Spray-Dried Cellulose Nanofibril-Reinforced Polypropylene Composites for Extrusion-Based Additive Manufacturing

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SPRAY-DRIED CELLULOSE NANOFIBRIL-REINFORCED
POLYPROPYLENE COMPOSITES FOR EXTRUSION-
BASED ADDITIVE MANUFACTURING

By

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A DISSERTATION
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
(in Forest Resources)

The Graduate School
The University of Maine
December 2017

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By Lu Wang

Dissertation Advisor: Dr. Douglas J. Gardner

An Abstract of the Dissertation Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (in Forest Resources)

December 2017

Compared to conventional manufacturing process, additive manufacturing (AM) offers free-form design, lighter and more ergonomic products, short lead time and less waste. Extrusion-based AM can be used to print thermoplastics. However, extrusion-based AM has processing challenges in printing semi-crystalline thermoplastics, for instance, polypropylene (PP). Cellulose nanofibrils (CNF) are one type of cellulose nanofibers that are produced from pulp fibers. CNF has extraordinary properties which make it an ideal candidate to reinforce polymers. Spray-dried CNF (SDCNF) is able to be incorporated into thermoplastic matrices without modifying conventional processing procedures.

The mechanical properties of 3D printed plastic parts have been considered significantly weaker than injection molded parts because the former contains more pores. However, with proper printing parameter selection, the mechanical properties of 3D printed parts can be very close to that of injection molded parts. What’s more, 3D printed
parts have lower density than injection molded parts, making it an ideal material for lightweight applications.

The shear rate involved in extrusion-based AM is reported to be much smaller than that during injection molding. Adding fillers would empirically increase the viscosity. However, the incorporation of SDCNF, up to 10 wt.%, did not significantly increase the viscosity of PP melts, even at a smaller shear rate.

Isotactic polypropylene (IPP) crystallizes much faster than other semi-crystalline thermoplastics used in extrusion-based AM. The overall crystallization rate depends on the nucleation rate and crystal growth rate. Adding fillers should increase the nucleation rate by providing more heterogeneous nucleation sites. Meanwhile the fillers decrease the crystal growth rate by reducing the available space for crystals to grow. At 10 wt.% loading level of SDCNF, the increase in nucleation rate was smaller than the decrease in crystal growth rate. So 10 wt.% SDCNF retarded the overall crystallization rate of iPP.

PP printed at a bed temperature of 120 ºC showed both α and β-crystal forms while injection molded PP only showed α-crystals. The heat deflection temperatures (HDT) of 3D printed parts were higher than injection molded parts because the voids in the 3D printed parts acted as thermal insulators that delayed heat transfer during the HDT test.
DEDICATION

First, I dedicate my dissertation work to my parents who provide me with a decent childhood, fundamental education and all the support they can give.

The person I most want to dedicate this dissertation work to is my wife, Yan Liu, who takes care of most housework and babysitting so I can focus on my research and thesis. By the way, she was in her graduate program in the past two years too.

I also want to dedicate this dissertation work to my parents-in-law who were here to help with babysitting so my wife and I can get most of our work done.

In addition, I want to dedicate this dissertation work to my daughter Ella M. Wang. It has been a very wonderful experience since she joined the family. I also want to thank my son, Aiden L. Wang, who gave the family another hope to look forward to during the last year of my Ph.D. study.

Without all of you, this thesis work would not be possible.
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Being a foreign student, I want to thank the staff from the Office of International Program, especially Ms. Mireille Le Gal and Ms. Sarah Joughin. Without them, my study in Maine or internship in Michigan was not possible.

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1.1 Thermoplastics

Plastics are the most commonly used materials now. Over 350,000 million pounds of plastics were consumed during the start of the 21st century (Rosato et al. 2010). There are about 35,000 types of plastics, 200 families, but fewer than 20 are widely used (Rosato et al. 2010). Among consumed plastics, 90% are thermoplastics and the rest are thermosets. Comparisons of the advantages and disadvantages of thermoplastics and thermosets are shown in Table 1.1. The major merit of thermoplastics over thermosets is their recyclability. Plus, thermosets contain partially uncured monomers that can possibly cause toxic emissions later. With the increasing concern on environmental issues, thermoplastics have more advantages over thermosets. Thermoplastics are further categorized into commodity and engineering plastics. Commodity thermoplastics, often cheaper than $1/pound, account for 2/3 of all thermoplastic sales. Major types are low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) and polyvinyl chlorides (PVC) (Harper, 2000, Rosato et al. 2010).
<table>
<thead>
<tr>
<th>Advantages</th>
<th>Thermoplastics</th>
<th>Thermosets</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>highly recyclable</td>
<td>more resistant to high temperature</td>
</tr>
<tr>
<td></td>
<td>high-impact resistance</td>
<td>highly flexible design</td>
</tr>
<tr>
<td></td>
<td>remolding capabilities</td>
<td>high dimensional stability</td>
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<tr>
<td></td>
<td>chemical resistant</td>
<td>good fiber wet-out</td>
</tr>
<tr>
<td></td>
<td>emission-free manufacturing</td>
<td>creep resistant</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>prone to creep</td>
<td>brittle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>not recyclable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>not re-moldable</td>
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</tbody>
</table>

Table 1.1 Comparisons between thermoplastics and thermosets.

PP is a commodity thermoplastic which comes from naphtha cracking, gasoline refining and propane dehydrogenation. Many advantages (low price, low weight, good processability, resistance to weathering and recyclability) make PP accepted worldwide with a demand of over 21 million pounds per year (Harper, 2000). However, the mechanical properties of PP are not comparable to engineering plastics, limiting its usage in the engineering fields. Filling PP with inorganic particles like glass fiber and talc can enhance the stiffness and strength of PP, extending the applications of PP composites to exterior automotive (dome lights, mount and engine covers) and structural areas (Harper 2000). The unrecyclable nature of inorganic fillers usually causes trouble in the recycling process of PP. Increasing mechanical properties, as well as keeping recyclability and sustainability require more attention.

1.2 Additive manufacturing

Additive manufacturing (AM), commercially known as 3D printing, is a dynamic processing technology which fabricates materials layer by layer from bottom to up (Wendel et al. 2008). Usually an object is drawn in software like AutoCAD and stored as a stereolithography (STL) file. The slicing software slices the object and converts it to
readable commands for the printer. After that, the printer builds each layer according to the preset pattern (Wendel et al. 2008). AM exceeds conventional manufacturing techniques in several aspects: 1) it is able to build materials with complex geometries which is impossible by traditional methods; 2) it doesn’t require additional tools like dies; 3) it doesn’t require a lot of assemblies because products are directly fabricated by printers; 4) it generates less waste, which is only 10% loss of raw material; 5) it helps companies save up to 70% of the manufacturing costs; 6) sometimes products made by AM can be up to 60% lighter and 7) composites made from different materials can be manufactured using multiple-material AM (http://calipermedia.com/the-advantages-of-3d-printing/, http://augmentedtomorrow.com/9-benefits-3d-printing/, Vaezi et al. 2013)

The International Committee on Additive Manufacturing Technologies has classified seven major AM techniques: photopolymer vat, material extrusion, powder bed fusion, directed energy deposition, sheet lamination, material jetting and binder jetting (Vaezi et al. 2013). Each type of AM is suitable for certain types of raw materials. Techniques can be used for polymers include stereolithography (SLA), 3D-printing (3DP), selective laser sintering (SLS), selective mask sintering (SMS), laminated object manufacturing (LOM) and fused deposition modeling (FDM) (Wendel et al. 2008). SLS has very limited applicable polymer sources (Nylon12, PC, PS) attributable to its strict requirements for processing conditions. LOM seems to have problems with printing complex shapes with embedded functional inserts. Parts from 3DP have almost 50% of porosity, which requires further infiltration by resin to enhance their mechanical properties. Several terms are named for the materials-extrusion-type of AM. The earliest and most widely used one is fused deposition modeling (FDM) which is a brand of the
Stratasys Ltd. To avoid conflicts, fused filament fabrication (FFF) was developed by RepRap (http://reprap.org/wiki/Fused_filament_fabrication). The recent ASTM standard (ISO/ASTM 52900:2015) called this technique as material extrusion. In a published book, the author called it fused layer modeling (FLM) (Gebhardt, 2012). During FLM processing (Figure 1.1), a polymer filament is continuously melted in a chamber and extruded through a nozzle according to the preset drawing in the software. After the first layer is built, the platform lowers a certain distance to receive the deposition of the second layer. By keeping doing this, the final part can be made. Compared to AM methods, FLM is cheaper and easier to operate (Drummer et al. 2012, Korpela et al. 2013). Moreover, the lower cost of FLM technology and its ability to manufacture waste polymers makes directly recycling plastics waste in-house possible. Remember, the collection, transport and transfer of recycling waste to be deposed of centrally are time, labor and money consuming and cause greenhouse gas emissions, compromising the benefits of recycling these wastes (Baechler et al. 2013).

Figure 1.1 Configuration and deposition method of FLM printer
Like other AM techniques, there are still obstacles to be overcome for using FLM for real-life production. First of all, plastics from FLM technology usually have inferior properties compared to those from conventional methods (Ivanova et al. 2013). During FLM, layers are made by laying down strands that are adjacent but not fully in contact with each other (Figure 1.1). Therefore, voids are formed, which can lower the parts’ mechanical properties. A degradation of 30%-53% on strength and modulus, depending on printing orientation, was found in FLM polycarbonate material (Smith and Dean 2013). Moreover, not all thermoplastics are suitable for FLM. Commercial available polymers for FLM mainly include acrylonitrile-butadiene-styrene (ABS), Nylon 12, polyphenylsulfone (PPSF), polylactic acid (PLA), polycarbonate (PC), polycaprolactone (PCL), ABS/PC blends, acrylonitrile-styrene-acrylate (ASA) (http://www.stratasys.com/materials/fdm.). Largely used regular polypropylene (PP) and polyethylene (PE) are rarely reported in the literature and commercial marketplace.

1.3 Processing control of FLM

To strengthen these weaknesses of FLM, processing control is one of the solutions. By adjusting manufacturing parameters, mechanical properties of each laid down strand, as well as the adhesion between each layer can be enhanced. Processing-related factors influencing properties of FLM parts are strand width, air gap, extrusion temperature, build direction, raster angle, color, envelope temperature, slice height, nozzle diameter, location, humidity, filament diameter, deposition speed (Anitha et al. 2001, Ahn et al. 2002, Sun et al. 2008, Gurrala and Regalla 2014, Hill and Haghi 2014). Slice height in the vertical direction is similar to the strand width and is also related to nozzle diameter (Ahn et al. 2002).
Build direction refers to the position of made parts where it can either be sitting down flat or on its side (Lee et al. 2007). Build direction sometimes has the same effect as raster angle (Smith and Dean 2013). Raster angle refers to the direction of laid-down strand relative to the reference plane of the specimen (Hill and Haghi 2014). Longitudinal deposition has the best performance, followed by default, diagonal and transverse direction in descending order.

Air gap means the space between strands (Ahn et al. 2002). A positive value means strands do not contact each other. Zero means strands just touch. A negative value means strands partially overlap. Negative air gap gave better adhesion among roads, therefore, is good for mechanical properties. Extrusion temperature and color didn’t affect mechanical properties (Ahn et al. 2002).

Processing factors affecting the bonding quality between roads by FLM were evaluated (Sun et al. 2008). Generally, the temperature of the bottom layer rises abruptly when a new layer is deposited above, but it drops quickly too. The mean temperature of bottom layer increases as layer number increases. Necks grow better on the bottom layers so that voids in the bottom are smaller than in top layers. This is because of a longer thermal history and a larger creep deformation by gravity. Higher extrusion temperature did not increase $T_{\text{min}}$ (the average of lowest temperature of each deposition path). Higher envelope temperature can increase $T_{\text{min}}$. High $T_{\text{min}}$ is good for intermolecular diffusion and better bonding quality. Average temperature is higher at the center of the build plate than the edge. Parts built near the center have larger neck growth than near the edge and have a corresponding higher failure load.
A mathematical model was developed to understand how part strength evolves with bonding between filaments in FLM (Gurrala and Regalla 2014). A direct proportional relation was found between diffusion time \((t)\) and half-angle of neck \((\theta)\). If given enough time for the diffusion between two strands to occur under desired temperature, two roads will finally coalesce into one. In reality, the active diffusion time won’t exceed a few seconds. Thus two roads cannot completely coalesce into one before solidification. Given initial radius \((r_0)\) and length \((l_0)\) of strand, yield strength of the strand \((\sigma)\), the relation between half-angle of neck \((\theta)\), number of roads and ultimate load \((F)\) can be obtained as: 

\[
F = \sigma \times 2r_0 \sin \theta \times l_0 \times (n - 1). \quad \text{Because } \theta \text{ is proportional to } t, \text{ ultimate tensile load } (F) \text{ will increase given longer diffusion time } (t). \text{ However, } t \text{ won’t be longer than a few seconds, so } F \text{ would reach maximum. This again tells how important the thermal history is for FLM parts.}
\]

A methodology was used to determine the stiffness matrix of a part built by FLM using classic lamination theory (CLT) (Bellini and Güçeri 2003, Ahn et al. 2003). Predicted results fit reasonably well with experimentally tested results. Discrepancy can be reduced by using a more detailed failure model. However, the results showed that failure was underestimated by using a finite element analysis when considering the FLM part as isotropic.

### 1.4 Filler as the reinforcement

Fillers have been added into the FLM filaments, aiming at enhancing the mechanical and functional properties of printed parts. Investigated fillers included: carbon fibers (Ning et al. 2015, Tekinalp et al. 2014, Tian et al. 2016, Yang et al. 2017),
thermotropic liquid crystalline polymers (Gray et al. 1998a, Gray et al. 1998b), glass fibers (Zhong et al. 2001, Carneiro et al. 2015), minerals (Drummer et al. 2012, Corcione et al. 2017), metals (Nikzad et al. 2011, Hwang et al. 2015), natural fibers (Duigou et al. 2016, Murphy and Collins 2016, Tao et al. 2017, Milosevic et al. 2017, Stoof et al. 2017). Nanofillers are outstanding in reinforcing polymers. Recently, nanofillers also have been applied in polymers made by FLM for performance enhancements (Ivanova et al. 2013). Investigated nanofillers include graphene (Dul et al. 2016, Prashantha and Roger 2017), carbon nanotubes (Shofner et al. 2003a,b, Daver et al. 2016), nanoclay (Weng et al. 2016, Francis and Jain 2016) and cellulose nanofiber (Dong et al. 2017). Moduli of the FLM polymer composites were higher than the molded pure polymers (Shofner et al. 2003, Tekinalp et al. 2014, Weng et al. 2016, Yang et al. 2017). Strength of FLM polymer composites can be higher (Tekinalp et al. 2014, Yang et al. 2017), similar (Shofner et al. 2003a, Carneiro et al. 2015) or lower (Duigou et al. 2016, Weng et al. 2016, Daver et al. 2016) than molded pure polymers. As molded polymer composites, the strain at break of FLM composites was lower than molded pure polymers (Shofner et al. 2003). Interfacial strength among strands was decreased because of weak fiber-polymer interaction (Yang et al. 2016). The degradation source of mechanical property are the voids formed inside the printed parts (Duigou et al. 2016). The increase in strength is caused by the molecular orientation induced by the printing nozzle and the fiber reinforcement (Tekinalp et al. 2014, Yang et al. 2017). Functionality was imparted to the polymer matrices once different fillers were added. Metals improved the thermal conductivity of the polymer matrices (Nikzad et al. 2011, Hwang et al. 2015). Carbon nanotubes increase the electric conductivity of the polymer (Daver et al. 2016).
1.5 Cellulose nanofibrils (CNF)

Nanocellulose possesses excellent mechanical properties and is deemed to be environmental friendly and very low cost compared to other nanofibers (Moon et al. 2011). Depending on how it is manufactured, nanocellulose can be categorized into three groups typically: cellulose nanofibrils (CNF), cellulose nanocrystals (CNC) and bacterial cellulose (BC) (Wang et al. 2016). Because of their fibril structure that forms entanglement in polymer matrices, CNF was reported to be a better reinforcement (Xu et al. 2013). All nanocellulose is originally produced in a suspension form (Peng et al. 2012a). To incorporate nanocellulose into thermoplastic matrices using current melting compounding process, a dried form is desired (Peng et al. 2012b). Spray drying was reported to potentially produce dried CNF at commercial scale with relatively lower cost (Peng et al. 2012a).

To date, there is no publication dealing with CNF reinforced PP filaments for FLM. However, research using CNF as a reinforcement in PP using conventional processing methods has been reported in several review articles (Hubbe et al. 2008, Siro and Plackett 2010, Siqueira et al. 2010, Moon et al. 2011, Khalil et al. 2012, Miao and Hamad 2013, Gardner et al. 2015, Wang et al. 2017). Generally, two methods are used for making the composites: solvent casting and molding (Hubbe et al. 2008). Molding is an industrially favorable process because of its cost and production rate. Therefore, only CNF-PP composites made by molding processes were reviewed here. A comparison on the mechanical property of CNF-PP composites from previous research is listed in Table 1.2.
Table 1.2 Mechanical property change of PP after adding CNF and MAPP.

<table>
<thead>
<tr>
<th>Fiber preparation</th>
<th>Freeze-dried</th>
<th>Spray-dried</th>
<th>In situ fibrillated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composites Composition (PP/MAPP/CNF)</td>
<td>(90/0/10)</td>
<td>(87/3/10)</td>
<td>(94/0/6)</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>↑19%</td>
<td>↑21%</td>
<td>↑43%</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>↑10%</td>
<td>↑35%</td>
<td>↑20%</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>↑12%</td>
<td>↑7%</td>
<td>↓5%</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>↓25%</td>
<td>↓7%</td>
<td>↑3%</td>
</tr>
<tr>
<td>Impact strength</td>
<td>↑19%</td>
<td>↑23%</td>
<td>↑74%</td>
</tr>
</tbody>
</table>

A comparison among cellulosic fillers: CNC, CNF and microcrystalline cellulose (MCC), was done to study their influences on the characteristic impact resistance of PP (Yang et al. 2011). Fibers and PP were compounded and extruded by a Brabender Prep-mixer where fiber loading level varied from 0-10 wt.%. As fiber content increased, the impact strength decreased because fillers aggregated at higher loading level. The agglomeration of fillers made cracks easier to propagate since no crack initiation energy was required. Adding filler to PP increased its fracture resistance, but decreased its crack sensitivity. CNC/PP was found to have the highest characteristic impact resistance.

