A Biobased Multifaceted Polymeric Material: A Case for Poly(butylene succinate)

by

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ABSTRACT

A BIOBASED MULTIFACETED POLYMERIC MATERIAL: A CASE FOR POLY(BUTYLENE SUCCINATE)

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University of Guelph, 2018

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An investigation into the adoption and use of bio-based poly(butylene succinate) (BioPBS) in a variety of applications. Polymers derived from biological monomers represent a new route to develop sustainable bio-based materials. BioPBS was combined with pyrolyzed miscanthus microparticles and graphene nanoplatelets to create a hybrid nano-biocomposite. Two methods were used to incorporate graphene nanoplatelets into the blends resulting in different internal morphologies which subsequently impacted their thermo-mechanical properties. BioPBS was also electrospun into fibers that have high porosity at the micro- and nano-scale resulting in a hierarchical structure that has sufficient mechanical properties for potential applications in wound healing and soft tissue engineering. An increase in BioPBS concentration resulted in the reduction of bead defects, which at 15 (\%w/v) resulted in bead-free uniform fibers and increased the porosity of the fibers while reducing pore size. This delve into various parameters affecting the polymer’s properties illustrate its potential for widespread use.
Acknowledgments

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I would also like to give a big thank you to my family members especially my mother, without her support and encouragement I would not be where I am today. A special thanks to my grandfather, the late Robert Cooper, for teaching me to do what is right and just, not for the gratification or praise of others but for what it bestows upon oneself.

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<th>Full name</th>
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<tr>
<td>AAES</td>
<td>Alkyl ammonium ethyl sulfate</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BC</td>
<td>Biocarbon</td>
</tr>
<tr>
<td>BioPBS</td>
<td>Bio-based poly(butylene succinate)</td>
</tr>
<tr>
<td>CHCL$_3$</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CLTE</td>
<td>Coefficient of linear thermal expansion</td>
</tr>
<tr>
<td>DC</td>
<td>Direct compounding</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMF</td>
<td>$N,N$-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EC</td>
<td>Entanglement concentration</td>
</tr>
<tr>
<td>EG</td>
<td>Electrode gap</td>
</tr>
<tr>
<td>FC</td>
<td>Film grade BioPBS in CHCL$_3$</td>
</tr>
<tr>
<td>FF</td>
<td>Film grade BioPBS in CHCL$_3$/DMF</td>
</tr>
<tr>
<td>FO</td>
<td>Film grade BioPBS in CHCL$_3$/DMSO</td>
</tr>
<tr>
<td>GnP</td>
<td>Graphene nanoplatelet</td>
</tr>
<tr>
<td>HDT</td>
<td>Heat deflection temperature</td>
</tr>
<tr>
<td>IC</td>
<td>Injection grade BioPBS in CHCL$_3$</td>
</tr>
<tr>
<td>IF</td>
<td>Injection grade BioPBS in CHCL$_3$/DMF</td>
</tr>
<tr>
<td>IO</td>
<td>Injection grade BioPBS in CHCL$_3$/DMSO</td>
</tr>
<tr>
<td>MB</td>
<td>Masterbatch</td>
</tr>
<tr>
<td>MFI</td>
<td>Melt flow index</td>
</tr>
<tr>
<td>MWD</td>
<td>Molecular weight distribution</td>
</tr>
<tr>
<td>PBS</td>
<td>Poly(butylene succinate)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PHB</td>
<td>Poly(3-hydroxybutyrate)</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMA</td>
<td>Thermomechanical analysis</td>
</tr>
<tr>
<td>TPP</td>
<td>Toughened polypropylene</td>
</tr>
</tbody>
</table>
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Chapter 1.
Introduction

1.1 Overview of Plastics

The last century has seen unprecedented scientific and technological progress. Nowhere is this more prominent than the emergence and widespread commercialization of plastics. The first totally man-made polymer was synthesized from a condensation reaction of phenol with formaldehyde, to form the first synthetic thermoset in 1907\(^1\). With little over a century of innovation and industrialization, knowledge and techniques have been developed to control the structure, properties, and function of plastics - leading to the widespread adoption of plastics within countless industries.

Our addiction to plastic has already manifested itself in the geology of this planet, recently a new form of stone has been classified based on the presence of plastics\(^2\). Plastiglomerate are rocks formed by the combination of ocean sediments such as volcanic rock, seashells, corals, or beach sand combined with plastics\(^2\). These anthropogenic markers will persist long after humanity ceases to exist. Drastic steps are needed to deal with the existing plastic throughout our planet and to establish new industries and infrastructure to create environmentally friendly materials.

Polymers derive their unique properties from their molecular structure which consist of long chains of repeating molecular units known as ‘mers’\(^3\). Both plastics and rubbers are classified as polymers, this broad definition also includes natural polymers such as cellulose, chitin, collagen, and DNA to name a few\(^3\). No other material has seen such an exponential adoption into society, plastics are now an essential part of everyday life, replacing countless conventional materials\(^1\). This exponential growth of both plastics and rubbers is a testament to the materials performance, versatility and cost effectiveness\(^1\). Plastics offer good value as their performance is comparable to conventional materials, but their cost is substantially less. However, this market cost is substantially less than the true cost of the material which reflects the global resources used and externalities related to the full life cycle of the product. Many materials, including conventional materials have not had a comprehensive lifecycle analysis to quantify their ‘true’ cost to society and the planet.
1.1.1 Environmental Concerns

Millions of tons of plastics and resins are produced annually worldwide, the majority derived from feed stocks such as: petroleum, natural gas and coal\(^1\). In fact, nearly half of all polyolefins produced in the United States are derived from petroleum feedstocks, the remainder coming from natural gas feedstocks \(^1\). This process perpetually adds emissions to our already over stressed carbon cycle, most notably the environmental cost associated with post-consumer waste \(^1\). This, of course, is not unique to plastics but with all manufacturing and services. The use of plastics in consumers goods is most prevalent in developed countries, as plastic consumption is highly correlated to the country’s gross national product \(^1\). However, it is estimated that future consumption will grow rapidly in developing countries, even small increases of per capita plastic consumption will translate into a disproportionately large increase in plastic usage \(^1\). One of the largest growing and healthiest markets for plastics is packaging, replacing glass and metal containers. Arguments can be made for both traditional packages and plastic packages in terms of sustainability. Traditional packages like glass jars or aluminum cans often have a longer product lifespan and can be reused multiple times, however, their initial extraction, processing and manufacturing costs are high. Plastics on the other hand often have shorter lifespans but require less processing and manufacturing costs \(^4\), while also saving on the costs of transportation, compared to other heavier packaging materials. More research needs to be conducted on the ‘true’ cost of the materials we often take advantage of in everyday life.

