, architectural industries for structural models, art fields for artifact replication, and medical fields for organs regeneration [2]. As of today, several 3D printing approaches, including fused filament fabrication (FFF), stereolithography (SLA), and selective laser sintering (SLS), have been well developed in both research laboratories and industrial facilities [3]. Among all types of 3D printing approaches, FFF certainly attracts tremendous interests due to its low cost, ease of use, and large commercial availability in the market. The FFF printing process is heat-assisted, during which the 3D printing filaments are driven into a heat block and heated up to a certain temperature (i.e., melting point), and then are extruded through a nozzle underneath the heat block. Extruded 3D printing materials deposit on a low temperature platform, cooling down, solidifying, and forming one layer. Using a movable 3D printing head, components are built up in a layer-by-layer manner.

For 3D printed semi-crystalline thermoplastics, annealing treatment between glass transition temperature (\(T_g\)) and \(T_m\) is straightforward to increase polymer crystal size and perfection [4]. Annealing has been found to improve polymer degree of crystallinity by developing nucleation and growing spherulitic superstructures. Upon heat, polymer chain movement was set to reach a
certain extent, leading to a crystallization process (either recrystallization or cold crystallization) [5]. As a result, enhanced crystallinity further improved the mechanical properties [6]. The more perfect arrangement of crystallites is obtained, the higher the crystallinity and mechanical performances will be achieved. Specifically, annealing contributes to the rapid increase in crystallinity in two stages. First is the growth of crystallites in the already existing nuclei spots; and the second stage is for the smaller crystallites combining to form bigger ones [7]. Annealing variants like time, temperature, applied stress together determine the annealing efficiency. Annealing temperature is closely associated with the substantial motion of polymer chain. High temperature could cause rupture of secondary bonds, resulting in poor mechanical properties. If annealing temperature is too high, thermal degradation could happen, especially in the crystalline regions containing tie molecules, which will significantly harm polymer mechanical behaviors [8].

1.1.2 Modification of Cellulose Nanofibers

Cellulose abundantly exists on earth. It is a linear homopolymer composed of D-glucopyranose units linked by β-1,4-glycosidic bonds. It has been very broadly used for hundreds of years, mainly in the paper and textile industries [9]. Cellulose nanomaterials – nanocellulose, is separated from cellulose microfibrils in wood, plants, algae, and bacteria [10]. It contains cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs) in terms of dimension and crystalline structures. CNF has 5-100 nm in diameter and several microns in length, yielding a high aspect ratio and unique features including high surface area, crystallinity, and overall strength [11].

Modification is critical to further tailor the CNF properties to meet more specific demanding applications. CNF surface is composed of a periodical distribution of hydroxyl groups, leading to two undesirable effects: strong self-assembled hydrogen bonding interactions and high hydrophilicity. Surface functionalization is very commonly applied for CNF modification. In this
study, polymer grafting as well as carbonization are briefly introduced to alter the properties of CNFs.

“Grafting from” approach proceeds by growing polymer chains from the active sites (i.e., hydroxyl groups) on cellulose backbone [6]. Various methods have been reported, such as free-radical polymerization, direct oxidation on cellulose backbone, ionic graft polymerization, ring opening polymerization, atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) [11]. Among all the polymerization methods, ring-opening polymerization is an interesting choice for grafting poly(lactic acid) (PLA) and polycaprolactone (PCL) as they are key materials for FFF, having L-lactic acid ε-caprolactone as monomers, respectively.

In general, CNF carbonization refers to the thermochemical process that turning organic molecules into inorganic solid carbon. After carbonization, the non-volatile matter of carbonized cellulose is a carbon-rich material composed of a complex mixture of polycyclic aromatic carbon sheets [12]. Pyrolysis is the most common method for producing carbonized cellulose nanofibers (CCNFs). Depending on the heating rate, the yield of carbonaceous material may vary. In the slow pyrolysis process, the main product is the carbonaceous solid, which is accounted for a relatively high yield range of 35-50 wt%. The fast pyrolysis generates a high yield of bio-oil with only 15-25 wt% of carbon solid residue. Regardless of the heating rate, the main mechanism associated with the carbon network formation keeps unchanged [13]. There are three stages involved from low to high temperature: dehydration, decarboxylation, and polycondensation [14]. The obtained carbonaceous material is often referred as bio-carbon which can be used as the substitute for petroleum-based carbon nanomaterials (e.g., carbon nanotubes). In order to achieve this goal, it is important to ensure that the synthesized bio-carbon have comparable properties, which are closely
related to the precursor types and treatment condition. Carbonization of cellulose typically yields a non-graphitized carbon phase. However, the graphitization capability for cellulose-derived carbon can be achieved by using high crystallized cellulose (i.e., CNFs) at high carbonization temperatures [15].

1.1.3 Applications of CNFs Integrated Polymer Composites

Theoretical longitudinal elastic modulus of CNFs is estimated to be ~167.5 GPa [16], which is stronger than steel. For this reason, CNF is considered as an ideal nanoscale reinforcing agent for most polymer matrices. CCNFs is moderate electrically conductive. Unlike conventional polyacrylonitrile based carbon nanofibers, CCNFs show no skin-core structure as the nanoscale precursor overcomes the incomplete oxidation of the core region during stabilization and the radial temperature gradient in the fiber during carbonization process [17]. Electromagnetic interference (EMI) shielding material is able to reflect or absorb EM radiations. Metals are commonly used in EMI shielding devices because of their high electrical conductivity. However, metals are expensive, rigid, heavy, and chemically active (e.g. oxidation and corrosion), so they are currently being replaced by carbon nanomaterials [18], which are lightweight, low cost, chemical stable, and easy to process. CCNFs may also find applications as sensing material. In terms of strain sensing, a wide range of applications have been demonstrated including: health monitoring, wearable electronics, and movement sensor [19]. From the perspective of designing and manufacturing a strain sensor, the electrical response of the CCNF conductive network is known to be related to the structural evolution. Microwave heating is the most efficient volume-heating process due to its excellent depth of penetration for the polymers [20]. CCNFs, as a dielectric nanofiller, can efficiently absorb microwave radiation and convert it into molecular vibrations/rotations through dipole moments, as an outcome of dipolar polarization [21]. The vibrations can subsequently add
to the heating level in polymer surrounding the CCNFs by friction mechanism. Such heat can be used for thermoset curing, thermoplastic annealing, or polymer thermal degradation [22].

1.2 Objectives

The objectives of this work are:

- To graft PLA onto CNFs and create a homogeneous dispersion of CNFs within PLA matrix, and as an outcome, enhancing both static and dynamic behaviors of 3D printed PLA.
- To develop a new CNF drying method in order to attain CCNFs with fibrous morphology. In the meanwhile, to discover CCNF multi-functionalities (i.e., reinforcing, conducting, EMI shielding, and deformation sensing) for 3D printed PCL composites.
- To develop a rapid thermal annealing method for 3D printed PLA, in order to enhance crystallinity and tensile strength in a rapid way.

1.3 Organization of Dissertation

- Chapter 1 provides an overall background information and the structure of this dissertation.
- Chapter 2 introduces the fabrication of PLA-g-CNFs/PLA bi-component filaments for 3D printing.
- Chapter 3 discusses the effect of annealing on the elastic features of 3D printed PLA using dynamic mechanical analysis.
- Chapter 4 describes the synthesis of CCNFs and discovers its multi-functionalities for 3D printed PCL composites.
- Chapter 5 presents a rapid annealing method for 3D printed PLA via microwave assisted heating.
1.4 References


CHAPTER 2. POLY(LACTIC ACID) GRAFTED CELLULOSE NANOFIBERS

2.1 Introduction

Bio-based polymers and polymer composites have been attracting enormous attentions for decades. Aliphatic bio-polyester - poly(lactic acid) (PLA), particularly draws interest due to its reasonable cost and moderate processability [1-3]. PLA is broadly used in automotive [4], additive manufacturing [5, 6], and biomedical [7] industries, where PLA parts are required to maintain demanding integrity under mechanical deformations.

A series of fillers, such as collagen [8], layered silicate [9], and montmorillonite [10], have been reported to strengthen PLA effectively. Nanocellulose is extracted from wood and plant cell walls, which are abundantly available on earth [11]. Nanocellulose includes cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs), and both have been studied extensively for reinforcing relatively weak materials such as starch [12], oil well cement [13], polyurethane [14], poly(vinyl acetate) [15], and PLA [1, 3, 16-20]. However, the enhancement of mechanical properties is generally limited, mainly because hydrophilic nanocellulose aggregates within hydrophobic polymers. To resolve this problem, chemical treatments, including urethanization, silylation and polymer grafting [21] were applied to alter CNF functional groups of nanocellulose. Chemically modified nanocellulose terminates with hydrophobic groups, holding a similar polarity as hydrophobic polymers, and thus, leading to a more uniform distribution in the polymer matrix. Compared with CNCs, CNFs are more suitable for reinforcing polymers (i.e., poly(ethylene oxide) [11], and polycaprolactone [22]) due to their great advantages of larger dimension and lower cost.

---

Thermal annealing is often used as a post-fabrication method to improve polymer mechanical properties [23]. Annealing parameters including time, temperature, and applied stress, are closely associated with polymer crystallinity [24]. Annealing is conducted below polymer melting point, at which stage polymer amorphous regions and less-perfect crystalline regions reorganize and combine into more perfect crystalline regions. Lower annealing temperature requires a much longer annealing time to achieve the maximum crystallinity, which is not ideally feasible from a practical prospective [25]. However, with the incorporation of nanofillers (e.g., WS2 nanotubes [26], and tunicin whiskers [27, 28]), polymers were observed to crystallize easier at lower annealing temperatures due to the nucleating effect of nanofillers.

The main objective of this work is to investigate the influence of chemical modified CNFs and the post-extrusion annealing treatment on the properties of PLA filaments. L-lactide monomers were first grafted onto CNFs via ring-opening polymerization. The synthesized poly(lactic acid) grafted cellulose nanofibers (PLA-g-CNFS) was compatible and dispersed evenly with the PLA matrix. From the incorporation of PLA-g-CNFS to the post-extrusion annealing treatment, and then to the crystallinity and mechanical properties alternation, a structure-process-property relationship was established, and the interactions among various factors were systematically evaluated.

2.2 Experimental

2.2.1 Materials

PLA (Ingeo Biopolymer 4032D) was purchased from NatureWorks (Minnetonka, MN, USA). 3,6-dimethyl-1,4-dioxane-2,5-dione (L-lactide), tin(II)2-ethylhexanoate (Sn(Oct)2), and organic solvents including toluene, acetone, methanol and chloroform were purchased from Sigma-Aldrich.
(St. Louis, MO, USA). CNFs were purchased from Daicel FineChem (Tokyo, Japan). All materials were used directly without further purification.

2.2.2 Preparation of PLA-g-CNFS

As-purchased CNFs (containing 25 wt% solid CNFs and 75 wt% water) were dried in vacuum at 65 °C for 24 hours because both catalyst (Sn(OCt)2) and L-lactide monomers were sensitive to moisture. Dry CNFs, toluene/acetone (3:1 volume/volume), and liquid Sn(OCt)2 mixed together and applied with a bath sonication (Ultrasonic Processor, MTI Corp, Richmond, CA, USA) for 30 min. L-lactide monomers were magnetically stirred in toluene at room temperature for 1 hour before mixing with the CNF suspension. The mass ratio of CNFs, L-lactide monomers and Sn(OCt)2 in the final mixture suspension was 1: 4: 0.1. Ring-opening polymerization took place in a three-neck round-bottom flask in a nitrogen atmosphere. The reaction temperature was controlled at 80 °C and stirring speed at 450 rpm. Polymerization was terminated after 24 hours, and the final products (PLA-g-CNFS) were obtained after rinsing with hot deionized water and cold methanol, filtering and drying to remove unreacted L-lactide residuals and homo-polymerized PLA.

2.2.3 Preparation of PLA-g-CNFS Composite Filaments

PLA and PLA-g-CNFS were separately suspended in chloroform and were magnetically stirred at 60 °C for 24 hours. The obtained PLA solution and PLA-g-CNNF suspension blended together and were stirred at room temperature for another 24 hours. The mixture suspension was kept in a conventional oven at 40 °C for a few hours to completely evaporate the chloroform. The obtained solid master batch was crushed into small pieces using a mechanical granulator (CIT-FW-200, Col-Int Tech, Irmo, SC, USA). Melt compounding was then conducted by blending the master batch with neat PLA pellets in a kinetic blender (Plasti-corder, C.W. Brabender Instruments,
Inc., South Hackensack, NJ, USA) at 180 °C for 15 minutes, with a mixing speed of 30 rpm. The well-mixed compounds were crushed again using a Granu-Grinder (C.W. Brabender Instruments, Inc.) and the grounding materials were fed into a filament extrusion system (Filabot EX2, Filabot, Barre, VT, USA) for producing filaments. Extrusion temperature was set at 165 °C and the nozzle diameter at 1.75 mm. A filament winding system (Filabot Spooler, Filabot, Barre, VT, USA) was used to collect the extruded filaments. The collected filaments were annealed in a vacuum oven at 120 °C for 1 hour and then gradually cooled down to room temperature in the vacuum for another 24 hours.

2.2.4 Characterizations of PLA-g-CNFs

CNF features before and after grafting PLA were compared using the Fourier transform infrared spectroscopy (FTIR, Bruker Alpha, Bruker Optics Inc., Billerica, MA, USA). The FTIR analysis was carried out with transmittance mode using a germanium tip which directly contacted the sample. The spectrum was measured between 3800-800 cm\(^{-1}\), with 64 scans and a resolution of 4 cm\(^{-1}\). X-ray photoelectron spectroscopy (XPS, Kratos Axis 165, Kratos Analytical Ltd, Manchester, UK) was carried out to determine the main elements (i.e., survey) and carbon-based bonds (i.e., C-C or C-H, C-O, O-C-O or C=O, and O-C=O) of the CNFs before and after grafting PLA. XPS data was analyzed using XPSPEAK software (version 4.1, Informer Technologies, Inc.). Thermal properties of CNFs, PLA and PLA-g-CNFs were measured using a differential scanning calorimetry (DSC, TA Q100, TA Instruments, New Castle, DE, USA) and a thermogravimetric analysis (TGA, TA Q50, TA Instruments, New Castle, DE, USA). Both DSC and TGA tests were conducted in nitrogen. The temperature ramp rates for DSC and TGA were 10 °C/min and 20 °C/min, respectively, and temperature ranges were 30-220 °C and 30-600 °C, respectively. For DSC test, the samples were rapidly heated up to 220 °C to eliminate the thermal history prior to
recording data. First cooling and second heating DSC thermograms were used for measurements. TGA data was used to calculate CNF concentration in PLA-g-CNPs [29]:

\[ W_{CNFs} \% = 1 - W_{at \ 255^\circ C} \% \]  

(1)

where \( W_{at \ 255^\circ C} \% \) is the weight percentage of PLA-g-CNPs at 255 \(^\circ\)C in TGA.

Transmission electron microscopy (TEM, JEM 1400, JEOL USA, Inc., Peabody, MA, USA) was used to observe morphologies of CNFs before and after PLA grafting. CNFs/water and PLA-g-CNPs/chloroform suspensions were prepared at concentrations of 0.05 wt%, followed by ultrasonic treatment for 30 minutes. Suspension droplets were deposited onto TEM grids and dyed with negative charged uranyl acetate for 5 minutes. TEM grids were dried in air for a few hours prior to the TEM observations.