CNF-PP nanocomposite was made through melt compounding and extrusion (Peng et al. 2016). To improve the compatibility between PP and CNF, maleic anhydride PP (MAPP) was used as the coupling agent. A loading level of 30 wt.% CNF was first made according to a masterbatch formulation. Then the masterbatch was diluted to final loading level with fresh PP. The compound was extruded and chopped into pellets. Those pellets were then injection molded into testing samples. The best result showed increases of 36 % in tensile modulus, 11% in tensile strength, 21 % in flexural modulus, 7% in
flexural strength and 23% in impact strength were observed for reinforced PP at a fiber content of 6 wt.%. Improved impact strength was attributed to the coupling agent which decreased the amount of separate surfaces and increased the interaction between matrix and reinforcement.

The mechanical properties of CNF reinforced PP composites using MAPP as coupling agent via melt compounding were investigated. Freeze-dried CNF was added into PP at 2.5 wt.%, 5 wt.%, 7.5 wt.% and 10 wt.% loading levels (Hassan et al. 2013). Tensile modulus of the CNF-PP (10/90) composites was 10% larger than PP, whereas the tensile strength of the composite was degraded by 25%. The reduced tensile strength was partially caused by a lowered crystallinity (measured by X-ray diffraction calorimetry) of PP when CNF was present. The tensile modulus and tensile strength of CNF-MAPP/PP (10/2/88) composite were 33% higher and 7% weaker than PP, respectively.

Cellulose was nanofibrillated and melt compounded with PP and MAPP in-situ by processing water slurry containing refiner treated kraft pulp and powdered PP resin (Suzuki et al. 2013, Suzuki et al. 2014). Modulus and strength of PP increased as CNF content increased. Tensile modulus and strength of CNF-PP (30/70) composite were 33% and 17% higher than PP. Flexural modulus and strength of CNF-PP/MAPP composites were 57% and 28% larger than PP at a composition of 30/66.7/3.3. Izod impact strength of CNF-PP composite, at the same composition increased by 74%. The addition of 2 wt.% MAPP to CNF-PP (30/70) composites improved the flexural strength by 41% without changing the flexural modulus.
Another study used spray-dried CNF to reinforce PP at a fiber content of 6 wt.% (Peng et al. 2016). Tensile modulus of CNF-PP (6/94) composites was 20% larger than PP with no significant improvement in tensile strength. Flexural modulus and flexural strength of CNF-PP (6/94) composites were 19% and 12% higher than PP. Izod impact strength of the composite was similar to PP. The addition of 2 wt.% MAPP significantly improved the impact strength of CNF-PP composites without changing the flexural properties.

Influences on the mechanical properties of PP by CNF with surface coating of polyoxyethylene nonylphenyl ether (PNE) was investigated (Iwamoto et al. 2014). Coating was done in 5 wt.% water suspension of CNF and PNE (weight ratio of 1:4). The suspension was dried, mixed with PP and MAPP and compounded in a twin-screw extruder. The composite had higher strain-at-break value than neat PP. This may be because CNF dispersed very well in the matrix with the coating, which toughened the composite. Good dispersion facilitated by PNE at 10 wt.% and good compatibility induced by MAPP at 10 wt.% resulted in the CNF-PP composites showed 45% higher in Young’s modulus and 50% higher in yield strength than neat PP.

1.6 Dissertation objectives and approach

The overall goal of the proposed research is to address fundamental issues related to processing CNF-PP composites via extrusion-based AM. The specific objectives are as follows: 1) explore the relation between processing parameters and mechanical properties of printed PP; 2) investigate how SDCNF changes the rheological properties of iPP; 3)
study how SDCNF influences the crystallization kinetics and thermal expansion of iPP; 4) test the thermal properties of CNF-PP composites made by extrusion-based AM.

Chapter 2 characterized the effect of three printing parameters: layer height, extrusion temperature and printing speed on the mechanical properties of printed parts using a commercially available PP filament. Differential scanning calorimetry (DSC) was used to understand how different processing conditions affected the crystal form of samples. Scanning electron microscopy (SEM) was applied to study the inner structure of samples. Mechanical tests were done to compare strength and stiffness properties of the printed samples and their injection molded counterparts. Chapter 3 revealed the effects of CNF contents and maleic anhydride polypropylene (MAPP) coupling agent on the rheological properties of CNF-PP composites. A parallel-plate rheometer is sufficient to provide useful rheology information. Chapter 4 examined the effect of cellulose nanofibrils (CNF) and maleic anhydride polypropylene (MAPP) addition on the nonisothermal crystallization kinetics and thermal expansion of iPP. A DSC was used for the crystallization kinetics study. Chapter 5 studied the thermal properties of SDCNF-PP composites from extrusion-based AM. Thermogravimetric analysis (TGA), DSC and dynamic mechanical analysis (DMA) were used to obtain relevant information.
CHAPTER 2

EFFECT OF FUSED DEPOSITION MODELING PROCESS PARAMETERS ON
THE MECHANICAL PROPERTIES OF POLYPROPYLENE

2.1 Chapter summary

Few commodity pure semi-crystalline thermoplastics are used in fused deposition modeling (FDM) because they can experience dimensional instability (warping) during printing. In this study, a commercially available polypropylene (PP) composite for FDM processing was used to print tensile and flexural test samples. Three printing parameters were investigated: 1) extrusion temperature (200 °C, 250 °C), 2) printing speed (45 mm/s, 90 mm/s) and 3) layer height (0.1 mm, 0.3 mm). Differential scanning calorimetry (DSC) showed that FDM printed PP samples had less α-crystal and more β-crystal than injection molded (IM) PP samples. Scanning electron microscopy (SEM) indicated that higher extrusion temperature, slower printing speed and smaller layer height facilitated the molecular diffusion at the interfaces and created smaller neck size within the printed parts. Density measurements showed that IM PP samples were denser than FDM PP. No difference in density was found among the FDM PP samples. Compared to the IM PP, mechanical properties decreased less for the PP printed at higher extrusion temperature (<11.5%). However, the FDM PP had similar or even increased flexural modulus than the IM PP.
2.2 Introduction

Additive manufacturing (AM), commercially known as 3D printing, is a dynamic processing technology which fabricates materials layer by layer from the bottom up. Usually an object is drawn using software and stored as a stereolithography (STL) format file. The printer software reduces an object into slices and converts it to a readable format for the printer. After converting the designed part into a readable format, the printer builds each layer according to the preset pattern (Wendel et al. 2008). AM exceeds conventional manufacturing techniques in several aspects: 1) it is able to build materials with complex geometries which is impossible by traditional methods; 2) it does not require additional tools like dies and 3) it does not require much assembly because products are directly fabricated by printers (Vaezi et al. 2013). Different materials require different AM techniques. Techniques that can be used for polymers include stereolithography (SLA), selective laser sintering (SLS), selective mask sintering (SMS), laminated object manufacturing (LOM) and fused layer modeling (FLM) or fused deposition modeling (FDM) (Wendel et al. 2008). During FDM processing (Figure 2.1), a polymer filament is continuously melted in a chamber and extruded through a nozzle. After the first layer is built, the platform lowers a certain distance to receive the deposition of the second layer. By repeating this process, the final part can be made. Compared to other rapid prototyping methods (RP), FDM is cheaper and easier to operate (Korpela et al. 2013).
Figure 2.1 Configuration of the 3D printer used in this study.

Within an FDM printed part, an interface forms when the adjacent laid-down polymer strands come into contact with each other. The interfacial width increases and interface gradually disappears as polymer molecular diffusion develops, resulting in mechanical properties increase (Kim and Wool 1983). The interface and pores that are generated in an FDM part are beneficial for cell reproduction, thus easily fit the technology into medical applications, for example, implants and tissue engineering (Drummer et al. 2012). However, these voids degrade the mechanical properties of the printed parts compared to their injection molded counterparts.

There are commercially available thermoplastics can be used for FDM. However, some commodity thermoplastics are not widely used in FDM, for instance, isotactic polypropylene homopolymer (PP). Neat PP is a very versatile polymer and is among the most utilized thermoplastic in commercial production for materials (Harper 2000, Rosato et al. 2001). Adding PP to the material scope of FDM is desirable and beneficial. A few papers reported on the production of PP composites by FDM (Shofner et al. 2003, Carneiro and Gomes 2015, Wang and Gardner 2017; Milosevic et al. 2017). Investigated printing parameters included deposition orientation, different infill degrees and layer
thickness. Samples were stronger and stiffer when all the filaments were printed along the long axis of the sample. The tensile properties increased as the infill density increased. Layer thickness was found to insignificantly affect the mechanical properties of samples.

In this study, we evaluated the effects of layer height (LH), extrusion temperature (ET) and printing speed (PS) on the mechanical properties of printed parts using a commercially available PP filament. Differential scanning calorimetry (DSC) was used to understand how different processing conditions affected the crystal form of samples. Scanning electron microscopy (SEM) was applied to study the inner structure of samples. Mechanical tests were done to compare strength and stiffness properties of the printed samples and their injection molded counterparts.

2.3 Materials and Methods

2.3.1 Materials

PP homopolymer filament (1.75 mm in diameter), Moplen HP741T, was purchased from Gizmodorks, Temple City, CA. The HP741T is nucleated, with a modified molecular weight and high flow index (60 g/10 min at 230 °C/2.16 Kg). Its flexural modulus is 1.75 GPa. It features a balance between rapid cycle time and good mechanical properties. Food containers are its typical applications. Ash content (30 wt.%) of this PP was determined first according to ASTM D5630-13. Then a metal analysis was done on the ash and the major components are listed in Table 2.1.
Table 2.1 Major metals contained in the PP ash and their percentages.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Al</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>26.4</td>
<td>0.02</td>
<td>1.3</td>
<td>0.04</td>
<td>0.03</td>
<td>0.07</td>
</tr>
</tbody>
</table>

2.3.2 Fused deposition modeling (FDM) of PP

The models of testing samples were first drawn in Auto CAD (2014) according to the dimensions specified in ASTM D638-14 (Type I) for tensile tests, ASTM D790-10 for flexural tests. Those files were saved as the STL format for further configuration. The 3D printer used for this study was a Makerbot Replicator 2X Experimental 3D Printer (MakerBot Industries, LLC, NY, USA). Features of this type of 3D printer are shown in Figure 2.1. Compared to other FDM devices, this device has two extrusion heads, enabling the printing of two different filaments within one building process. To start a printed part, the STL file was opened in Makerware software (Version: 3.9.0), centered, laid flat and printed with the right-side nozzle. Printing parameters were changed in “settings” in the software. Advanced parameters were altered in a customized profile. To achieve a 0° orientation, “infillorientationoffset”, “infillorientationinterval”, "solidfillorientation offset" and "solid fill orientation interval" were set in the customized profile at 90°, 0°, 90° and 0° respectively. Air gap was changed by varying the number of “gridspacemultiplier” between 0 and 1. A complete overlap between two adjacent filaments is achieved by choosing 0; while a simple contact happens when 1 is selected. According to the manufacturer, both an extrusion temperature ranges of (210, 230 °C) and (250, 280 °C) would result in a good printing quality. Thus, two temperatures within
those ranges were chosen. A platform temperature of 130 °C was chosen as it is in accordance with the upper limit of the printer software. The default printing speed is 90 mm/s. As a lower level, 45 mm/s was chosen for comparison. Infill density was set to 100% to make solid samples. The number of shells was reduced to 1 to minimize its influence on the mechanical properties. The layer width was fixed at 0.4 mm regardless of the layer height. To improve the adhesion between the first PP layer and platform, a piece of office packing tape (Office Depot®, OfficeMax # 24767995) was laid down on the platform before printing. The total experimental design is shown in Table 2.2.

Table 2.2 Experimental design and sample nomenclature.

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Denomination</th>
<th>ET/°C</th>
<th>PS/(mm/min)</th>
<th>LH/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection molding</td>
<td>IM</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FDM</td>
<td>A</td>
<td>250</td>
<td>90</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>250</td>
<td>90</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>250</td>
<td>45</td>
<td>0.3</td>
</tr>
<tr>
<td>Fused deposition modeling</td>
<td>D</td>
<td>250</td>
<td>45</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>200</td>
<td>90</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>200</td>
<td>90</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>200</td>
<td>45</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>200</td>
<td>45</td>
<td>0.1</td>
</tr>
</tbody>
</table>

ET: extrusion temperature; PS: printing speed and LH: layer height

2.3.3 Injection molding

Filaments were pelletized in a Hellweg MDS 120/150 granulator (Hackensack, NJ). Pellets were then processed in an injection molder Model #50 “Minijector” with a ram pressure of 17 MPa at 200 °C and held in the molds for 10s to cool. Molds provide sample with dimensions specified in ASTM D638-14 (Type I) and ASTM D790-10. The samples were then put into plastic containers and stored in desiccators to maintain
dryness. Before testing, samples were conditioned in a chamber for at least 40 h at 23 °C±2 °C and 50% ±10 % RH.

2.3.4 Differential scanning calorimetry (DSC)

Melting behavior of the processed PP was studied by DSC using a TA Instruments Q 2000 Calorimeter (New Castle, Delaware, USA). All measurements were performed under nitrogen (nitrogen flow = 50 mL/min) to avoid degradation of PP upon heating. 8-10 mg of each sample was put in a sealed aluminum pan. Samples were heated up from 25 to 200°C at a rate of 10°C/min.

2.3.5 Scanning electron microscopy (SEM)

SEM studies on the morphologies of FDM samples were carried out using a Hitachi TM 3000 SEM (Tokyo, Japan). All samples were cryofractured within liquid nitrogen to prepare the surface because either microtome or hand trimming smeared the surface severely. Because of the low definition requirement in this research, no sputter-coating was done before the microscopic observations. SEM images were taken at an accelerating voltage of 15 kV at various magnifications.

2.3.6 Density

A QMS X-ray densitometer (Knoxville, Tennessee) was used to measure the density profiles of both injection molded and printed samples. Sample dimensions were 63.5*12.5*3.2 mm. Density determination by the scanning system is based on the relationship between X-ray attenuation and density as expressed in the following equation (Jeong 2005).
\[ \frac{I}{I_0} = \exp(\mu \rho t) \]  \hspace{1cm} (1)

where \(I\) = intensity of radiation beam after passing through the sample, \(I_0\) = intensity of radiation beam before passing through the sample, \(\mu\) is the material mass attenuation coefficient (\(m^2/kg\)), \(\rho\) is the material density (\(kg/m^3\)) and \(t\) is material thickness (m). At least five samples were tested for each group.

2.3.7 Mechanical properties

Tensile and flexural tests were performed according to ASTM D 638-14 and ASTM D 790-10 to obtain data on tensile and flexural properties. Tests were conducted at room temperature 23 ± 2 °C and 50 ± 10 % RH. A universal testing machine (Instron 5966) with a 10 kN load cell was used for the tests. An extensometer was mounted to measure the elongation of the samples. The tensile test speed was set at 50 mm/min to break the sample within 5 min. The span for the flexural test was 51 mm. The outer fiber strain rate for flexural tests was 0.01/min, resulting in a flexural test speed of 1.4 mm/min. Five replicates of each sample were tested. The average and standard deviation of Young’s modulus and strengths from tensile and flexural tests were calculated.

\[ \text{specific mechanical properties} = \frac{\text{mechanical properties}}{\text{density}} \]  \hspace{1cm} (2)

2.3.8 Statistical Analysis

The density, tensile and flexural properties and specific mechanical properties were analyzed using a three-way analysis of variance (ANOVA) along with a student test at \(\alpha=0.05\). All the analysis was done in JMP statistical analysis program (JMP Statistical...
Discovery Software Version 8 2008). A statistical model was used to represent the properties of PP.

\[ Y_{ijkl} = \mu + \alpha_i + \beta_j + \gamma_k + (\alpha \beta)_{ij} + (\beta \gamma)_{jk} + (\alpha \gamma)_{ik} + (\alpha \beta \gamma)_{ijk} + e_{ijkl} \]  (3)

Where \( i=1,2; j=1,2, k=1,2 \) and \( l=1,2,3,4,5 \). \( Y_{ijkl} \) is the mean of each property; \( \mu \) is the population mean of each property. The effects of extrusion temperature, printing speed and layer height on each property were represented by \( \alpha_i, \beta_j \) and \( \gamma_k \). Effects of interaction between two of the three factors on each property are represented by \( (\alpha \beta)_{ij}, (\beta \gamma)_{jk} \) and \( (\alpha \gamma)_{ik} \). The three-way interaction is represented by \( (\alpha \beta \gamma)_{ijk} \). \( e_{ijkl} \) is the error for this model.

After the ANOVA test was done, a t-test was used to investigate whether statistically significant differences existed between the IM PP and one of the FDM PP.

2.4 Results and Discussion

2.4.1 Crystal form

![DSC results of IM and FDM PP at scanning rate of 10 °C/min.](image)

Figure 2.2 DSC results of IM and FDM PP at scanning rate of 10 °C/min.
The DSC curves of PP samples are shown in Figure 2.2. In each case, at least two endothermic peaks are shown around 120 °C and 165 °C, which correspond to the melting temperatures of a proprietary gradient and the α-crystal in isotactic PP (iPP) (Tordjeman et al. 2001, Bourbigot et al. 2013). FDM PP produced at a higher extrusion temperature have less α-crystal character compared to IM PP, however, displaying a new peak around 150°C. This peak was reported to be the β-crystal of PP (Tordjeman et al. 2001). Factors causing the formation of β-crystal include special nucleating agent and processing strategy (Xiao et al. 2009, Bourbigot et al. 2013). β-crystal grows faster than α-crystal when crystallized between 100 and 130°C (Tordjeman et al. 2001). In this study, the printer build platform was always set at 130°C, which favored the β-crystal growth. It’s important to point out that the percentage of β-crystal is much higher in PP from lower extrusion temperature. This is because once the extrusion head temperature was at 250°C, the crystallization temperature for PP during printing exceeded 130°C which suppressed the β-crystal. Because of the formation of two different crystal forms during the DSC running, the crystallinity of the whole sample cannot be readily achieved (Li et al. 1999, Bourbigot et al. 2013).
2.4.2 Morphology of FDM PP

Figure 2.3 SEM micrographs of FDM PP printed using different parameters.
Figure 2.4 PP molecular diffusion across the road interfaces at different layer heights.