The vast majority of the organic chemicals (90\%) and the energy (80\%) we use to power our everyday lives are derived from fossil fuels \(^4\), our increasing population perpetually adds to this demand, dwindling a finite resource while increasing the price of these fuels \(^5\). These fossil fuels are created from ancient organic matter which ultimately derive its energy from the photosynthesis of ancient plants, as illustrated in Figure 1. Over millennia this organic matter is converted into basic hydrocarbons through intense heat and pressure \(^6\). In present day, these fossil chemicals are extracted and used as fuels and to create materials, this process adds additional carbon into the atmosphere, black arrows in Figure 1. The green arrows in Figure 1 represent a manageable carbon cycle while the black arrows represent excess carbon that cannot be naturally managed. If demand for these fossil resources continues to rise it is projected that our supply will be exhausted by 2050 \(^7\).
A paradigm shift must occur to move away from a petroleum based socioeconomic system to one that is circular and environmentally sustainable. This circular economy utilizes resources that exist within the biosphere, shown by green arrows in Figure 1. This economy would utilize carbon sources that are not fossilized and that are within our current carbon cycle, known as new carbon. Utilizing fossil fuels (ie., old carbon) adds additional carbon to the current carbon cycle that has been naturally sequestered over millennia. This excess atmospheric carbon puts our current carbon cycle out of balance, leading to countless environmental problems.
Table 1. Comparison of new and old carbon.

<table>
<thead>
<tr>
<th>TYPE OF CARBON</th>
<th>NEW CARBON</th>
<th>OLD CARBON</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
<td>Plants and animals</td>
<td>Fossil fuels</td>
</tr>
<tr>
<td><strong>Derivative</strong></td>
<td>Biomass</td>
<td>Petroleum</td>
</tr>
<tr>
<td><strong>Method</strong></td>
<td>Agriculture</td>
<td>Extraction</td>
</tr>
<tr>
<td><strong>Supply</strong></td>
<td>Renewable</td>
<td>Finite</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td>Biofuels, biochemicals and biomaterials</td>
<td>Fuels, chemicals and materials</td>
</tr>
<tr>
<td><strong>Disposal</strong></td>
<td>Composting</td>
<td>Landfill and/or incineration</td>
</tr>
<tr>
<td><strong>Carbon Cycle</strong></td>
<td>Closed cycle</td>
<td>Open and increasing</td>
</tr>
</tbody>
</table>

The differences between new and old carbon can be seen in Table 1. The major disadvantages in using old carbon are the environmental concerns previously mentioned, difficulty in extraction, finite supply which leads to increasing prices, and end of life disposal. Current disposal methods such as landfilling or incineration perpetuate the strain these products put on the environment. This being said, the chemicals and materials that can be synthesised from these resources are immense and have increased the standard of living for billions of people across the world, including the advancements seen in the agricultural industry which are used for the improved production of biomass. On the other hand, with proper management the supply of new carbon could be completely renewable. Methods to produce and refine new carbon will help stimulate the agricultural sector by valorizing resources that have been traditionally considered waste products. Current manufacturing processes will need to be updated to handle these new resources. Once the material or product has reached its end of life, it can decompose and re-enter the green circular economy to be utilized later to create new fuels and products. Some major concerns with introducing new carbon as replacement for fossil fuels is the fact that the current infrastructure is in place for fossil fuels, this will need to be updated to accommodate new source materials. Another major concern is the ‘fuels vs food’ debate, first generation bioproducts, specifically biofuels, were produced directly from food crops by fermentation. This problem has been overcome in second
and third generation biofuels, which utilize non food crops to produce bioproducts with the goal of becoming cost competitive with fossil fuels.  

Roughly 4% of fossil fuels produced globally are used to create chemicals and materials, the vast majority being of fossil fuels are used for transportation and various fuels. However, this 4% is responsible for over 40% of fossil fuel revenues, roughly equivalent to the revenues earned from transportation fuels. It is prudent then to focus on this sector for several reasons. Focusing on replacing petroleum-based products will disproportionally reduce the revenue available to the petroleum industry. A large percentage of these materials are single-use or disposable plastics which are often disposed of incorrectly. Globally, 4.8 to 12.7 metric tonnes of plastics enter our water ways from mismanaged waste systems. Restricting the use of single-use plastics and promoting bio-based and compostable plastics could be an effective strategy to mitigate the environmental costs of these everyday materials. By not only focusing on replacing fossil-based fuels but also fossil-based products we can fully divest our society from this dwindling resource.

1.2 Biodegradable Plastics

Polymers derived from biomass can be divided into three categories: natural polymers such as, cellulose, chitin, collagen, starches or other proteins; synthetic polymers created from biomass such as, poly(lactic acid) (PLA) or poly(butylene succinate) (PBS), and polymers produced from microbial fermentation like poly(3-hydroxybutyrate) (PHB). Polymers derived from biological monomers represent a new route to develop sustainable bio-based materials, their properties can be improved by blending together or with fillers to create composites. Fibrous reinforcement actually began with cellulose in phenolics in 1908, by the 1940s the majority of fibrous reinforcement were derived from petroleum resources like glass or aramid fibers. Due to the aforementioned environmental concerns research and development has shifted focus back to utilizing these natural fibers and materials to meet our societal needs.

PBS is a compostable, biocompatible and currently partial bio-based aliphatic polyester that has a lot of potential in many fields. This thermoplastic has good mix of properties: a density of 1.25 g/m³, a glass transition temperature (T₉) between -45 to -10 °C, a melt temperature (Tₘ) between 90 to 120 °C and most importantly can be processed in similar conditions (160 to 200 °C) to petroleum based
polyolefins\textsuperscript{19}. In terms of mechanical properties PBS has a tensile strength between that of polyethylene (PE) and polypropylene (PP), and a stiffness between high and low-density PE\textsuperscript{19}. Some of the major shortcomings of PBS are its low impact strength (toughness) and poor gas and liquid barrier properties\textsuperscript{19}. Research is being conducted to improve these properties through a number of strategies\textsuperscript{20}, including reinforced with fillers like nanoparticles\textsuperscript{21,22} and natural fibers\textsuperscript{23}. PBS’s versatility is one of its greatest strengths, for this reason PBS was chosen as a case study on bio-based compostable polymeric materials. This thesis will explore two main applications for PBS, specifically its use as a commodity plastic with the goal of increasing its thermo-mechanical properties, and second, its potential use in the biomedical field as a biocompatible biomaterial.
1.3 Thesis Structure

This thesis is separated into multiple chapters which are connected through the problem statement below. This first chapter served as an introduction into plastics and the global problems associated with them. The second chapter will provide a thorough literature review for both the materials and processes used throughout this work. Chapters three and four delve into specific applications for bio-based poly(butylene succinate) (BioPBS). The final chapter will conclude the significance of this work as well as provide insight into future research.

