# NIECTION MOLDING

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Chair's Message Rick Puglielli



As the anxiety begins to rise this holiday season amidst the pandemic, the Injection Molding Division of SPE will continue to focus on our mission of delivering quality content to the injection molding community and the future scientists and engineers who will develop new technology that will use plastics in a safe and responsible manner with respect for the environment. Contrary to the war on plastics, the industry has been making great strides at achieving this goal. Just like a vaccine for Covid-19 being developed in less than one year, we can achieve great things if we act like our lives depend on it. Our lives benefit from plastics in so many ways, so rather than starting a war, we need to act like our lives depend on it. However, our lives and well-being for future generations also depend on a clean, healthy environment with a sustainable ecosystem so together we all need to work at warp speed to find a safe and responsible way to reap the benefits of plastics before we make them obsolete. We can all achieve this together. The plastics industry must continue to push the envelope with new designs and invest in technologies and materials that support these efforts. As consumers we can support this effort at least for the short term by sacrificing the convenience and low prices that we have all been accustomed to.

Have Safe, Healthy and Happy Holiday Season!

Sincerely,

Rick Puglielli 2020-2021 SPE Injection Molding Division Chair

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Keep the connection! Join us on:



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#### FEBRUARY 2021

#### INTELLECTUAL AGREEMENT FUNDAMENTALS FOR SCIENTISTS, ENGINEERS AND MANAGERS

WEEK 1: February 5, 2021 12:00 PM (EST) - 1:00 PM (EST)
WEEK 2: February 12, 2021 12:00 PM (EST) - 1:00 PM (EST)
WEEK 3: February 19, 2021 12:00 PM (EST) - 1:00 PM (EST)
WEEK 4: February 26, 2021 12:00 PM (EST) - 1:00 PM (EST)

Are you planning on communicating or collaborating with individuals and/or entities outside of your organization on technical information or technology development? Learn how to protect your technology and intellectual property (IP) interests by making sure an appropriate IP agreement is put in place with the other party prior to such communication or collaboration. Don't be caught off guard and have your IP rights compromised when working with others by learning the fundamentals of IP agreements and their use!

This workshop series is intended as an introductory primer in intellectual property agreements for scientists, engineers and managers involved in business and technology. It introduces the participants to the fundamentals of contracts with a focus on those relating to intellectual property (confidential / proprietary information, trade secrets, inventions and patent applications). The course will provide an overview of the major sections of a contract and common types of IP related agreements, including confidentiality/non-disclosure, material transfer and testing, collaborative research, joint development, technical services, consulting, and patent / trade secret licensing. Participants will learn the appropriate type of agreement to use for a certain business scenario involving technology and intellectual property. Participants will also learn approaches for protecting and allocating IP rights when working with outside parties. The course will also cover how to extract further value from your IP assets through creative technology licensing efforts with others.

#### **GET MORE DETAILS>**

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#### Meet the Technical Manager for iD Additives Foaming Agents, Ron Bishop!

With over 35 years of experience in the plastics industry, Ron has helped countless processors reduce part weight and cycle times by adding foaming agents to their injection molding, extrusion, blow molding and other applications. Contact him with your questions at **708-588-0081 x2898** or **rbishop@idadditives.com**.





#### **ON-DEMAND WEBINAR**

#### **REIMAGINE WHAT SIMULATION CAN DO FOR YOUR BUSINESS**

#### TZERO® INNOVATIVE DELIVERABLES AND CASE STUDIES

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#### ON-DEMAND WEBINAR HOW TO INTERPRET YOUR INJECTION MOLDING PROCESS DATA

#### DISCOVER HOW TO IDENTIFY MACHINE AND PROCESS PROBLEMS FROM YOUR EDART® DATA

Process monitoring software can collect data all day long, but if you don't know how to interpret that data and put it to work for you, then your technology is not reaching its full potential. This webinar will walk through several examples of process problems and show you how to analyze the data points and use them to take corrective action.