Cryofractured FDM PP surface micrographs are shown in Figure 2.3. The observed white particles in the SEM micrographs are metal salts inside the PP matrix. Each polymer strand laid down is called a “road”. Generally, “necks” are formed by incomplete diffusion among four adjacent roads as shown in Figure 2.4. Several important observations can be made by comparing groups. Samples with smaller layer height (Figure 2.3 B, D, F and H) have more interfaces but smaller neck size than those with larger layer height. As layer height decreases, the distance between the centers of two adjacent roads (up and down direction) decreases. The smaller layer height shortens the distance required to achieve the same degree of diffusion compared to larger layer height (Figure 2.4). Also, the total time for printing a sample increases if layer height is smaller. This gives the sample longer heat exposure duration during printing. Therefore, if other parameters are controlled, roads with smaller layer height have better diffusion on the interfaces and smaller neck size. However, in some areas, roads of smaller layer
height do not touch each other. A possible reason for that is the printer does not have enough accuracy control on layer width once the layer height is as small as 0.1 mm.

A comparison between higher extrusion temperature groups (ABCD) and lower extrusion temperature groups (EFGH) verifies that a higher extrusion temperature is able to produce denser bottom layers without interfaces. The bottom layers are in contact with the platform that is maintained at 130 °C during printing. Those layers have the highest temperature for the polymer to diffuse. This phenomenon was also reported in FDM fabricated ABS parts (Sun et al. 2008). A higher extrusion temperature can also increase the interfacial width and reduce neck sizes across the whole cross section because it enables the roads to diffuse more.

Upon comparing A and C (B and D, E and G, F and H), a slower printing speed would result in a larger interfacial width and a smaller neck size. When printing speed is slower, the total printing time for a sample increases. Each layer receives a longer time of heat exposure. The degree of diffusion is higher compared to a faster printing speed.

**2.4.3 Density profile**

As seen in Table 2.3, among all the three printing factors, only extrusion temperature has a significant effect on the density of FDM PP. The results in Figure 2.5a show that samples made at 250 °C, except Group D, have no significant difference from those printed at 200 °C. The effect of the printing setting on the density is possibly covered by the existence of metal salts which have much higher density than PP. As seen in Figure 2.5b, even Group D, the densest sample, is less dense than IM PP.
Table 2.3 Selected values from the ANOVA for densities of PP.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of freedom</th>
<th>Sum of squares</th>
<th>F value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected total model</td>
<td>39</td>
<td>0.0939</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ET</td>
<td>7</td>
<td>0.031</td>
<td>2.2535</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>1</td>
<td>0.0027</td>
<td>1.3855</td>
<td>0.2478</td>
</tr>
<tr>
<td>LH</td>
<td>1</td>
<td>0.0081</td>
<td>4.1366</td>
<td>0.0504</td>
</tr>
<tr>
<td>ET*PS</td>
<td>1</td>
<td>0.0024</td>
<td>7.5433</td>
<td>0.0098*</td>
</tr>
<tr>
<td>PS*LH</td>
<td>1</td>
<td>0.0018</td>
<td>1.2226</td>
<td>0.2771</td>
</tr>
<tr>
<td>ET*LH</td>
<td>1</td>
<td>0.0000025</td>
<td>0.9275</td>
<td>0.3427</td>
</tr>
<tr>
<td>ET<em>PS</em>LH</td>
<td>1</td>
<td>0.0011</td>
<td>0.0013</td>
<td>0.9718</td>
</tr>
<tr>
<td>Error</td>
<td>32</td>
<td>0.0629</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ET: extrusion temperature; PS: printing speed and LH: layer height.
* indicates significant level at $\alpha=0.05$

Figure 2.5 Densities of PP from the different FDM processing parameters (a) and a comparison between the IM PP and a FDM PP (b).
Density profiles of IM and FDM PPs are displayed in Figure 2.6. Densities of all samples are larger than 1080 kg/m³. The normal density of PP is around 900 kg/m³. As mentioned previously, the metal salts increase the density. Compared to IM PP, which shows density across the thickness is very consistent, the density values of FDM PP fluctuate all the way through the thickness direction. Samples printed with a smaller layer height have higher densities compared to those printed at larger layer height. A reason for this is that samples with smaller layer heights have a higher degree of diffusion and smaller void percentage compared to those with larger layer heights. For samples printed at 250 °C, regardless of printing speed or layer height, their density profiles all display a similar trend: density decreases from bottom to the top of a sample. On the contrary, samples printed at 200 °C do not show this trend. This finding is consistent with the SEM results. At 250 °C, neck size on the bottom side of the samples is smaller than those printed at 200 °C. Therefore, the bottom has a higher density than the top. In other words, density is more heterogeneous in samples printed at higher temperature and more homogeneous in samples printed at lower temperature.

Figure 2.6 Density profiles of FDM PP samples made using different process parameters and compared to IM PP samples.
2.4.4 Mechanical properties

Table 2.4 Selected values from the ANOVA for mechanical properties of PP.

<table>
<thead>
<tr>
<th>Sources</th>
<th>DF</th>
<th>Sum of squares</th>
<th>p value</th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TS</td>
<td>TM</td>
<td>FS</td>
<td>FM</td>
<td>TS</td>
<td>TM</td>
<td>FS</td>
<td>FM</td>
</tr>
<tr>
<td>Corrected total</td>
<td>39</td>
<td>38.9</td>
<td>1.7</td>
<td>75.9</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>model</td>
<td>7</td>
<td>32.5</td>
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<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ET</td>
<td>1</td>
<td>28.1</td>
<td>1.1</td>
<td>44.9</td>
<td>0.1</td>
<td>&lt;0.05*</td>
<td>&lt;0.05*</td>
<td>&lt;0.05*</td>
<td>0.08</td>
</tr>
<tr>
<td>PS</td>
<td>1</td>
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<td>0.0</td>
<td>1.0</td>
<td>0.1</td>
<td>0.08</td>
<td>0.08</td>
<td>0.09</td>
<td>0.02*</td>
</tr>
<tr>
<td>LH</td>
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<td>0.1</td>
<td>0.1</td>
<td>14.6</td>
<td>0.1</td>
<td>0.75</td>
<td>0.06</td>
<td>&lt;0.05*</td>
<td>0.15</td>
</tr>
<tr>
<td>ET*PS</td>
<td>1</td>
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<td>0.1</td>
<td>1.9</td>
<td>0.1</td>
<td>0.51</td>
<td>0.10</td>
<td>0.02*</td>
<td>0.07</td>
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<tr>
<td>PS*LH</td>
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<td>0.0</td>
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<td>0.35</td>
<td>0.34</td>
<td>0.02*</td>
<td>0.12</td>
</tr>
<tr>
<td>ET*LH</td>
<td>1</td>
<td>3.2</td>
<td>0.2</td>
<td>0.6</td>
<td>0.0</td>
<td>&lt;0.05*</td>
<td>0.05*</td>
<td>0.18</td>
<td>0.24</td>
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<tr>
<td>ET<em>PS</em>LH</td>
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<td>0.1</td>
<td>0.0</td>
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<td>10.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TS: tensile strength, TM: tensile modulus, FS: flexural strength, FM: flexural modulus

Results of the ANOVA test on the mechanical properties of PP are shown in Table 2.4. For tensile properties, the extrusion temperature*printing speed interaction has a significant influence on mechanical properties. For flexural strength, the extrusion temperature*printing speed interaction and the printing speed*layer height interaction show significant effects. Regarding the flexural modulus, only printing speed is the significant factor. No other individual factors or interactions show statistical significance.
<table>
<thead>
<tr>
<th>Processing method</th>
<th>Tensile properties</th>
<th>Flexural properties</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Strength (MPa)</td>
<td>Modulus (GPa)</td>
</tr>
<tr>
<td>IM</td>
<td>17.5 (0.4)</td>
<td>2.7 (0.04)</td>
</tr>
<tr>
<td>A</td>
<td>15.5 (0.2)</td>
<td>2.5 (0.07)</td>
</tr>
<tr>
<td>B</td>
<td>15.9 (0.7)</td>
<td>AB 2.6 (0.1)</td>
</tr>
<tr>
<td>C</td>
<td>15.6 (0.2)</td>
<td>B 2.64 (0.05)</td>
</tr>
<tr>
<td>D</td>
<td>16.4 (0.7)</td>
<td>A 2.7 (0.2)</td>
</tr>
<tr>
<td>E</td>
<td>14.1 (0.6)</td>
<td>D 2.4 (0.06)</td>
</tr>
<tr>
<td>F</td>
<td>13.8 (0.1)</td>
<td>D 2.2 (0.1)</td>
</tr>
<tr>
<td>G</td>
<td>14.8 (0.3)</td>
<td>C 2.3 (0.1)</td>
</tr>
<tr>
<td>H</td>
<td>13.8 (0.3)</td>
<td>D 2.2 (0.1)</td>
</tr>
</tbody>
</table>

The mechanical properties of PP are shown in Table 2.5. The flexural strength of PP, either IM or FDM, are 1.5 to 2 times larger than the tensile strengths, which was also found in a previous study on polymer mechanical behavior (Landel and Nielsen 1993). According to the “weakest link” theory, the tensile strength is the strength where the weakest element reaches its limit and breaks (Hodgkinson 2000). The flexural strength is the stress on the surface of a sample when it fails. Therefore, the flexural property of a surface affects that of a whole sample greatly (Hodgkinson 2000). This phenomenon is especially prominent in FDM. As seen from the SEM graphs, FDM PP has dense bottom layers attributed to the annealing which increases the properties of polymer. The flexural modulus of IM PP is close to the provided values in the material data sheet. But the tensile modulus of both PP is significantly higher than flexural modulus. One thing to note is the testing speed for tensile properties was set at 50 mm/min instead of 5 mm/min. This gives a higher value because the polymer is more elastic than viscous at higher testing speed. A combination of higher extrusion temperature and smaller layer height creates higher tensile strength. A combination of higher extrusion temperature and
smaller layer height results in better tensile modulus. A combination of higher extrusion temperature and slower printing speed produces higher flexural strength. A combination of slower printing speed and smaller layer height leads to better flexural strength. A slower printing speed produces a higher flexural modulus, however, this influence is not obvious. These findings correspond well to DSC, SEM and density profile results.

As seen in Figure 2.7, FDM PP is lower in tensile properties and flexural strength than IM PP. The decrease ranges of tensile strength, tensile modulus and flexural strength are respectively (6.1%, 21.1%), (-0.3%, 19.2%) and (3.2%, 16.6%). Decreases in strength are related to the existence of interfaces between roads, acting as stress concentration and initiating breaks (Sun et al. 2008). Among all the three factors studied, extrusion temperature has the most obvious effect on the mechanical properties loss. Higher extrusion temperature leads to smaller property loss. Although no significant differences are found among ABCD in terms of the mechanical properties, Group D appears to have
the highest mechanical properties. Group D also has comparable mechanical properties to IM PP except its tensile strength is lower by 6% (Figure 2.8). On the other hand, Groups BCDFGH have higher flexural modulus than IM PP. One research indicated that the flexural modulus of FDM ABS was also close to typical values of IM ABS (Ning et al. 2015). In other research, the bottom layer of FDM PLA was found to have a higher crystallinity compared to rest of the part (Drummer et al. 2012). Therefore, the properly annealed bottom layer may account for the good flexural modulus of FDM PP.

Figure 2.8 Comparisons on the mechanical properties between IM and FDM PP (Group D).

The percentage change of the specific mechanical properties of IM and FDM PP is shown in Figure 2.9. Clearly, the specific mechanical property loss is smaller than mechanical property loss. The influence of extrusion temperature on mechanical properties is still discernable. Higher extrusion temperature leads to less mechanical property loss. However, the influence of extrusion temperature is weakened by the normalization over density. Group B shows a slightly better overall specific mechanical
properties compared to ACD. Figure 2.10 states that Group B is as robust as IM PP, with a 16% enhancement in specific flexural modulus.

Figure 2.9 Change percentages of the specific mechanical properties of FDM PP compared to IM PP.

Figure 2.10 Comparisons on specific mechanical properties between IM and FDM PP (Group B).
2.5 Conclusions

In this study, three printing processing parameters; extrusion temperature, printing speed and layer height were explored to test their influence on the mechanical properties of FDM PP. The results obtained in this study clearly indicated that FDM, with proper processing control and material selection, has the capacity to make parts that are almost equally strong to their injection molded counterparts. The specific mechanical properties of FDM parts were mostly higher than their injection molded counterparts. FDM has the potential to be used for direct manufacturing, instead of prototyping, especially for lightweight applications.

DSC revealed that FDM PP had $\alpha$ and $\beta$-crystal forms while IM PP only had the $\alpha$-crystal. SEM results showed higher extrusion temperature, slower printing speed and smaller layer height resulted in denser internal structures with an increased interfacial width. FDM PP parts were lighter than injection molded PP. PP printed at 250°C was denser than PP printed at 200°C. Compared to injection molded PP, FDM PP parts had weaker tensile properties and flexural strength because the interfaces in printed PP acted as stress concentrating areas, initiating breakage during mechanical testing. PP printed at 250°C showed a smaller decrease in mechanical properties compared to IM PP than PP printed at 200°C. The mechanical properties of Group D were not significantly different from IM PP except its tensile strength was weaker by 6%. The specific mechanical properties of Group B parts revealed no difference from IM PP except its specific flexural modulus was significantly higher by 16%.
CHAPTER 3

CELLULOSE NANOFIBRIL-REINFORCED POLYPROPYLENE COMPOSITES
FOR MATERIAL EXTRUSION: RHEOLOGICAL PROPERTIES

3.1 Chapter summary

Polypropylene (PP) is not typically utilized in 3D printing material extrusion because PP shrinks and warps during the printing process. Cellulose nanofibrils (CNF) have the potential to make PP 3D printer processable and also enhance mechanical properties of PP printed parts. The rheological behavior of CNF-PP composites during material extrusion requires study because it is different from injection molding and compression molding processes. This study revealed the effects of CNF contents (3 wt.% and 10 wt.%) and maleic anhydride polypropylene (MAPP) coupling agent on the rheological properties of CNF-PP composites. Morphological analysis showed that CNF agglomerated during spray drying and a spherical structure was formed. Rheological tests showed that the elastic modulus, complex viscosity, viscosity, transient flow shear stress of PP were increased by the addition of 10 wt.% CNF, while the creep strain of PP was reduced. The damping factor and stress relaxation time remained the same when 10 wt.% CNF was added to the PP. Incorporation of MAPP into the CNF-PP composites impacted the rheological properties of the CNF-PP composites. Flexural strength and modulus of PP were improved by 5.9% and 26.8% by adding 10 wt.% CNF compared to the control.
3.2 Introduction

Rheological characterization of thermoplastics is critical to understand the fundamental flow behavior as well as provide information on processing. Several articles investigated the flow behavior of CNC/PP composites during melt compounding. The complex viscosity and storage modulus of PP increased dramatically with small addition of spray-freeze-dried CNC (5 wt.%) (Khoshkava and Kamal 2014). The increase came from the web-like morphology of spray-freeze-dried CNC and a good dispersion of fillers inside the polymer matrix. Meanwhile, spray-dried CNC at 5 wt.% addition level did not change the complex viscosity of PP significantly. This result can be attributed to CNC agglomeration and failure to form an interconnected web structure. Increasing the fiber content may be a solution to form such a structure inside the polymer matrix according to previous research on microcrystalline cellulose (Kiziltas et al. 2013). An increase in storage modulus and a decrease in transient flow stress of a PP melt with the addition of 1 wt.% CNC were also reported (Hassanabadi et al. 2015). On the other hand, the storage modulus, loss modulus and complex viscosity were reported to decrease as CNC content in the polymer increased, attributed to a dilution effect (Nagalakshmaiah et al. 2016). It was reported that the addition of 20 wt.% CNF increased the storage modulus of PP melt by a factor of three at 160 °C using a parallel-plate rheometer (Suzuki et al. 2016). In another study, 6 wt.% CNF in PP was found to increase the melt flow index (MFI), but the MFI decreased once 2 wt.% MAPP was incorporated (Peng et al. 2016). Information on the rheological properties of CNF-PP composites need further investigation.

In this study, CNF at two different addition levels (3 wt.% and 10 wt.% based on the weight of total material) with MAPP (2 wt.% based on the weight of total material)
were compounded into PP to prepare composite filaments for material extrusion. For a bench-scale material extrusion device, the shear rate ($s^{-1}$) involved in the printing process is much smaller compared to injection molding and extrusion. Because the diameter of the printing nozzle is smaller than that of the extrusion barrel, shear rate on the polymer at the nozzle is larger than that in the barrel. The shear rate at the printing nozzle was estimated to be in the range of 100-200 $s^{-1}$ (Turner et al. 2014). Therefore, a parallel-plate rheometer is sufficient to provide useful rheology information. The objective of this work is to report on the parallel-plate rheological behavior of CNF/MAPP/PP composites for material extrusion.

3.3 Materials and Methods

3.3.1 Materials

Cellulose nanofibrils (~3 wt.% suspension) were provided by the Process Development Center of the University of Maine. The CNF suspension is produced by a disk refining method. The suspension was diluted to 1.2 wt.% for spray drying using a pilot-scale spray dryer (GEA-Nitro). The drying was done at a temperature of 250 °C, a disk spinning rate of 30,000 rpm, and a pump feeding rate of 0.4 L/min. Homopolymer PP (H19G-01) was purchased from Ineos Olefins & Polymers USA (League City, TX). Its density is 0.91 g/cm$^3$ with a melting point of 160 °C and a MFI of 19 g/10min (230 °C/2.16 kg). Maleic anhydride polypropylene (MAPP) pellets (Polybond 3200) were obtained from Chemtura Corporation (Lawrenceville, GA). The MA content in the MAPP is about 1.0 wt.%. Density, melting point and MFI (190 °C/2.16kg) of the MAPP is 0.91 g/cm$^3$, 190 °C and 115 g/10min.
3.3.2 Morphology

Morphological information on the dried CNF was obtained by performing a particle size analysis using a microscope based image analysis system (Morphologi G3S, Malvern, UK). 5 mm$^3$ samples were loaded into a special holder with both sides sealed by 25 µm aluminum foil. The holder was placed in a dispersion unit and fibers were evenly dispersed on a glass plate with a pneumatic pressure of 0.5 MPa, injection time of 10 ms and settling time of 60 s. A 50X objective lens was used for measuring the CNF. The software converted the 2D projection of a particle to a circle with the same area. The diameter of the circle is called circle equivalent diameter (CE diameter) (Peng et al. 2012a). The morphologies of the spray-dried CNF were visualized using a Hitachi Tabletop Microscope SEM (Tokyo, Japan) at an accelerating voltage of 5 kV. The environmental SEM does not require sputter coating for observation. The same SEM was also used to visualize the CNF distribution within PP by observing the impact-fracture surfaces of injection molded specimens.