1.3.1 Problem Statement

The exponential increase in the use of plastics is taking a large toll on the global environment and natural systems. Bio-based and compostable plastics have immense potential to replace petroleum-based plastics. Current limitations to bio-plastics include increased costs and inferior thermo-mechanical properties compared to petroleum counterparts. Further research is required to improve these properties, while further innovation and industrialization is needed to lower the cost.

1.3.2 Overall Objective

The principal objective of this research is to prove BioPBS’s capabilities in a variety of applications, including commodity plastics, advanced hybrid nano-biocomposites and its potential use as a biomaterial.

1.3.3 Significance

The development of improved polymeric materials will further advance bio-based materials, ultimately expediting the replacement of petroleum resources. The addition of an under-utilized bio-filler, such as biocarbon, will promote the biofuels industry by valorizing this co-product. While increasing the thermo-mechanical properties of the composite, simultaneously lowering the composites cost.
Chapter 2. 
Literature Review

2.1 Materials

These aforementioned concerns have prompted mankind to search for more sustainable resources to fuel our ever-growing societal needs. Biomass is one of the few resources that could potentially create sustainable energy and material systems. The planet’s biosphere is capable of producing 1300 megatonnes of biomass annually without interfering with the food supply or current agricultural practices\(^\text{24}\). As of 2015, only 3-4\% of biomass available globally is used by humans for food or non-food purposes\(^\text{25}\). The main chemical compounds found in biomass are carbohydrates (75\%) with the remainder being proteins, lignin and fats\(^\text{26}\). The chemical structure of biomass is essential for its integration as a resource for energy and materials, it also represents a large hurdle to overcome before biomass can be utilized as a replacement to fossil fuels. The chemical structure of biomass is relatively more diverse and complex compared to fossil fuels, making it more difficult to refine and create products from\(^\text{27}\). Biorefineries, manufacturing systems similar to petrol refineries, have been proposed to refine these complex chemical compounds into useful fuels and materials\(^\text{4,5,25}\).

2.1.1 Bio-based Aliphatic Polyesters - PBS

Biodegradable aliphatic polyesters have seen an increase in popularity across a wide variety of fields, due in part to increases in global carbon dioxide levels and immense amounts of plastic waste. These polymers are in high demand in many applications from packaging to biomedical applications such as implant devices, tissue scaffolds, and wound dressings\(^\text{28}\). They are ideal for biomedical applications due to their biodegradability, biocompatibility and high capacity for drug loading\(^\text{28}\).

PBS is produced by the esterification of succinic acid with 1,4-butanediol (See Figure 2). The current industrial process utilizes approximately 54\% bio-based content in the production of PBS in the form of bio-succinic acid (Bio-SA)\(^\text{29}\). However, with further industrialization, Bio-SA can be used to produce 1,4-butanediol\(^\text{30}\), which would lead to 100\% BioPBS, outlined in green in Figure 2.
PBS has been mainly commercialised to be used in biodegradable packaging and containers. However due to its biocompatibility properties it has gained much attention as a promising biomaterial. Thin films have been successfully created, mainly through compression molding. While scaffolds have been produced through many techniques, namely salt leaching, electrospinning or extrusion. These studies mainly focused on the synthesis and characterization of these new materials, however Gigli et al. prepared an extensive review showing that PBS is biocompatible with many cell types.

2.1.2 Biofuel Co-product - Biocarbon

Charred biomass, referred to as biocarbon (BC) or biochar, is one of the three main products produced from the pyrolysis of biomass. Pyrolysis is the direct thermal decomposition of materials in the absence of oxygen, this produces three products, bio-oil, syngas and reduced solids (BC). Product yield of pyrolysis is dependent on process conditions, namely temperature, low temperature pyrolysis produces more char, while higher temperature processes favor liquid and gas components. Further, pyrolysis occurs more quickly at higher temperatures, seconds compared to hours at lower temperatures. Interestingly, modern pyrolysis units can run off the energy they produce, requiring only 15% of the energy produced.
BC has been traditionally used as a carbon sink or soil amendment \(^{39}\). More recently BC has been used as bio-filler for composite applications \(^{38,41–43}\). It has recently been shown that the temperature at which pyrolysis occurs also impacts the functionality of the BC produced, high temperature pyrolysis eliminates more functional groups on the surface of BC while increasing the surface area of the BC \(^{38}\). In composite applications it is advantageous to have both surface functionality and high surface area to create blends with good thermo-mechanical properties, therefore pyrolysis conditions are very important when using BC. Research has shown that using high and low temperature BC in a toughened polypropylene (TPP) composites resulted in drastically different mechanical properties \(^{44}\). High temperature pyrolysis resulted in a stiffer BC, compared to low temperature BC, this increased stiffness resulted in a stiffer composite \(^{44}\). High temperature BC also resulted in tougher (measured through impact strength) composites, this was attributed to the better affinity between BC and the matrix \(^{44}\). Researchers found the opposite trend when high and low temperature BC was added to a nylon 6 matrix \(^{45}\). In this case the higher functionality of the low temperature BC was attributed to the increased properties observed in the composites \(^{45}\). These studies emphasise the differences between both the BC filler used and the matrix in which they reinforce, demonstrating a wide variety of thermo-mechanical properties, dependent on both the filler and matrix.