#### VIEW NOW>

#### **ON-DEMAND WEBINAR**

#### USING SYSTEM AND HOT RUNNER BALANCE IN THE MOLD QUALIFICATION PROCESS

System balance plays an important role in the optimization of an injection molding process and can be the limiting factor in the production of high quality parts from every cavity. In this webinar Husky will present the process fundamentals of system and hot runner balance and its impact on mold qualification. They will look at the factors that enable well designed balanced hot runners as well as the causes of unbalanced systems. Attendees will learn about the factors that influence short shot balance, how to measure system balance and how to set system balance expectations based on specific applications.

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#### **ON-DEMAND WEBINAR**

#### HOW TO REDUCE RISK IN PLASTIC PART DESIGN AND MANUFACTURING

In this webinar Autodesk will explore how companies today use simulation workflows to identify potential issues, detect the significance of interaction effects between variables, and define custom quality criteria to produce a part with the least amount of risk. The information from simulation results can even be transferred to set up injection molding machine processes for quicker start up. Join Autodesk to find out more.

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#### Recordings from all SPE virtual events are now available for viewing 24/7!

If you missed any of SPE's virtual events, you can now purchase event recordings by visiting the website and choosing which event(s) you would like!



# Spe ANTEC® 2021 THE HYBRID EDITION

# CHOOSE THE EVENT THAT'S RIGHT FOR YOU!

#### ANTEC® Industry Insights March 22–23, 2021

Kicking off ANTEC® 2021, must-hear plastics leaders will share their valuable industry insights. Join us for this two-day event via SPE's exclusive live-streaming service to your remote location.

#### Program includes:

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- Plastics & The Environment It's not just bags, bottles and straws
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#### ANTEC® Classic March 29-April 9, 2021

ANTEC® Classic, slated for March 29 to April 9, will offer real-time, remote presentations occurring over 10-days with 20 technical tracks. Additionally, it will include International Spotlights with real-time global presentations broadcast online from various regions around the world, including Asia, India, Australia/New Zealand, Europe, and the Middle East. Dates for International Spotlights will be forthcoming.

Hear from the industry's top researchers as they discuss their latest findings. In the traditional ANTEC® format, 200+ papers across a wide variety of topics will be presented. Watch the presentations real-time, with Q&A after each presentation, or watch the recorded sessions on-demand on your schedule.

For more information visit: www.injectionmoldingdivision.org/antec/



It's much more than a "Plastics Race"... it's the SPE Plastics Winter Olympics!!!

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- Test your plastics knowledge by answering a wide variety of questions (hints available)
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- Contestants try to medal in as many events as they choose
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- Points are awarded for each correct answer, and deducted for hints used

Speed matters! Tiebreaker is the amount of time spent answering the questions

• Students and Plastics Professionals compete in separate competitions

Student Chapters with the highest average score from at least 3 participants will receive the coveted plastic Olympics Traveling Trophy

- SPE's Plastics Winter Olympics is open for 4 days (December 18-21) compete at your convenience
- Watch the leader board and see if you'll be taking your spot on the winner's podium
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Click here to reserve your spot in the SPE Plastics Winter Olympics!



# THIS #GIWINGTUESDAY CHANGE THE PERCEPTION OF PLASTICS

# Giving Tuesday is a national movement to support programs and initiatives we believe in.

Today, we are asking support for our SPE Foundation PlastiVideos Program!

With a generous gift from SPE Detroit, PlastiVan shifted gears last spring to begin producing virtual content in an effort to reach more students during this unprecedented year.

With exciting topics as marine debris, foam, and manufacturing, PlastiVideos provide engaging lessons in plastics science.

But, we need your help!

It costs \$5,000 to produce one PlastiVideos learning module.

Help us reach our goal of raising \$10,000 to create two new learning modules for students and educators.

This #GivingTuesday, make a gift and help us in our mission to change the perception of plastics one classroom at time.

#### **GIVE WONDER. GIVE AWARENESS.**



Thanks to help from the SPE Detroit Section, SPE Automotive Section, and Plastics Pioneers Association, PlastiVan is shifting gears during this time and using our resources to create new online offerings for our stakeholders. PlastiVideos transform our exciting PlastiVan program into virtual modules. It costs \$5,000 to develop and tape each PlastiVideo module. We need YOUR help to bring PlastiVideos to more classrooms!