3.3.3 Composites manufacturing

Before compounding, CNF and PP pellets were oven dried for 2h at 105 °C. CNF was added into PP pellets and mixed by hand. A masterbatch containing 30 wt.% CNF was first made by starve-feeding the mixture into a twin-screw co-rotating extruder (C. W. Brabender Instruments, South Hackensack, NJ) attached to a drive system (Intelli-Torque Plastic-Corder). The material feeding rate was 8 g/min. The L/D of this extruder is 40/1. Previous work in our research group used a C. W. Brabender Prep Mixer (C. W. Brabender Instruments, South Hackensack, NJ) to prepare a PP masterbatch (Peng et al. 2016). The mixing method resulted in good distribution of CNF into the PP matrix.
Increasing the screw rotational speed from 200 rpm to 1000 rpm was found to improve the dispersion of nanoclay in PP (Peltola et al. 2016). However, better exfoliation of nanoclay did not create higher mechanical properties possibly attributable to more chain scission at the higher screw speed. Therefore, a screw speed of 250 rpm was adopted in this study and the process is referred to as a “fast masterbatch production process”. The extrusion temperature was set at 200 °C for all the five zones of extruder barrel. After exiting the extruder, the masterbatch was ground using a granulator (Hellweg MDS 120/150, Hackensack, NJ). The composite pellets, fresh PP and MAPP were oven dried at 105 °C before the second extrusion with the formulations in Table 3.1. During the second extrusion, the masterbatch was diluted with fresh PP pellets to the desired CNF filler contents. The extrusion temperature was 200 °C and screw speed was 250 rpm. The composite extrudate passed through a two-nozzle die with a nozzle diameter of 2.7 mm. The extrudate was carried by a 2200 Series End Drive Conveyor (Dorner, Hartland, WI) and finally chopped by a pelletizer. Pellets were made into flexural bars using an injection molder (Model #50 “Minijector”) with a ram pressure of 17 MPa at 200 °C. A mold with dimensions of 180 mm×55 mm×75 mm (length×width×height) was used. Samples were held in the mold at ambient temperature for 10s before demolding. To make the control sample, the as-received PP pellets went through the same extrusion and injection molding process for manufacturing.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Labels</th>
<th>PP</th>
<th>CNF</th>
<th>MAPP</th>
</tr>
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<tbody>
<tr>
<td>PP</td>
<td>PP</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PP+MAPP</td>
<td>PP-MA</td>
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<td>2</td>
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<td>PP+3% CNF</td>
<td>PP-3%</td>
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<td>0</td>
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<tr>
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<td>PP-3%-MA</td>
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<td>88</td>
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</table>

### 3.3.4 Rheological tests

Rheological tests were done using a stress-controlled Bohlin Gemini rheometer (Malvern Instruments, UK) at a temperature of 200 °C under air. Parallel plates with a diameter of 25 mm were selected. Sheet-shaped samples were cut from flexural bars and placed between the plates. A gap size of 1 mm was chosen for all tests. Before the small amplitude oscillation shear (SAOS) test, a strain sweep test was performed to check the linear viscoelastic regime of all specimens and strain amplitude of 1% was selected. The elastic modulus ($G'$), viscous modulus ($G''$) and complex viscosity ($\eta^*$) were recorded at a frequency range of (0.1, 100) Hz. A steady shear flow test was conducted in the 0.001 s$^{-1}$ to 5 s$^{-1}$ range to investigate the nonlinear behavior of the samples. A transient flow test was performed at a shear rate of 0.5 s$^{-1}$. The relationship between flow time and shear stress was recorded. A stress relaxation test was done at a shear strain of 1%. Elastic modulus was recorded as a function of time. Finally, creep/creep recovery tests were conducted with a shear stress of 10 Pa and a creep time of 60 s. After that, the stress was removed and the strain recovery was recorded for 30 s. All tests were performed at two replicates to ensure repeatability.
3.3.5 Flexural testing

The applicability of the “fast masterbatch production process” method was demonstrated by producing injection molded flexural bars that were tested according to ASTM D 790-10. Flexural bar dimensions were 125 mm×12.7 mm×3.2 mm. The span-to-depth ratio is 16:1. Tests were conducted at room temperature of 23 ± 2 °C and relative humidity of 50 ± 10 % RH. A universal testing machine (Instron 5966) with a 10 kN load cell was used for the tests. The span of the flexural test was 52 mm. With an outer fiber strain rate of 0.01/min, the flexural test speed was 1.4 mm/min. Flexural strength and Young’s modulus of the specimens were determined. Five replicates of each sample were tested. The flexural properties were analyzed using a two-way analysis of variance (ANOVA) along with a student test at α=0.05. The analysis was done in JMP statistical analysis program (JMP Statistical Discovery Software Version 8 2008). A statistical model was used to represent the properties of PP.

\[ Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + e_{ijk} \]  

Where i=1, 2, 3; j=1, 2 and k=1, 2, 3. \[ Y_{ijk} \] is the mean of flexural property; \[ \mu \] is the population mean of flexural property of pure PP. The effects of filler content and coupling agent on flexural property were represented by \[ \alpha_i \] and \[ \beta_j \]. Effects of interaction between two factors on flexural property was represented by \( (\alpha\beta)_{ij} \). The \[ e_{ijk} \] is the error for this model.
3.4 Results and Discussion

3.4.1 Morphology

Figure 3.1 SEM micrographs of spray-dried CNF.

Figure 3.2 Particle size distribution frequency curves of spray-dried CNF.

Table 3.2 Morphological properties of spray-dried CNF.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CE diameter (µm)</th>
<th>Aspect ratio</th>
<th>HS Circularity</th>
<th>Convexity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF</td>
<td>9.58 (0.90)</td>
<td>1.25 (0.007)</td>
<td>0.84 (0.03)</td>
<td>0.96 (0.009)</td>
</tr>
</tbody>
</table>

The morphology of the dried cellulose nanofibers is critical to modifying the rheological properties of resulting polymer composites. Spray-freeze-dried CNC from 1 wt.% suspension produced a web-like structure after drying (Khoshkava and Kamal, 2014). The microscopic features gave the CNC/PP composites a percolation threshold (2.5 wt.%) above which the rheological properties changed dramatically. The change is caused by improved particle-particle and particle-polymer interactions. Similar results
were obtained by studying freeze-dried CNC reinforced PLA via solution casting (Bagheriasl et al. 2016). Unlike spray-freeze drying and freeze-drying, spray drying tends to generate spherical particles attributable to agglomeration (Peng et al. 2012a). As seen in Figure 3.1, both spherical and fibril CNF particles are created during spray-drying. Most CNF particles lose nanoscale dimensions because of the agglomeration from capillary forces, hydrogen bonding and van der Waals forces during drying (Khoshkava and Kamal 2014). Unlike spray-freeze-dried CNC, no high-porosity or web like structure is created inside the spray-dried CNF (Khoshkava and Kamal 2014). Based on the frequency curve in Figure 3.2, a certain portion of the dried particles remain in the nanoscale dimension (smaller than 1 µm). The majority of the CNF particles are smaller than 10 µm. A few percent of the particles are in the millimeter length scale. Morphological properties of the spray-dried CNF particles are listed in Table 3.2. Mean diameter of the CNF particles is in the micron scale dimensions. High sensitive (HS) circularity depicts how close the shape is to a perfect circle. A perfect circle has a circularity of 1 while a spike or irregular object exhibits circularity closer to 0 (Peng et al. 2012b). Convexity is the measurement of the edge roughness of a particle. A smooth shape has a convexity of 1 while a spike or irregular object has a convexity closer to 0. Because of the aspect ratio, HS circularity and convexity are closer to 1, the shape of the spray-dried CNF is more spherical than fibril. The smooth surface indicated by large convexity value implies that the spray-dried CNF has less porosity.
Figure 3.3 Spray-dried CNF distribution within PP after melt compounding.
The distribution of CNF within PP after injection molding is shown in Figure 3.3. Higher magnification graphs were taken, zooming into possible aggregation areas in the low magnification micrographs. In general, CNF powders distribute fairly well in the PP matrix. This indicates the “fast masterbatch production” method is of high efficiency in distributing CNF in PP. The addition of MAPP does not change the distribution of CNF in the PP. Also observed are large agglomerates of CNF as well as many finer CNF particles, indicating of a lower degree of dispersion of CNF. The morphology of CNF embedded in the PP is similar to that of CNF powder before compounding, meaning no significant dispersion of CNF can be achieved with our method. This is because the shear forces involved in the compounding cannot disrupt the forces which produce the agglomeration of CNF during spray drying.

3.4.2 Rheology

3.4.2.1 SAOS

![Complex viscosity of specimens as a function of frequency.](image)

Figure 3.4 Complex viscosity of specimens as a function of frequency.
Figure 3.5 Elastic modulus of specimens as the function of frequency.

Figure 3.4 and 3.5 show the development of complex viscosity (η*) and storage modulus (G’) as a function of frequency for the CNF-PP composite samples. In general, the change in η* and G’ of PP after adding CNF is modest compared to previous studies where percolation was formed (Khoshkava and Kamal 2014). The reason is CNF agglomeration caused by spray drying diminishes the particle-particle and particle-polymer interaction (Khoshkava and Kamal 2014). As seen in Figure 3.4, the η* decreased as frequency increased for pure and filled-PP, implying a non-Newtonian behavior over the entire tested frequency range (Kiziltas et al. 2013). The PP-10% composite has a higher η* while the PP-3% composite has a similar η* compared to pure PP. For instance, at a frequency of 0.1Hz, the η* of the PP-10% is 25% larger than the pure PP and PP-3%. The higher addition percentage of CNF imparts the composite with more CNF-CNФ and CNF-PP contacts, which increases the η*. No significant difference was found for the shear thinning behavior among all samples during the SAOS test. The MAPP can be a lubricant and a coupling agent, determined by its weight percentage in PP composites (Twite-Kabamba et al. 2009). At a moderate addition level, MAPP is an effective compatibilizer that improves the interfacial adhesion between PP molecules and CNФ, impeding the disentanglements of PP molecules. When MAPP addition is
excessive, it acts as a lubricant that facilitates the disentanglement and reptation of PP molecules (Khassanabadi et al. 2015). These conclusions are confirmed by this study. For PP-MA, the $\eta^*$ decreases compared to pure PP. For PP-10%-MA, the addition of MAPP increases the $\eta^*$ of the composite melt.

As seen in Figure 3.5, the $G'$ of the PP-10% is larger than the pure PP and PP-3%. For example, at a frequency of 0.1 Hz, $G'$ of PP-10% is 33% higher than the PP and PP-3%. This is mainly attributable to the rigid nature of the CNF which restricts the deformation of PP (Kiziltas et al. 2016). No non-terminal behavior (pseudo solid-like) of CNF-filled PP was observed, indicating that no 3D microstructure is formed at those filler content levels. Three reasons account for this: 1) there is no strong CNF-PP interaction because of their different polarities; 2) the spherical structure of spray-dried CNF prevents the formation of an effective CNF network inside the PP matrix and 3) the low porosity of spray-dried CNF cannot facilitate the polymer melt infiltration to improve dispersion and particle-polymer interaction. The lack of 3D microstructure of cellulose nanofibers reinforced polymer systems was also reported by previous research (Kiziltas et al. 2016). The PP-10%-MA samples show improved $G'$ compared to PP-10% samples. At a higher CNF to MAPP ratio, the interfacial bonding is enhanced by MAPP (Zhou et al. 2013). Stress transfer from the PP molecules to CNF is more efficient. Therefore, CNF exhibits a better reinforcing effect in PP.
Figure 3.6 Damping factor of specimens as the function of frequency.

The damping factor (tan δ) is the ratio of viscous modulus (G’’) to storage modulus (G’). The material acts as viscous liquid when tan δ>1 and appears elastic solid when tan δ < 1 (Ching et al. 2016). As seen in Figure 3.6, the melts are viscous liquid below 20 Hz. The addition of CNF marginally changes the behavior of the PP melt. The crossover point (tan δ=1) is the transition from liquid-like to solid-like behavior. The inverse of the crossover frequency is the characteristic relaxation time of a polymer chain (Khoshkava and Kamal 2014). The crossover frequencies for all the samples without MAPP are identical (24 Hz), corresponding to a characteristic relaxation time of 0.042 s for PP chains and is comparable to a previous finding on pure PP melts (Khoshkava and Kamal 2014). This indicates that PP chain relaxation was not significantly affected by the addition of CNF because the particle-polymer interaction is weak. This interaction is incapable of retarding the relaxation of the PP molecules significantly. When MAPP is added into pure PP, it facilitates the relaxation of PP chains as indicated by a higher crossover frequency (25 Hz). When MAPP is introduced into the composite melt, the damping factor is decreased. The crossover frequency of PP-10%-MA (23 Hz) is lower than the PP-10%. This indicates that PP chain relaxation is slightly retarded by the
presence of MAPP. The nature of MAPP is to couple PP molecules with CNF, thus more restriction is applied to the mobility of PP molecules.

3.4.2.2 Steady shear flow

![Figure 3.7 Viscosity of specimens as a function of shear rate.](image)

Nonlinear rheological properties of the polymer melt can be obtained by performing steady-state shear tests up to high shear rates. As seen in Figure 3.7, at low shear rates, all samples display Newtonian behavior. The PP-10% possesses higher viscosity than the PP and PP-3%. For example, the viscosity of PP-10% at 0.001 s\(^{-1}\) is 15% higher than pure PP. The increase in viscosity stems from the fact that larger filler content offers more hindrance to the movement of polymer chains (González-Sánchez et al. 2011). At higher shear rates, all samples display shear thinning behavior. The higher the fiber content, the more shear thinning the sample exhibits. For a fiber reinforced polymer, the gradual alignment of fibers to the flow direction at high shear rate was reported to account for the increased shear thinning (Yokozeki et al. 2012). However, spray-dried CNF is nearly spherical thus does not show considerable orientation even under fluid flow. The change in shear thinning behavior results from the disrupted CNF-PP interaction at higher shear rates. The addition of MAPP to the PP-3% and PP-10%
composite improves the interaction between CNF and PP molecules and increases the viscosity of the composite melt. Because the difference between the viscosity of CNF-PP composites and PP becomes much smaller after a shear rate of 5 s\(^{-1}\), the composites will have no difficulty to flow in a typical material extrusion device where the shear rate is normally above 100 s\(^{-1}\) (Turner et al. 2014).

3.4.2.3 Transient flow

![Figure 3.8 Shear stress of specimens as a function of time.](image)

During a transient flow test, polymer chains disentangle and reptate (Hassanabadi et al. 2013). For an entangled material, the shear stress first experiences a rising then a drop and eventually attaining a steady state. The peak shear stress depends on the how easily the disentanglement and reptation occur. Figure 3.8 shows the shear stress as a function of shear time. All samples rapidly disentangle their polymer chains and start to flow after 1.2 s. PP-10% has a higher shear stress than PP and PP-3%. Shear stress during transient flow was reported to increase as fiber content increased in polymer composites (Kagarise et al. 2010, Yokozeki et al. 2012). The occurrence of a stress peak is mainly created by the fiber alignment to the flow direction of polymer molecules (Yokozeki et al. 2012). As discussed before, fiber alignment is not the reason for the stress peak observed.
When a certain amount of CNF is present in the PP melt, the frictional force between CNF and PP molecules or the attachment of PP chains to the CNF surface reduces the mobility of the PP molecules (Hassanabadi et al. 2015). Therefore, higher stress is required to disentangle the PP chains. In addition, the shear stress of the PP-10% at steady state is larger than PP and PP-3%. The steady state shear stress depends on the equilibrium of disentanglement and entanglement of polymer chains (Hassanabadi et al. 2015). In the PP-10%, the disentanglement is more difficult because of increased CNF-PP and CNF-CNF interactions. Finally, the shear stress at peak and steady state of PP-3%-MA and PP-10%-MA is higher than PP-3% and PP-10% because of the enhanced interaction between the CNF and PP molecules that impedes the disentanglements of the PP chains.

3.4.2.4 Stress relaxation

![Graph showing the elastic modulus of specimens as a function of relaxation time.](image)

Figure 3.9 Elastic modulus of specimens as a function of relaxation time.

The stress relaxation test is another way to detect the interaction between polymer chains and fillers. In a system where particle-polymer interaction is strong, polymer chains will relax more slowly than the pure polymer because the particles retard the movement of the polymer chains (Khoshkava and Kamal, 2014). Based on the results
shown in Figure 3.9, all samples relax rapidly within the first second, again implying that the CNF-PP interaction is weak. The PP and PP-3% samples reach the zero-stress state in 9 s while PP-10% sample achieved zero-stress state at 12 s. The PP-10% has more CNF-PP interactions because the higher filler content results in more contact among CNF and PP molecules. The PP-3%-MA and PP-10%-MA relaxed slightly slower than the PP-3% and PP-10% attributable to improved CNF-PP interactions. Neither the addition of CNF nor MAPP significantly affects the stress relaxation behavior of PP. This confirms the finding from tan δ results.

3.4.2.5 Creep/creep recovery

![Creep/creep recovery diagram](image)

Figure 3.10 Strain development of specimens as a function of creep/creep recovery time.