2.2.5 Characterizations of Composite Filaments

The distribution of PLA-g-CNPs within the composite filaments were observed on the filament cross-sections by TEM. Selected composite filaments were carved to ultrathin slices using an ultramicrotome (Leica EM UC7, Leica Microsystems Inc., Buffalo Grove, IL, USA). The prepared slices deposited on the TEM grids, dyed and observed using the same procedure as for the CNF droplets. All TEM images were analyzed using ImageJ (NIH ImageJ Software). PLA crystallinity was calculated from the second heating thermograms:

\[ \chi_c = (\Delta H_m + \Delta H_c)/(1 - \emptyset)\Delta H_{m0} \times 100\% \]  

(2)

where \( \chi_c \) is crystallinity, \( \Delta H_m \) is enthalpy of fusion, \( \Delta H_c \) is cold crystallization enthalpy, \( \emptyset \) is the mass fraction of CNFs, and \( \Delta H_{m0} \) is the melting enthalpy for 100% crystalline PLA (i.e., 93 J/g) [2].

Thermomechanical properties of the composite filaments were measured using a dynamitic mechanical analyzer (DMA, TA Q800, TA Instruments, New Castle, DE, USA) in a 3-point
bending mode at a fixed frequency (i.e., 1 hz). Test temperature ranged from 30 to 120 °C with a heating rate of 3 °C/min. Tensile properties were measured using an universal tensile testing machine (Instron 5582 and Bluehill Software, Norwood, MA, USA). The filaments were cut to 20 mm long and fixed between two grips with a gauge length of 10 mm. The crosshead speed was 2 mm/min and load cell was 10 kN [2]. Six samples were tested for each composition to report average values.

2.3. Results and Discussion

2.3.1 Chemical Structure, Thermal Properties and Morphologies of PLA-g-CNFs

FTIR curves (Figure 2.1a) illustrate that PLA-g-CNFs had a highly pronounced peak at 1723 cm$^{-1}$ in comparison with neat CNFs. This peak represented distinguished carbonyl group (C=O) only existed in PLA [1, 30], which proved a successful grafting of PLA on CNFs. In the meantime, the diminished peak at 3310 cm$^{-1}$ corresponded to the reduced hydroxyl group (O-H) in PLA-g-CNFs, which suggested the substitution of O-H with grafted PLA.

XPS survey spectra reveals that carbon and oxygen were the two major elements for PLA-g-CNFs. In the high-resolution carbon spectra (Figure 2.1b-d), the carbon signals split into several component peaks, reflecting the local environments of carbon-based bonds. The mass concentration of C-C/C-H in CNFs before and after grafting PLA was calculated to be similar, indicating that ring-opening polymerization barely had influence on the composition of CNF backbones. It is clearly observed that only PLA-g-CNFs (Figure 2.1d) exhibit O-C=O and C=O/O-C-O peaks at 289.32 eV and 287.49 eV, respectively. In such a case, the noticeable presence of O-C=O in PLA-g-CNFs was attributed to the grafted PLA. Therefore, XPS results further confirmed the grafting of PLA on CNFs.
Figure 2.1. Spectra of FTIR (a) for CNFs and PLA-g-CNFs; and high resolution XPS carbon spectra for (b) PLA, (c) CNFs, and (d) PLA-g-CNFs

DSC thermograms (Figure 2.2a-b) show no evidence of glass transition temperature ($T_g$) or melting temperature ($T_m$) for CNFs due to the strong hydrogen bonding [14]. As a semi-crystalline polymer, PLA exhibited $T_g$ at 60.6 °C, cold crystallization temperature ($T_{cc}$) at 138.8 °C, and $T_m$ at 166.4 °C. PLA-g-CNFs had a highly pronounced crystallinity at 85.8%. Those crystalline regions were probably developed from C-C bonds between grafted PLA and crystalline parts of CNFs [31]. Presence of such interaction led to re-arrangements of grafted PLA chains along CNFs, transforming amorphous regions to crystalline regions. At the same time, the reduced onset melting temperature ($T_{m\text{, onset}}$) of PLA-g-CNFs indicated that newly formed crystallites tended to be small or imperfect crystals, which thereby leading to a low temperature melting process. In the cooling curves, PLA-g-CNFs had noticeable exothermic peaks in terms of crystallization process, which was also in an agreement with the statement that CNF crystalline parts prompted re-folding of
grafted PLA chains, driving the amorphous regions to crystalline regions. Nevertheless, PLA-g-CNFs exhibited no obvious glass transition behavior in either cooling or heating curve, which was because the sporadic crystalline regions of the grafted PLA hampered segments movement.

![DSC and TG curves for PLA, CNFs, and PLA-g-CNFs](image)

Figure 2.2. DSC and TG curves for PLA, CNFs, and PLA-g-CNFs: (a) first cooling; (b) second heating; (c) TGA; and (d) DTGA.

As shown in Figure 2.2c, both PLA and CNFs experience thermal degradations at ~350 °C, however, the degradation for PLA-g-CNFs could be separated to two stages [28, 32]. The first stage was the degradation of grafted PLA from 172 to 254 °C. Left shifted degradation temperature ($T_d$) was probably ascribed to the relatively low molecular weight of grafted PLA (Figure 2.2d). This was critical because grafted PLA chains were not expected to entangle heavily on the surface of CNFs, forming an essential thin layer of PLA shell would protect CNFs from agglomerations, and simultaneously kept CNFs to their original shape and size without lessening its hardening effect as a reinforcement agent. The second stage was the degradation of CNFs from 280 to 377
°C. Slightly left shifted T_d was probably ascribed to the fact that grafted PLA chains penetrated into CNF amorphous regions [32], increasing free space between CNF backbones and as a result, causing damages to secondary bonding (such as hydrogen bonding). In addition to the thermal stability, concentration of CNFs in PLA-g-CNFS was calculated at 67 wt% by Equation 1.

Figure 2.3. TEM images of CNFs and cross-sections of composite filaments after annealing: (a) CNFs; (b) PLA-g-CNFS; and (c–f) composite filaments with PLA-g-CNFS content at 0, 1, 3, and 5 wt %, respectively.

TEM images (Figure 2.3a-b) demonstrate that CNFs have a diameter of 6.7±2.0 nm while PLA-g-CNFS are 6.9±1.5 nm. Although the diameters of the two types of CNFs remained indifferent, CNF surface morphology changed from smooth to rough after grafting PLA. This was
caused by inhomogeneous ring-opening polymerization on the CNF surface as the amorphous parts were more flexible to react with L-lactide monomers.

2.3.2 Morphologies of Composite Filaments

Compared to neat PLA filaments (Figure 2.3c), the cross-sections of composite filaments (Figure 2.3d-f) exhibit significant presence of PLA-g-CNFs. The diameter of PLA-g-CNFs in composite filaments were in consistence with that from the suspension (~6.9 nm). The PLA-g-CNFs were homogeneously distributed in PLA with the loading level up to 5 wt%. Higher PLA-g-CNf content led to agglomerations, which were considered as defects and reduced the hardening effect. Moreover, aggregated PLA-g-CNFs reduced the number of available nucleating sites for crystallite growth.

2.3.3 Thermal Properties and Crystallinity of Composite Filaments

As shown in Table 2.1 and Figure 2.4, composite filaments display a constant $T_g$ (~62 °C) before (Figure 2.4a) and after annealing (Figure 2.4b). As discussed above, grafted PLA chains were highly crystallized, the consistent $T_g$ for all composite filaments were from PLA matrix, which was not affected by neither the incorporation of PLA-g-CNFs nor the annealing treatments. $T_m$ values for composite filaments were also comparable considering sample-to-sample variation. Because PLA chains normally had an incomplete conformational rearrangement via cooperative segmental movements from the rubbery state, at relatively low temperatures (i.e., below $T_m$), amorphous PLA chains had the potential to undergo an additional crystallization process (i.e., cold crystallization [26]). In this case, as the incorporated PLA-g-CNFs served as nucleating sites for crystallite growth and the C-C bonds limited free molecule motion of PLA chains in the discrete amorphous regions, as a result, amorphous PLA re-arranged to form small and imperfect PLA crystalline along the CNFs [33, 34]. The formation of this type of crystalline regions directly
reduced T_{m \text{ onset}} by \sim 4 \, ^\circ \text{C}. The decrease of T_{cc} also provided the evidence that composite filaments were easier to conduct cold crystallization at low temperatures than neat PLA filaments. Crystallinity of composite filaments increased as a function of PLA-g-CNFS content due to the increased availability of nucleating sites. Crystallinity of the 3 wt% composite filaments reached 7\% before annealing and 27.6\% after annealing, respectively. For neat PLA filaments, because of the lack of nucleating sites, crystallinity was rarely improved after annealing.

Figure 2.4. DSC thermograms for composite filaments with various PLA-g-CNFS content (0, 1, 3, and 5 wt \%): (a) before and (b) after annealing.

2.3.4 Mechanical Properties of PLA-g-CNFS Composite Filaments

As shown in Figure 2.5a-b, storage modulus (E’) of the composite filaments increased as a function of PLA-g-CNFS content in both glassy (30 \, ^\circ \text{C}) and rubbery (90 \, ^\circ \text{C}) states. The increase of E’ in the rubbery state was explained by the fact that PLA matrix became mechanically weak above T_g and PLA-g-CNFS made the major contributions to keep the E’ at a high level. In this case, PLA-g-CNFS content was the dominating factor in determining E’ in the rubbery state, and the reinforcing mechanism was most probably the tangling effect of cellulose network within the matrix [16, 35]. At 90 \, ^\circ \text{C}, unannealed 3 wt\% composite filaments had an E’ twice as much as neat PLA filaments. Similar polarity of grafted PLA and PLA matrix made them tightly entangled together, promoting
the adhesion between matrix and reinforcement as well as efficient stress transfer at the interface.

Solvent blending together with melt compounding had grafted PLA served as vehicles to introduce CNFs to the entire PLA matrix. Therefore, the higher uniformity of CNFs dispersed in PLA matrix was another reason for the increase of $E'$. The decrease of $E'$ in the 5 wt% composite filaments was related to the inhomogeneous dispersion of PLA-g-CNFS. As discussed above, incorporation of PLA-g-CNFS initiated the formation of small and imperfect PLA crystallites. It is these newly formed crystals that optimally keep composite filaments highly elastic in the glassy state.

According to Tables 2.1 and 2.2, the positive correlation between $E'$ at 30 °C and crystallinity also validates this statement. It should be noted that the $T_g$ (Figure 2.5c-d) of all conditions fall into a comparable temperature range (~86 ± 3 °C), which is in an agreement with DSC results.

Table 2.1. DSC results for CNFs, PLA and PLA-g-CNFS; and composite filaments with various PLA-g-CNFS content before and after annealing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_{m,onset}$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>PLA</td>
<td>60.6</td>
<td>138.8</td>
<td>-10.7</td>
<td>158.6</td>
<td>166.4</td>
<td>14.8</td>
<td>4.4</td>
</tr>
<tr>
<td>PLA-g-CNFS</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>144.6</td>
<td>162.8</td>
<td>26.3</td>
<td>85.8</td>
</tr>
<tr>
<td>Before annealing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 wt%</td>
<td>62.1</td>
<td>127.1</td>
<td>-33.5</td>
<td>157.9</td>
<td>167.2</td>
<td>38.5</td>
<td>5.4</td>
</tr>
<tr>
<td>1 wt%</td>
<td>61.2</td>
<td>103.5</td>
<td>-42.5</td>
<td>156.0</td>
<td>168.3</td>
<td>49.7</td>
<td>7.9</td>
</tr>
<tr>
<td>3 wt%</td>
<td>61.0</td>
<td>104.4</td>
<td>-36.7</td>
<td>155.1</td>
<td>167.9</td>
<td>43.3</td>
<td>7.2</td>
</tr>
<tr>
<td>5 wt%</td>
<td>61.2</td>
<td>102.6</td>
<td>-35.7</td>
<td>155.8</td>
<td>168.7</td>
<td>46.6</td>
<td>12.4</td>
</tr>
<tr>
<td>After annealing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 wt%</td>
<td>62.0</td>
<td>122.2</td>
<td>-33.7</td>
<td>158.8</td>
<td>166.5</td>
<td>39.2</td>
<td>6.0</td>
</tr>
<tr>
<td>1 wt%</td>
<td>60.9</td>
<td>103.6</td>
<td>-31.0</td>
<td>155.5</td>
<td>167.7</td>
<td>45.9</td>
<td>16.2</td>
</tr>
<tr>
<td>3 wt%</td>
<td>61.1</td>
<td>102.4</td>
<td>-25.7</td>
<td>156.3</td>
<td>168.4</td>
<td>50.8</td>
<td>27.6</td>
</tr>
<tr>
<td>5 wt%</td>
<td>60.7</td>
<td>102.0</td>
<td>-24.9</td>
<td>155.8</td>
<td>168.0</td>
<td>39.6</td>
<td>16.4</td>
</tr>
</tbody>
</table>

To better demonstrate the temperature dependence on reinforcement efficiency, $E'$ ratio of composite filaments to PLA filaments versus $E'$ of PLA filaments are plotted and the results are
shown in Figure 2.5e-f. Basically, reinforcement efficiency increased in the rubbery state and decrease in the glass state as a function of temperature. Consistent trends for all composite filaments illustrated that the incorporation of PLA-g-CNFs enhanced mechanical properties at all temperature ranges. However, PLA-g-CNFs agglomerations happened at 5 wt% loading, not only impairing the reinforcement efficiency in the rubbery state, but deferring PLA crystal growth in the glassy state.

Figure 2.5. Storage modulus, tan delta and reinforcement efficiency for composite filaments with various PLA-g-CNFn content (0, 1, 3, and 5 wt %): (a, c, and e) before and (b, d, and f) after annealing.

Tensile properties for composite filaments are shown in Figure 2.6 and Table 2.2. Similar to DSC and DMA results, the 3 wt% composite filaments after annealing possessed the highest Young’s modulus (~1.3 times of neat PLA) and tensile strength (~1.6 times of neat PLA). Theoretical models including Halpin-Tsai and Krenchel models were applied to compare the predicted value with experimental data. The Halpin-Tsai equation is given as below [3, 11]:

\[ E_{cm} = E_m(1 + \xi \eta \theta)/(1 - \eta \theta) \]  

(3)
\[ \eta = \frac{(E_r/E_m - 1)}{(E_r/E_m + \xi)} \]  \hspace{1cm} (4)

\[ \xi = \frac{(0.5 \times l)}{d} \]  \hspace{1cm} (5)

where \( E_{com}, E_m \) and \( E_r \) are the moduli of composite filaments, PLA matrix, and PLA-g-CNFs, respectively. \( \theta \) is the volume fraction of PLA-g-CNFs; \( \zeta \) is a shape parameter, which depends on the geometry and aspect ratio of PLA-g-CNFs. The length \( (l) \) of individual PLA-g-CNF was estimated to be 10 \( \mu m \) [3] and the diameter was 6.8 nm, leading to \( \zeta \) of 735.3.

Table 2.2. A comparison of DMA data and static tensile data of composite filaments before and after annealing.