2.1.3 Graphene

Graphene was first discovered, more appropriately, isolated by Novoselov, Geim and others in 2004 \(^{46}\), they demonstrated that individual, single atom thick, layers of graphite (graphene) could be isolated through mechanical cleavage \(^{46}\). Graphene is an allotrope of carbon with sp\(^2\) hybridized carbon atoms arranged in a hexagonal lattice structure. When these layers stack on each other they form graphite. Discovering the thinnest material known to humankind, which also exhibited exemplary electrical properties, lead to Novoselov and Geim winning the Nobel Prize for Physics in 2010. Researchers proved shortly after that not only is graphene the smallest material known to man, it is also the strongest material currently known, with an intrinsic tensile strength of 130.5 GPa and a Young’s modulus of 1 TPa \(^{47}\). Not surprisingly the addition of graphene into polymeric matrices leads to substantial improvement in stiffness and strength \(^{21,48–50}\). Graphene reinforced polymers are already in use in many applications in motor vehicles and sporting goods \(^{51}\). The fundamental mechanisms of this reinforcement are: the effects of lateral dimensions of the graphene, number of layers, surface chemistry, and orientation of the graphene within the composite \(^{22}\). Further research is being conducted to source graphene from natural sources, specifically kraft lignin \(^{52}\).
The reinforcement capabilities of nanomaterials are far superior to macroscale reinforcement, low volume fractions, less than 5 wt% are equivalent to 40-50 wt% by macro reinforcement \(^{53}\). However, these amazing benefits provided from nanomaterials do not come without their challenges, the main challenges are associated with controlling the elemental composition, stoichiometry, preventing aggregation, and achieving even distribution and dispersion.

### 2.2 Processes

Compounding nanomaterials into macroscopic products can be difficult. Proper compounding is essential because nanomaterials lose their advantageous properties when aggregated, forming microscopic particles \(^{54}\). Distribution refers to the distance between particles and their surroundings. While dispersion refers to the distance between two or more particles, without regard for the overall surrounding. The concept of distribution and dispersion can be seen in Figure 3.

![Figure 3. Dispersive vs distributive mixing. Ideal case highlighted with the red box.](image-url)
Compounding must be distributive and dispersive, with the ideal case being homogenously distributed with high dispersion and no aggregates or agglomeration\textsuperscript{56}. This case is highlighted by the red box in Figure 3. Research is currently being conducted on novel ways to efficiently compound nano-fillers. Both chemical and physical methods can be utilized to improve dispersion. Physical methods can include grinding, applying shear forces, or folding. While chemical methods can include, oxidation or polymer chain cleavage. Many nanomaterials are created from the top down, meaning the materials start as large agglomerations and are broken down into smaller and smaller particles. An elevated level of dispersion is needed to prevent agglomeration of the broken-down particles.

2.2.1 Compounding Through Extrusion

Extruders are the primary industrial processing technology used to compound materials for a wide variety of applications. Extruders come in a variety of configurations depending on the material. Extruders heat the polymer, via conduction, while simultaneously compounding the polymer using, most commonly, a helical screw. The residence time of the extruder can affect the properties of the finished product and can be controlled through speed, inherent polymer properties, or length of the extruder\textsuperscript{57}. The extrusion process begins with the polymer resin being fed into the hopper. The rotating screw forces the polymer through the barrel which is heated. The molten polymer is forced through the end of the extruder which is capped with a die which is used to give the desired shape to the final product. Extruders have four main zones that the polymer melt passes through\textsuperscript{58}. First the polymer passes through the feeding zone where the solid polymer is moved into the beginning of the barrel and begins heating. The second zone is known as the compression zone, the polymer continues to be heated, forming a polymer melt, the profile of the screw has also changed, resulting in higher compression forces which force air out of the polymer melt. The third zone is the metering zone, in this section of the extruder the polymer melt is consistently pumped through the extruder to ensure uniform flow, which is needed to get consistent products. The last zone, the die zone, gives the final shape to the polymer melt and reduces melt expansion\textsuperscript{58}.

Although extruders are predominant in industry they do have some limitations. Extruders rely on purely mechanical force to distribute the filler within the polymer matrix. This type of mixing is not ideal for nano-fillers as the type and distribution of forces applied in an extruder can cause agglomeration\textsuperscript{56}. They also require relatively high temperatures to ensure the polymer remains in a liquid state. Traditional methods to improve mixing with extruders include twin screw configurations as well as modifications to the screw profile.
Twin screw extruders create far superior compounding compared to their single screw counterparts. This is due to the intermeshing zone between the two screws which creates large shear forces. The two screws can be used in a co-rotating regime or a counter-rotating regime, co-rotation offers more uniform shear rates throughout the entire profile of the screw, while counter-rotation, provides higher shear, but requires a lower screw speed. The other conventional alteration done to extruders is configuring the screw profile. Changing the screw profile allows the customization of the extruder zones mentioned above. This is very useful for the compounding of nanomaterials as specific modular units can be designed specifically for nanomaterials.

Other alternatives for improving compounding are using longer residence times, slower processing rates, or the addition of additives to enhance the miscibility between the polymer and nanomaterial. These options are not industrially feasible due the increase in production time associated with longer residence times and lower feed rates, even tiny amounts of additives are often very expensive. These conventional methods still lead to inconsistencies and restrictions in compounding, especially when using nanomaterials, the adoption of novel and innovative methods is needed to efficiently compound nanomaterials.
2.2.2 Electrospinning

Electrospinning is a process used to create micro and nano-diameter fibers from ether a polymer solution or polymer melt, the later requires elevated temperatures, while the former requires the use of a solvent. The electrospinning process begins when an electric charge penetrates a polymer solution from the metallic needle, causing instabilities within the solution. A typical electrospinning setup consists of a high voltage source (1-30kV), a needle or capillary, a syringe pump, and a grounded collector, as shown in Figure 4. The electric field strength controls the Coulombic and electrostatic forces. A critical point is reached when the electrostatic forces overcome the solution forces, resulting in a charged fluid spray or stream ejected from the orifice. At the tip of the needle (capillary), a hemispherical droplet of the polymer solution forms, which is held suspended by surface tension. When the electrical forces overcome the effects of surface tension, the hemispherical droplet changes shape into what is known as a Taylor cone. As the jet travels towards the collector plate it undergoes a whipping or bending motion due to the uneven distribution of surface charges. This instability causes the simultaneous elongation of fibers and removal of solvent by evaporation. This elongation results in a thin fiber randomly oriented on the collector’s surface. The main forces that the Taylor cone and subsequent fibers experience include drag, gravity, surface tension, viscoelastic force, and Coulombic repulsion forces. Drag forces are present as a result of the interaction between the moving jet and surrounding air. Expansion of the jet is due to Coulombic forces, whereas shrinkage is due to surface tension and viscoelastic forces.