By Brian Love

## Revisiting Boltzmann Kinetics in Applied Rheology

The dynamic viscosity of resins undergoing soft gelation shows a marked sigmoidal shape, suggesting that similarly shaped functions might be considered for model predictions.

We have all encountered instances where failure to characterize the complete physical state of formulated polymer-resin mixtures limits our ability to describe rheological advancement (gaining new insights into deformation and the flow of matter) from a more fundamental perspective. The presence of co-monomers, fillers, compatibilizers, and orientation all affect the thermodynamics of the glass transition. As monomers and formulated resins form longer chain lengths, the transition from small- to larger-molecule behavior is often tracked and observed based on rheological analysis, combined with the corresponding parametric studies, to resolve how fillers, formulation, cure temperature, and pressure affect the dynamics of these processes. The analysis might lack a true interpretation of free volume, for example, but the parametric sensitivity can be resolved, thus helping process engineers define routine and robust cure schedules.

There is no shortage of models describing cure advancement, either from a rheological or a curekinetics perspective. Several practical reviews have summarized specific models that are based in part on both kinetics and thermodynamics.<sup>1,2</sup> They interpret how the glass transition is affected by growing chain lengths. Further complications arise for network formation as the kinetics of polymerization also affect the induction time and rheological advancement.<sup>3, 4</sup> On the one hand, phenomenological relationships interpret the shapes of various rheological profiles.5-7 On the other, ab initio calculations from first principles, aimed at resolving the contributions of entanglements and size to the path length of single polymer chains,



**Figure 1:** Data of gelation for a 9% (by weight) acrylamide gel crosslinked in the presence of ammonium persulfate, and compared with a corresponding sigmoidal model for polymerization. Eta: Crosslinked viscosity, in units of Pa · s. **Revisiting Boltzmann Kinetics in Applied Rheology** 

are used to study rheology.<sup>8</sup> The power-law model has a particular allure to describe time-dependent viscosity because of its simplicity. Predictions have been made using power-law coefficients to control polymerization conditions and avoid thermal runaway associated with auto-accelerating reactions<sup>9, 10</sup>

We have been investigating whether other mathematical models could represent a wider range of dynamic rheology data. The Austrian physicist Ludwig Boltzmann elegantly described the toggling between two states following some sort of sigmoidal curve. He resolved the mathematics to describe such a function,  $\eta(t)$ , which yields four parameters, two time constants and two physical constants attributed to the initial and terminal physical states,

$$\log \eta(t) = \log \eta_{\infty} + \frac{\log(\eta_0) - \log(\eta_{\infty})}{(1 + e^{\frac{t - t_0}{\Delta t}})}.$$
 (1)

For a cure curve, these states are related to the viscosities of the resin in the uncured ( $\eta_0$ ) and cured ( $\eta_\infty$ ) states, respectively. One time constant corresponds to the induction time for the viscosity to traverse though the midpoint between the cured and uncured conditions ( $t_0$ ) and the second relates to the time associated with the rate of viscosity rise ( $\Delta t$ ) at the midpoint. Interpretations of the gel time similar to the power-law model are described as algebraic expressions of the two time constants.

We have evaluated rheological advancement using this sigmoidal model of pre-polymers measured in our own laboratory and reanalyzed other published data sets, including epoxies,<sup>11–13</sup> acrylics,<sup>14, 15</sup> polyurethanes,<sup>16</sup> polyacrylamides,<sup>17</sup> and even network gels based on denatured and misfolded proteins such as insulin. An example of the analysis for an acrylamide gel with its corresponding Boltzmann fit is shown in **Figure 1**. We use the model in logarithmic form given the large range of most rheological data, as it seems to capture a wider array of resin behavior.

The model is nimble in resolving dynamic viscosity from a phenomenological perspective. It is encouraging that the Boltzmann parameters have some physical significance. On one level, the allure of including one simple equation into process models such asMoldflow® to describe time-dependent materials conveyance in reaction-injection molding and polymerization vessels as a function of time is compelling. Unresolved issues remain to be addressed. For one, it is not fair to consider the upper limit of viscosity accurate in the Boltzmann model if it is extracted from data in which the torque limit of the rheometer is reached. A more rugged rheometer would yield a different dynamic curve, which would result in different Boltzmann constants. This is one motivation to redirect our efforts to focus on weaker gels such as the acrylamides, which have gel stiffnesses well below the torque limit of the rheometer. The sigmoidal model should be more accurate for foodstuffs and other protein mixtures that have lower terminal viscosities. Our work is just the first step of a more comprehensive effort to justify and compare the sigmoidal model in terms of what we already know of other fundamental gelation models from a thermodynamic and kinetic point of view, incorporating cure temperatures, exothermic evolution, dynamic conversion, and free volume within the growing polymer.