<table>
<thead>
<tr>
<th>Filament Sample</th>
<th>DMA Data</th>
<th>Static Tensile Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E' )@30(^\circ)C</td>
<td>( E' )@90(^\circ)C</td>
</tr>
<tr>
<td>Before annealing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 wt%</td>
<td>2522.8</td>
<td>615.6</td>
</tr>
<tr>
<td>1 wt%</td>
<td>3117.8</td>
<td>937.4</td>
</tr>
<tr>
<td>3 wt%</td>
<td>4226.9</td>
<td>1081.2</td>
</tr>
<tr>
<td>5 wt%</td>
<td>3549.4</td>
<td>880.8</td>
</tr>
<tr>
<td>After annealing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 wt%</td>
<td>2364.0</td>
<td>661.5</td>
</tr>
<tr>
<td>1 wt%</td>
<td>4045.1</td>
<td>1099.0</td>
</tr>
<tr>
<td>3 wt%</td>
<td>5894.0</td>
<td>1702.9</td>
</tr>
<tr>
<td>5 wt%</td>
<td>3599.3</td>
<td>961.3</td>
</tr>
</tbody>
</table>

Krenchel equation is also given [3]:

\[ E_{comp} = E_m(1 - \theta) + \eta_l\eta_0 E_r \theta \]  \hspace{1cm} (6)

\[ \eta_l = 1 - ((\tanh (\beta l/2)/(\beta l/2)) \]  \hspace{1cm} (7)

\[ \beta = \frac{1}{(r(E_m / 2E_r \ln(R/r))^{1/2})} \]  \hspace{1cm} (8)

where \( \eta_l \) is the length correction factor, and \( \eta_0 \) is orientation factor, which is 3/8 when fibers are randomly distributed in matrix. \( r \) is the radius and \( R/r \) equals \((K_r/\theta)^{1/2}\), where is \( K_r \) is \( \pi/4 \) while considering the square packaging. \( \theta \) is calculated by:
\[ \theta = \frac{(W_r/\rho_r)}{((W_r/\rho_r) + (1 - W_r)/\rho_m)} \]  

where \( W_r \) is weight percent of PLA-g-CNPs in composite filaments, \( \rho_r \) is the density of PLA-g-CNPs and \( \rho_m \) is the density of PLA matrix. The following values are used for theoretical calculation: \( E_m = 2.7 \) GPa, \( E_r = 33 \) GPa [3, 36], \( \rho_m = 1.25 \) g/cm\(^3\), and \( \rho_r = 1.58 \) g/cm\(^3\).

Figure 2.6. Composite filaments (before vs. after annealing) tensile properties as a function of PLA-g-CNPs content: (a) tensile modulus; and (b) tensile strength.

The experimental and simulated Young’s modulus are compared in Figure 2.6a. For the PLA-g-CNPs content ranging 0 to 3 wt\%, both models predicted an acceptable trend of Young’s modulus in agreement with the experimental data. The Krenchel model was mainly used for simulating random fiber composites, leading to a reasonable estimate of Young’s modulus on composite filaments before annealing. The Halpin-Tsai model was mainly used for aligned fiber composites [3], thereby giving a higher estimate of Young’s modulus than the Krenchel model. Owing to the annealing treatment, composite filament Young’s modulus after annealing was comparable to the simulated value from the Halpin-Tsai model. At high PLA-g-CNPs content (i.e., 5 wt\%), PLA-g-CNPs agglomerations negatively influenced Young’s modulus, leading to difference between experimental and simulation. Although annealing was suggested to have a noticeable impact on modulus, the tensile strength was not that highly influenced according to Figure 2.6b.
2.4 Conclusions

L-lactide monomers were successfully grafted onto CNFs via ring-opening polymerization. Compared to CNFs, PLA-g-CNFS had a better dispersion in PLA with surface modification. The grafted PLA chains were highly crystallized, providing optimal nucleating sites for crystal growth. The extruded composite filaments had crystallinity increased from ~6 to ~12% before annealing and to ~28% after annealing. Higher crystallinity led to better mechanical properties for the composite filaments in the glass state. At 30 °C, the storage modulus for the composite filaments increased from ~2450 to ~4227 MPa before annealing and to ~5894 MPa after annealing. At 90 °C, the hardening effect of PLA-g-CNFS enhanced storage modulus for composite filaments from ~630 to ~1081 MPa before annealing and to ~1703 MPa after annealing. Composite filaments had a comparable Young’s modulus to the simulated values from Halpin-Tsai and Krenchel models. By combining chemical modifications of CNFs with post-extrusion annealing treatment, we demonstrated a strategy to prepare PLA composite filaments with CNFs evenly distributed within, achieving promising mechanical properties at a broad temperature range.

2.5 References


3.1 Introduction

3D printing technologies, consisting of fused filament fabrication (FFF), stereolithography (SLA), and selective laser sintering (SLS), have been well established in the personal, educational and professional aspects [1, 2]. Specifically, FFF 3D printing attracts a tremendous amount of interests due to its low cost, easy-to-use, and large commercial availability. Two dominant FFF 3D printing materials are acrylonitrile butadiene styrene (ABS) and poly (lactic acid) (PLA) [3]. Compared with petroleum-based ABS, PLA is more sustainable as it is originally derived from corn starch and biodegradable in compost [4]. Moreover, 3D printed PLA components have no thermal warping or curling issues, and the relevant mechanical properties are noticeably superior to ABS [5]. However, it should be noted that some disadvantages of 3D printed components such as poor layer adhesion [6] and high porosity [7] could result in inadequate mechanical performance in comparison with conventionally manufactured parts (e.g., from injection molding).

Cellulose nanofibers (CNFs) are extracted from biomass such as wood and plant. CNF has been extensively used as filler for polymer resins due to its extraordinary mechanical, physical and chemical properties [8]. However, strong hydrogen bonds within CNFs usually cause dispersion issues when mixing with hydrophobic polymers (e.g., PLA) [9]. CNF surface modification could be applied to resolve this issue. Our previous work reported the substitution of CNF terminated hydroxyl groups with grafted PLA short chains, which achieved a more homogeneous dispersion of CNFs in PLA matrix [10].

PLA experiences several heating-cooling cycles (e.g., resin synthesis, filament fabrication, extrusion) prior to end products. As a semi-crystalline polymer, PLA crystallite structures and
mechanical properties are dramatically influenced by its thermal history. Thermal annealing treatment is an approach to diminish the thermal history effect and rebuild PLA crystallinity, crystallite size, and mechanical properties by releasing frozen PLA molecular chains and letting them reorient and recrystallize [11]. With the incorporation of organic nanofillers, PLA should crystallize more easily due to the nucleation effect. For example, tunicin whiskers [12] and nanocellulose [13] were reported to successfully support the development of PLA crystallites through annealing.

PLA displays versatile viscoelastic behaviors in terms of time, temperature, force, and frequency. In this paper, we reported a strategy to improve the flexural properties of 3D printed PLA by introducing PLA-g-CNFs to the formulation and applying thermal annealing treatment after 3D printing. Using dynamic mechanical analysis (DMA) technique, the effects of PLA-g-CNFs and annealing treatment on the responses of 3D printed PLA to dynamic temperature and frequency changes, and static bending force were thoroughly investigated. Creep and recovery behaviors were also compared among composites with respect to PLA-g-CNFs loading rate and testing temperature. In the meantime, the size and structure of the annealing-induced crystallites, and layer morphologies after bending test were also compared.

3.2 Experimental

3.2.1 Materials

PLA (Grade: Ingeo Biopolymer 4032D) was purchased from NatureWorks Inc. (Minnetonka, MN, USA). (3S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione (L-Lactide), tin (II) 2-ethylhexanoate (Sn(OCt)₂), and organic solvents (i.e., toluene, acetone, methanol, and chloroform) were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). CNFs were purchased from Daicel FineChem Co. (Tokyo, Japan). All materials were used directly without further purification.
3.2.2 Preparation of PLA-g-CNFS/PLA Composite Filaments for 3D printing

The detailed procedure for producing PLA-g-CNFS/PLA composite filaments were reported in our previous work [10]. Briefly, PLA-g-CNFS were first synthesized via ring-opening polymerization, and then solvent-mixed with PLA to produce PLA-g-CNFS/PLA master batch. The master batch was diluted by compounding with PLA granules, and eventually extruded into PLA-g-CNFS/PLA composite filaments.

3.2.3 3D Printing Composites

3D printing parameters listed in Table 3.1. 3D printed composites had PLA-CCNFs concentrations at 1, 2, and 3 wt% for comparison. For the post-fabrication thermal annealing treatment, as-3D printed composites were placed in a vacuum oven (OV-DZF-6020, MTI Corp, Richmond, CA) at 120 °C for 12 hours. The composites were kept in the oven for another 24 hours for the cooling process.

3.2.4 Characterizations of 3D Printed Composites

DMA (Q800, TA Instruments Inc., New Castle, DE) temperature ramp, frequency sweep, static bending, and creep-recovery tests were carried out to study the relevant dynamic, static and viscoelastic properties. All tests were conducted in a 3-point bending mode with a span distance of 20 mm. For temperature ramp, the heating rate was set at 5 °C/min, and temperature range was between 30 and 100 °C, with a single frequency at 1 Hz. Glass transition temperature (T_g) was determined from the DMA tan delta curve. For frequency sweep, temperature was set at 35 and 70 °C, respectively, and frequency range was between 1 and 50 Hz. Power law equation was applied to analyze the frequency dependence of storage modulus:

\[ E' = K' \cdot \omega^{n'} \]  

(1)
where $K'$ is the power law constant, representing the elastic and viscous properties; $\omega$ is the frequency; and $n'$ is the frequency exponent. For static 3-point bending test, stress control mode was used with a ramp force rate at 0.5 N/min. Stress-strain behaviors were compared between two temperatures (35 vs. 70 °C). Replicated runs (i.e., three composites) were carried out for each formulation to obtain average values.

### Table 3.1. Configuration data of FFF technique used in this study.

<table>
<thead>
<tr>
<th>Printer model</th>
<th>FlashForge Creator Pro (Flashforge USA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient relative humidity (%)</td>
<td>58±3.5</td>
</tr>
<tr>
<td>Ambient temperature (°C)</td>
<td>22±3.0</td>
</tr>
<tr>
<td>Build direction</td>
<td>Y-direction (flat)</td>
</tr>
<tr>
<td>Build plate surface material</td>
<td>kapton blue tape</td>
</tr>
<tr>
<td>Build plate temperature (°C)</td>
<td>60</td>
</tr>
<tr>
<td>Cooling fan speed (%)</td>
<td>60</td>
</tr>
<tr>
<td>Design software</td>
<td>Autodesk Fusion 360</td>
</tr>
<tr>
<td>Filament diameter (mm)</td>
<td>1.75±0.17</td>
</tr>
<tr>
<td>Print temperature (°C)</td>
<td>210</td>
</tr>
<tr>
<td>Infill pattern</td>
<td>rectilinear (45°, -45°)</td>
</tr>
<tr>
<td>Infill rate (%)</td>
<td>100</td>
</tr>
<tr>
<td>Layer height (mm)</td>
<td>0.2</td>
</tr>
<tr>
<td>Nozzle diameter (mm)</td>
<td>0.6</td>
</tr>
<tr>
<td>Nozzle material</td>
<td>copper</td>
</tr>
<tr>
<td>Print speed (mm/min)</td>
<td>1800</td>
</tr>
<tr>
<td>Rectangular dimensions (L<em>W</em>T in mm)</td>
<td>60.0<em>12.8</em>3.2 (ASTM D790)</td>
</tr>
<tr>
<td>Retraction speed (mm/min)</td>
<td>1000</td>
</tr>
<tr>
<td>Slicer software</td>
<td>Simplify3D</td>
</tr>
</tbody>
</table>

Creep and recovery behaviors were investigated using the identical DMA setup. The 3D printed composites were firstly equilibrated at the target temperature (i.e., 30 or 70 °C), followed by an isothermal step for 5 minutes, a creep step for 30 minutes with a 1 MPa 3-point bending stress, and finally a recovery step for 90 minutes. The creep data were simulated using the four-parameter Burger’s model [14, 15],

$$\varepsilon = \frac{\sigma_0}{E_M} + \frac{\sigma_0}{E_K} \left(1 - e^{-\frac{t}{\tau}}\right) + \frac{\sigma_0}{\eta_M} t$$

(2)
where \( \varepsilon \) is the creep stain; \( \sigma_0 \) is the bending stress (i.e., 1MPa); \( \tau \) is the ratio of \( \eta_K \) to \( E_K \), which is the retardation time taken to produce 63.2\% or \((1 - e^{-1})\) of the total deformation in the Kevin unit; and \( t \) is the creep time. Four parameters \( E_M, E_K, \eta_M \) and \( \tau \) were defined by fitting the experimental data in Eq. (2) using the Gauss-Newton algorithm.

The recovery data was simulated by the Weibull distribution function,

\[
\varepsilon = \varepsilon_{KV} \left( exp \left( - \left( \frac{t-t_0}{\eta_r} \right)^{\beta_r} \right) \right) + \varepsilon_{\infty}
\]

where \( \varepsilon \) is the recovery strain after the removal of the applied force; \( \eta_r \) and \( \beta_r \) are the characteristic life and shape parameters over recovery time \( t \), respectively; \( t_0 \) is the recovery starting time (i.e., 35 min); \( \varepsilon_{KV} \) is the strain of the Maxwell dashpot; and \( \varepsilon_{\infty} \) is the strain of the Kelvin-Voigt element (i.e., permanent deformation).

Recoverable strain rate \( (X_{\text{recovery}}) \) was calculated by:

\[
X_{\text{recovery}} = \frac{1-\varepsilon_{\infty}}{\varepsilon_{\text{max creep}}} \times 100\%
\]

OriginLab software (version 9.0, OriginLab Corp., Northampton, MA) was used to fit experimental data to the models.

Edges of the 3D printed composites after static 3-point bending test were sputter coated (EMS 550X, Electron Microscopy Sciences Inc., Hatfield, PA) with a thin layer of gold prior to observation at the scanning electron microscope (SEM, JSM-6610LV, JEOL USA Inc., Peabody, MA). SEM was operated at a voltage of 10 kV using the secondary electron imaging (SEI) mode, and the images were acquired at magnification levels of 15x and 100x. The obtained SEM images were analyzed by ImageJ (NIH ImageJ Software). PLA crystal structures were examined by X-ray diffraction (XRD, Empyrean XRD, PANalytical Inc., Westborough, PA) with 2\( \theta \) angles.
ranging from 5 to 40° and a step size of 0.02°. The average crystallite size was calculated using the Scherrer equation [8]:

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]  \hspace{1cm} (5)

where \( \tau \) is the mean size of crystallite; \( K \) is the shape factor (i.e., 0.9); \( \beta \) is the full width at half-maximum intensity (FWHM); and \( \theta \) is the diffraction angle.

### 3.3 Results and Discussion

#### 3.3.1 Composite Response to Temperature

As shown in Figure 3.1a, the storage modulus (\( E' \)) of unannealed composites increased with PLA-g-CNFS loading rate. This reinforcement was achieved due to the incorporated PLA-g-CNFS restricting PLA mobility. However, the \( E' \) values decreased dramatically at 60 °C and yielded a failure at ~70 °C. This was probably because the matrix PLA chains started to move unrestricted above \( T_g \) despite of the presence of grafted PLA-matrix PLA interfacial bonding [10]. Likewise, the annealed composites (Figure 1b) first underwent a glassy plateau at low temperatures, after which the \( E' \) values decreased gradually from 70 to 100 °C. Table 3.3 shows that the \( E' \) values were significantly greater for annealed composites at any given temperature. For example, the \( E' \) values of the 1 wt% annealed composites were 35% and 158% greater than 1 wt% unannealed composites at 35 °C and 70 °C, respectively.