Figure 4. Schematic representation of a basic electrospinning setup.
The polymer concentration of the solution was found to have the greatest affect on fiber properties. Solutions with higher polymer concentrations were found to have higher fiber diameters, and a wide distribution of fiber sizes. Interestingly, an electrostatic effect was found to influence macroscale morphology of electrospun fibers and could result in the formation of three dimensional structures. Flow rate is a crucial parameter for both morphology and throughput. Generally, a lower feed rate is desirable, as this ensures enough time for sufficient solvent evaporation. A higher feed rate can lead to beaded fibers or other abnormalities due to insufficient evaporation. One of the primary obstacles regarding industrial electrospinning has been the speed of fiber production, and is commonly seen as the most significant hurdle in the way of electrospun fibers being adopted in commercial applications. The electrospinning process must be scaled-up for fibers to be produced in commercially viable amounts. There are two main methods which have achieved this scaled-up production: multi-needle electrospinning and needleless electrospinning. Perhaps the most widely electrospun polymer is poly(ethylene oxide) (PEO). It is often combined with other biopolymers like chitosan and lignin to improve their electrospinnability.

Several factors affect the electrospinning processes, which can be broken down into process, solution, and ambient parameters. Process parameters are those that are controlled by the electrospinning setup, such as the applied electric field, electrode gap, and flow rate. Solution parameters include polymer concentration, viscosity, molecular weight of the polymer, conductivity, and surface tension. Ambient parameters include temperature and humidity. These parameters and their impact on fiber/particle morphology are summarized in Table 2.
Table 2. Parameters affecting the electrohydrodynamic process.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effect on fiber morphology</th>
<th>Explanation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solution parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>Increase in fiber diameter and disappearance of beads with increased viscosity. Too high a viscosity and no jet will form.</td>
<td>The jet elongation becomes more difficult and slower at higher viscosities.</td>
<td>72–74</td>
</tr>
<tr>
<td>Polymer concentration</td>
<td>Increasing concentration increases fiber diameter.</td>
<td>At low concentration beads form and too high a concentration inhibits flow.</td>
<td>60,75</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Reduction of beads with increasing molecular weight.</td>
<td>Molecular weight represents the polymer entanglements present in a solution, thus it is directly related to solution viscosity.</td>
<td>72,76</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Decrease in fiber diameter with increasing conductivity.</td>
<td>The electrical charge in the jet increases, thus increasing electric force.</td>
<td>77,78</td>
</tr>
<tr>
<td>Surface tension</td>
<td>Low surface tension encourages the electrospinning process to happen in lower electric fields.</td>
<td>Viscelastic effects dominate surface tension.</td>
<td>79</td>
</tr>
<tr>
<td><strong>Processing parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied voltage</td>
<td>Decrease in fiber diameter with increasing voltage.</td>
<td>A higher applied voltage ejects more fluid.</td>
<td>80,81</td>
</tr>
<tr>
<td>Electrode gap</td>
<td>Fiber diameter and jet current both decrease with an increasing electrode gap, produces beads with small and large distances.</td>
<td>Jet elongation time is increase.</td>
<td>82,83</td>
</tr>
<tr>
<td>Flow rate</td>
<td>Decrease in fiber diameter with decrease in flow rate High flow rate generates beads</td>
<td>A lower flow rate ejects less fluid.</td>
<td>84</td>
</tr>
<tr>
<td><strong>Ambient parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Decrease in fiber size with increase in temperature.</td>
<td>An inverse relationship between temperature and viscosity.</td>
<td>73,85</td>
</tr>
<tr>
<td>Humidity</td>
<td>High humidity results in porous fibers.</td>
<td>Increase in relative humidity reduces the evaporation rate of the solvent.</td>
<td>86</td>
</tr>
</tbody>
</table>
Chapter 3.
Processing-Property Relationship of Bio-based Poly(butylene succinate) Reinforced with Pyrolyzed Perennial Grass Microparticles and Graphene Nanoplatelets

3.1 Abstract

BioPBS was combined with pyrolyzed miscanthus microparticles and graphene nanoplatelets to create a hybrid nano-biocomposite. Pyrolyzed biomass, known as biocarbon, was incorporated into a BioPBS matrix to improve the thermo-mechanical properties of the bioplastic while simultaneously increasing the value of this co-product. Biocomposites loaded with 25 wt% biocarbon showed 57, 13, and 32% improvements in tensile modulus, heat deflection temperature and thermal expansion, respectively. Further improvements were found when graphene nanoplatelets were added to the biocomposite forming a hierarchical hybrid nano-biocomposite. Two processing methods were used to incorporate GnPs into the composites: graphene was first added directly to BioPBS and biocarbon components and compounded. Second, a masterbatch of graphene and BioPBS were compounded together, the masterbatch was then diluted to the same ratios used in the direct compounding method. The two methods resulted in different internal morphologies which subsequently impacted the mechanical properties of the composites, little change was observed in the thermal properties studied. Composites processed using the direct compounding technique showed the greatest increase in tensile strength and modulus, 17 and 120% respectively. Composites processed using a masterbatch technique had slightly lower strength and modulus but almost twice the impact strength compared the direct compounding method. This masterbatch technique was found to have a superior balance of stiffness and toughness likely due to the presence of superclustered graphene platelets.
3.2 Introduction

Polymers are dominating the material landscape across the world, owing in part to their low density, low cost, and easy formability. Traditionally highly correlated with GDP \(^1\) (essentially a convenience of first world), however, it is estimated that future consumption will grow rapidly in developing countries, even small increases of per capita plastic consumption will translate into a large increase in plastic usage \(^1\). This increase in global plastic usage will have a devastating effect on the global environment. Drastic steps must be taken to replace these materials with environmentally friendly products.

Biodegradable aliphatic polyesters have seen a surge in popularity across a number of industries. PBS is produced by the esterification of succinic acid with 1,4-butandiol. The current industrial process utilizes approximately 54\% bio-based content in the production of PBS in the form of bio-succinic acid \(^{29}\). However, with further industrialization, bio-succinic acid can be used to produce 1,4-butandiol \(^{30}\), which would lead to 100\% bio-based PBS.