I would like to acknowledge the contributions of Thibaut Savart and Caroline Dove, who conducted the acrylamide-cure experiments and the corresponding rheometry

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### Mechanical Characterization and Effect of Water Absorption on PLA Carbon Fiber Composites in Injection Molding

This study investigated the mechanical behaviors of injection molded polylactic acid (PLA) composites reinforced with carbon fiber (CF) at different fiber loading levels (5 wt%, 10 wt%, 15 wt% & 20 wt%). PLA, a biodegradable thermoplastic derived from renewable resources, has been replacing petroleum-based plastics in many applications due to its sustainability and low environmental impact. However, the low mechanical strength limits its wide structural applications. The addition of small amount of CF significantly increased the tensile strength and modulus while leading to reducedductility. Compared to pure PLA, the composites with 5 wt% CF content had a 40% increase of tensile modulus and a 63% decrease of elongation-at-break. The effects of water absorption on the mechanical properties of PLA/CF composites were also studied.

#### Introduction

PLA is a biodegradable plastic material derived from renewable sources. The demand for ecologically friendly material makes PLA a promising material. However, the relatively weak mechanical properties of PLA limit its wide structural applications. Incorporating fibers into the PLA matrix is one of effective ways to tailor and enhance the mechanical properties. To create green composites, natural fibers such as kenaf fiber, hemp fiber, flax fiber, have been added to PLA to tailor its properties. Ochi et al 1 studied mechanical properties of kenaf/PLA composites, and reported that the tensile strength and flexural strength of the composites increased linearly up to a fiber loading of 50 vol.%. The kenaf/PLA composite specimens were produced by heating prepregs in metallic mold and then hot pressing. Oksman et al <sup>2]</sup>conducted a study on PLA/flax composites and PP/flax composites. It was reported that flax can be used as a reinforcing material with the PLA and the strength of PLA/flax composites are about 50% better compared to similar PP/flax composites. The test samples were produced in a two-step process. The composite materials were extruded with a twin-screw extruder and then compression molded. Huda et al<sup>3</sup> conducted a study on PLA composites reinforced with recycled newspaper cellulose fiber (RNCF) and chopped glass fibers through a twin-screw extruder and then an injection molding machine. It was reported that mechanical properties of the PLA composites were favorable compared to the properties of PP composites. Guo et al<sup>4</sup> studied statistically the effects of molding conditions on the mechanical behavior of PLA/wood-fiber composites with response surface methodology.

Use of natural fibers to reinforce PLA is not sufficient for structural applications. Conventional fibers, glass fiber (GF) and carbon fiber (CF), are excellent reinforcements for enhancing mechanical properties. CF has a density of about 1.6 g/cc, and is lighter than GF which has a density of 2.1-2.7 g/cc. Developing lightweight structural composites is important in automotive engineering to improve fuel efficiency. In literature, a few studies were conducted on PLA/CF composites. Shen et al <sup>5</sup> studied the mechanical properties of hydroxyapatite (HA)/PLA composite reinforced with 20 vol.% CF. The CF/PLA/HA composite was prepared by hot pressing a prepreg which consisting of PLA, HA and CF. Wan et al <sup>6</sup> studied the influence of surface treatment on the mechanical properties of PLA/CF composites. It was reported that surface treatment of oxidized CF with nitric acid improved mechanical properties of the CF/PLA composites. PLA/CF composites were produced by compression molding. Another paper <sup>7</sup> reported the mechanical and thermal properties of PLA and recycled carbon fiber composites. The composite studied were produced by compounding PLA and recycled CF in micro-compounder and then processing the composite material in injection molding machine.