![Figure 3.1](image)

**Figure 3.1.** Storage modulus vs. temperature for the composites: (a) unannealed (unann.) and (b) annealed (ann.).
As shown in Figure 3.2, XRD patterns of unannealed composite are typical amorphous halo shapes ($2\theta$ between 7 and 26°) [16]. Such PLA amorphous region was generated as extruded PLA experienced limited time to arrange completely before immobilizing on the low-temperature platform. As the PLA-g-CNPs loading rate increased, the amorphous halo exhibited a tendency to convert to a peak at $2\theta = \sim 18^\circ$ (the inset in Figure 2), indicating the potential to form PLA crystallites.

Figure 3.3. Storage modulus vs. frequency for the composites: (a) unannealed at 35 °C, (b) annealed at 35 °C, and (c) annealed at 70 °C.
During the annealing treatment, PLA chains had sufficient time to rearrange and induced well-packed spherulite structures [11]. Especially for the composites with the incorporation of PLA-g-CNFs, multiple intensive diffraction peaks were observed at \(2\theta = 14.68, 16.43, 18.75, 22.13, 24.48, \) and \(28.7^\circ\), corresponding to the crystal planes \((010), (110/200), (203), (015), (206), \) and \((018)\), respectively [17]. Crystal plane \((206)\) represented disordered \(\alpha'\) form crystallites, which normally generated at low temperatures (i.e., \(\leq 120^\circ\)C); whereas the others were associated with the ordered \(\alpha\) form crystallites that generated at high temperatures (i.e., \(> 120^\circ\)C) [18, 19]. As shown in Table 4, annealing induced crystallites had two sizes at \(~150\) and \(~300\) Å. Compared to large crystallites remained at the same size level, small crystallites slightly grew up as PLA-g-CNFs loading rate increased. It is believed that both types of crystallites contributed to enhancing composite performances as small crystallites limited the mobility of PLA chains and increased \(T_g\); while large crystallites helped composites maintain stable shapes and integrities above \(T_g\) (in the rubbery state).

### 3.3.2 Composite Response to Frequency

Figure 3.3a shows typical viscoelastic curves for semi-crystalline polymers under DMA frequency sweep [20, 21]. At 35 °C, the \(E'\) values of unannealed composites increased for a short period of time before reaching a stable glassy state. Annealed composites showed a similar trend (Figure 3.3b), but with a significantly higher \(E'\) values in the entire frequency range. For example, the \(E'\) values of 3 wt% annealed composites at 1 Hz were 2.2x times of 3 wt% unannealed composites.

The experimental frequency sweep data essentially fitted the power law function for both annealed and unannealed composites. As shown in Table 3.2, increased \(K'\) values suggested that the incorporated PLA-g-CNFs effectively enhanced both elastic and viscous properties for the
composites. The indifferent $n’$ values indicated that composite reasonability to frequency was mainly determined by matrix regardless of incorporated PLA-g-CNFs or annealing treatment.

Table 3.2. Power law modeling parameters of the frequency sweep results for the printed composites before and after annealing.

<table>
<thead>
<tr>
<th>PLA-g-CNFs weight fraction (%)</th>
<th>$K’$ (Pa S$^n$)</th>
<th>$n’$</th>
</tr>
</thead>
<tbody>
<tr>
<td>before annealing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>651.55</td>
<td>0.012</td>
</tr>
<tr>
<td>1</td>
<td>1077.77</td>
<td>0.012</td>
</tr>
<tr>
<td>3</td>
<td>1425.05</td>
<td>0.023</td>
</tr>
<tr>
<td>after annealing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2378.56</td>
<td>0.012</td>
</tr>
<tr>
<td>1</td>
<td>2292.22</td>
<td>0.017</td>
</tr>
<tr>
<td>3</td>
<td>3239.30</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Time, temperature, and frequency together determine PLA viscoelastic performance. Increased temperature has the same effect on the measured viscoelastic properties as increased time or decreased frequency. When frequency sweep was carried out above $T_g$ (i.e., 70 °C), unannealed composites failed immediately. Annealed composites remained intact (Figure 3.3 c) with the $E’$values dropping initially in the 1-2 Hz frequency range, followed by a gradual increase, and eventually reaching a plateau at high frequency. This observation could probably be interpreted by a three-step first-order transition of PLA chains[22]. Time and temperature were the dominating factors at low frequency. For the first step, the “frozen” PLA was supposed to move unrestricted at 70 °C, but under low frequency (which is long time), PLA chains were more likely to release restraints from previous thermal history through energy dissipation, and thereby leading to the decrease of the $E’$values. For the second step, increased frequency dominated the $E’$values in a similar way to decreased temperature. The $E’$values gradually increased as the composites shifted from the rubbery state back to the glassy state. For the last step, annealed composites
completed the first-order transition, stabilized, and reached a glassy plateau. Regardless of temperature, $E'$ values of annealed composites were only frequency dependent at high frequency, which resulted in a comparable $E'$ values for annealed composites at 35 and 70 °C.

### 3.3.3 Composite Response to Static Bending Force

Figure 3.4 shows composite stress-strain curves from static 3-point bending under DMA maximum loading capacity (i.e., 18N total force). At 35 °C (Figure 3.4a), composite flexural moduli increased with PLA-g-CNFS loading rate (Table 3.3). As expected, annealing treatment further amplified such increase. For example, 3 wt% annealed composites had a flexural modulus of ~1538 MPa, which was 2.6 times of 0 wt% unannealed composites, and 1.9 times of 3 wt% unannealed composites. On the contrary, the same amount of 3-point bending force influenced composites significantly at 70 °C. As shown in Figure 3.4b, stress-strain curves of unannealed composites were rubber-like concave upwards shape with large flexural strains at ~5 MPa, while annealed composites displayed a linear elastic stress-strain curve with much reduced strains. Annealing treatment also significantly improved composite flexural properties at high temperature. For example, flexural modulus of 3 wt% annealed composites at 70 °C was ~9000% larger than 3 wt% unannealed composites. It should be noted that the reinforcement effect of PLA-g-CNFS on composite flexural properties was unnoticeable compared to the annealing treatment at 70 °C.

Figure 3.5a clearly shows that 0 wt% unannealed composites were partially damaged after 3-point bending test at 70 °C, as a result of layer-to-layer separation and single layer rupture. As shown in Figure 3.5b-c, 1 wt% and 3 wt% unannealed composites retained their layer integrities but were significantly bent under the applied force. The bending angles (Figure 3.6) were measured at 112°, 88°, and 84° for 0 wt%, 1 wt%, and 3 wt% unannealed composites, respectively. For annealed
composites, the 3D printed layers were tightly attached to each other, neither damages nor noticeable deformations were observed at the given loading levels as shown in Figure 3.5d-f.

Figure 3.4. Stress-strain curves for the composites: (a) at 35 °C, and (b) at 70 °C.

Figure 3.5. SEM images of the edges for the composites after static bending test: (a-c) unannealed with 0, 1, and 3 wt% PLA-g-CNFS contents, respectively; and (d-f) annealed with 0, 1, and 3 wt% PLA-g-CNFS contents, respectively. Insets show higher magnification images.
3.3.4 Composite Creep and Recovery Behavior

Figure 3.7a, c and Figure 3.8a, c show comparisons of creep behaviors in terms of the annealing treatment at 70 and 30 °C. Creep stages, including instantaneous deformation, primary, and secondary creeps, were observed. Comparing with annealed composites, creep strains were significantly increased at 70 °C for unannealed composites. This observation indicated that annealing treatment positively correlated to creep resistance, especially at high temperatures.

![Figure 3.6. Bending angles (i.e., angles between composite deflection and original position) of the composites after static bending test.](image)

Parameters from the Burger’s model, $E_M$ and $E_K$, increased with PLA-g-CNFs loading rate at a given temperature (Table 3.5). Since $E_M$ and $E_K$, respectively, represent the instantaneous elastic deformation and the stiffness of amorphous polymer chains, such increases indicated the improved composite elasticity. Both $E_M$ and $E_K$ values were sufficiently small for unannealed composites at 70 °C, which was ascribed to unannealed composites losing the relevant elasticity in the rubbery state. Likewise, small $\eta_M$ values were observed from the absence of either crystalline regions or structural orientation in amorphous regions at the second creep stage [15, 23-26]. At 30 °C, $\tau$ values were comparable among composites regardless of annealing treatment, which suggested
similar changing rates of $\eta_K$ and $E_K$ values. Increased $\tau$ values at 70 °C resulted from improved composite viscous properties.

Figure 3.7. Creep and recovery strain vs. time for the composites at 70 °C: (a-b) unannealed, and (c-d) annealed.

Figure 3.8. Creep and recovery strain vs. time for the composites at 30 °C: (a-b) unannealed, and (c-d) annealed.
Table 3.3. A comparison of storage modulus ($E'$), flexural modulus ($E$), and flexural strain ($\varepsilon_{\text{max}}$) at the maximum applied load (i.e., 18N) for the printed composites before and after annealing.

<table>
<thead>
<tr>
<th>PLA-g-CNFS weight fraction (%)</th>
<th>Dynamic</th>
<th>Static</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E'$ at 35 °C (MPa)</td>
<td>$E'$ at 70 °C (MPa)</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0</td>
<td>1952.45*</td>
<td>872.23</td>
</tr>
<tr>
<td></td>
<td>(169.37)</td>
<td>(330.29)</td>
</tr>
<tr>
<td>1</td>
<td>2257.55</td>
<td>1131.38</td>
</tr>
<tr>
<td></td>
<td>(435.64)</td>
<td>(172.12)</td>
</tr>
<tr>
<td>3</td>
<td>2691.49</td>
<td>742.68</td>
</tr>
<tr>
<td></td>
<td>(211.37)</td>
<td>(20.64)</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
</tbody>
</table>

Before Annealing

<table>
<thead>
<tr>
<th>PLA-g-CNFS weight fraction (%)</th>
<th>Dynamic</th>
<th>Static</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E'$ at 35 °C (MPa)</td>
<td>$E'$ at 70 °C (MPa)</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0</td>
<td>2274.23</td>
<td>1990.79</td>
</tr>
<tr>
<td></td>
<td>(79.47)</td>
<td>(70.35)</td>
</tr>
<tr>
<td>1</td>
<td>3038.97</td>
<td>2918.95</td>
</tr>
<tr>
<td></td>
<td>(182.51)</td>
<td>(325.43)</td>
</tr>
<tr>
<td>3</td>
<td>3354.25</td>
<td>2618.74</td>
</tr>
<tr>
<td></td>
<td>(83.76)</td>
<td>(181.09)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PLA-g-CNFS weight fraction (%)</th>
<th>Dynamic</th>
<th>Static</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E'$ at 35 °C (MPa)</td>
<td>$E'$ at 70 °C (MPa)</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0</td>
<td>298.1/0.27</td>
<td>161.5/0.50</td>
</tr>
<tr>
<td>1</td>
<td>298.1/0.27</td>
<td>164.8/0.49</td>
</tr>
</tbody>
</table>

Table 3.4. Calculated average crystal size and FWHM corresponding to different crystal planes.

<table>
<thead>
<tr>
<th>PLA-g-CNFS weight fraction (%)</th>
<th>Average crystal size (Å)/FWHM (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(110/200)</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------</td>
</tr>
<tr>
<td>before annealing</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Amorphous</td>
</tr>
<tr>
<td>1</td>
<td>Amorphous</td>
</tr>
<tr>
<td>3</td>
<td>Amorphous</td>
</tr>
<tr>
<td>after annealing</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Amorphous</td>
</tr>
<tr>
<td>1</td>
<td>298.1/0.27</td>
</tr>
<tr>
<td>3</td>
<td>298.1/0.27</td>
</tr>
</tbody>
</table>

As shown in Figure 3.7b, d and Figure 3.8b, d and Table 3.6, improved creep recovery for 3D printed composites was validated by the fact that $\varepsilon_{\infty}$ decreased as PLA-g-CNFS loading rate increased. Comparing with unannealed composites, annealed composites were protected from permanent damage at high temperature, which was in an agreement with the SEM observations.
However, in terms of $x_{\text{recovery}}$ at a given temperature, incorporated PLA-g-CNFs and annealing treatment had no obvious impact on the recovery rate.

3.4 Conclusions

PLA/PLA-g-CNFs composites were 3D printed via FFF technique. Surrounding the PLA-g-CNFs nucleation sites, both $\alpha$ and $\alpha'$ phases matrix PLA crystallites were induced and developed during post-fabrication thermal annealing treatment. Annealing induced crystallites, together with the PLA-g-CNFs, helped confine the free motion of matrix PLA molecular chains, upshifted $T_g$, and improved composite resistance to thermal, dynamic oscillation, and static bending forces at both low and high temperatures. In particular, dynamic storage and static flexural moduli of 3 wt% annealed composites were, respectively, 72% and 156% larger at 35 °C, and 200% and 15194% greater at 70 °C in comparison with as-3D printed composites (i.e., 0 wt% unannealed composites).

Experimental creep and recovery data fitted in the four-parameter Burger’s model and Weibull distribution function. Both experimental data and simulated parameters confirmed the increased creep resistance and recovery properties of the 3D printed composites with the incorporation of PLA-g-CNFs and applied annealing treatment. This work provides a facile strategy to enhance flexural properties of FFF 3D printed PLA composites and demonstrates the synergetic effect of the incorporated PLA-g-CNFs and post-fabrication annealing treatment.

3.5 References


CHAPTER 4. CARBONIZED CELLULOSE NANOFIBERS FOR 3D PRINTED
CONDUCTIVE POLYCAPROLACTONE COMPOSITES

4.1 Introduction

Polymer-nanofiller conductive composites can be found as crucial parts for batteries [1], sensors [2], electromagnetic interference (EMI) shielding [3], and electrostatic discharge (ESD) protection [4]. The conductive nanofillers are generally one-dimensional carbon nanomaterials such as carbon nanofiber [5], carbon nanotube [6], and graphene [7]. Carbon nanofibers are compatible with both isotropic and anisotropic polymer systems, providing polymer matrix with enhanced conductivity as well as mechanical, thermal, and dielectric properties. Polymer composites obtain benefits from carbon nanofibers such as chemical stability, competitive cost, and high aspect ratio [8]. Industrial carbon nanofibers with controllable structure and diameter are growing from hydrocarbon feedstock or carbon monoxide on metal catalyst [9]. However, chemical vapor deposition approach is considered as energy consuming, process complicated, and costly for small-scale processing. An alternative way to produce carbon nanofibers is by pyrolyzing carbon nanofiber precursors (e.g., polyacrylonitrile (PAN) [10], pitch [11], and cellulose [12]) at an inert atmosphere. The precursors are normally required to have fibrous morphology such that the obtained carbon nanofibers would be competitive with vapor grown carbon nanofibers in terms of dimension, structure, and properties.