Structure-property relations and the processing steps that result in this structure have lead to large breadth of knowledge in multifaceted polymeric materials \(^{87}\). However the addition of nanomaterials such as graphene, carbon nanotubes, nanofibers, and nanoclays have complicated this field \(^{88}\). Graphene or a graphene nanoplatelet (GnP) is a nanoscale platelet of multiple graphene sheets (a single graphene sheet is roughly 4nm thick \(^{89}\)) with a thickness between 0.34 and 100 nm \(^{90}\). Graphene is the strongest material known, with an intrinsic tensile strength of 130.5 GPa and a Young’s modulus of 1 TPa \(^{47}\). The addition of graphene into polymeric matrices, not surprisingly, leads to great improvement in stiffness and strength \(^{21,48–50}\), likely due to a combination of high aspect ratio, alignment during stretching, and promotion of strain induced crystallization \(^{91}\). However, to take full advantage of this incredible material it must be evenly dispersed and well distributed within the polymer matrix. This is not easily obtainable due to GnP large surface area, Van Der Waals forces holding sheets together \(^{92}\), low solubility in organic solvents and polymers which results in low levels of dispersion and exfoliation when using conventional manufacturing processes like solution or melt blending \(^{93}\). Many advanced techniques have shown excellent levels of dispersion including ultrasound assisted extrusion \(^{94}\), addition of surfactants \(^{95}\), water \(^{96}\), or supercritical CO\(_2\) \(^{97}\), and in situ polymerization \(^{98}\).
Melt mixing or melt compounding is a process in which a polymer melt and filler are compounded together in a high shear environment, conventionally done in an extruder. Compared to solution mixing, which requires the use of solvents, melt mixing is more economical, more environmentally friendly, and does not require a distinct processing line in a manufacturing setting. However, to date, the literature suggests that melt mixing does not provide the same level of dispersion as the previously mentioned advanced methods.

In the production of polymer nanocomposites, Dennis et al. showed that an increase in the residence time during compounding encourages exfoliation, but an excessive amount of shear or back mixing causes poor dispersion. Back mixing is commonly used in micro compounders and will be present in this study. Villmov et al. also showed that the residence time and throughput had an effect on the dispersion of a carbon nanotubes masterbatch in a poly-caprolactone matrix. They found that an increase in throughput, which corresponds to a decrease in residence time and less shear, resulted in worse dispersion and poor electrical properties. Most researchers agree that composites with well dispersed exfoliated structures ultimately lead to better composite properties. However, significant improvements are not observed in every system, including nanoclay and GnP systems. Gong et al. showed that multilayer graphene was superior to single layer graphene in reinforcing epoxy systems.

In this study, BioPBS and BC were melt compounded, extruded and injection molded to create a biocomposite with superior thermo-mechanical properties compared to the neat matrix. GnP were also added to the composite using two different processing methods to compare the relationship between processing conditions and the resulting properties. A masterbatch technique where GnP were first compounded with BioPBS at a relatively high weight percent extruded, dried and then re-compounded with BioPBS and BC to the desired ratios, and a direct compounding method where BioPBS, BC, and GnP were compounded together directly. The process-property relationship was explored through tensile and flexural properties, impact strength, morphology, rheology, and thermodimensional properties. The two different processes could have affected the dispersion and distribution of GnP within the matrix which would result in different thermos-mechanical properties.
3.3 Experimental

3.3.1 Materials

Injection grade BioPBS (PBS FZ71PM), product of PTT MCC BIOCHEM CO., Ltd., Thailand, was obtained from Competitive Green Technologies, Canada. The injection grade BioPBS had a melt flow index (MFI) of 22 g/10 min at 190°C with 2.16 kg, a density of 1.26 g/cm³, and a melting point of 115 °C. Miscanthus grass BC was received from Genesis Industries, USA, the miscanthus BC was produced through a two-stage slow pyrolysis process at 500 °C and sifted to ~ 6.35mm. Once received the BC was ground in a planetary ball mill (Retsch PM100, Germany) with 50 10 mm diameter balls at 250 rpm for 1 hr, resulting in particles with an average size of 16.25 μm ± 14.68 μm. GnP with a particle diameter of 2 μm, thickness of 1-5 nm, and surface area of 500 m²/g was used as received, purchased from XG Sciences, USA.

3.3.2 Processing of Hybrid Biocomposites

Prior to processing BioPBS and BC was dried for 8 hr at 80 °C and 105 °C, respectively, the remaining moisture content was determined using an infrared moisture analyzer (Sartorius MA37-1, Germany). The moisture content prior to processing of the BioPBS, BC and GnP was less than 0.1, 1.0, and 2.0 wt.%, respectively. Compounding and injection molding took place in a 15-cc co-rotating, twin screw micro compounder paired with a 12-cc micro injection moulder (Xplore Instruments, The Netherlands). Compounding was conducted at 140 °C with a screw speed of 100 rpm. Injection molding was conducted using a mold temperature of 30 °C, an injection pressure of 10 bar and an injection time of 10 sec. First, BioPBS pellets (roughly 5 mm in radius) and BC powder were briefly mixed together by hand in BioPBS/BC ratios of 90/10 through 75/25 wt.% and directly compounded for 2 min in the above conditions. Second, two different processing techniques were utilized to compound BC and GnP into a BioPBS matrix to create hybrid nanocomposites. Direct compounding (DC) where BioPBS/BC/GnP were mixed by hand in ratios of 75/24/1 and 75/20/5 and compounded directly for 2 min in above conditions. A masterbatch (MB) of BioPBS and GnP was prepared by compounding in the same conditions for 2 min, to form a BioPBS blend with 25 wt.% GnP content. The masterbatch was then diluted with BioPBS pellets and compounded again for 2 min to form the same BioPBS/BC/GnP blend ratios 75/24/1 and 75/20/5 wt.% In both processing methods samples were injection molded immediately after the final compounding step and conditioned following ASTM D618 prior to further characterization.
Direct compounding is a common method used industrially to mix components together, all components are added together directly into the hopper and mixed through two intermeshing screws. As previously mentioned this normally results in poor dispersion and intercalation for nanomaterials. Commonly, a masterbatch is also utilized to compound large amounts of fillers to form a concentrated mixture filler. The masterbatch is then remixed and diluted to form the desired blend ratio. This process is commonplace in the plastic industry, for both colourants and additives.

### 3.3.3 Thermo-mechanical Analysis

Tensile and flexural tests were conducted using an Instron 3382 (Instron, USA) following ASTM D638 and D790, respectively. Impact strength of the materials was measured using a 5 ft-lb pendulum in a TMI Monitor Impact Tester (Testing Machines Inc, USA), following ASTM D256. Samples were notched immediately after processing using a TMI Notching Cutter (Testing Machines Inc, USA). Five samples were used for each test.