The conventional injection molded composites are typically produced by a two-step process, which includes pre-compounding of polymer with additives and then processing with an injection molding machine. There were studies conducted on a one-step injection molding <sup>8,9</sup> process, where composite parts are molded directly from a dry blend of the resin, reinforcement, and fillers. Moriwaki et al [8] reported that the breakage of GFs is smaller in a one-step injection molded GF/PA composite. The advantages for one-step injection molding are the reduced operation cost and the reduced fiber breakage occurred in high-shear compounding process. Nakao et al <sup>10</sup> studied direct fiber feeding injection molding (DFFIM) by using CF and commingle yarn as reinforcing fibers with PA6 and PA66. The fiber feeding is done through a vent opening on the resin metering equipment.

It was reported that the fiber was uniformly dispersed in the polymer matrix with both CF and commingle yarn. It has not been reported in the literature about the single-step injection molding of PLA/CF composites with a low content of CF. PLA is naturally hydrophilic due to its polar oxygen linkages and is prone to hydrolytic degradation in the presence of water. Studies were conducted to investigate the effects of water absorption on PLA composites. Tham et al <sup>11</sup> studied the effects of water absorption on the thermal and impact properties of PLA/halloysite nanotube (HNT) composites at three different temperatures. It was reported that the water uptake increased with an increase in water temperature, and the diffusion coefficient of pure PLA is higher than that of the PLA/HNT composites due to the presence of HNT in the composites. PLA/HNT composites were prepared with melt compounding followed by compression molding. Ndazi et al <sup>12</sup> reported that the water uptake of PLA/rice hulls composites increased with an increase in water temperature when subjected to water absorption test. Also, the increase of rice hulls content increased the diffusion of water into the composites. There were no studies to understand the effects of water absorption on the PLA/CF composites. This paper investigates the effects of water absorption on the mechanical properties of PLA/CF composites and the effect of CF on the water absorption behavior of PLA/CF composites.

#### **Experimental**

#### Materials

The plastic material used in this study was PLA (3052D Ingeo grade, with MFR = 14 g/10min, Specific Gravity = 1.24), The CF used was Panex<sup>®</sup> 35 chopped fiber (Type-65) from Zoltek Corp., the normal fiber length is 6 mm. All the materials were used as received. The material formulation for the injection molding experiments is shown in **Table 1**.

Туре	No.	PLA (wt%)	<b>CF (wt%)</b>
Pure PLA	0	100	0
PLA/CF Composites	1	95	5
	2	90	10
	3	85	15
	4	80	20

#### **Mold Design and Fabrication**

A two-part family mold was designed according to the ASTM D638<sup>13</sup>, as shown in **Figure 1**. The fan gate was selected to achieve a uniform material flow, minimize backfilling and part warpage, and keep the cross sectional area constant. It is also suitable for rapid filling of large parts or fragile section mold area with large entry area. The steel insert mold base from DME (Model 08/09 U Style Frame) was cut with a CNC machining center.

#### **Injection Molding Machine**

The injection machine used for making the composite specimens was Engel E-victory 30 with a 30-ton clamping force. The screw diameter is 22 mm with L/D ratio of 30. The injection process parameters, shown in **Table 2**, were used for all the experiments.

#### **Experimental Design**

The PLA and CF were dry blended according to the material formulation in **Table 1**. This blended material was directly put into the hopper of injection molding machine to process composite specimens. For all the experiments, the injection processing parameters were kept the same. Before switching from one experiment to another, a sufficient amount of pure

Figure 1: Fabricated Mold According to ASTM.

#### **Table 2: Injection Molding Parameters**

230
15
560
200
15
25
24.8

PLA was used to purge the system. Specimens were collected for each material formulation according to ASTM D638.

Tensile tests were performed on an MTS tensile testing machine with the load cell capacity of 250 kN. The grip distance was 115 mm and the crosshead speeds of 5 mm/min. 10 specimens were tested for each material formulation. The data reported were the average values of the measurements.

A water absorption test was conducted by placing the specimens in water for 24 hours at room temperature. Immediately, after the water absorption test, specimens were weighed and subjected to a tensile test. 10 specimens were tested for each material formulation and the data reported were the average values of the measurements.