Cellulose molecules are self-assembled to form microfibril structures that avoid additional spinning steps to form fibers which is normally required by PAN and pith. Cellulose microfibrils can be further separated to yield cellulose nanofibers (CNFs) via combined chemical hydrolysis and mechanical homogenization. CNFs have nano-scale diameters (5-20 nm), micro-scale lengths, and unique fiber properties [13], which create an opportunity for producing carbon nanofibers.
Carbonization of cellulose fibers is essentially a thermochemical decomposition process that turns organic cellulose into inorganic carbon. Cellulose carbonization process is mainly associated with four continuous stages from low to high temperature [14]: desorption of free water and structure water; cleavage of cellulose side groups; session of cellulose backbones; and graphitization. Relevant studies were completed in the 1960s, however, only until very recently, an Australian group first reported carbonization of CNFs for producing carbon nanofibers [15]. The most critical step for CNF carbonization is to obtain dry CNF precursors. Improper drying approaches can cause intensive CNF agglomerations, which will lead to material heterogeneity after carbonization. Carbonized CNFs (CCNFs) produced from improper form of precursors tend to lose their unique fibrous morphology and desirable properties as a functional nanomaterial.

Unfortunately, commonly used CNF drying approaches including freeze drying [16], oven drying [17], spray drying [18], and supercritical drying [19] seem to be inappropriate for producing qualified dry CNFs for carbonization. In this work, we developed a solvent drying approach to acquire dry CNFs from the relatively concentrated aqueous suspension. For the first time, we synthesized carbonized solvent dried CNFs without loss of fibrous morphology. We investigated CCNF fundamental properties and explored its prospect to serve as a multifunctional filler for thermoplastic polycaprolactone (PCL) composites. Demonstrated applications included reinforcing PCL composite films for improving tensile performances, combining with carbon black (CB) for producing a highly electrically conductive hybrid, and 3D printing conductive composites for EMI shielding and deformation sensing.
4.2 Experimental

4.2.1 Materials

PCL pellets (Capa 6800) were purchased from Perstorp (Malmö, Sweden). CNFs (containing 75 wt% of water) were purchased from Daicel FineChem (Osaka, Japan). Carbon black (TIMCAL SUPER C65) was purchased from MTI corp. (Richmond, CA). Polyvinylpyrrolidone (PVP, $M_w=40000$) was purchased from Sigma-Aldrich (St.Louis, MO). Organic solvents including acetone, toluene, and chloroform were purchased from Hach (Loveland, CO), and were used directly without further purification.

4.2.2 Synthesis of CCNFs

Three approaches were applied to desiccate CNFs from aqueous suspension. Oven drying was carried out by removing water in vacuum oven at 95 °C for 12 hours. Freeze drying was carried out by sublimating 3 wt% CNF-ice solids. Solvent drying was a solvent exchange process which transmitted CNF from water to acetone, and finally to toluene. Obtained CNF-toluene suspension was applied to a high intensity ultrasonication (MTI MSK-USP-3N-LD Ultrasonic processor) treatment for 30 min and vaporized toluene at room temperature to acquire dry CNFs. Acetone was recycled by rotary evaporator (Yamato RE 300) and reused for solvent drying approach. Dry CNF precursors were stabilized at 240 °C in air for 8 hours, followed by a carbonization process at 1000 °C under the protection of nitrogen for 2 hours in a furnace (MTI GSL 1100x). Fundamentals of CCNFs (e.g., morphology, crystal structure, and elemental composition) were characterized using scanning electron microscopy (SEM, FEI Quanta 3D Focused Ion Beam), high-resolution transmission electron microscope (HRTEM, JEOL 2011), X-ray diffraction (XRD, PANalytical Empyrean XRD), X-ray photoelectron spectroscopy (XPS, Scienta Omicron ESCA 2SR XPS), and particle size measurement (Microtrac S3500).
4.2.3 Fabrication of CCNF-PCL Composite Film

Composite films were fabricated by a solution casting method using CCNF-PCL-chloroform solution. Tensile testing samples were sliced to dumbbell shape to meet the requirement of ASTM D638 standard (type V). Tensile data (i.e., toughness, modulus, strength, and strain at break) were collected by a tensile test machine (Instron model 5582) and analyzed by Bluehill software (Version 2.0). Instron was equipped with a 1 kN load cell. Tensile test employed two grips (with a distance of 7.62 mm) to hold the two wide ends of the dumbbell shaped composite film. The specific testing speed were set at 10 mm/min. Average tensile values were obtained from five samples of which fractured at the narrow part. Composite film fracture surfaces after tensile test were observed by an optical microscope (Zeiss Axiovert 200 Inverted Microscope) and SEM.

4.2.4 Synthesis of PVP@CCNF-CB Hybrid

CNFs mixed with Polyvinylpyrrolidone (PVP) and stirred in water for 12 hours. Similar to the solvent drying process for CNFs, PVP-CN formation was transferred from water to acetone, and subsequently mixed with carbon black (CB). The solid mixture (PVP-CN-CB) was centrifuged to remove acetone and re-dispersed in toluene. After an ultrasonication treatment, toluene was evaporated at room temperature for a few days. Dry PVP-CN-CB was obtained and later carbonized to produce PVP@CCNF-CB hybrid.

4.2.5 Fabrication of 3D Printing Conductive Filament

Conductive fillers (i.e., CB, CCNF-CB, and PVP@CCNF-CB) mixed with PCL pellets and extruded into 3D printing conductive filaments at 90 °C. Extrusion temperature, and nozzle diameter were set at 90 °C, and 1.75 mm for the single screw extruder (Filabot EX2). Extruded filaments were cut into small segments and refed in the extruder for three times to obtain filaments
with conductive fillers homogeneously dispersed. Four-probe method was used to measure filament electrical resistivity ($\rho$) by:

$$\rho = \frac{R A}{l}$$

where $l$ is 3cm, $A$ is filament cross-section area, and $R$ is resistance measured by a digital multimeter (Keithley 2100).

**4.2.6 Fabrication of EMI Shielding Composites**

EMI shielding samples were 3D printed in a cylinder shape with 1.5 mm inner diameter, 3.5 mm outer diameter, and 2 mm thickness. EMI shielding properties were measured with a vector network analyzer (Agilent N5230c). A coaxial line method was used for the scattering parameter measurements in a frequency range of 4-26 GHz. 3D printing EMI shielding sample outer surface morphology were observed by SEM.

**4.2.7 Fabrication of Deformation Sensor**

Electromechanical behaviors of conductive filaments were investigated by simultaneously measuring real-time change of resistance during the stretching-bending test. Deformation sensors were made from 20 wt% CCNF-CB-PCL and compared in terms of fabrication methods. Film-type sensor was simply fabricated by drop casting CCNF-CB-PCL-chloroform suspension onto glass petri dish and sliced into rectangular after chloroform was evaporated. 3D printing sensor was overall in a rectangular shape identical to film-type sensor, but with hexagon array located in the center region. Finite element analysis (FEA) (ANSYS Workbench) was performed to compare stress distribution on sensor surface in terms of fabrication methods. Autodesk Fusion 360 software was used to sketch 3D models of two types of sensors. FEA parameters were based on the obtained mechanical properties of neat PCL films. Mesh refinement of the numerical analysis were employed with 990 and 198 elements for film-type sensor and 3D printing sensor,
respectively. The simulated results were presented in normal stress and von Mises stress maps, as an outcome of 3% tensile strain applied in the longitudinal direction. Stress maps used false-color non-linear scales. The length of filament sample for cyclic stretching-bending was in the range of 10-15 mm. Electrical resistance was measured using a four-probe method. Electromechanical stability in response of cyclic mechanical deformations was evaluated by repeatedly (5 cycles) stretching and bending the filaments with a tensile test setup. Maximum tensile and bending strains were set at 3% and 2%, respectively. The electromechanical data including short-term (i.e., 5 cycles) cyclic stretching-bending, electrical resistance, and long-term (i.e., 300 cycles) cyclic tensile data were all collected within composite elastic regime (strain = 3%).

4.3 Results and Discussion

4.3.1 Fundamentals of CCNFs

Figure 4.1a shows TG curves for the dry CNF precursors from three drying approaches (i.e., oven, freeze, and solvent drying). Rapid weight loss between 240 and 390 °C was due to CNF thermal decomposition [20]. For solvent dried CNFs, slightly lower (~15 °C) onset degradation temperature and less char residue at 800 °C indicated a higher sensitivity to temperature as heat flow penetrated and decomposed the internal CNFs easily through the exposed large surface area [21]. Both oven and freeze dried CCNFs are absence of fibrous morphologies after forming agglomerated particulates and flakes, respectively. Solvent dried CCNFs preserve their fibrous morphology (Figure 4.1b), having both single fiber and tangled fiber bundles observed. By measuring the sizes of CCNFs in their water suspensions (Figure 4.1c), it is concluded that solvent dried CCNFs remain in nanoscale (< 1 μm.), while the majority of the freeze dried CCNFs fall in the range of 1-5 μm. Not surprisingly, oven dried CCNFs possessed not only the largest sizes but also the most widespread size distribution from 5 to 20 μm.
Figure 4.1. Fundamentals of CCNFs. (a) TG curves of CNFs from three drying approaches. Insets show that oven and freeze dried CNFs heavily aggregated while solvent dried CNFs lied in fibrous form. (b) SEM image of solvent dried CCNFs. (c) Number fraction distributions of three types of CCNFs sizes from 0.1 to 100 μm. Insets show photographs of dispersion state of CCNFs in 0.5 wt% water suspensions. (d) Schematic of proposed CNF solvent drying process. (e) FTIR spectra of three dry CNFs. Insets show magnified spectra at wavenumbers of 3600-3100, and 1750-1550 cm⁻¹. (f) XRD patterns of solvent dried CNFs and CCNFs. Insets show deconvolution of CCNF diffraction peak (002), and HRTEM image of CCNFs with short-ranged carbon lattice highlighted in red boxes.

A schematic (Figure 4.1d) is introduced to illustrate the proposed mechanism for the fibrous structure of solvent dried CCNFs. Solvent drying approach was indeed a solvent exchange (disperse-centrifuge) process that transferred CNFs from water to acetone and subsequently to toluene²⁰. CNF-water suspension exhibits an opaque appearance by forming hydrogen bonds with
water molecules. After being re-dispersed, acetone accepted CNF self-assembled intrinsic *intra*
and *inter* hydrogen bonds [22] and provided CNFs with a similar dispersion environment like
water. In CNF-toluene suspension, toluene infiltrated into CNF molecular chains and discharged
CNF *inter* hydrogen bonds, leading to a clear appearance. Toluene molecules occupied spaces
were preserved after solvent evaporation. As a result, solvent dried CCNFs attained fibrous
structures instead of agglomerations. In the meantime, carbonization induced the cleavage of CNF
side groups, which destroyed *intra* hydrogen bonds [23] and place more distances between
individual CCNF. Our hypothesis is supported by the FTIR result (Figure 4.1e). Decreased
intensity of the solvent dried CNF peak at 3600-3150 cm\(^{-1}\) indicated diminished CNF self-
assembled *inter* hydrogen bonds [24]. The absorbance bands at 1750-1680 cm\(^{-1}\) and 1650-1600
cm\(^{-1}\) were reported to be attributed to the C=O group from CNF impurities (e.g., pectin) and the
hydroxyl group from CNF absorbed water molecules, respectively [22]. Likewise, decreased
intensity of these bands in solvent dried CNFs indicated that conserved free spaces prevented
forming *inter* hydrogen bonds of CNFs-impurities and CNF-absorbed water [25].

Three diffraction peaks (101), (10\(\overline{1}\)) and (200) of solvent dried CNFs (Figure 4.1f) represent
the transverse arrangement of the crystallites in cellulose I, while diffraction peak (040) represents
CNF longitudinal structure [26]. The newly generated diffraction peak (002) in CCNFs was a
mixture of sharp crystalline peak and amorphous halo, associated with the graphitized carbon [27]
and amorphous carbon [28], respectively. The intermediate carbon phase of CCNFs is also
confirmed by the HRTEM image (Figure 4.1f inset) that disordered and short-ranged carbon
structures simultaneously distribute along the fiber. XPS survey spectrum shows that CCNFs
mainly consist of carbon and oxygen, while sodium, nitrogen, and sulfur are contaminations from
the alkali purification and acid hydrolysis processes during CNF preparation. Increased C/O ratio
was ascribed to the loss of oxygen during CNF carbonization (i.e., dehydration and depolymerization). Oxygen in CCNFs crosslinked with the carbon microstructures (i.e., C-O and C=O), forming the amorphous carbon region. The graphitized carbon region comprised a high concentration of sp2 carbon, represented by the C-C peak with a broad, asymmetric tail towards higher binding energy [29].

4.3.2 CCNF-PCL Composite Films

Solvent dried CCNFs noticeably reinforce PCL composite films as the tensile performances gradually improve with the CCNF loading rate from 1 to 7 wt% (Figure 4.2a). Composite film maximum tensile toughness (317.0 MJ/m³), modulus (117.7 MPa), strength (30.5 MPa), and strain at break (1959.4%) were achieved at CCNF loading rate of 7 wt%, which were 2.9, 1.4, 1.9, and 1.9 times of the neat PCL film. Figure 4.2b compares the tensile constants for three CCNFs filled composite films. It is clearly observed that the solvent dried CCNFs provided PCL with superior tensile properties over both oven a freeze dried CCNFs at any given loading rate. It also should be noted that the tensile strength of our 7 wt% CCNF-PCL composites was remarkably higher in comparison with other types of reinforcing agents for PCL.

Improved tensile properties were strongly associated with the uniform dispersion state of solvent dried CCNFs in the PCL matrix. Owing to the fibrous morphology, solvent dried CCNF-PCL composite films show a smooth fracture surface (Figure 4.2d), on which pull-out fibers are distinctly distributed (Figure 4.2e), indicating the good compatibility between fibers and matrix. On the contrary, rough fracture surfaces are observed for oven dried (Figure 4.2f) and freeze dried (Figure 4.2h) CCNF-PCL composite films, indicating the significantly poor dispersion state resulting from the agglomerated fibers. In this case, not only the oven and freeze dried CCNFs are not able to reinforce PCL, but tend to initiate failures at fiber rich regions (Figure 4.2g-i).
4.3.3 Conductive CCNF-CB Hybrid

Carbonized cellulose from low pyrolysis temperature (<1400 °C) is normally lack of electrical conductivity. A combination with other conductive materials [30] is necessary to boost their conductivity [31]. Here, we integrate CCNFs with CB to synthesis a conductive hybrid, in which CCNFs serve as bridges to connect CB aggregates (Figure 4.3a). Moreover, CNF surface was decorated with PVP coating via hydrogen bonds before carbonization. As CNFs turn into CCNFs
after carbonization, another carbon derived from PVP was attached on the CCNF surface. The XRD pattern of PVP coated CCNF (PVP@CCNF) is identical to that of CCNFs, indicating PVP derived carbon lied in an amorphous state [32]. From the HRTEM image (Figure 4.3b-c), the 17.3 nm PVP carbon layer covers the CCNFs continuously, which plays a similar role like a binder that couples CCNFs and CB. Therefore, free charges may move among CB aggregates through either the PVP derived carbon layer or the CCNF linked CB pathway (Figure 4.3d), which led to a much enhanced conductivity for the PVP coated CCNF-CB hybrid (PVP@CCNF-CB).

Figure 4.3. Conductive PVP@CCNF-CB-PCL 3D printing filaments. (a) SEM image showing CCNF “bridging” CB aggregates in CCNF-CB hybrid. (b) TEM image of PVP@CCNF-CB hybrid structure. (c) TEM image of PVP derived carbon layer on the surface of CCNF. (d) Schematic of free charges transporting between CB aggregates in PVP@CCNF-CB hybrid. (e) The ability of 30 wt% conductive fillers-PCL filaments to power four colors LEDs. and (f) Comparative study on electrical resistivity of conductive filaments (this work) and CB based commercial products.