Creep tests are used for measuring the elasticity of polymer melts over time (Kiziltas et al. 2016). As seen in Figure 3.9, the strains of all samples increase almost linearly with creep time. The addition of CNF decreases the strain of pure PP, indicating a higher elasticity induced by the intrinsic rigidity of CNF that restricts the movement of the polymer melt (Kiziltas et al. 2016). In the creep recovery test, elastic deformation is restored. The recoverable strain $\gamma_R$ is defined as follows (Romero-Guzmán et al. 2008):
\[ \gamma_R = \frac{\gamma_c - \gamma_r}{\gamma_c} \times 100\% \]  

(2)

Where \( \gamma_c \) is the strain at the end of creep test and \( \gamma_r \) is the strain developed at the end of recovery test. The strain from creep recovery test further confirms the finding from the creep tests. The recoverable strains for PP, PP-MA, PP-3%, PP-3%-MA, PP-10% and PP-10%-MA are 1.5%, 1.2%, 1.9%, 1.4%, 2.6% and 1.9%. For groups without MAPP, pure PP displays the smallest recovery strain. These strain values from the recovery test are close to what was reported for polyethylene containing similar CNF content using a creep stress of 200 Pa (Kiziltas et al. 2016). The recovery strain of pure PP is smaller than those (~10%) obtained in previous study using a creep stress of 10 Pa (Romero-Guzmán et al. 2008). That PP had a MFI of 3.8 g/min (230 °C/2.16 kg) which is five times lower than our PP. The low MFI indicates a higher molecular weight, larger molecular entanglement density and higher elasticity, which leads to higher recovery strain. The recoverable strain of the PP melt increases with the incorporation of CNF attributed to the increase of elasticity caused by CNF. MAPP slightly increases the strain of composite melts during the creep test and decreases recoverable strain during the recovery test. This is the only situation in this study where the rheological property of CNF filled-PP is adversely affected by MAPP and the results are contradictory to a previous finding on wood/PP/PE composites (Gao et al. 2012). For the other tests in this study, polymer chains undergo large disentanglement under the applied testing conditions. However, a small shear force (10 Pa) was applied during the creep test. The deformation of the melt was modest and no significant chain sliding occurred. The rule of mixtures explains that the elastic modulus of the composite is roughly the sum of the elastic modulus of each component multiplied by their volumetric percentage in the composite
Since MAPP is a low molecular weight polymer compared to PP, it is mechanically less stiff than PP and CNF. Consequently, the incorporation of MAPP to CNF-PP decreases the elastic modulus.

### 3.4.3 Flexural properties

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of squares</th>
<th>F value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected total model</td>
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<td>263.04</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>228.49</td>
<td>1.36</td>
<td>31.75</td>
</tr>
<tr>
<td>CNF content</td>
<td>2</td>
<td>36.28</td>
<td>0.71</td>
<td>12.60</td>
</tr>
<tr>
<td>MAPP</td>
<td>1</td>
<td>10.36</td>
<td>0.003</td>
<td>7.20</td>
</tr>
<tr>
<td>CNF content*MAPP</td>
<td>2</td>
<td>46.05</td>
<td>0.001</td>
<td>15.60</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>34.54</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

*a degree of freedom, *b flexural strength, c flexural modulus, 
* indicates significant level at α=0.05.

Concern may rise when the mixing time is dramatically reduced with a fast extrusion speed during the masterbatch production procedure. Improper mixing is detrimental to the mechanical properties of the composites. The SEM graphs proved the efficiency of our method visually. As a supplemental support, the flexural properties of injection molded CNF-PP composites from the “fast masterbatch production process” method were tested. Analysis of variance on the flexural properties of PP and its composites are shown in Table 3.3. The interactive effect of CNF content and MAPP is important to the flexural strength. Different combinations of CNF content and MAPP content will generate CNF-PP composites with varied flexural strength. While for flexural modulus, only CNF content is critical, meaning the MAPP cannot improve the flexural modulus of CNF-PP composites. The finding on flexural modulus further confirmed the results from the creep/creep recovery test.
Table 3.4 Flexural properties of specimens from injection molding.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Strength (MPa)</th>
<th>Significance</th>
<th>Young’s Modulus (GPa)</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>48.14 (1.09)^a</td>
<td>CD^b</td>
<td>1.68 (0.03)</td>
<td>B</td>
</tr>
<tr>
<td>PP-MA</td>
<td>45.91 (1.72)</td>
<td>E</td>
<td>1.68 (0.05)</td>
<td>B</td>
</tr>
<tr>
<td>PP-3%</td>
<td>47.09 (0.54)</td>
<td>DE</td>
<td>1.66 (0.04)</td>
<td>B</td>
</tr>
<tr>
<td>PP-3%-MA</td>
<td>49.26 (1.15)</td>
<td>BC</td>
<td>1.63 (0.09)</td>
<td>B</td>
</tr>
<tr>
<td>PP-10%</td>
<td>50.79 (1.43)</td>
<td>B</td>
<td>2.13 (0.08)</td>
<td>A</td>
</tr>
<tr>
<td>PP-10%-MA</td>
<td>54.35 (0.91)</td>
<td>A</td>
<td>2.09 (0.05)</td>
<td>A</td>
</tr>
</tbody>
</table>

^a values in the parentheses stand for standard deviation.  
^b Capital letters represent for statistical differences. Values with different letters are significantly different.

As can be seen from Table 3.4, the addition of 3 wt.% CNF into PP insignificantly affects the flexural properties of pure PP regardless of the presence of MAPP. After 10 wt.% CNF is incorporated into PP, the flexural strength and modulus of the composite are 5.9% and 26.8% higher than the pure PP. Further addition of MAPP improves the flexural strength of PP by 12.9% compared to the pure PP. Those results are comparable to what were found before using a slower extrusion speed and a longer mixing time (Peng et al. 2016). Therefore, this “fast masterbatch production process” method is efficient for producing CNF-PP compounds. The improvement in Young’s modulus of PP components by the addition of 10 wt.% CNF is mainly attributed to the rigidity of CNF itself (Fu et al. 2008, Kiziltas et al. 2016). The mechanisms of improved strength in short fiber-filled polymer composites include 1) enhanced the stress transfer at interface, 2) lowered stress concentration at fiber ends and 3) crack deflection (Sato et al. 1988).

Meanwhile, short fibers can degrade a polymer matrix with fiber ends which initiates cracks. Whether the strength will increase or decrease depends on which factors dominate (Sato et al. 1988). Apparently, the enhancement of the flexural strength of CNF-PP composite by MAPP is attributed to the improved stress transfer at interfaces as
demonstrated by the rheological tests (Zhou et al. 2013). At higher CNF content, stress transfer at the interface is more effective attributed to increased fiber-polymer contact. The stress around a fiber is affected by other fibers. The stress concentration is reduced once the fibers are closer to each other which can be a result of higher fiber content. The addition of 10 wt.% CNF increases the crack initiation. At the same time, the larger number of CNF fibers increases the stress transfer at the interface and reduces the stress concentration at the fiber ends. The overall result is a slight increase in flexural strength of the PP.

3.5 Conclusions

The effects of CNF content and MAPP coupling agent on the rheological properties and flexural properties of CNF-PP composites for 3D printer filaments were studied. SEM showed that CNF agglomerated during drying and a spherical structure with low porosity was formed. Spray-dried CNF can be well distributed into PP using a “fast masterbatch production” method. Rheological tests showed that elastic modulus, complex viscosity, viscosity, transient flow shear stress of PP were increased by approximately 33%, 25%, 15% and 27% at the chosen frequency and shear rates after 10 wt.% CNF was added into the PP. The increase came from enhanced particle-polymer interaction at higher filler content. Creep strain was reduced with the addition of 10 wt.% CNF because of increased rigidity. The damping factor and stress relaxation time remained the same even at 10 wt.% CNF addition because the CNF-PP interaction is weak. MAPP increased the complex viscosity, elastic modulus, viscosity, transient flow shear stress and creep strain of CNF-filled PP but decreased the stress relaxation of these composites. The flexural strength and modulus of PP were increased by 5.9% and 26%
after 10 wt.% CNF was added into PP. This further confirms the efficiency of the “fast masterbatch production process” method used in this study. Adding 3 wt.% CNF into PP changed neither the rheological properties nor the flexural properties of PP significantly. In summary, the addition of CNF into PP, through a “fast masterbatch production process” method, marginally changed the rheological properties from a practical consideration. The small change in rheological properties at lower shear rate brought by CNF makes the resulting PP composites filament process friendly to material extrusion devices.
CHAPTER 4

CELLULOSE NANOFIBRIL- REINFORCED POLYPROPYLENE COMPOSITES FOR FUSED FILAMENT FABRICATION:

NONISOTHERMAL CRYSTALLIZATION KINETICS AND THERMAL EXPANSION

4.1 Chapter summary

Isotactic polypropylene (iPP) is difficult to print attributable to its rapid crystallization rate. In this study, cellulose nanofibrils (CNF) and maleic anhydride polypropylene (MAPP) addition were investigated to reveal their effects on the nonisothermal crystallization kinetics and thermal expansion of iPP. CNF at 3 wt.% and 30 wt.% accelerated the crystallization rate of iPP, while CNF at 10 wt.% retarded the crystallization rate. Additionally, adding MAPP into iPP/CNF composites accelerated the crystallization rate of iPP. The Jeziorny and Liu methods successfully described the nonisothermal crystallization kinetics of iPP/CNF composites while the Ozawa method failed. The effective activation energy of iPP increased when more than 10 wt.% CNF was added based on the Kissinger method. Polarized light microscopy results indicated that high CNF content led to a reduced particle gap which hindered the PP crystal growth. The coefficient of thermal expansion of iPP/CNF10% was 11.7% lower than neat iPP.
4.2 Introduction

Cellulose nanofibrils (CNF) are a type of cellulose nanofibers which are derived from wood pulp by mechanical disintegration (Wang et al. 2016). CNF was found to be a good mechanical reinforcement for polymers because of its high stiffness and fibril-like structure (Siqueira et al. 2008). The direct incorporation of CNF into a hydrophobic thermoplastic matrix by conventional manufacturing methods prefers the fiber in dried form to facilitate processing (Peng et al. 2012a). Spray drying was reported to be a good way of obtaining dried CNF in terms of drying cost and industrial scalability (Peng et al. 2012a). Fused filament fabrication (FFF) is one of the additive manufacturing methods that can be used to print thermoplastics. Because of its low cost and simple operation, FFF is the most popular 3D printing technique. However, FFF cannot print all thermoplastic polymers, for example, isotactic polypropylene (iPP) (Wang and Gardner 2017). Because iPP crystallizes quickly, the printed layers shrink and warp during the deposition of subsequent layers. Here is a comparison on the crystallization rate of iPP and poly(L-lactide) (PLLA). The crystallization half time (t1/2) of iPP with a number-based molecular weight (Mn) of 4.18×10^4 g/mol at 120 °C was 2.93 min (Seo et al. 2000). While the t1/2 of PLLA with a Mn of 4.5×10^4 g/mol at 120 °C was around 21.5 min (Fujsawa 2014). Because PLLA crystallizes much slower than iPP under the same processing conditions, PLLA is easier to use in the FFF process. To use iPP in the FFF process, retarding the crystallization rate is required.
During the FFF process, the crystallization temperature profile at the center of the bottom layer of a specimen is shown in Figure 4.1 (Sun et al. 2008). The printing orientation is along its long axis. The period within that increase-decrease circle corresponds to the time required to build each layer. The real-time temperature of one spot changes only drastically when the printing nozzle is close enough to it. When the printing nozzle moves away, the temperature change is small. The average temperature variation is also small. Therefore, two types of nonisothermal crystallization occur during the FFF process. One is the crystallization at high cooling rate (>20 °C/min), which only happens when the nozzle is close enough to the polymer. This accounts for a very small portion of the crystallization process. The other one is the crystallization at low cooling rate (5~10 °C/min), which dominates the crystallization time. When the temperature drops below the crystallization temperature ($T_c$) of the polymer, the shrinkage of the polymer is controlled by the thermal expansion of the amorphous portion. A previous study revealed that the shrinkage of iPP above the $T_c$ was much larger than the shrinkage below $T_c$ when iPP cooled from its melt state (Bozec et al. 2000). Therefore, the crystallization is the primary force that drives iPP to shrink.
The addition of higher amount of nanofillers in polymer systems was found to decrease the crystallization rate (Fornes and Paul 2003, Li et al. 2007, Deshmukh et al. 2015). After spray drying, the majority of CNF particles exhibit a spherical structure with a small aspect ratio and smooth surface (Peng et al. 2012b, Wang et al. 2017). Those morphological properties can diminish the nucleation ability of CNF. In that case, a large amount of spray-dried CNF can be used to decelerate the overall crystallization rate of iPP.

The addition of natural fibers into the iPP matrix is frequently reported to accelerate the crystallization of iPP in a nonisothermal condition by increasing the nucleating density (Grozdanov et al. 2007, Zhu et al. 2008, Phuong and Gilbert 2010, Xu et al. 2016). The effect of surface treatments on the crystallization kinetics of iPP depends on the type of treatment (Quillen et al. 1994, Janicek et al. 2014). Thermal expansion of iPP or PP/PE blends was found to decrease with increasing cellulose content (Ito et al. 2010, Huang et al. 2012). So far, a study on how spray-dried CNF affects the nonisothermal crystallization kinetics and thermal expansion of iPP has not been performed. This experiment was primarily designed to analyze the effect of CNF content and MAPP on the nonisothermal crystallization kinetics of iPP at four cooling rates (5, 10, 15, 20 °C/min). Thermal expansion analysis was performed on the group with the slowest crystallization rate. The results of this study can be helpful to address the warping of iPP during FFF, as well as provide useful information on processing iPP/spray-dried CNF composites via conventional methods.
4.3 Materials and Methods

4.3.1 Materials

iPP Homopolymer (H19G-01) was purchased from Ineos Olefins & Polymers USA (League City, TX). It was designed for the extrusion of continuous filament yarn. Basic properties include a density of 0.91 g/cm³, a melting point of 160 °C, a melt flow index of 19 g/10min (230 °C/2.16 kg), tensile strength (yield) of 37.2 MPa, flexural modulus of 1.78 GPa and notched Izod impact Strength of 2.8 kJ/m². MAPP pellets (Polybond 3200) with a MA content about 1.0 wt.% were obtained from Chemtura Corporation (Lawrenceville, GA). It has a density of 0.91 g/cm³ and a MFI of 115 g/10min (190 °C/2.16 kg). Cellulose nanofibrils suspension (~3 wt.%) was purchased from the Process Development Center of University of Maine. CNF powders were obtained through spray drying 1.2 wt.% CNF suspension using a pilot-scale spray dryer (GEA-Niro, Germany). Drying parameters include an inlet temperature of 250 °C, a disk spinning rate of 30,000 rpm and a pump feeding rate of 0.4 L/min.

4.3.2 Composite manufacturing

Table 4.1 Formulations of iPP/CNF composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Labels</th>
<th>iPP</th>
<th>CNF</th>
<th>MAPP</th>
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</thead>
<tbody>
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<td>iPP</td>
<td>iPP</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>iPP+MAPP</td>
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</tr>
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<td>iPP/CNF3%</td>
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<td>0</td>
</tr>
<tr>
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<td>2</td>
</tr>
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<td>iPP/MA/CNF30%</td>
<td>68</td>
<td>30</td>
<td>2</td>
</tr>
</tbody>
</table>
A “fast masterbatch production process” was adopted to manufacture CNF-reinforced iPP composites. More manufacturing details can be obtained from this reference (Wang et al. 2017). In brief, raw materials were first oven-dried for 2 h at 105 °C. CNF and iPP were mixed by hand at a fiber content of 30 wt.% and fed into a co-rotating twin-screw extruder (C. W. Brabender Instruments, South Hackensack, NJ) for compounding. The extruder operates at 200 °C across the heating sections with an extrusion speed of 250 rpm. Extrudates were collected continuously and cooled before grinding using a granulator (Hellweg MDS 120/150, Hackensack, NJ) to obtain masterbatch pellets. The masterbatch pellets, fresh iPP and MAPP were oven-dried, mixed and compounded using the same equipment and running parameters to make pellets containing 3 wt.%, 10 wt.% and 30 wt.% CNF with or without MAPP. Pellets were oven-dried before being transferred to an injection molder (Model #50 “Minijector”) with an injection pressure of 17 MPa at 200 °C. As-received iPP experienced the same processing cycle and served as a control specimen. The formulations of manufactured composites are shown in Table 4.1.

4.3.3 Nonisothermal crystallization study

The nonisothermal crystallization study was carried out using a TA Instruments Q2000 Calorimeter (New Castle, Delaware, USA). About 1-2 mg of samples were cut from the pellets and sealed normally in Tzero aluminum pans. The weight selected was to ensure that the pan lid was not broken by the sharp edges of samples during the sealing procedure. Samples were first heated up to 190 °C at a heating rate of 50 °C/min and held at that temperature for 5 minutes to erase their thermal history. Then at four cooling rates (5, 10, 15 and 20 °C/min), samples were cooled down to 50 °C and their curves were
recorded. The selection of cooling rate depends on the equipment cooling capacity and testing temperature. 20 °C/min is the fastest cooling rate the DSC achieves when the temperature is 50 °C. Any cooling rate above 20 °C/min cannot be maintained. Finally, samples were reheated from 50 °C to 190 °C at a ramp rate of 10 °C/min to obtain melting information. All measurements were performed in a nitrogen atmosphere with a flow rate of 50 ml/min. The crystallinity of iPP in the composites can be calculated based on the following equation:

$$X_c = \frac{\Delta H_m}{(\Delta H_f^0 \times \Phi)}$$  \hspace{1cm} (1)

where $\Delta H_m$ is melting enthalpy of iPP, $\Delta H_f^0$ is the fusion enthalpies of iPP with 100% crystallinity and was reported to be 209 J/g from the literature (Wang and Gardner 2017). The $\Phi$ is the percentage of the polymer in the composites. Different samples were used for the different cooling rates.

4.3.4 Microscopy

To evaluate the crystal morphology of iPP/CNF composites, a ME520 Series polarized light microscope (PLM) (AmScope, USA) was utilized. Sections of 3 µm-thick were obtained from the cross section of injection molded specimens using a Sorvall MT2-B Ultramicrotome. Each section was placed between a glass slide and a cover slip then transferred to a heating plate (Thermo Scientific) which operated at 200 °C. The section stayed on the hot plate for 2 min before it was set aside and cooled at room temperature.
4.3.5 Thermal expansion test

Thermal expansion measurements were conducted on injection-molded specimens along the flow direction according to the ASTM D 696-16. Because iPP has a glass transition temperature around 0 °C, thermal expansion measurement should be performed separately in a temperature range from -30 °C to 30 °C. The thermal expansion above \( T_g \) of iPP is larger than that below \( T_g \). For this study, the thermal expansion above \( T_g \) is more of interest. The equation used to calculate the coefficient of thermal expansion is

\[
\alpha = \frac{\Delta L}{L_0 \Delta T}
\]  

(2)

where \( \Delta L \) is the change in length of specimen caused by temperature change, \( L_0 \) is the length of specimen at room temperature and \( \Delta T \) is the change in temperature which is 30 °C. Three replicates were measured for evaluation.