#### **Results and Discussion**

#### Tensile Load vs. Extension

**Figure 2** shows the tensile test curves for the pure PLA and PLA/CF composites. The tensile strength and modulus increased with an increase in CF content from 5 wt% to 20 wt% when compared to those of pure PLA. The ductility of the composite materials decreased with the increase in CF content from 5 wt% to 20 wt%. **Figure 3** shows the fractured specimens after the tensile test, for all the formulations including pure PLA and PLA/CF composites.



Figure 2: Typical tensile load vs. extension.





#### **Density of Injection Molded Composites**

**Figure 4** shows the density of the PLA and PLA/CF composites. Compared to pure PLA, the density of composites increased gradually with the increase in CF content from 5 wt% to 20 wt%. It was also observed that the variability or standard deviation increased for the composites with 15 wt% and 20 wt% CF, which indicates the mixing and distribution of CF would become difficult when the CF content increased to 20 wt% in this single step injection molding process without pre-compounding.



#### **Tensile Strength and Tensile Modulus**

**Figure 5** shows the tensile strength of all the materials before and after they were subjected to the water absorption test. As the CF content increases, the tensile strength of the composites increases almost linearly. Compared with pure PLA, the composites with 20 wt% CF has about 54% increase in tensile strength. However, between the composites with 15 wt% and 20 wt%, the strength increase is not significant. This is probably due to the poor mixing at a relatively high CF content. The composites after water absorption show a slight decrease in tensile strength, it could be because the penetrated water would weaken the interfacial bonding between the fiber and the PLA matrix. Another contributor could be a slight degradation of the PLA from hydrolysis as water penetrates along the interfaces.



**Figure 6** shows the tensile modulus of all the materials before and after they were subjected to the water absorption test. Compared with pure PLA, the composites had a significant increase in tensile modulus with the increase of CF content from 5 wt% to 20 wt%. The addition of 5 wt% CF leads to an increase of 40% in tensile modulus. As the CF content increases to 20 wt%, the tensile modulus significantly increases to 2.4 times that of pure PLA.



#### Elongation at Break

Elongation at break, also known as fracture strain, is the ratio between the changed length and the initial length after breakage of the test specimen. It is also a measure of the ductility of the composites. **Figure 7** shows the elongation at break for all materials before and after they were subjected to the water absorption test. The elongation at break decreased significantly when the 5 wt% CF was incorporated in the PLA matrix. As the CF content increases, the elongation at break slightly decreases. After the water absorption test, the pure PLA shows a slight increase in elongation at break.



#### **Water Absorption**

**Figure 8** shows the water uptake of pure PLA and PLA/CF composites after they were subjected to water absorption test. The water uptake of the composites increased as the CF content increases. This could be because the increase of interfacial voids between the CF and the PLA matrix, as well as the increase of porous CF content. However, compared with pure PLA, the composites with 5 wt% CF has a decrease of 51% in water uptake. There could be two possible explanations. First, there could be micro cracks on the PLA surface adsorb water. Second, the addition of CF increases the crystallinity of PLA/CF composites, because it acts as a nucleating agent and promotes a faster formation of crystalline domains. As a result, higher crystallinity is considered as a barrier against the advance of penetrant and a reduction in the diffusion coefficient <sup>14</sup>. Further investigation is needed to clarify.



#### Conclusions

This paper investigated the mechanical characteristics of PLA and PLA/CF composites produced from a single injection molding process. The effects of water absorption on the mechanical characteristics of PLA/CF composites were studied.

Experimental results show an increase in tensile strength and tensile modulus of the composites, as the CF content increases. The addition of 5 wt% CF increased the tensile strength and tensile modulus by 19% and 40%, respectively. As the CF content increased to 20 wt%, the tensile strength and tensile modulus significantly increased by 54% and 243% respectively, compared to those of pure PLA. However, the increase in CF content led to the decrease of the elongation at break of the composites and the loss of ductility.

Water absorption has a larger influence on the tensile strength than the tensile modulus and the elongation at break of the composites. This paper suggests that a single step injection molding would be proper for making the composites with a CF loading less than 20 wt%. Moreover, the addition of small amount of CF (i.e., 5 wt%) would significant improve the tensile modulus and tensile strength.

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