Figure 4.3e compares the capability of conductive 3D printing filaments to illuminate LEDs in a closed loop. It is clearly observed that PVP@CCNF-CB-PCL filament powered all LEDs, in
contrast with the fact that yellow and green LEDs barely emitted light when connected with CB-PCL and CCNF-CB-PCL filaments. A comprehensive comparison between our conductive filament and commercial CB based conductive filaments is shown in Figure 4.3f. The electrical resistivity of PVP@CCNF-CB-PCL filament dramatically decreased from 1116.44 to 0.0159 Ω•m as PVP@CCNF-CB loading rate increased from 10 to 30 wt%, making it extremely conductive over both commercial and CB only conductive filaments. The results of such extraordinary conductivity proposed the potential to use this filament for 3D printing EMI shielding and deformation sensing components.

4.3.4 EMI Shielding

A conductive polymer composite is capable of weakening or totally shielding EM radiation due to material dielectric loss [33]. Material properties (e.g., permittivity), EM radiation characteristics (e.g., frequency), and geometries (e.g., thickness) together decided the EMI shielding effectiveness of a conductive composite [34]. Figure 4.4a-b show composite real (ε′) and imaginary (ε″) dielectric permittivity within the frequency range of 4-26 GHz. As PCL matrix was nonconductive, ε′ was only associated with composite interfacial polarization ability which was closely related to filler surface area and free charge mobility inside conductive composites [35]. Positive ε′ intended the interfacial polarization arising from the difference in electrical conductivities between filler and matrix [36]. CCNF based conductive filler tended to intertwine with CB to form a chain-like interconnected structure [8], which could help delocalize polarized charge at the filler-matrix interface instead of accumulation [37]. The values of ε′ and ε″ (Figure 4.4a-b) decrease in the frequency range of 4 to 26 GHz due to the possible interfacial polarization - a phenomenon resulting from insulated PCL creating boundaries within CCNF-CB network [38]. The dielectric loss tangent is a ratio of ε″ to ε′. Within the frequency range of 4-15 GHz, at any
given filler loading rate, dielectric loss tangent value has an order of CCNF-CB-PCL > PVP@CCNF-CB-PCL > CB-PCL > neat PCL (Figure 4.4c). At frequency higher than 15 GHz, this ranking changed to PVP@CCNF-CB-PCL > CCNF-CB-PCL > CB-PCL > neat PCL. The significant increase of dielectric loss tangent value for PVP@CCNF-CB led to a higher EM attenuation factor within the frequency range of 15-26 GHz [39].

Reflection and absorption are two dominant mechanisms for EMI shielding by conductive composites [40]. Specifically, reflection occurs when EM radiation interacts with composite surface charges, the amount of which directly determines the EMI shielding effectiveness by reflection ($SE_R$) [41]. Absorption is a dissipation of EM radiation energy into other internal energies [42]. EM radiation can be reflected multiple times, and the multi-reflected EM radiation residual are re-absorbable inside the material [34]. The total EMI shielding effectiveness ($SE_T$) is a sum of $SE_A$ and $SE_R$, which is also expressed by:

$$SE_T = 10 \log \left( \frac{P_I}{P_T} \right)$$

(2)

where $P_I$ and $P_T$ are the powers of incident and transmitted EM radiations, respectively.

Measured $S$ parameters, $S_{11}$ (power ratio of reflected ($P_R$) to incident EM radiation) and $S_{21}$ (power ratio of transmitted to incident EM radiation) are expressed by:

$$S_{11} = \frac{P_R}{P_I}$$

(3)

$$S_{21} = \frac{P_T}{P_I}$$

(4)

The reflection coefficient $R$, transmission coefficient $T$, and absorption coefficient $A$, are calculated by:

$$R = S_{11}^2$$

(5)

$$T = S_{21}^2$$

(6)
\[ A = 1 - R - T \] (7)

The \(SE_R\), \(SE_A\), and \(SE_T\) values are calculated by:

\[ SE_R = -10\log(1 - R) \] (8)

\[ SE_A = -10\log\left(\frac{T}{1-R}\right) \] (9)

\[ SE_T = SE_R + SE_A \] (10)

Figure 4.4d compares composite \(SE_T\) for three types of conductive fillers. As expected, neat PCL showed no EMI shielding effectiveness regardless of the EM radiation frequency. CCNFs integrated CB-PCL composites showed much improved \(SE_T\) with frequency than CB-PCL. For instance, the maximum \(SE_T\) values reached over 15 dB at 26 GHz for PVP@CCNF-CB-PCL. \(SE_A\) curves (Figure 4.4e) follow the tendency of the \(SE_T\) curves; whereas the \(SE_R\) curves shown in Figure 4.4f have a bell shape with the maximum reflection occurs at ~6 GHz. It is clearly observed that \(SE_A\) had the major contribution to \(SE_T\). The limited contribution by \(SE_R\) to \(SE_T\) was partially related to the poor surface morphology resulting from 3D printing. Voids between successive layers (Figure 4.4g) and excessive stringing or layer seams (Figure 4.4h) generate multi EM radiation scattering inside the sample and affect \(SE_A\). Skin depth is defined as the distance up to which EM radiation attenuates by 1/e or 37% [43]. It is calculated by:

\[ \delta = \frac{1}{\sqrt{\pi f \mu_r \mu_0 \sigma}} \] (11)

where \(f\) is EM radiation frequency; \(\mu_0\) is absolute permeability of free space, which equals \(4\pi \times 10^{-7}\) H/m\(^{-1}\); relative permeability \(\mu_r\) equals 1 for our non-magnetic composites; and \(\sigma\) is composite electrical conductivity. It is known that \(\delta\) is inversely proportional to \(SE_A\). PVP@CCNF-CB-PCL with the minimum \(\delta\) in the testing frequency range exhibited the maximum absorption. Alternatively, CB-PCL exhibiting the minimum absorption had the maximum \(\delta\).
4.3.5 Deformation Sensing

The real-time electrical resistance of 20 wt% CCNF-CB-PCL filament is measured during short-term a cyclic (5 cycles) stretching-bending test within filament elastic regime at three different strain rates (i.e., 1.5 (Figure 4.5a), 3.0 (Figure 4.5b), and 4.5 %/min (Figure 4.5c)). The $R/R_0$ peak value decreased after the first cycle, but reached a relatively stable state within the first five cycles. When the applied strain recovered to 0, the $R/R_0$ value dropped below 1, indicating the reduced electrical resistance [44] than the initial value. This changes of electrical resistance
from cycle to cycle could be ascribed to the formation of distortions/cracks during straining process and inconsistently re-bridging of such cracks or relaxation of distortions when the strain was released [45]. As expected, strain rate had no obvious influence on the \( R/R_0 \) peak value because composite electromechanical property was mainly determined by the geometrical effect [46]. Due to the uniform dispersion of conductive fillers within the filament, the structural integrity of conductive networks was well preserved under elastic regime. As a result, regardless of the strain rate, filament electrical resistance exhibited a noticeable decrease before yield point as CCNF-CB hybrid aligning along with PCL molecular chains, after which it started to increase due to the geometrical effect, and finally reached infinity at fracture. It should be noted that a hysteresis phenomenon was observed based on the stretching and bending results, which could be ascribed to the viscoelasticity of the PCL matrix as shown in the stretching-bending test curves.

In an attempt to investigate the effect of sensor geometry on sensor response to various deformations, a conventional solution casted film-type sensor was compared with a 3D printed sensor with a honeycomb structure. Both sensors comprised of the same composition (i.e., 20 wt% CCNF-CB-PCL) and dimensions (i.e., length, width, and thickness), while the 3D printed sensor was much lighter in weight due to the presence of hexagonal holes. FEA results show that under uniaxial force, the film-type sensor (Figure 4.5d) carried an unnoticeable load with stress mostly distributed at four corners. Conversely, stress distributes relatively uniformly across the entire honeycomb structure (Figure 4.5e), and the 3D printed sensor is noticeably deformed and was able to recover upon the release of strain. This phenomenon is also in consistence with the reproducible \( R/R_0 \) curves for 3D printing sensor from cycle to cycle (Figure 4.5f). A stable \( R/R_0 \) peak value of 0.93 was present after the 3D printing sensor was subject to 300 cycles at tensile strain of 1.5%/min, which was identical to the \( R/R_0 \) peak value in the first 50 cycles. Figure 4.5g demonstrates the
flexibility and durability of the 3D printing sensor that can be bent under force and recover to its original position upon the release of deformation. In the meantime, the R/R₀ value shifted to the original value when the 3D printing sensor was bent at a same angle in the opposite direction.

Figure 4.5. Sensing properties of CCNF-CB-PCL composites. Electrical resistance changes (R/R₀) in response to stretching-bending for 20 wt% CCNF-CB-PCL conductive filaments. (a) At a stretching-bending strain rate of 1.5 %/min⁻¹. (b) 3.0 %/min⁻¹. and (c) 4.5%/min⁻¹. FEA results of normal stress distribution on sensor surface. (d) Film-type sensor, and (e) 3D printing (3DP) sensor. (f) Comparative study on R/R₀ for film-type and 3D printing sensors under cyclic tensile test for 500 cycles, at a strain rate of 1.5 %/min⁻¹. Insets show detailed R/R₀ curves for the 50th and 250th cycles. and g) Sensor sensitivity and reliability to deformations. Insets show photographs of sensor flexibility in response to stretching and bending.
4.4 Conclusions

In summary, a novel approach for drying CNFs from aqueous suspension was introduced through a modified three-step solvent exchange process. The majority of the CNF self-assembled inter hydrogen bonds were discharged by toluene molecules, which offered sufficient free spaces between CNF molecular chains. Obtained solvent dried CCNFs lied in an intermediate state between hard and amorphous carbons, having both short-ranged and disordered carbon lattices distributed along single fiber or tangled fiber bundles. Retained fibrous morphology was essential for solvent dried CCNFs, as reinforcing fillers, to disperse homogeneously in PCL matrix, and remarkably improved composite film tensile performance. CCNFs helped form 3D network in CCNF-CB hybrid, creating bridges for free charges to move between CB aggregates. Highly electrically conductive composite containing CCNF-CB based hybrids (i.e., CCNF-CB and PVP@CCNF-CB) were suitable for EMI shielding. EM radiation was mainly absorbed owing to CCNF interconnected structure effectively delocalizing free charges. This conductive composites were also used for 3D printing honeycomb geometric deformation sensors which exhibited excellent stability and durability in response to long-time cycles and various deformations.

4.5 REFERENCES


CHAPTER 5. ACCELERATED ANNEALING FOR 3D PRINTED POLYLACTIC ACID VIA MICROWAVE HEATING

5.1 Introduction

Crystallite size, phase, structure, and degree of crystallinity together determine the macroscopic properties of semi-crystalline thermoplastic polymers [1]. Thermoplastic polylactic acid (PLA), as a typical semi-crystalline polymer, is widely used in food packaging industry [2]. It is derived from natural resources (e.g., corn starch) and is biodegradable in soil [3]. Recently, PLA finds applications for fused filament fabrication (FFF) 3D printing technology [4]. The superior mechanical strength of PLA significantly helps prevent 3D printed parts from curling and warping [5]. However, 3D printed PLA still has low crystallinity as the extruded PLA solidifies at the low temperature (i.e., < glass transition temperature, T_g) platform so rapidly that it has little time to crystallize completely.

Post-processing thermal annealing treatment applied between T_g and melting temperature (T_m) is designed to enhance the crystallinity for semi-crystalline polymers. Annealing induces the nucleation as well as the growth of existing crystallites, converting amorphous region and less perfect crystallites into larger or more perfect crystallites [6]. For this reason, annealed polymers behave properly at high service temperatures [7]. Annealing time and temperature are negatively correlated in terms of crystallinity. To reach a high crystallinity, a longer time is required if the temperature is low. However, annealing temperature should not be too close to T_m in case of polymer melting, which would result in an overall decrease of crystallinity [8].

Annealing methods for polymers mainly consist of oven annealing [6], solvent vapor annealing [9], zone annealing [10], and photothermal annealing [11]. Oven annealing is easy-to-use as annealing takes place in an oven or an autoclave, in which heat propagates from polymer
surface to the interior. However, for PLA with low thermal conductivity and thermal diffusivity, oven heat may take a long time to penetrate inside the printed part, which is less promising from a practical perspective. Solvent vapor annealing is mostly used for synthesizing organic electronic polymers blend and block copolymers [12]. It exposes polymers in a solvent atmosphere, having molecular chains relaxed until the desired morphology is obtained. Solvent vapor annealing significantly reduces the risk of polymer melting or polymer thermal degradation as it carries out at low temperatures by using fast evaporating solvent. Zone annealing is originally designed for treating metals and started to apply for semiconducting polymers recently [13]. Unlike oven heat reaching polymers in all directions, zone annealing is subjected to generate localized heat by a hot wire and apply to polymers only in one direction. Xue also suggested that zone annealing was inherently extendible following a roll-to-roll technology for continuous fabrication of semiconducting polymers [10]. Photothermal annealing is conducted by using photothermal materials. For example, Viswanath used embedded gold nanoparticle to convert incident light energy to thermal energy and use that heat to perform annealing on polyethylene oxide films [1].

As an alternative heating route, microwave heating has great advantages such as no-contact energy transfer, low cost, and selective heating for composite containing both low and high dielectric loss components [14]. Microwave heating has been extensively used to synthesize semiconducting nanomaterials [15], or to extract energy-dense products (e.g., biofuels) from biomass [16]. Carbonaceous materials exhibit high dielectric loss, which enables them to absorb microwave radiation and convert it into thermal energy efficiently [17]. Cellulose microfibrils in wood and plant cell walls, can be further separated into nanofibers named cellulose nanofibers (CNFs) [18]. Organic CNFs can be transformed to inorganic carbonized CNFs (CCNFs) via a continuous carbonization process. In this work, we first validated the microwave absorbing
potential of CCNFs, and subsequently fabricated PLA-CCNF (CCNF concentration: 0.5 wt\%) composites via 3D printing. When irradiating with microwave, the input microwave energy was selectively absorbed by CCNFs, while the PLA part remained unchanged. The absorbed microwave energy was converted into localized heat surrounding CCNFs, and subsequently transferred to adjacent PLA for carrying out annealing treatment. In the meantime, we systematically investigated the influence of annealing parameters including method (oven vs. microwave annealing), time (0-120 min), and temperature (80 vs. 120 °C) on the resulting cold crystallization phenomenon, crystallinity, crystallite size and structures, and tensile properties of 3D printed PLA. A crystallinity-tensile strength relationship was also established to seek the optimal annealing conditions.

5.2 Experimental

5.2.1 Preparation of CCNFs

CNF-water suspension (containing 3.8 wt\% solid CNFs) was purchased from the University of Maine (Orono, ME). CNF suspension concentration was further diluted to 1 wt\% and homogenized using a homogenizer (T25, IKA Works, Inc., NC) at 8000 rpm for 5 min. Dry CNF precursors were acquired using a lab-scale mini spray-dryer (B-290, Buchi Corp., DE). Spray drying parameters included inlet temperature of 190 °C, aspirator rate of 90\%, pump rate of 20\%, and air flow of 30 m\(^3\)/h. Spray drier outlet temperature was measured at 130 °C. The obtained dry CNFs were placed in an alumina crucible and carbonized in a tube furnace (GSL 1100x, MTI Corp., CA). Carbonization process involved with a stabilization process in air at 280 °C for 8 h, followed by a graphitization process at 1000 °C in N\(_2\) for 2 h, and a cooling process to room temperature under the protection of N\(_2\). The obtained CCNFs was subjected to ball milling (M301,
Retsch USA Verder Scientific, Inc., PA) for 15 min at a frequency of 15 Hz using a 25 mm diameter grinding ball.