4.4 Results and Discussion

4.4.1 Nonisothermal crystallization kinetics

The crystallization kinetics of iPP and its composites are displayed in Table 4.2. As a basic trend, the onset temperature (\( T_o \)), crystallization peak temperature (\( T_p \)) and crystallinity of iPP (\( X_c \)) of all samples decrease as the cooling rate increases. At a slower cooling rate, more crystal nuclei can be activated at the same time interval. Therefore, the crystallization occurs more completely during slow cooling than fast cooling (Phuong and Gilbert 2010). No consistent trend in the change of \( T_o \) and \( T_p \) caused by the addition of CNF can be found at different wt.%e. The increase in \( X_c \) induced by the CNF is slight
The degree of natural fiber being a nucleating agent in iPP matrix depends on factors like fiber size, chemical composition, surface polarity and surface topography where the surface topography is a decisive factor (Wang et al. 2011). A coarse fiber is a better heterogeneous nucleation agent. Based on our previous study on the morphology of spray-dried CNF, CNF is mostly a spherical particle with a smooth surface (Peng et al.}

### Table 4.2 Nonisothermal crystallization parameters at various cooling rates.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\lambda$ (K/min)</th>
<th>$T_o$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$X_c$ (%)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP</td>
<td>5</td>
<td>135</td>
<td>126</td>
<td>49</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>131</td>
<td>123</td>
<td>50</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>129</td>
<td>121</td>
<td>48</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>127</td>
<td>119</td>
<td>46</td>
<td>0.46</td>
</tr>
<tr>
<td>iPP/CNF3%</td>
<td>5</td>
<td>134</td>
<td>126</td>
<td>50</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>132</td>
<td>123</td>
<td>48</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>130</td>
<td>121</td>
<td>46</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>128</td>
<td>119</td>
<td>48</td>
<td>0.47</td>
</tr>
<tr>
<td>iPP/CNF10%</td>
<td>5</td>
<td>135</td>
<td>126</td>
<td>52</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>132</td>
<td>123</td>
<td>48</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>130</td>
<td>121</td>
<td>49</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>129</td>
<td>120</td>
<td>49</td>
<td>0.49</td>
</tr>
<tr>
<td>iPP/CNF30%</td>
<td>5</td>
<td>134</td>
<td>126</td>
<td>56</td>
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</tr>
<tr>
<td></td>
<td>10</td>
<td>132</td>
<td>123</td>
<td>54</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>130</td>
<td>121</td>
<td>58</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>129</td>
<td>120</td>
<td>48</td>
<td>0.42</td>
</tr>
<tr>
<td>iPP/MA</td>
<td>5</td>
<td>133</td>
<td>126</td>
<td>53</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>131</td>
<td>123</td>
<td>52</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>129</td>
<td>121</td>
<td>49</td>
<td>0.56</td>
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<tr>
<td></td>
<td>20</td>
<td>127</td>
<td>119</td>
<td>47</td>
<td>0.41</td>
</tr>
<tr>
<td>iPP/MA/CNF10%</td>
<td>5</td>
<td>133</td>
<td>125</td>
<td>52</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>131</td>
<td>122</td>
<td>50</td>
<td>0.83</td>
</tr>
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<td></td>
<td>15</td>
<td>129</td>
<td>120</td>
<td>49</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>127</td>
<td>118</td>
<td>49</td>
<td>0.46</td>
</tr>
</tbody>
</table>

$^a$ $\lambda$-cooling rate, $^b$ $T_o$-onset temperature, $^c$ $T_p$-peak temperature, $^d$ $X_c$-crystallinity and $^e$ $t_{1/2}$-half crystallization time.
This explains the weak nucleation ability of CNF for iPP and makes the spray-dried CNF a suitable additive for iPP targeting FFF processing.

During nonisothermal crystallization, the relative degree of crystallinity \( X_t \) is a function of crystallization temperature that can be calculated from the following equation (Herrero and Acosta 1994):

\[
X_t = \int_{T_0}^{T} \left( \frac{dH_c}{dT} \right) dT / \int_{T_0}^{T_{\infty}} \left( \frac{dH_c}{dT} \right) dT
\]

(3)

where \( T_0 \) is the onset temperature, \( T \) is the temperature at time \( t \), \( T_{\infty} \) is the temperature when crystallization completes. \( dH_c \) is the enthalpy of crystallization. The \( X_t \) can also be associated with the crystallization time considering the conversion from \( T \) to \( t \):

\[
t = (T_0 - T) / \lambda
\]

(4)

where \( \lambda \) is the cooling rate.

In Table 4.2, the \( t_{1/2} \) refers to the time when 50% \( X_t \) was achieved. As cooling rate increases, the \( t_{1/2} \) decreases. This trend is consistent with a previous study on iPP and natural fiber-filled iPP composites. The driving force is the dependence of nucleation and crystal growth rate on the degree of undercooling (Phuong and Gilbert 2010, Ou et al. 2011). In other words, higher undercooling makes the polymer nucleate and grow faster. With the incorporation of CNF at 3 wt.%, the \( t_{1/2} \) of iPP was decreased by 9% when \( \lambda=5 \) K/min. At 30 wt.% CNF content, the \( t_{1/2} \) of iPP was reduced by 11% when \( \lambda=5 \) K/min. CNF at those loading levels accelerated the crystallization rate of iPP. However, at 10 wt.% loading level of CNF, the \( t_{1/2} \) of iPP was alleviated by 6%, indicating CNF retarded the crystallization rate of iPP. Based on the analysis, CNF at 10 wt.% can be used as an
additive in iPP during FFF to help the shrinkage issue. The addition of MAPP into iPP/CNF composite increased the crystallization rate of iPP by 14% when \( \lambda = 5 \) K/min. There are three possible reasons. First, MAPP alone is reported to be a nucleating agent for iPP that helps to form more spherulitic sites and smaller spherulites (Seo et al. 2000). This is confirmed by the shorter \( t_{1/2} \) of iPP/MA composites in Table 4.2. Second, MAPP was found to increase the equilibrium melting point of wood flour/PP composites thus enlarging the degree of undercooling for the system by facilitating the chain relaxation at the interfaces (Wang et al. 2011). This is proven by the slightly increased crystallinity of the iPP/MA/CNF10% compared to iPP/CNF10%. A higher degree of undercooling is directly associated with faster crystallization. Lastly, MAPP can improve the compatibility between CNF and iPP, distributing CNF better in iPP and thus enhancing the nucleation ability of CNF. Therefore, MAPP is not necessarily an appealing additive for FFF processing of iPP. The overall crystallization rate of iPP depends on nucleation rate and crystal growth rate (Hiemenz and Lodge 2007). The addition of CNF at various loading levels affects the nucleation rate and crystal growth rate in different ways, yielding the observed results. Microscopy of the crystal structure can help explain these results and will be discussed in a subsequent section. To help understand how the crystallization kinetics behaved, in the next section, nonisothermal crystallization kinetic models were applied to fit the experimental data.
4.4.2 Nonisothermal crystallization kinetics modeling

4.4.2.1 Jeziorny method

![Diagram showing ln(-ln(1-Xt)) against ln(t) for different cooling rates.]

Figure 4.2 Plot of $\ln(-\ln(1-X_t))$ against $\ln(t)$ of iPP/CNF10% composites according to Jeziorny model during crystallization at various cooling rates.

Both isothermal and nonisothermal crystallization processes can be described by the Avrami’s model (Ou et al. 2011). The relation between relative degree of crystallinity ($X_t$) and elapsed crystallization time ($t$) is as follows:

$$1 - X_t = \exp(-K t^n)$$

(5)

where $K$ is the kinetic constant related to nucleation and crystal growth and $n$ is the Avrami exponent that is determined by the geometry of the nucleated and grew crystals. The higher the $K$, the faster the crystallization rate. In practice, the above equation is expressed in its double logarithmic form:

$$\ln \left[ -\ln(1-X_t) \right] = n \ln t + \ln K$$

(6)

A plot $\ln(-\ln(1-X_t))$ against $\ln(t)$ within the $X_t$ range of (0.01~63%) yields a straight line (Figure 4.2). At higher $X_t$, curves lose linearity because secondary crystallization and impingement of crystals dominate the process, which makes the Avrami’s method
inapplicable (Gopakumar et al. 2002, Khoshkava et al. 2015)). The slope of the line is $n$ and the interception with y axis is $ln K$. Because the crystallization temperature changes during nonisothermal crystallization, $n$ and $K$ are merely curve-fitting parameters with no physical meaning (Ou et al. 2011). Modification of the Avrami’s model was made by Jeziorny to make it meaningful to describe the nonisothermal crystallization kinetics (Jeziorny 1978). The parameter $K$ was corrected to consider the effect of cooling rate during the test. The modified crystallization rate constant $K_J$ was calculated by

$$ln K_J = \frac{(ln K)}{\lambda} \tag{7}$$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Samples</th>
<th>n</th>
<th>$K_J$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP</td>
<td>iPP</td>
<td>5</td>
<td>5.33</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>1.11</td>
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<td>4.57</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>iPP/CNF3%</td>
<td>5</td>
<td>4.33</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>5.07</td>
<td>1.02</td>
</tr>
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<td>1.10</td>
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<td>iPP/CNF10%</td>
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<td>0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>3.98</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>4.23</td>
<td>1.08</td>
</tr>
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<td></td>
<td>iPP/CNF30%</td>
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<td>4.26</td>
<td>0.62</td>
</tr>
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<td>10</td>
<td>4.41</td>
<td>1.00</td>
</tr>
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<td></td>
<td></td>
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</tr>
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<td></td>
<td></td>
<td>20</td>
<td>3.16</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>iPP/MA/CNF10%</td>
<td>5</td>
<td>4.23</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>4.69</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>3.98</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>3.90</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Data from fitting the curves obtained from Jeziorny method are displayed in Table 4.3. Generally, $n$ decreases and $K_J$ increases as cooling rate increases. For iPP, $n$ varied from 4.57 to 5.33, indicative of a tridimensional, homogeneous crystal growth (Zhu et al. 2003).
Similar $n$ values were reported by previous research on natural fiber-filled PP (Grozdanov et al. 2007, Xu et al. 2016, Quillin et al. 1994). After CNF was added, $n$ decreases. This is because CNF, being a nucleating agent, changed the nucleation from homogeneous to heterogeneous. iPP/CNF3%, iPP/CNF30% and iPP/MA/CNF10% have larger $K_J$ than iPP at a slower cooling rate. This is consistent with the $t_{1/2}$ values in Table 4.2. A similar change in the $K_J$ of iPP caused by the addition of microcrystalline cellulose was reported (Zhu et al. 2008). The increase of $K_J$ at faster cooling rate is not significant probably because undercooling overwhelms nucleation density, becoming the dominant crystallization driving force. iPP/CNF10% has a smaller $K_J$ than iPP, which is consistent with the results in Table 4.2. Therefore, the Jeziorny method is effective in describing the nonisothermal crystallization kinetics of iPP/CNF composites.

4.4.2.2 Ozawa method

The Ozawa method considers the nonisothermal crystallization process as a sum of many isothermal crystallization processes occurring at an infinitesimal time over the crystallization period (Ozawa 1971). His mathematical model was also based on the Avrami equation:

$$1 - X_t = \exp[-K(T)/\lambda^m]$$

(8)
Where $K(T)$ is the crystallization constant, depending on the crystallization temperature. And $m$ is the Ozawa exponent. A double logarithmic form can also be converted from above equation:

$$\ln[- \ln(1 - X_t)] = \ln K(T) - m \ln(\lambda)$$

(9)

A plot of $\ln[-\ln(1-X_t)]$ versus $\ln \lambda$ at different crystallization temperatures should give linear curves (Figure 4.3). Then $K(T)$ and $m$ can be obtained from the intersection and slope. As seen from the Ozawa graphs, the curves are relatively linear at lower crystallization temperature. At high crystallization temperature, the curves lose their linearity. The Ozawa method does not consider the secondary crystallization which can occur at the early stage during the crystallization (Grozdanov et al. 2007). Therefore, the Ozawa method is not effective in describing the nonisothermal crystallization of iPP/CNF composites. This conclusion is consistent with previous findings (Grozdanov et al. 2007, zhu et al. 2008, Phuong and Gilbert 2010). No additional analysis was performed.

4.4.2.3 Liu method

4.4.2.3 Liu method

Figure 4.4 Plots of $\ln \lambda$ as a function of $\ln t$ at different $X_t$ for iPP/CNF10% composites based on the Liu method.
Liu et al. proposed a method to exactly describe the nonisothermal crystallization kinetics by combining Avrami and Ozawa methods (Liu et al. 1997). The equation is

\[
\ln \lambda = \ln F(T) - \alpha nt, \tag{10}
\]

\[
F(T) = \left[ \frac{K(T)}{K} \right]^{1/m}, \tag{11}
\]

\[
\alpha = \frac{n}{m}, \tag{12}
\]
Where $F(T)$ is the degree of cooling rate required during unit crystallization time when the polymer has a certain degree of crystallinity. The smaller the $F(T)$, the faster the crystallization. $K$ is the Avrami constant, $n$ is the Avrami exponent, $K(T)$ is the Ozawa constant, $m$ is the Ozawa exponent and $\lambda$ is the cooling rate. Plotting $ln \lambda$ against $ln t$ gives a linear curve as shown in Figure 4.4. The $\alpha$ and $ln F(T)$ can be achieved from the slope and intercept of these curves. Kinetic parameters from the Liu method are shown in Table 4.4.

The $\alpha$ values of iPP and iPP/CNF are close to 1, meaning the Jezioney and Ozawa methods are similar in modeling the nucleation mechanism and crystal geometry, especially at low $X_t$. $F(T)$ increases monotonically with the increase of $X_t$, indicating that crystallization becomes more difficult at higher $X_t$. iPP/CNF3%, iPP/CNF30% and iPP/MA/CNF10% slightly decreases $F(T)$ of iPP when compared at the same $X_t$, meaning that CNF at these loading levels accelerates the crystallization rate of iPP. iPP/CNF10% has the opposite effect on $F(T)$ of iPP compared to the other loading levels, meaning CNF10% retards the iPP crystallization rate. These findings are consistent with the information provided by $t_{1/2}$ in Table 4.2. Therefore, the Liu method is effective in describing the nonisothermal crystallization kinetics of CNF/iPP composites.
4.4.3 Effective activation energy

![Graph showing the relationship between ln(λ/T_p^2) and 1/T_p for obtaining ΔE based on Kissinger method.](image)

Figure 4.5 Plot of \( \ln (\lambda / T_p^2) \) against \( 1/T_p \) for obtaining ΔE based on Kissinger method.

Table 4.5 Effective activation energy calculated based on the Kissinger method.

<table>
<thead>
<tr>
<th>Samples</th>
<th>iPP</th>
<th>iPP/CNF3%</th>
<th>iPP/CNF10%</th>
<th>iPP/CNF30%</th>
<th>iPP/MA/CNF10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE (kJ/mol)</td>
<td>264.1</td>
<td>262.5</td>
<td>291.6</td>
<td>305.5</td>
<td>265.2</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.997</td>
<td>0.989</td>
<td>0.999</td>
<td>0.999</td>
<td>0.988</td>
</tr>
</tbody>
</table>

The effective activation energy (ΔE) during polymer crystallization refers to the energy required to transport macromolecular segments to the surface of a crystal (Phuong and Gilbert 2010). The Kissinger equation has been used to calculate ΔE using crystallization peak temperature (\( T_p \)) and cooling rate (\( \lambda \)) (Kissinger 1956). The Kissinger method equation is:

\[
d[\ln(\lambda / T_p^2)] = -\frac{\Delta E}{R} d(1/T_p),
\]

where \( \lambda \) is the cooling rate, \( T_p \) is the peak crystallization temperature and \( R \) is the universal gas constant (8.314 J/(K*mol)). Plotting \( \ln (\lambda / T_p^2) \) against \( 1/T_p \) yields a linear curve as in Figure 4.5. ΔE can be obtained from the slope. Activation energies of
different samples are listed in Table 4.5. These activation energy values are similar to what were reported for natural fiber-filled iPP (Phuong and Gilbert 2010). $\Delta E$ of iPP/CNF3% is similar to iPP. On the other hand, iPP/CNF10% and iPP/CNF30% increase the $\Delta E$ of iPP. CNF at 30 wt.% appears more likely to retard the crystallization speed of iPP. Moreover, adding MAPP into iPP/CNF10% largely reduced the $\Delta E$. These seemingly conflicting results can be explained by considering the two components that determine the overall crystallization rate and transcrystallization phenomenon which are analyzed in next section.

4.4.4 Microscopy

Figure 4.6 shows the crystal morphology of iPP and iPP/CNF composites obtained by polarized light microscope. Because no cold-crystallization peaks were observed in the DSC scans for all specimens, the crystal morphology caused by the micrograph preparation was negligible. As CNF content increases in the iPP matrix, nucleation density increases, but spherulite size decreases. Typical crystal diameters of iPP, iPP/MA, iPP/CNF3%, iPP/CNF10%, iPP/CNF30% and iPP/MA/CNF10% are about 33 µm, 27 µm, 21 µm, 12 µm, 8 µm and 10 µm. A previous study on the isothermal crystallization kinetics of cellulose nanocrystals (CNC)-filled PP found that adding 1 wt.% spray-freeze-dried CNC increased the chain-folding work of PP significantly (Khoshkava et al. 2015). This implies that the CNC restricted the folding motion of polymer chains during crystallization and made the re-entry of polymer chains into the crystal face more difficult, resulting in smaller crystals (Khoshkava et al. 2015). Hence, steric hindrance attributed to the large amount of CNF is the reason for the higher $\Delta E$ for iPP as shown in Table 4.5.
Figure 4.6 Polarized light micrographs of iPP and iPP/CNF composites. Inside the circles are the Maltese-cross patterns of iPP spherulites. The last two graphs show the effect of MAPP on transcry stallization.
As a compatibilizer, MAPP helps PP to wet the natural fiber better (Wang et al. 2011). Also, MAPP is reported to facilitate the transcrystallization, a process where spherulites grow perpendicularly to the surface (Yin et al. 1999). Transcrystallization can improve the attachment of polymer segments to the crystal surface, thus reducing the $\Delta E$. However, the method used here to prepare sections for PLM observation involved a fairly fast cooling rate (~80 °C/min), which may create thin transcrystalline layers. Thin crystal layers are not readily seen in PLM at high magnification because of their weak light intensity. A possible site of CNF transcrystallization was identified for iPP/MA/CNF10% in Figure 4.6. As a comparison, the morphology of PP spherulites on CNF surface in PP/CNF3% composite is also shown which is almost identical to that in the iPP matrix. This may prove the role of MAPP in transcrystalline layer formation. The PLM micrographs confirmed kinetic results obtain in previous sections.