The heat deflection temperature (HDT) was determined under three-point bending following ASTM D648 using a DMA Q800 (TA Instruments, USA). Samples were tested at heating rate of 2 °C/min until a deflection of 250 μm was reached. The coefficient of linear thermal expansion (CLTE) was measured using a TMA Q400 (TA Instruments, USA), following ASTM E831. Tests were conducted in a temperature range from – 60 °C to 100 °C at a heating rate of 5 °C/min, samples were cut to ~ (6 mm x 6 mm x 3 mm). The expansion probe was set normal to the injection flow direction with an applied force of
0.05N. Further thermal properties were analyzed using a DSC Q200 (TA Instruments, USA) in a nitrogen atmosphere. First, the sample (5 - 10 mg) was heated to 180 °C at 10 °C/min and held for 2 min, then cooled to -60 °C at 5 °C/min and held for 2 min. This cycle was repeated to erase the thermal history of the first cycle, the second heating scan and first cooling scan are used for analysis. Percentage crystallinity of biocomposites were calculated using the same method as Chen et al. 107. Two samples were used for each test.

3.3.4 Rheology and Morphological Analysis

Two methods were used to determine the rheological properties of the composites. First the MFI was measured following ASTM D1238 procedure A, at 190 °C under 2.16 kg. Frequency dependent viscosity was determined using a MCR302 rheometer (Anton Paar GmbH, Austria), a frequency sweep was conducted from 500 – 0.1 rads/s at 150 °C. Zero shear viscosity was obtained using a Carreau regression. Two samples were used for each test. The impact fracture surface of the composites was observed using a Phenom ProX SEM (Phenom-World, The Netherlands) with a 15 kV acceleration voltage. Prior to imaging, samples were gold sputter coated for 5 s using a 108 manual sputter coater (TED PELLA, Inc)
3.4 Results & Discussion

3.4.1 Mechanical Properties

3.4.1.1 Mechanical Properties of BC Reinforced BioPBS Biocomposites.

The mechanical properties of a material, specifically the strength, stiffness and toughness, are crucial to how the material will be adopted to specific applications. These properties are influenced by a few parameters namely: particle size, the particle matrix interaction, and particle loading (amount of particles) \(^{108}\). An increase in tensile and flexural properties is observed when BioPBS is reinforced with BC, observed in red in Figure 6a and 6b. An increase in strength suggests good bonding between the BioPBS matrix and the particulate filler and that the particles are able to carry some load within the composite \(^{44}\). This is highly depends on the effective stress transfer between the matrix and filler \(^{109}\). The higher modulus of BC compared to the BioPBS matrix is attributed to the increase in the composites stiffness \(^{110}\). Further, it can be seen that the flexural strength of the neat BioPBS was lower than the tensile strength, 34.15 MPa compared to 41.5 MPa. However, after the addition of BC into the matrix the composites flexural strength increased by 59\%, compared to neat BioPBS while the composites tensile strength increased by 6\%. This suggests that the BC reinforcement is not uniaxial in nature. Flexural strength accounts for not only the tensile stresses within a material but also the compressive stresses \(^{111}\). For this reason flexural strength values are normally higher than tensile strength and is also more characteristic of everyday applied stress \(^{111}\).

Impact toughness corresponds to the energy absorbed by the material before failure. BC reinforcement also improved the toughness of the biocomposite, measured through impact strength, seen in Figure 6c. There is often a trade-off between strength and toughness in composites and simultaneous increase is often not observed \(^{38,112}\). Impact toughness is dependent on many factors and is a highly complicated mechanism \(^{113,114}\) often misrepresented. However, generally impact toughness in filler reinforced composites can be attributed to the size of the filler, the orientation and distribution of the filler, and the adhesion between the filler and matrix \(^{111}\). In order to see improved toughness, the energy needs to be effectively transferred to the filler, enabling it to absorb said energy \(^{111}\). During fracture, the crack propagates through the matrix and is momentarily stopped, known as crack pinning, due to the
heterogeneities of the filler \textsuperscript{109}. If there is good adhesion between the filler and the matrix some of the energy of the crack will be transferred to the filler, leading to a tougher composite \textsuperscript{113}. Impact toughness normally decreases when fillers are added \textsuperscript{38,115}, however, it was found that the size of filler has a large affect on the impact toughness of the composite, where smaller particles (irrespective of volume) increased impact toughness \textsuperscript{108,116}. It is seen in Figure 6c that initial loadings of BC into the BioPBS matrix resulted in increased impact strength, up until 20\% loading, however, above this level (25\%) the impact strength decreased below that of the neat BioPBS matrix. Kumar \textit{et al.} \textsuperscript{117} found that initial loading of fillers (up to 7.5\% aluminium cenospheres) increased impact strength, but further loading (10\%) resulted in lower impact strength. Lange and Radford \textsuperscript{118} similarly showed in an epoxy-alumina trihydrate system in which the fracture energy across several sizes of alumina trihydrate particles also peaked at a certain volume fraction and decreased after that. The decrease in fracture energy after the peak is attributed to the fact that the particles are packed too closely to effectively interact with the propagating crack, reducing the effects of crack pinning \textsuperscript{118}.