5.2.2 Characterization of CCNFs

CCNF surface morphology was observed with a scanning electron microscope (SEM, FEI Quanta 3D Focused Ion Beam) at a voltage of 10 kV. CCNFs were coated with a thin layer of gold by a sputter coating machine (550X, Electron Microscopy Sciences, PA) prior to the SEM observation. Dielectric properties of dry CNFs and ball milled CCNFs were measured using the open-ended coaxial-line dielectric probe (85070E dielectric probe kit, Keysight Technologies, CA). The instrument (Agilent E5071C Network Analyzer, Keysight Technologies, CA) was calibrated using air and distilled water as references. Testing frequency range was set between 0.2 and 4.5 GHz. It should be noted that the frequency of 2.45 GHz was selected for this study as it is the most commonly used frequency for both industrial and scientific microwave setups. Particle sizes of CNFs, CCNFs, and ball milled CCNFs were measured by Microtrac S3500 (Microtrac Inc., PA) with 0.05 wt% fiber-water suspensions.

Figure 5.1. Schematic of microwave annealing method. Photograph CCNFs-PLA specimen in dumbbell shape, with two wide ends covered by a thin layer of copper tapes. Specimen narrow section reached a high temperature after annealed by microwave heating at 120 °C for 3 min.
5.2.3 Annealing for 3D Printed CCNFs-PLA

Ball milled CCNFs mixed well with PLA pellets (NatureWorks, MN), and the mixture was fed into a single screw extruder (EX2, Filabot, VT) at 165 °C for producing 1.75 mm diameter 3D printing composite filaments. The extruded filaments were cut into small segments and refed in the extruder three times to attain a homogeneous CCNF dispersion [19]. Dumbbell shape specimens for tensile test were 3D printed using a CR-10 3D printer. 3D printing parameters listed in Table 5.1. A type K thermocouple wire was mounted on the surface of tensile specimen and the real-time temperature was monitored by a digital thermometer (RS 232, Fisher scientific, NH). A conventional oven (1370fm, VWR Corp., PA) was pre-heated to the target temperature (i.e., 80 or 120 °C) before oven annealing. Two selected annealing temperatures fell in two temperature regions (i.e., T_g - T_cc, and T_cc - T_m. T_cc refers to cold crystallization temperature). After the annealing process, specimens were removed out of oven and placed in the ambient atmosphere for a cooling process. The temperature changes during cooling process was also recorded until the temperature dropped below T_g. For microwave annealing, a 1.2 kW microwave generator (Richardson electronics, IL) irradiated 2.45 GHz microwave on the dumbbell specimen, which was placed in a customized WR 340 aluminum waveguide (75 mm (L) x 10.5 mm (W) x 10.5 mm (H)). The USB power sensors (PWR-SEN-6G+, Mini-Circuits, NY) were attached to monitor the forward and reflected microwave power levels. An infrared thermos camera (A40, FLIR Systems Inc., OR) was mounted above the waveguide to collect specimen temperatures. Figure 5.1 shows the microwave annealing setup. Annealing temperature was adjusted by controlling forward microwave power manually. A high-power level (700 W) was firstly employed to elevate specimen temperature to the target temperature in a short time (i.e., <1 min), and subsequently temperature was maintained steadily for the entire microwave annealing process. Due to a
significant mass difference between the wide ends and the narrow section of the dumbbell specimen, an imbalance microwave absorption and heat generation could occur between the two regions. Since the narrow section was designed to hold stress and break (according to ASTM D638) in the tensile test, specimen two wide ends were covered with one layer of copper tape (Figure 5.1) to shield the microwave, having only the narrow section annealed at target temperatures. After microwave annealing, specimen cooling process was continuously recorded by the thermal camera until temperature dropped below $T_g$.

Table 5.1. 3D printing parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printer model</td>
<td>Creality3D CR-10</td>
</tr>
<tr>
<td>Build plate surface material</td>
<td>Glass</td>
</tr>
<tr>
<td>Build plate temperature (oC)</td>
<td>70</td>
</tr>
<tr>
<td>Cooling fan speed (%)</td>
<td>100</td>
</tr>
<tr>
<td>Filament diameter (mm)</td>
<td>1.75</td>
</tr>
<tr>
<td>Printing temperature (oC)</td>
<td>220</td>
</tr>
<tr>
<td>Infill pattern</td>
<td>rectilinear (45°, -45°)</td>
</tr>
<tr>
<td>Infill rate (%)</td>
<td>100</td>
</tr>
<tr>
<td>Layer height (mm)</td>
<td>0.2</td>
</tr>
<tr>
<td>Nozzle diameter (mm)</td>
<td>0.4</td>
</tr>
<tr>
<td>Nozzle material</td>
<td>copper</td>
</tr>
<tr>
<td>Print speed (mm/min)</td>
<td>2400</td>
</tr>
<tr>
<td>Retraction speed (mm/min)</td>
<td>1200</td>
</tr>
<tr>
<td>Slicer software</td>
<td>Simplify3D</td>
</tr>
</tbody>
</table>

5.2.4 Characterization of Annealed Composites

Specimen tensile properties were characterized using an Instron (5582, Instron, MA) with a 30 kN load cell and a constant strain rate of 5 mm/min. Specimen thickness was measured using a digital caliper (Mitutoyo 500-133). Five replicates were run to report average values. Differential scanning calorimetry (DSC, Q200, TA Instruments, DE) was used to determine PLA crystallinity. DSC samples were from the specimen narrow section and were subjected to a heating scan from
25 and 250 °C with a heating rate of 5 °C/min. TA Universal Analysis software was used to analyze the data from the first heating curve. PLA crystallinity (χ) was calculated by:

\[
\chi (\%) = \frac{\Delta H_m^* - \Delta H_c}{\Delta H_m^*} \times 100
\]

where \( \Delta H_m^* \), \( \Delta H_m \), and \( \Delta H_c \), are the melting enthalpy for 100% crystalline PLA (i.e., 93 J/g) [6], melting enthalpy, and cold crystallization enthalpy, respectively. Isothermal DSC also carried out to imitate the annealing process. Specifically, PLA pellets, 3D printed neat PLA, and 3D printed CCNFs-PLA were held at annealing temperatures for 300 min to record the change of heat flow.

PLA crystal structures were characterized by X-ray diffraction (XRD, PANalytical Empyrean XRD) with 2θ angles ranging from 5 to 50° and a step size of 0.02°. The average crystallite size was calculated using the Scherrer equation [11]:

\[
\tau = \frac{K \lambda}{\beta \cos \theta}
\]

where \( \tau \) is the mean size of crystallite; \( K \) is the shape factor (i.e., 0.9); \( \beta \) is the full width at half-maximum intensity (FWHM); and \( \theta \) is the diffraction angle.

5.3 Results and Discussion

5.3.1 Morphology and Dielectric Properties of Ball Milled CCNFs

Drying methods including oven drying, freeze drying, supercritical drying, and spray drying were reported for dehydrating CNF-water suspensions [20]. Spray drying method was selected for this work as the obtained powdery CNFs were easy to compound with PLA pellets through extrusion. As shown in Figure 5.2a, spray dried CNFs agglomerate to form irregular particles at micron-scale, with more than 90% having diameters between 1-5 μm (Figure 5.2d). After carbonization, CCNFs showed a similar particulate morphology (Figure 5.2c), but had diameters increased to the range of 2-10 μm. After ball milling, CCNFs had diameters significantly reduced.
(Figure 5.2c) as more than 75% were measured at sub-micron scale (< 1 µm) and more than 95% smaller than 2 µm. Small fiber size helps ball milled CCNFs disperse more homogeneously in the water suspension as shown in Figure 5.2e.

Figure 5.3 compares dielectric properties (i.e., real - $\varepsilon'$ (Figure 5.3a), and imaginary - $\varepsilon''$ parts of permittivity (Figure 5.3b), and dielectric loss tangent (Figure 5.3c)) between dry CNFs and ball milled CCNFs. As expected, organic CNFs showed unnoticeable frequency dependence of dielectric properties, which was in an agreement with literature [21]. On the contrary, dielectric constant value of ball milled CCNFs was observed decrease with frequency in the entire testing frequency range as an outcome of material polarization relaxation, which led charged CCNFs to undergo dielectric lags behind applied electric field [17]. As frequency increased, the total number of charged CCNFs decreased, resulting in a reduce in dielectric constant. The $\varepsilon'$ and $\varepsilon''$ values of ball milled CCNFs decreased ~30 and ~70%, respectively, from frequency of 0.2 to 4.5 GHz. Dielectric loss tangent ($\tan \delta = \varepsilon''/\varepsilon'$) represents material capability in dissipating microwave energy into heat. Good microwave absorbing material possesses a high $\varepsilon''$ and moderate $\varepsilon'$ [17]. At frequency of 2.45 GHz, the average loss tangent value of CCNFs was 6 times of CNFs, which indicated a great potential for ball milled CCNFs to serve as an appropriate microwave absorbing material. Moreover, even compared with some carbonous materials such as biochar [22], activated carbon [23], and graphite [24], our ball milled CCNFs still showed highly pronounced dielectric properties within the microwave frequency range.

5.3.2 Brief Background of PLA Crystallization

As shown in Figure 5.4a, the addition of CCNFs seems to have no influence on PLA transition temperatures as both filament and 3D printed specimens have almost identical $T_g$ of ~ 57 °C, $T_{cc}$ of ~95 °C, and $T_m$ of ~162 °C. The virgin PLA pellets showed a higher $T_g$ of ~66 °C and an absence
of cold crystallization peak. A much higher crystallinity was observed for PLA pellets (Figure 5.4b), which in fact interpreted that the high T_g was ascribed to crystallites hampered PLA chain mobility. After a series of thermal processing (i.e., extrusion and 3D printing), PLA filaments and 3D printed PLA experienced melting and recrystallization, resulting in insufficient crystallinity [25].

Table 5.2. Microwave absorption and reflection at different levels of forward microwave power.

<table>
<thead>
<tr>
<th>Microwave power</th>
<th>Forward (W)</th>
<th>Reflected (W)</th>
<th>Absorbed (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>73</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>113</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>115</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>137</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>140</td>
<td>160</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.2. SEM images of fiber morphologies. (a) CNFs; (b) CCNFs; and (c) Ball milled CCNFs. (d) Number fraction distributions of sizes of CNFs, CCNFs, and ball milled CCNFs. (e) Photographs of fiber-water suspensions (fiber concentration = 0.05 wt%).
Figure 5.3. Measured dielectric properties of dry CNFs and ball milled CCNFs. (a) Dielectric constant; (b) Dielectric loss factor; and (c) Dielectric loss tangent.

Figure 5.4c shows the isothermal crystallization behaviors of PLA at two target temperatures. No obvious crystallization peak was observed at 80 °C (below T_{cc}), indicating that 3 h treatment was not long enough to trigger PLA re-crystallization. At 120 °C, 3D printed PLA and CCNFs-PLA specimens exhibited visible exothermal peaks at ~90 and ~150 min, respectively, corresponding to the cold crystallizations. Zhai [26] reported a similar result, and suggested that PLA crystallization became difficult at 140 °C as PLA chain rearrangement was significantly interfered by chain mobility. An appropriate annealing temperature range might locate between 110-130 °C in order to accomplish a higher crystallinity.

5.3.3 Annealing of PLA

Figure 5.5 shows a positive correlation between the power of forward microwave and the temperature of the 3D printed CCNFs-PLA. Table 5.2 presents that only a small portion of the forward microwave was absorbed while the rest was reflected (considering no leakage). The specimen warmed up slowly when microwave forward power was lower than 200 W. Temperature reached a steady state eventually, where no temperature gradient was observed between specimen narrow section and wide ends. A remarkable faster heating was observed when microwave power was set higher than 250 W. Temperature reached ~150 °C within 20 min using a 250 W power, and ~250 °C within 10 min using a 300 W power. In these scenarios, temperature gradient was
clearly distributed across the dumbbell shape specimen with a much higher temperature at the wide end. Moreover, specimen displayed a self-accelerated heating at temperatures above $T_{cc}$ due to PLA dielectric dependence of temperature. Ren [27] suggested that PLA dielectric constant showed a marginal relaxation as only some short side chains were free to rotate at temperatures below $T_g$. PLA backbone segments might have an increased mobility as temperature increased above $T_g$, however, such movements were hindered by the PLA cold crystallization process around $T_{cc}$. Only at temperatures above $T_{cc}$, PLA dielectric constants increased intensely toward the interface polarization effect [28].

Figure 5.4. Crystallization properties of PLA pellet, PLA filament, PLA-CCNFs filament, 3D printed PLA, and 3D printed CCNFs-PLA. (a) Non-isothermal DSC thermograms; and (b) Measured crystallinity. (c) Isothermal DSC thermograms of as-3D printed PLA and as-3D printed CCNFs-PLA at 80 or 120 °C.

The cooling process after annealing is compared among oven annealed PLA, oven annealed CCNFs-PLA, and microwave annealed CCNFs-PLA. From Figure 5.6, we can conclude that the annealing method perceptibly affect specimen cooling rate, especially at low temperatures. For example, for cooling down to 80 °C, where PLA rarely crystallized, microwave annealed specimen took a slightly longer cooling time (~ 1 min) than oven annealed specimen. Compared with the much longer annealing time, it is assumed that specimen cooling profile was identical to both annealing methods. For this reason, the cooling process should not impact the resulting crystallinity and tensile strength.
Figure 5. Response of temperature to forward microwave power for 3D printed CCNFs-PLA (not covered with copper tape). Insets show IR images of specimens at maximum temperatures.

Figure 5.7a compares specimen crystallinity as a function of annealing time at 120 °C. For both oven and microwave annealing methods, specimen crystallinity was observed to increase initially and leveled off in despite of the increased annealing time. This general trend can be interpreted as follows. At the start of annealing, amorphous PLA chains released thermal stress and repacked to form crystallites, and thereby enhanced crystallinity. As heat accumulated at specimen with increased time, PLA chain movement turned out faster, which hampered the crystallization process. Specimen maximum crystallinity was not related to either annealing method or composition. For all three conditions, the same maximum crystallinity was achieved at ~57%. However, microwave annealing yielded a significant faster crystallization rate than oven annealing. For example, 3D printed CCNFs-PLA achieved the maximum crystallinity within 1 min via microwave annealing, while 6 min treatment was required via oven annealing.
Table 5.3. Specimen crystallinity and tensile strength as a function of annealing time for different annealing temperatures using oven or microwave annealing.