The overall crystallization rate is dependent on nucleation rate and crystal growth rate (Hiemenz and Lodge 2007). For iPP/CNF3%, the presence of CNF increased the nucleation density without affecting the crystal growth. This made CNF at 3 wt.% accelerate iPP’s crystallization rate. For iPP/CNF10%, nucleation density for iPP was increased by the CNF. At the same time, crystal growth rate was impeded by CNF. The overall effect was CNF at 10 wt.% retarded iPP’s crystallization rate. After MAPP was introduced to iPP/CNF10%, nucleation density furthered increased because of the coupling effect. Moreover, the formation of transcrystalline layers facilitated crystal growth. Therefore, iPP/MA/CNF10% accelerated the crystallization rate of iPP. For iPP/CNF30%, the nucleation density of iPP was improved dramatically. Though CNF
limited the crystal growth, the overall effect was CNF at 30 wt.% accelerated iPP’s crystallization rate.

4.4.5 Thermal expansion

Table 4.6 Coefficient of thermal expansion of iPP and iPP/CNF composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\alpha^a (10^{-6}/^\circ\text{C})$</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP</td>
<td>80.1 (3.1)$^b$</td>
<td>A$^c$</td>
</tr>
<tr>
<td>iPP/CNF10%</td>
<td>70.7 (2.4)</td>
<td>B</td>
</tr>
</tbody>
</table>

* $^a$ coefficient of thermal expansion, $^b$ standard deviation
  and $^c$ capital letters represent statistical differences. Values with different letters are significantly different at 95% confidence level.

Based on the results from nonisothermal crystallization kinetics study, CNF at 10 wt.% without MAPP was selected to be incorporated into iPP for FFF. The effect of CNF on the thermal expansion of iPP was investigated and the results are listed in Table 4.6. The CTE of iPP is within the CTE range of iPP reported by previous research (Yang et al. 2005, Kalaitzidou et al. 2007). After adding 10 wt.% CNF into the iPP, the CTE decreased by 11.7%. This change is comparable with a previous study where the CTE of iPP containing 10 wt.% wood flour was reduced by 16.9%. Because cellulose possesses a small CTE and the addition of CNF replaces a portion of iPP, the composite displays a smaller CTE (Huang et al. 2012). This would help reduce the iPP shrinkage caused by temperature changes below the crystallization temperature during the FFF.

4.5 Conclusions

This study investigated the CNF content and the use of MAPP on the nonisothermal crystallization kinetics of CNF reinforced iPP composites. iPP/CNF3% and iPP/CNF30% reduced the $t_{1/2}$ of iPP. This implied that CNF at these two levels
accelerated iPP’s crystallization rate. In contrast, iPP/CNF10% increased the $t_{1/2}$ of iPP, retarding iPP’s crystallization rate. The addition of MAPP into iPP/CNF10% composites reduced the $t_{1/2}$ of iPP. This is because MAPP is a nucleating agent and can facilitate transcrystallization. The Jeziorny and Liu methods were proven to be valid in describing the nonisothermal crystallization process of iPP reinforced by spray dried CNF where the Ozawa method failed. The $\Delta E$ of iPP, calculated based on Kissinger method, was similar to that of iPP/CNF3%, but smaller than those of iPP/CNF10% and iPP/CNF30%. The existence of CNF at high loading level restricts the diffusion and folding of polymer chains during crystallization, decelerating the crystal growth rate. The addition of MAPP into iPP/CNF10% lowered the $\Delta E$ probably because MAPP facilitated the occurrence of transcrystallization. The PLM graphs further confirmed that large amount of spray-dried CNF can impede the crystal growth. Generally, the nucleation rate was increased by the addition of CNF. At 10 wt.% CNF, the increase in nucleation rate was compromised by the decreased crystal growth rate, making CNF a crystallization rate retardant. Moreover, the CTE of iPP/CNF10% composites was 11.7% smaller than iPP. Based on this study, spray-dried CNF at 10 wt.% loading level can help to reduce the shrinkage iPP caused by temperature changes during the FFF processing.
CHAPTER 5

THERMAL PROPERTIES OF SPRAY-DRIED CELLULOSE NANOFIBRIL-REINFORCED POLYPROPYLENE COMPOSITES FROM EXTRUSION-BASED ADDITIVE MANUFACTURING

5.1 Chapter summary

Polypropylene block copolymer (PPco) is easier for extrusion-based additive manufacturing (AM) compared to isotactic PP homopolymer (iPP) because it shrinks and warps less during printing. This study investigated the thermal properties of PPco and spray-dried CNF (SDCNF)-PPco composite pellet formulations. Thermogravimetric analysis (TGA) data showed that the addition of SDCNF lowered the thermal degradation onset temperature and increased the residual mass content (at 450°C) of PPco pellets. The peak degradation temperatures of SDCNF and PPco remained the same. The peak crystallization temperature and relative crystallinity of PPco were increased by the addition of SDCNF and MAPP. The peak melting temperature of PPco was not significantly changed. Printed specimens showed three melting peaks (β, β' and α crystals) while injection molded PPco only showed one (α crystal) melting peak. Dynamic mechanical analysis (DMA) results showed that the heat deflection temperatures (HDTs) of printed SDCNF-PPco composites were higher than injection molded PPco. SEM micrographs showed that the addition of SDCNF increased the number of voids inside the printed parts.
5.2 Introduction

Extrusion-based additive manufacturing (AM) has been used to print thermoplastics and their composites (Wendel et al. 2008). Other names for extrusion-based AM include fused deposition modeling (FDM), fused layer modeling (FLM), fused filament fabrication (FFF) and material extrusion (Wang et al. 2017a). Because of its low cost and simple operation, extrusion-based AM is being extensively investigated (Wang and Gardner 2017). However, extrusion-based AM is not suitable for printing isotactic PP homopolymer (iPP) because it warps significantly as compared to other popular thermoplastics for AM, for example, Poly(L-lactic acid) (PLLA). The rapid crystallization rate is the major reason for iPP’s warping. Impact-modified polypropylene, or polypropylene block copolymer (PPco), was reported to crystallize more slowly than iPP (Nandi and Ghosh 2007). Therefore, PPco can be printed more easily. Figure 5.1 shows the comparison of the 3D printing processability of iPP and PPco.

Figure 5.1 IPP (back) and PPco (front) specimens from 3D printing.

Cellulose nanofibers typically refer to cellulose nanofibrils (CNF), cellulose nanocrystal (CNC) and bacterial cellulose (BC) (Moon et al. 2011). CNF is produced through mechanical fibrillation of pulp fibers and possesses a diameter on the nano scale and lengths on the micron scale (Wang et al. 2016). CNC is obtained via acid hydrolysis of pulp whose diameter and length are both on the nano scale. Attributed to its high
aspect ratio, CNF was reported to outperform CNC in reinforcing various polymers (Xu et al. 2013). To facilitate the compounding of CNF with thermoplastics, dried CNF is desired (Peng et al. 2012). Spray-dried CNF (SDCNF) was found to be an effective way to obtain dried powder (Peng et al. 2012).

Thermal analysis of natural fiber-filled polymer composites has been reported widely (Huda et al. 2005, Tajvidi and Takemura 2010, Kiziltas et al. 2011, Tajvidi et al. 2013, Reixach et al. 2015). Cellulose nanofibers are distinct from natural fibers based on their chemical composition, surface properties and fiber morphology. CNF and CNC were reported to increase the peak crystallization temperature (T_c) of PP (Ljungberg et al. 2006, Panaitescu et al. 2007). In other studies, CNC increased the crystallinity (X_c). The peak melting temperature (T_m), T_c and residual mass of PP were unchanged (Nagalakshmaiah et al. 2016, Bahar et al. 2012). However, CNC or CNF was also reported to decrease the X_c of PP (Ljungberg et al. 2006, Hassan et al. 2014). Cellulose nanofibers reduced the onset temperature (T_o) of PP composites because they are less thermally stable than PP (Yang et al. 2013, Khoshkava and Kamal 2014). Meanwhile cellulose nanofibers retarded the thermal degradation weight loss of PP at high temperatures (Yang et al. 2013). Cellulose nanofibers did not affect the X_c of PP. A coupling agent, maleic anhydride polypropylene (MAPP) is often used in making cellulose nanofiber-filled PP composites. However, the influences of MAPP on thermal properties (T_m, T_c, X_c) varies among reported research most likely attributable to chemical make-up of the coupling agent (Ljungberg et al. 2006, Panaitescu et al. 2007, Bahar et al. 2012, Hassan et al. 2014).
In this study, thermal analysis was performed to better understand the processing of SDCNF-PPco composites in extrusion-based AM. Thermogravimetric analysis (TGA) was used to obtain the $T_o$ of such composites to avoid thermal degradation during printing. Differential scanning calorimetry (DSC) was utilized to determine the $T_m$ and $T_c$ of SDCNF-PPco pellets to help choose proper printing and build bed process temperatures. DSC was also performed on manufactured SDCNF-PPco parts to obtain $X_c$. Dynamic mechanical analysis (DMA) was conducted to measure heat deflection temperature (HDT) of the processed composites. HDTs of printed PPco and SDCNF-PPco composites were compared with injection molded PPco. Scanning electron microscopy (SEM) was used to visualize the inner morphological structure of the printed parts.

5.3 Materials and Methods

5.3.1 Materials

CNF suspension (~3 wt.%) was produced by the Product Development Center at the University of Maine via a mechanical grinding process. This original CNF suspension was diluted to 1.2 wt.% solids content for spray drying. A pilot-scale spray dryer (GEA-Niro, Germany) was used to dry the CNF suspension at a chamber temperature of 250°C, pump feeding rate of 0.4L/min and a disk spinning rate of 30,000 rpm. The mean diameter of SDCNF is around 10 μm. The aspect ratio of SDCNF is 1.25. The polypropylene impact copolymer (ExxonMobil TM PP7414) formulated for automotive applications was purchased from ExxonMobil (Texas, USA). The PPco had a melt flow index (MFI) of 20 g/10min, a density of 0.9 g/cm$^3$, Izod impact strength of 180 J/m and a
HDT of 85.1°C. MAPP pellets (Polybond 3200) were purchased from Chemtura Corporation (Lawrenceville, GA). It has a MA content of 1.0 wt.%, a density of 0.91 g/cm$^3$ and a MFI of 115 g/10min.

5.3.2 Compounding

To improve the distribution and dispersion of SDCNF within the PPco, a masterbatch process was adopted. The detailed description of this process can be found in a previous paper (Wang et al. 2017a). PPco, MAPP and SDCNF were conditioned at 105°C for at least 2h. PPco, MAPP and SDCNF (30 wt.%) were hand mixed and fed into a co-rotating twin-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ) at an approximate feeding rate of 7 g/min, a screw speed of 200 rpm and a temperature of 200°C for all five heating zones. Extrudates were granulated using a grinder (Hellweg MDS 120/160, Hackensack, NJ). During the second extrusion, fresh PPco was added to the masterbatch to dilute it to the final composite formulation weight percentages which are listed in Table 5.1. Feeding rate, screw speed and heating-zone temperatures for the second extrusion were kept the same as the first extrusion. Extrudates were again granulated. Composite granules were fed into the extruder outfitted with a nozzle die (2.7 mm) to make filaments during the third extrusion. The feeding rate was about 3 g/min, screw speed was 60 rpm and five-heating zone profile was 185°C, 180°C, 175°C, 172°C, 170°C and the die temperature was 165°C. After the die, the composite extrudate passed through a water tank (25 °C) to solidify the shape of filament and were wound on spools.
Table 5.1 SDCNF-PPco composite formulations.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Labels</th>
<th>PP (wt.%)</th>
<th>MAPP (wt.%)</th>
<th>SDCNF (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPco</td>
<td>PPco</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PPco+MAPP</td>
<td>PPcoMA</td>
<td>98.7</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>PPco+7.5%SDCNF</td>
<td>PPcoSDCNF7.5</td>
<td>92.5</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>PPco+MAPP+7.5%SDCNF</td>
<td>PPcoMASDCNF7.5</td>
<td>91.2</td>
<td>1.3</td>
<td>7.5</td>
</tr>
<tr>
<td>PPco+15%SDCNF</td>
<td>PPcoSDCNF15</td>
<td>85</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>PP+MAPP+15%SDCNF</td>
<td>PPcoMASDCNF15</td>
<td>83.7</td>
<td>1.3</td>
<td>15</td>
</tr>
</tbody>
</table>

5.3.3 Composite parts manufacturing

Composite and pure PPco parts were printed using a LulzBot TAZ 6 (Aleph Objects Inc., Colorado, USA) with Cura printing software (Version 21.03). All specimens were printed one at a time at the same location on the printing bed. To adhere the extruded PPco strands to the bed, a strip of packing tape (Office Depot®, OfficeMax #24767995) was adhered on top of the bed. Important printing settings were: extrusion temperature of 200°C, bed temperature of 120°C, extrusion speed of 45 mm/s, infill density of 100%, layer height of 0.3 mm, number of shell of 2, with brim, orientation of ±45° and air space of 0%. Only pure PPco pellets obtained from the PPco filament were injection molded and used as a control specimen (PPcoIM). Injection molding was done on a “Minijector” (Model #50) at a temperature of 200°C, a pressure of 17 MPa and a holding time of 10s with a room-temperature mold. Additional composite filaments were also chopped into pellets for thermal analysis.

5.3.4 Thermogravimetric analysis (TGA)

TGA measurements on PPco and SDCNF-PPco composites pellets were conducted using a TA Instruments Q500 (New Castle, Delaware, USA). About 5-10 mg
samples were used for each measurement. Samples were heated from 30°C to 450°C at a heating rate of 10°C/min under nitrogen to avoid oxidation. Derivative thermogravimetric (DTG) analysis results were obtained simultaneously. At least three individual samples for each formulation were randomly picked from the granules for testing.

5.3.5 Differential scanning calorimetry (DSC)

The DSC was performed on both pellets and printed samples using a TA Instruments Q 2000 (New Castle, Delaware, USA). In each case, a piece of 1-3 mg was cut from the larger sample, placed in a pan, and sealed. For pellets, they were heated to 190°C at a rate of 10°C/min and held at that temperature for 5 min to erase thermal history before being cooled down to 30°C. T_c was obtained during the cooling process. Then samples were again heated up to 190°C to obtain T_m and X_c. For printed samples, they were directly heated to 190°C at a rate of 10°C/min. The X_c of composite pellets and injection molded PPco were calculated from the following equation (Wang and Gardner 2017),

\[ X_c = \frac{\Delta H_m}{(\Delta H_f^0 \times \phi)}, \]

where \(\Delta H_m\) is melting enthalpy of PP, \(\Delta H_f^0\) is the fusion enthalpies of PP which displays 100% crystallinity and was reported to be 209 J/g from the literature (Wang and Gardner 2017). The \(\phi\) is the percentage of the polymer in the composites. Because no information regarding the percentage of rubber phase in the PPco was provided by the polymer provider, we considered the percentage of PP inside PPco as 100% and named the X_c as relative crystallinity (RX_c). Three replicates were tested for each sample.
5.3.6 Dynamic mechanical analysis (DMA)

DMA was used to obtain the heat deflection temperature (HDT) of PPco and its printed composites using the TA Instruments Q 800 (New Castle, Delaware, USA). A dual-cantilever mode was used for the testing which was performed according to ASTM D 648. A constant force was exerted on the sample bar which later experienced a temperature change from 40°C to 120°C at a heating rate of 2°C/min. The HDT was defined as the temperature where the test bar deflects by 0.25 mm. The constant force can be calculated from the following equation,

\[ F = 2\sigma T^2 W / 3L, \]  

where \(\sigma\) is the maximum stress (0.455 MPa), \(T\) is thickness, \(W\) is width, and \(L\) is length (35 mm) of the sample. Three replicates were measured for each specimen.

5.3.7 Scanning electron microscopy (SEM)

SEM (TM 3000, Hitachi High-Technologies Corporation, Tokyo, Japan) was used to observe the morphological structure of specimens obtained from injection molding and AM. The testing was done on impact-fractured surfaces at an accelerating voltage of 5 kV.
5.4 Results and discussion

5.4.1 TGA

![TGA and DTG graphs](image)

Figure 5.2 TGA (a) and DTG (b) graphs of PPco, SDCNF and SDCNF-PPco composites.
Table 5.2 TGA data for SDCNF, PPco and SDCNF-PPco pellets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_o$ $^{\text{a}}$ ($^\circ$C)</th>
<th>$T_{\text{DTG-SDCNF}}$ $^{\text{b}}$ ($^\circ$C)</th>
<th>$T_{\text{DTG-PPco}}$ $^{\text{c}}$ ($^\circ$C)</th>
<th>Residual Mass at 450$^\circ$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF</td>
<td>283 (3)$^{d}$</td>
<td>340 (3)</td>
<td>-</td>
<td>15 (0)</td>
</tr>
<tr>
<td>PPco</td>
<td>302 (5)</td>
<td>378 (4)</td>
<td>0 (0)</td>
<td></td>
</tr>
<tr>
<td>PPcoMA</td>
<td>308 (4)</td>
<td>392 (5)</td>
<td>0 (0)</td>
<td></td>
</tr>
<tr>
<td>PPcoSDCNF7.5</td>
<td>301 (2)</td>
<td>336 (3)</td>
<td>387 (6)</td>
<td>1 (0)</td>
</tr>
<tr>
<td>PPcoMASDCNF7.5</td>
<td>284 (3)</td>
<td>341 (2)</td>
<td>383 (2)</td>
<td>1 (0)</td>
</tr>
<tr>
<td>PPcoSDCNF15</td>
<td>278 (3)</td>
<td>345 (1)</td>
<td>379 (2)</td>
<td>2 (0)</td>
</tr>
<tr>
<td>PPcoMASDCNF15</td>
<td>285 (1)</td>
<td>344 (1)</td>
<td>387 (3)</td>
<td>2 (0)</td>
</tr>
</tbody>
</table>

$^{\text{a}}$ Onset temperature, $^{\text{b}}$ SDCNF degradation peak temperature, $^{\text{c}}$ PPco degradation peak temperature, $^{\text{d}}$ standard deviation.