<table>
<thead>
<tr>
<th>Temperature (^\circ\text{C})</th>
<th>Annealing method</th>
<th>Time (min)</th>
<th>Crystallinity (%)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 (CCNFs-PLA)</td>
<td>oven</td>
<td>5</td>
<td>23.9 ± 4.1</td>
<td>42.2 ± 11.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>25.2 ± 0.1</td>
<td>37.0 ± 8.6</td>
</tr>
<tr>
<td></td>
<td>microwave</td>
<td>5</td>
<td>27.9 ± 5.4</td>
<td>49.1 ± 2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>25.9 ± 0.3</td>
<td>53.9 ± 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>39.5 ± 4.2</td>
<td>54.7 ± 0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>58.9 ± 1.9</td>
<td>55.3 ± 0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>50.5 ± 3.1</td>
<td>56.5 ± 1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>50.2 ± 7.7</td>
<td>44.5 ± 3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>45.2 ± 0.8</td>
<td>24.3 ± 5.5</td>
</tr>
<tr>
<td>120 (CCNFs-PLA)</td>
<td>oven</td>
<td>1</td>
<td>27.9 ± 6.5</td>
<td>29.6 ± 5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>16.5 ± 1.7</td>
<td>25.2 ± 5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>21.9 ± 2.9</td>
<td>35.9 ± 7.0</td>
</tr>
<tr>
<td></td>
<td>microwave</td>
<td>5</td>
<td>38.3 ± 2.1</td>
<td>28.7 ± 8.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>52.8 ± 2.5</td>
<td>46.4 ± 7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>49.5 ± 1.3</td>
<td>52.6 ± 5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>56.4 ± 3.5</td>
<td>28.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>51.2 ± 1.9</td>
<td>21.2 ± 3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>56.7 ± 2.2</td>
<td>31.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>54.3 ± 0.6</td>
<td>35.7 ± 3.6</td>
</tr>
<tr>
<td></td>
<td>microwave</td>
<td>0.5</td>
<td>37.4 ± 3.2</td>
<td>49.6 ± 5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>55.9 ± 3.8</td>
<td>50.7 ± 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>54.6 ± 4.4</td>
<td>47.1 ± 3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>53.7 ± 3.4</td>
<td>56.3 ± 1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>57.6 ± 2.3</td>
<td>35.5 ± 7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>57.0 ± 2.9</td>
<td>30.1 ± 9.0</td>
</tr>
<tr>
<td></td>
<td>microwave</td>
<td>10</td>
<td>57.0 ± 3.0</td>
<td>23.1 ± 5.8</td>
</tr>
<tr>
<td>120 (PLA)</td>
<td>oven</td>
<td>5</td>
<td>50.3 ± 10.3</td>
<td>29.0 ± 5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>55.6 ± 6.3</td>
<td>38.5 ± 3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>55.4 ± 1.9</td>
<td>43.4 ± 3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>54.7 ± 5.4</td>
<td>35.1 ± 8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>52.9 ± 2.6</td>
<td>40.8 ± 6.4</td>
</tr>
</tbody>
</table>
Figure 5.6. Cooling curves for 3D printed specimen via oven or microwave annealing at 120 °C.

Polymer cold crystallization peak in non-isothermal DSC thermogram normally diminishes or disappears after annealing being applied. The shorter the time requests to eliminate the cold crystallization peak, the higher the annealing efficiency is. Oven annealing had heat penetrated from outside in, and thus, took ~6 min to entirely eliminate the cold crystallization peaks (Figure 5.7b-c). On the contrary, the spatial specificity of microwave annealing enabled the heat to be generated inside, and thus, cold crystallization peaks disappeared after microwave annealing for 1 min (Figure 5.7d). A second melting peak was developed at lower temperature for oven annealed specimens. Nijenhuis [29] suggested that the low temperature melting peak essentially represented less perfect crystallites derived from chain reorientation. It was structurally identical to perfect crystallites (corresponding to the high temperature melting peak), but with smaller lamella dimensions. A similar phenomenon was also observed for microwave annealed specimen. From
annealing time 0.5 to 10 min, the main melting peak at ~162 °C first split into two peaks at 161 and 164 °C, and the two peaks gradually re-merged in one peak toward higher melting temperature at ~163 °C. Tábi [30] suggested that two melting peaks were associated with PLA α’ and α crystalline phases. The combination of two peaks indicated the completion of α’ to α disorder-to-order phase transition.

Figure 5.7. (a) Specimen crystallinity measured as a function of annealing time at 120 °C for 3D printed neat PLA and CCNFs-PLA composite via oven or microwave annealing method. (b-d) DSC thermograms of oven annealed PLA, oven annealed CCNFs-PLA, and microwave annealed CCNFs-PLA, respectively, as a function of annealing time at 120 °C.

Figure 5.8a compares specimen crystallinity as a function of annealing time at 80 °C. Table 5.3 suggests that a much longer time is needed to achieve the maximum crystallinity at annealing temperature of 80 °C, particularly for oven annealing. However, low temperature and long-time oven annealing provided PLA with the maximum crystallinity at ~67% (Table 5.4), which was the highest among all annealing conditions (i.e., annealing time, temperature, and method). Unlike
oven annealed specimen that had crystallinity continuously increased as a function of annealing time, microwave annealed specimen had reduced crystallinity after reaching the maximum crystallinity at 30 min. At 60 min, the remaining crystallinity was ~ 70% of the maximum value. This was probably because small crystallites packed together and formed large crystallites which decreased the overall volume of crystalline regions. Alternative explanation was the accumulated heat enhanced the thermal motion of PLA chains, especially at the CCNFs surrounding spots, and melted the already existing crystallinities [31]. Interestingly, only one melting peak was observed during all annealing time for both annealing methods, referring to unlikely formation of new crystallites. But the melting peak still shifted to a higher temperature, which was probably ascribed to the growth of already existing crystallites.

![Figure 5.8](image)

Figure 5.8. (a) Specimen crystallinity measured as a function of annealing time at 80 °C for 3D printed CCNFs-PLA composite via oven or microwave annealing method. (b-c) DSC thermograms of oven annealed CCNFs-PLA, and microwave annealed CCNFs-PLA, respectively, as a function of annealing time at 80 °C.

### 5.3.4 Tensile Properties and Crystal Structures

As shown in Figure 5.9a, as-3D printed neat PLA displays a comparable tensile strength in comparison with as-3D printed CCNFs-PLA (time = 0 min), indicating that the integrated ball milled CCNFs had no influence on PLA tensile strength at this small loading level (0.5 wt%). Microwave annealed specimen achieved the maximum tensile strength of ~56 MPa at 3 min, at which time the maximum crystallinity (~58%) was also achieved. After 3 min, although specimen
crystallinity remained relatively stable, the tensile strength started to drop until reaching the minimum value of 23 MPa at 10 min. As discussed above, long-time annealing had the overt heat constantly transmitted and led to the consolation of PLA crystallites. The newly formed large crystallite shortened the length of tie molecules in the crystalline regions and made specimen brittle. In the meantime, PLA bulk melting or even thermal degradation was likely to happen at the heat accumulated CCNFs-PLA interface, which also resulted in the decrease of tensile strength. Similar to the maximum crystallinity, the maximum tensile strength of oven annealed specimen was achieved at a comparable value as microwave annealed specimen, but with a longer annealing time (i.e., 6 min). For specimen annealed at 80 °C, the general trend of tensile strength with time is just following the trend of crystallinity with time (Figure 5.9b). Microwave annealed specimen had tensile strength initially increased and subsequently decreased, while oven annealed specimen had tensile strength increased and maintained steady.

Table 5.4. Annealing time to the maximum crystallinity and tensile strength for different annealing temperatures using oven or microwave annealing.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Annealing method</th>
<th>Time to max. crystallinity (min)</th>
<th>Time to max. tensile strength (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>oven</td>
<td>120</td>
<td>60</td>
</tr>
<tr>
<td>80</td>
<td>microwave</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>120</td>
<td>oven</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>120</td>
<td>microwave</td>
<td>15</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 5.10a shows the diffraction patterns of microwave annealed specimen at 120 °C. Diffraction peaks at 2θ = 14.7, 16.4, 18.8, 22.1, and 28.7° corresponded to crystal planes (010), (110/200), (203), (015), and (018), respectively [32]. For both (110/200) and (203) crystal planes, as expected, the increased integral peak area from 0.5 to 3 min was ascribed to the formation and combination of crystallites, while the subsequent decrease from 3 to 5 min was ascribed to the
melting of crystallites. This also explained the changes of crystallite size of microwave annealed specimen at 120 °C (Table 5.5). The (010), (015) and (018) diffraction peaks were absent for microwave annealed specimen at 80 °C (Figure 5.10b). At 5 min, XRD pattern showed a convoluted halo shape, indicating the presence of the majority amorphous regions. Crystallite size slightly increased after longtime annealing as an outcome of crystallite growth. In general, the XRD results was in consistence with the tensile test results.

Table 5.5. Average crystal size of microwave annealed 3D printed CCNFs-PLA at different annealing temperature and time.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(110)/(200)</td>
</tr>
<tr>
<td>80</td>
<td>30</td>
<td>19.97</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>20.46</td>
</tr>
<tr>
<td>120</td>
<td>0.5</td>
<td>14.98</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18.24</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>14.98</td>
</tr>
</tbody>
</table>

Figure 5.9. Specimen tensile strength measured as a function of annealing time. (a) At 120 °C; and (b) At 80 °C.

Polymer crystallinity directly determines crystallite morphology (e.g., size and perfection), crystallite phase, and molecular chain orientation in both amorphous and crystalline regions [33]. Figure 5.11 shows the complex interplay between specimen crystallinity and tensile strength. At higher annealing temperature (i.e., 120 °C), although annealing was able to enhance crystallinity
in a short time, the tensile strength was highly dependent on crystallite morphology. The formed large crystallites from either growth of new crystallites or merge of already existing crystallite deeply impacted specimen tensile strength. Shorter annealing time and higher crystallinity tended to provide specimen with a proper tensile strength. However, such annealing conditions, especially via microwave annealing, had to be very carefully manipulated as overheating could occur easily at 120 °C. At lower annealing temperature (i.e., 80 °C), the crystallinity and tensile strength became positively correlated. Issues like overheating and crystallite combination showed no evidence of occurrence at a temperature below \( T_{cc} \) as long as annealing time was strictly controlled.

Figure 5.10. XRD patterns of microwave annealed specimen as a function of annealing time. (a) At 120 °C; and (b) At 80 °C.

Figure 5.11. Crystallinity-tensile strength relationship at all annealing conditions.
5.4. Conclusions

Microwave energy was selectively absorbed by CCNFs and distributed heterogeneously within 3D printed PLA composites, where temperature was higher in the CCNF rich regions. The heat enabled amorphous PLA to reorient to form crystallites, and simultaneously supported the growth of already existing less perfect or small crystallites into larger ones. Long-time annealing at high temperature accelerated crystallite combination process, but could impair relevant tensile strength. An optimal crystallinity and tensile strength could be achieved at lower annealing temperature. Specifically, microwave annealing at 80 °C helped 3D printed PLA composites accomplish high crystallinity as well as high tensile strength in an accelerated manner. This research demonstrated the efficiency of microwave heating for annealing 3D printed PLA composites, and also extended a scientific understanding of using CCNFs as localized heat sources within other manufactured thermoplastics to manipulate product crystallinity and mechanical properties upon an exposure to microwave radiation.

5.5 References


CHAPTER 6. OVERALL CONCLUSIONS

6.1 Main Conclusions

In this study, functionalized CNFs were integrated within thermoplastic polymer composites through 3D printing. On one hand, surface modified CNFs were synthesized for reinforcing 3D printed PLA composites; On the other hand, CCNFs were processed through pyrolysis for functionalizing 3D printed thermoplastics. The conclusions of this study are as follows:

In comparison with neat CNFs, PLA-g-CNFs had a better dispersion in PLA after surface modification. The grafted PLA chains were highly crystallized, providing sufficient nucleating sites to grow crystallites for matrix PLA. Higher crystallinity resulted in better mechanical properties for the composite filaments in both glassy and rubbery states. For example, at 30 °C, the storage modulus increased from ~2450 to ~4227 MPa, while at 90 °C, the storage modulus increased from ~630 to ~1081 MPa. Composite filaments also had a comparable Young’s modulus to the simulated values from Halpin-Tsai and Krenchel models. For 3D printed PLA/PLA-g-CNFs composites, both α and α’ phases PLA crystallites were induced and developed during post-processing thermal annealing treatment. Annealing induced crystallites, together with the PLA-g-CNFs, helped confine the mobility of matrix PLA molecular chains, upshifted T_g, and improved composite resistance to thermal, dynamic oscillation, and static bending forces at both low and high temperatures. In the meantime, composite creep resistance and recovery behaviors were significantly improved due to the synergetic effect of the incorporated PLA-g-CNFs and post-fabrication annealing treatment.

Other than surface modification, a novel approach was introduced to dry CNFs from aqueous suspension, and subsequently synthesized CCNFs through a continuous carbonization process. The obtained CCNFs lied in an intermediate state between hard and amorphous carbons, having
both short-ranged and disordered carbon lattices distributed along single fiber or tangled fiber bundles. Retained fibrous morphology was essential for solvent dried CCNFs, as reinforcing fillers, to disperse homogeneously in PCL matrix, and remarkably improved composite film tensile performance. CCNFs helped form 3D network in CCNF-CB hybrid, creating bridges for free charges to move between CB aggregates. Highly electrically conductive composite containing CCNF-CB based hybrids (i.e., CCNF-CB and PVP@CCNF-CB) were suitable for EMI shielding. EM radiation was mainly absorbed owing to CCNF interconnected structure effectively delocalizing free charges. This conductive composites were also used for 3D printing honeycomb geometric deformation sensors which exhibited excellent stability and durability in response to long-time cycles and various deformations. CCNFs was also an excellent microwave absorber, that selectively absorbed microwave energy and created localized heat within 3D printed CCNFs-PLA. The heat enabled amorphous PLA from the matrix to reorient to form crystallites, and simultaneously supported the growth of already existing less perfect or small crystallites into larger ones. Long-time annealing at high temperature accelerated crystallite combination process, but could impair relevant tensile strength. An optimal crystallinity and tensile strength could be achieved at lower annealing temperature. Specifically, microwave annealing at 80 °C helped 3D printed PLA composites accomplish high crystallinity as well as high tensile strength in an accelerated manner.

6.2 Future Work

Understanding the fundamental effects of carbonization parameters on CNFs-based carbon would give better tuning on the properties of the carbon materials and allow the CCNFs to be more competitive. CCNFs are moderate conductive, which normally requires to combine with other conductive nanofillers to boost conductivity. Other than physical blending with CB as suggested
in Chapter 4, an alternative approach would be surface modification on CCNFs, such as surface chemistry and heteroatoms doping. Surface chemistry, including oxidation, amination, and sulfonation, is mainly used as a preliminary step for further chemical grafting. Heteroatoms doping is carried out by incorporating non-carbon atoms (e.g., nitrogen, phosphor, sulfur, and boron) to replace some carbon atoms in the carbon network. Recombination with other nanomaterials via chemical bonds has great potential to improve the utilization diversity of CCNFs. Therefore, I would suggest the future work to focus on developing innovative recombination approach for CCNFs towards novel applications.
VITA

Ju Dong was born and grew up in Zibo, Shandong province, China. He received his B.Eng. degree in Light Chemical Engineering from the Jiangnan University, China, in 2012. He received his M.S. degree in Textile Chemistry from North Carolina State University, in 2014. His master thesis work was about the utilization of photo-thermal effect of gold nanoparticles for curing liquid epoxy-PMMA core-sheath electrospun fibers. He started his doctoral study at Louisiana State University in 2016. Since then, he has been working under the guidance of Dr. Qinglin Wu in the school of Renewable Natural Resources. He is also pursuing a minor in Mechanical Engineering as his Ph.D. project is closely related to enhancing mechanical performances of 3D printed thermoplastic composites by integrating with cellulose nanofibers.