The TGA and DTG graphs of SDCNF, PPco and SDCNF-PPco composites are shown in Figure 5.2. Because all SDCNF-PPco composites displayed similar graphs, only the PPcoMASDCNF15 sample was shown for simplicity purposes. Important information extracted from TGA and DTG curves are listed in Table 5.2. The $T_o$ of SDCNF is lower than PPco. Therefore, once SDCNF was added into PPco, the $T_o$ of the composites decreased compared to PPco. The $T_{\text{DTG-SDCNF}}$ remains similar between SDCNF and SDCNF-PPco composites. The $T_{\text{DTG-PPco}}$ remains close between PPco and SDCNF-PPco composites. These findings are consistent with a previous study on the thermal stability of CNF reinforced PPco (Yang et al. 2013). This is because the degradation peak temperature of SDCNF or PPco, as an intrinsic property, is not affected by the compounding process. As seen from Figure 5.2(b), adding SDCNF into PPco reduces the peak degradation rate of SDCNF without significantly changing the peak degradation rate of PPco. This indicates that once the SDCNF starts degrading, it decomposes more slowly in the PPco matrix than in the nitrogen atmosphere. This result was also found in a previous study (Yang et al. 2013). The $T_{\text{DTG-PPco}}$ in our work was ~380$^\circ$C which is lower
than a reported value (~430°C) (Yang et al. 2013). The PPco used here went through 3 extrusion processes where two of them were performed at high screw speed (200 rpm). Multiple extrusions, especially at high screw speed, were reported to cause chain scission and molecular weight reduction. Those changes make PP less thermally stable (González-González et al. 1998, Hermanová et al. 2009). Lower mechanical properties (not shown) obtained from the processed PPco as compared to that of as-received PPco confirmed our assumption. During the TGA testing, both 380°C and 420°C peaks appeared for the T_DTG-PPco. This reflects the different processing history of PPco because some PPco were added before and some PPco were added after the masterbatch process. Samples with lower T_DTG-PPco are analyzed here because they are more likely to be degraded in the next process. The addition of SDCNF increased the residual mass content of PPco at 450°C. This implies that SDCNF hinders the thermal degradation of PPco at higher temperature (Yang et al. 2013). The purpose of running TGA was to predict whether or not the thermal degradation occurred during the AM process. During AM, filaments flow continuously through the liquefier for a short residence time. Moreover, much smaller shear rate was reported during extrusion-based AM as opposed to injection molding (Tuner et al. 2014). Additionally, the polymer was printed at 200°C. Based on this information, no severe thermal degradation was expected during printing.
5.4.2 DSC

Figure 5.3 Melting (a) and crystallization (b) processes of PPco pellets measured by DSC.

Table 5.3 Thermal properties of PPco and its composite pellets obtained from DSC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting temperature $T_m$ (°C)</th>
<th>Crystallization peak temperature $T_c$ (°C)</th>
<th>Relative crystallinity $RX_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPco</td>
<td>159 (0)</td>
<td>117 (0)</td>
<td>37 (1)</td>
</tr>
<tr>
<td>PPcoMA</td>
<td>160 (0)</td>
<td>118 (0)</td>
<td>39 (1)</td>
</tr>
<tr>
<td>PPcoSDCNF7.5</td>
<td>160 (0)</td>
<td>121 (0)</td>
<td>41 (2)</td>
</tr>
<tr>
<td>PPcoMASDCNF7.5</td>
<td>161 (0)</td>
<td>122 (0)</td>
<td>40 (1)</td>
</tr>
<tr>
<td>PPcoSDCNF15</td>
<td>161 (0)</td>
<td>122 (0)</td>
<td>40 (1)</td>
</tr>
<tr>
<td>PPcoMASDCNF15</td>
<td>161 (0)</td>
<td>122 (1)</td>
<td>42 (2)</td>
</tr>
</tbody>
</table>
DSC curves obtained from the melting and crystallization processes are shown in Figure 5.3. The related thermal properties are listed in Table 5.3. PPco and SDCNF-PPco composites all have a $T_m$ around 160°C which corresponds to the melting of $\alpha$ crystal (Wang and Gardner 2017). SDCNF does not appear to change the $T_m$ of coPP, which was also reported in previous research (Ljungberg et al 2006, Panaitescu et al. 2007, Nagalakshmaiah et al. 2016, Bahar et al. 2012). The addition of SDCNF gradually increases the $T_c$ of PPco, indicating SDCNF, under current testing conditions, acts as a nucleating agent for PPco. In a previous study, CNF was reported to be a nucleating agent, which increased the $T_c$ of PP (Panaitescu et al. 2007). The $R\chi_c$ of PPco with SDCNF is larger than pure PPco, which again confirms the nucleating ability of SDCNF for PPco. Generally, the addition of MAPP into either PPco or SDCNF-PPco composites promotes the $R\chi_c$ of PPco. First, MAPP alone was reported to be a nucleating agent for PP (Seo et al. 2000). Second, MAPP facilitates SDCNF to distribute better within PP, which increases the nucleation density. Based on above information, a printing temperature of 200°C should be sufficient for melting the PPco and its composites. A bed temperature of 120°C will improve the $R\chi_c$ of PPco as it constantly anneals the specimens during printing. An increase in $X_c$ of PLLA was reported using a bed temperature of 160°C (Wang et al. 2017b).
Figure 5.4. Melting curve of injection molded (IM) and additive manufactured (AM) PPco.

Table 5.4 Melting information for injection molded and printed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting temperature (β) ( T_{mβ}(°C) )</th>
<th>Melting temperature (α) ( T_{mα}(°C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPcoIM</td>
<td>-</td>
<td>162 (1)</td>
</tr>
<tr>
<td>PPco</td>
<td>146 (1)</td>
<td>160 (1)</td>
</tr>
<tr>
<td>PPcoMA</td>
<td>147 (0)</td>
<td>161 (0)</td>
</tr>
<tr>
<td>PPcoSDCNF7.5</td>
<td>146 (0)</td>
<td>160 (0)</td>
</tr>
<tr>
<td>PPcoMASDCNF7.5</td>
<td>147 (0)</td>
<td>160 (0)</td>
</tr>
<tr>
<td>PPcoSDCNF15</td>
<td>146 (1)</td>
<td>160 (0)</td>
</tr>
<tr>
<td>PPcoMASDCNF15</td>
<td>146 (1)</td>
<td>160 (0)</td>
</tr>
</tbody>
</table>

The melting curves of injection molded PPco (PPcoIM) and printed PPco (PPcoAM) are shown in Figure 5.4. As seen in Table 5.4, for PPcoIM, only one melting peak was observed at around 160°C which is the melting temperature of α crystal of PP (Tordjeman et al. 2011). For PPcoAM, they all show three peaks at about 145°C, 150°C and 160°C, corresponding to the β, β' and α crystals of PP (Wang and Gardner 2017,
Papageorgiou et al. 2015). The formation of β crystal can be promoted by a controlled crystallization temperature range (100-120°C), β-nucleating agent, directional crystallization in a temperature gradient field and shear-induced crystallization (Fujwara 1975). Based on our previous study of 3D printed PP, a controlled crystallization temperature is most likely the major reason for the formation of β crystal in this study as the printing bed temperature was kept at 120°C (Wang and Gardner 2017). β' crystal is formed when less stable β recrystallizes to more stable α crystal. β' crystal is a transitional phase that is caused by the heating used in the DSC test (Fujwara 1975), thus should not be used for calculating crystallinity. To calculate the RXc for PPcoAM, Equation (1) should not be used. Instead, the Xα and Xβ should be calculated separately because α and β crystals have different heats of fusion (Li et al. 1999). The contents of β and α crystal affect the mechanical properties of PP. Considering the mechanical properties are not the interest of this study and the complexity of calculations, Xc, Xα and Xβ were not obtained.

5.4.3 Heat deflection temperature (HDT)

Table 5.5 Heat deflection temperatures of PPco and its composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPcoIM</td>
<td>84 (5)</td>
</tr>
<tr>
<td>PPco</td>
<td>92 (1)</td>
</tr>
<tr>
<td>PPcoMA</td>
<td>103 (2)</td>
</tr>
<tr>
<td>PPcoSDCNF7.5</td>
<td>103 (2)</td>
</tr>
<tr>
<td>PPcoMASDCNF7.5</td>
<td>107 (7)</td>
</tr>
<tr>
<td>PPcoSDCNF15</td>
<td>104 (5)</td>
</tr>
<tr>
<td>PPcoMASDCNF15</td>
<td>100 (5)</td>
</tr>
</tbody>
</table>
Figure 5.5 SEM graphs of injection molded PPco (a), printed PPco (b), printed PPcoSDCNF7.5 (c) and printed PPcoSDCNF15 (d).

HDTs of injection molded PPco and printed PPco composites are displayed in Table 5.5. PPcoMA has a higher HDT than PPcoIM and PPco. HDT of a solid polymer is related to the T_m and X_c of the material (Landel and Nielson 1993). Because MAPP can increase the RX_c of PPco (Table 5.3), the addition of MAPP increases the HDT of PPco. Adding 7.5 wt.% SDCNF increases the HDT of coPP. There are two reasons. 1) It was reported that natural fibers in PP restricted the mobility of PP chains in the amorphous area, leading to a higher HDT (Chattopadhyay et al. 2010, Chattopadhyay et al. 2011). 2) As seen in Figure 5.5, the addition of SDCNF increased the number of voids in printed parts. Those voids acted as insulator that delayed heat transfer thus increased the HDT. An increase in HDT of foamed willow-fiber-filled PLA was reported compared to
unfoamed injection-molded PLA (Zafar et al. 2016). The number of voids inside printed Nylon 12 was also reported to increase when fillers were added (Abdullah et al. 2017). However, these voids will degrade the mechanical properties of printed parts, thus should be avoided to make better quality parts.

5.5 Conclusions

Thermal analysis was performed on PPco and SDCNF-PPco composite pellets and specimens.

1) TGA showed that the addition of SDCNF lowered the onset temperature and increased the residual mass content (at 450°C) of PPco pellets without significantly changing the peak degradation temperatures of SDCNF and PPco.

2) SDCNF and MAPP increased the peak crystallization temperature and relative crystallinity of coPP without changing its melting temperature. This indicated that SDCNF and MAPP were nucleating agents for PPco under the test manufacturing conditions.

3) Printed PPco and SDCNF-PPco composites exhibited three melting peaks that belong to β, β' and α crystals while injection molded PPco only showed a melting peak of α crystal. A bed temperature of 120°C was the major reason for the formation of β crystal in printed parts.

4) DMA displayed that printed PPcoMA had higher HDT than injection molded PPco because MAPP increased the crystallinity of PPco. Printed SDCNF-PPco composites had higher HDT than PPcoIM because SDCNF increased the number of voids and restricted the mobility of PP chain in amorphous areas.
CHAPTER 6

CONCLUSIONS AND FUTURE RESEARCH

6.1 Conclusions

The overall goal of the proposed research was to address fundamental issues regarding the printability of PP and SDCNF-PP composites using extrusion-based AM. The relations among structure, processing and properties of SDCNF-PP composites were investigated. Structure here refers to the morphology of SDCNF and composition of PP. Processing of the composites involved AM and injection molding. Properties studied included mechanical properties of printed parts, rheological properties of SDCNF-PP melts, nonisothermal crystallization kinetics and thermal expansion of SDCNF-PP composites and thermal properties of SDCNF-PP composites made by extrusion-based AM. A summary of the overall results are listed below.

1) The mechanical properties of printed PP can be comparable to injection molded PP if printing parameters are selected properly. Higher extrusion temperature, smaller layer height and slower printing speed resulted in smaller voids in printed parts, leading to minimal decreases in mechanical properties. The specific mechanical properties of printed PP were comparable or even higher than injection molded PP because the density of printed PP was smaller than injection molded PP.

2) The addition of SDCNF into PP increased the flexural properties of PP. For example, the flexural strength and modulus of PP were increased by 5.9% and 26% after 10 wt.% SDCNF was added into PP. Meanwhile, the viscosity of SDCNF-PP composites did not increase dramatically compared to PP, even at small shear rates. The small
increase in viscosity at lower shear rate brought by SDCNF makes the resulting PP composites filament friendly to extrusion-based AM devices.

3) The addition of 10 wt.% SDCNF into PP increased the t_{1/2} and reduced the overall crystallization rate of PP. Neither 3 wt.% nor 30 wt.% of SDCNF reduced the overall crystallization rate of PP. The addition of SDCNF all increased the nucleation density (rate) of PP as seen in the polarized light microscopy of SDCNF-PP composites. The addition of 10 wt.% and 30 wt.% SDCNF decreased the crystal growth rate by increasing the effective activation energy. Only at 10 wt.% SDCNF level, the increase in nucleation rate was smaller than the decrease in crystal growth rate of PP, resulting in a decreased overall crystallization rate. MAPP increased the crystallization rate of PP by acting as a nucleating agent. Jeziorny and Liu methods were valid in describing the nonisothermal crystallization kinetics of PP while the Ozawa method was invalid. Moreover, the CTE of PP was decreased by about 12% when 10 wt.% SDCNF was present.

4) Adding SDCNF into PP decreased the degradation onset temperature but increased the residual mass content of impact-modified PP. SDCNF acted as a nucleating agent for impact-modified PP by increasing the peak crystallization temperature and crystallinity of impact-modified PP. Printing impact-modified PP at a bed temperature of 120 °C created both α and β type crystals in the part while injection molded PP only had α crystal. The HDT of printed impact-modified PP was higher than injection molded equivalent. This is because small portion of voids in printed parts acted as thermal insulator that delays the heat transfer.
6.2 Future work

1) The biggest issue encountered during the thesis work was the printing quality of SDCNF-PP composites: the strands coming out of the nozzle kept breaking during deposition, resulting in extra pores. This issue has to be addressed to make functional parts. Our filaments were made in lab using a self-made take-up device. The resulting filament had an average diameter of 2.65 ±0.15 mm. The tolerance of the diameter of our filament was far bigger than that of the commercial filament (0.05 mm). The large diameter tolerance was thought to be the source that caused the poor printing quality. However, the pure PP filament which was made in the exact same way as SDCNF-PP composite filaments had good printing quality, indicating that the diameter and tolerance of our filament met the printing requirements. Another reason may cause the poor printing quality was the lack of melting and blending pressure in the printer that would drive the air out (Duigou et al. 2016). To test this speculation, a major modification (add screw in the liquifier) to the printer is needed. Another source for the extra pores was the incompatibility between fiber and polymer (Tekinalp et al. 2014). Fibers and polymers flow independently during extrusion, leading to the voids formation. Compatibilizer was suggested to be used to help with the issue. However, in our experiments, MAPP was used with SDCNF. The corresponding composite filaments did not show good printing quality. The last reason found in the polymer scientific literature was that the existence of fibers generated sporadic semi-blockage at the nozzle exit (Milosevic et al. 2017, Stoof et al. 2017). This problem was solved by increasing the nozzle diameter from 1 mm to 2 mm. Our printer has a nozzle diameter of 0.5 mm which may be too small for printing fiber composites smoothly. So the next step of this research is to explore use of nozzles
with larger diameters. However, attention is needed when choosing the nozzle diameter because the resolution of printed parts will decrease when nozzle diameter increases.

2) After spray drying, most CNF exhibited a spherical structure. This spherical structure did not increase the viscosity of the SDCNF-PP composite melts which was beneficial for processing. However, the SDCNF spheres lack the ability to form entanglements and percolation as other nanofibers system would do to greatly enhance the mechanical properties of polymer at small fiber loading level. The size of the SDCNF depends on the size of droplets which are produced by spray dryer breaking up the suspension film (Peng et al. 2012). Spray drying parameters can be further tested to reduce the droplet size.

3) The shear force involved during extrusion compounding did not disperse the SDCNF agglomerates even at a screw speed of 250 rpm. Several forces are responsible for the formation of such agglomerates (Wang et al. 2017). Among them, the H-bonding among cellulose molecules is the strongest. Dispersion methods used for other types of nanofibers should be investigated on SDCNF. These include ultrasonic treatment on SDCNF before compounding, ball-milling on the SDCNF before compounding (Perrin-Sarazin et al. 2009) and compounding SDCNF with other fillers to increase the shear force on the agglomerates.

4) Adding 10 wt.% SDCNF into iPP reduced the overall crystallization rate of iPP under nonisothermal condition, but only to a small extent. Therefore, the addition of SDCNF did not significantly reduce the warping of iPP during printing. However, there were other nanofillers investigated before which were able to reduce the crystallization
rate or crystallinity of a semi-crystalline polymer greatly (Fornes and Paul 2003, Boparai et al. 2016). The $t_{1/2}$ of a high-molecular-weight Nylon6 was reduced by 50% with the addition of 7.2 wt.% montmorillonite using melt compounding (Fornes and Paul 2003). The crystallinity of Nylon6 was reduced by 37% with the addition of 20 wt.% of Al-Al$_2$O$_3$ nano powders (Boparai et al. 2016). Compounding SDCNF with these nanofillers has the potential to further reduce the crystallization rate of iPP.

5) Compared to iPP homopolymer, iPP copolymer or impact-modified PP has already shown slower crystallization rate (Nandi and Ghosh 2007). The influence of adding SDCNF into iPP copolymer should be studied to conclude whether SDCNF can decrease the crystallization rate of iPP copolymer further more. Once the printing-quality issue is resolved, SCNF-PP composite specimens should be prepared to obtain mechanical properties and dynamic mechanical properties (elastic modulus, loss modulus and damping factor) of these composites. Interfacial strength of printed SDNCF-PP composites are also of great interest because few publications report this property for polymer composites made by extrusion-based AM. It was mentioned in one previous study that the existence of particles would decrease the interfacial strength as they hindered the molecular diffusion at the interfaces (Hwang et al. 2015). However, CNF with MAPP may increase the interfacial strength if the interfacial stress can be transferred to CNF effectively.


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Lu Wang was born in February 17\textsuperscript{th} of 1988 in China. He was raised in Changzhou, Jiangsu, until 2006. He attended Central South University of Forestry & Technology in China and received a Bachelor of Science degree in Wood Science and Engineering in 2010. After graduation, Lu continued his study at the Nanjing Forestry University as a master student. He achieved his Master of Science degree in Bamboo-based Engineering Materials in June, 2013. Lu started his new adventure in the School of Forest Resources and Advanced Structures and Composites Center at the University of Maine as a Ph.D. graduate research assistant. At Maine, Lu gradually sharpens his skill as a student researcher. Among these awards were the 2016-2017 Graduate Scholarship Award of Society of Plastic Engineers (SPE) Automotive Composites Conference & Exhibition (ACCE), 2016 first place poster competition award of the Northeast Agriculture and Biological Engineering Conference (NABEC) and the 2017-2018 Marquis Who’s who in American list. Lu is a candidate for the Doctor of Philosophy degree in Forest Resources from the University of Maine in December 2017.