\textbf{3.4.1.2 Mechanical Properties of the Hybrid Nano-biocomposites.}

GnPs were compounded into the composites in two different ways, this resulted in different tensile, flexural and impact properties. Regardless of the way the GnPs were compounded into the composites the addition of GnPs drastically increased the tensile and flexural properties of the composites. This is attributed to the high stiffness of graphene (1 TPa) \textsuperscript{47} and biocarbon (5 GPa). Researchers have shown that property improvement is highly dependent on processing conditions and morphology \textsuperscript{91}. However high levels of dispersion is hard to achieve in graphene composite systems \textsuperscript{93}. The main differences in the two processes, MB compared to DC, used were the increased total residence time (5 min) and initial GnP loading (25\%) of the MB technique. The major mechanical differences between the two compounding methods was the increased strength and stiffness seen in the DC method and the increased toughness (impact strength) seen in the MB methods shown in green (MB) and blue (DC) in Figure 6.
Figure 6. Mechanical properties of biocomposites, a) Tensile strength and modulus, b) Flexural strength and modulus, and c) Notched Izod impact strength and elongation at break. Where (A) BioPBS, (B) BioPBS/BC (90/10), (C) BioPBS/BC (85/15), (D) BioPBS/BC (80/20)
Researchers found that increasing the mixing length of compounding, equivalent to an increase in residence time in a micro compounder, almost doubled the dispersion levels of fibers from 14 to 30% \(^{119}\). This was not observed in this study, this could be for a number of reasons, first the initial loading of GnP in the MB was relatively high (25%) compared to DC blends which led to the formation of superclustered GnP domains, seen in Figure 9. Second, GnP platelets display a much higher affinity to one another than fibers \(^{120-122}\), leading to less dispersion. However some researchers have shown that aggregates of fillers is actually beneficial in the reinforcement of composites \(^{123,124}\), claiming that certain level of structural hierarchy may be needed to achieve the full reinforcement potential of graphene \(^{123,124}\). This hierarchical structure is achieved in the MB composites through the addition of larger BC particles, the GnP superclusters as well as the smaller GnP domains. Reinforcement through aggregation is observed in this study, through the marked increase in impact strength, superclusters of GnP are observed in the MB compounded composites which are most likely responsible for the increased impact strength. Differences are also observed in the complex and zero shear viscosities seen in Figure 11.

3.4.1.2.1 Statistical analysis

In order to determine if there was a significant difference between the two processing methods used as well as the amount of GnP a \(2^2\) analysis of variance (ANOVA) with replicates was done on Izod impact and tensile strength. A summary of the analysis can be seen in Table 3, Full ANOVA results can be seen in Tables 10 and 11 in the supporting information. P-values are much lower than the alpha value = 0.05 therefore, we reject the null hypothesis that the means of both factors (processing method and amount of GnP) are equal for both impact and tensile strength. Meaning there is a significant difference observed for both the processing method used and the amount of GnP added. The difference between F and \(F_{crit}\) is also much larger for impact strength relative to tensile strength. P-values for impact strength are also much lower compared to tensile strength, this suggests that both factors have a more significant effect on the impact strength of the blends compared to the tensile strength.
Table 3. Summary of $2^2$ ANOVA

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Impact strength</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>P-value</td>
</tr>
<tr>
<td>Process method</td>
<td>255.9819</td>
<td>2.33E-07</td>
</tr>
<tr>
<td>Amount of GnP</td>
<td>76.13656</td>
<td>2.33E-05</td>
</tr>
<tr>
<td>Interaction</td>
<td>43.17356</td>
<td>0.000175</td>
</tr>
</tbody>
</table>

It is interesting to note that there is a significant interaction effect between the processing method used and the amount of GnP added for impact strength only, evident from the significant difference between F and $F_{crit}$ as well as the difference between the P-value and alpha value. This could help explain why such a large increase in impact strength was observed in the MB blends. Figure 7 clearly shows two nonparallel lines between the impact strengths of 1 and 5% GnP content using the two different compounding methods, these nonparallel lines are characteristic of an interaction effect between the factors measured.

![Interaction plot between compounding method used and percent of GnP in blends.](image)

Figure 7. Interaction plot between compounding method used and percent of GnP in blends.
3.4.2 Morphological Investigation of the Biocomposites

The morphology of the composites was observed through SEM images of the impact fracture surface. Researchers have shown that it possible to distinguish, based on contrast, between different qualities of carbon, due to their intrinsic differences in conductivity. This principle was used in this study to differentiate between GnPs and the rest of the composite, specifically BC, as the BioPBS matrix is easily distinguishable in the matrix. Levels of dispersion of GnPs throughout the matrix are clearly different between the DC blends (Figure 8) and MB blends (Figure 9), although no quantitative analysis was conducted on the levels of dispersion it is apparent that superclusters of GnPs have formed in the MB blends while they are not apparent in the DC blends. These superclusters were formed in the initial MB process, observed in Figure 9. These superclusters reduced in size and dispersed substantially, more so in the 1% GnP MB composites (Figure 9c-d) compared to the 5% GnP MB composites (Figure 9a-b). It is known that the orientation of GnP and other high aspect ratio particulates have a significant effect on both the mechanical and gas barrier properties. Well orientated particles, that is orientated in the same direction, often flow induced, show increased mechanical properties in a parallel direction and increased barrier properties in a perpendicular direction. This is observed to a slight degree locally but not in the overall morphology of the composites, this infers that that there was some degree of flow induced orientation during extrusion process.
Figure 8. SEM images of the fracture surface of DC blended composites. a) 5% GnP content, 500x magnification, b) same surface at 10000x magnification, c) 1% GnP content, 500x magnification, b) same surface at 10000x magnification. All images taken at 15 kV.

BC particles show good levels of adhesion to the surrounding matrix given that there is no particle pullout observed after impact testing \(^{108}\). GnPs are also observed on the surface of BC particles, Figure 11, which could also assist in adhering to the BioPBS matrix, however this would need to be further investigated through atomic force microscopy.
Some degree of dispersion is observed in the higher magnification images of both DC and MB compounded, higher magnification images would be required to further investigate dispersion and intercalation. It is interesting to note that in the 25% GnP loaded masterbatch there is no dispersion within the supercluster domains, Figure 9, suggesting that the higher loading of GnP restrict dispersion.
3.4.3 **Rheological Behavior**

The flow behavior of polymer melts is of great interest to manufacturers of polymers and composites. It is important to understand these behaviors as the resulting material is affected by the processing environment. All blends showed signs of shear thinning, a non-Newtonian behavior, a drop in complex viscosity associated with increased shear rates. This shear thinning is most dramatic in the DC blends, shown in blue in Figure 12. The addition of BC into the BioPBS matrix increased both the complex and zero shear viscosities, while lowering the MFI of the composites. The addition of 1% GnP did not have an outward effect on any of the rheological measurements except in the DC blended systems where increased shear thinning is observed in the higher frequency domains of complex viscosity. It is interesting that in the DC 1% GnP blends zero shear viscosity decreased while MFI increased compared to 25% BC and 1% MB blends.
Figure 12. Complex Viscosity of BioPBS Composites. Inset: Zero shear viscosity (left) and melt flow index (right).

Where (A) BioPBS, (B) BioPBS/BC (90/10), (C) BioPBS/BC (85/15), (D) BioPBS/BC (80/20), (E) BioPBS/BC (75/25), (F-G) BioPBS/BC/GnP (MB) (75/24/1) and (F-G) BioPBS/BC/GnP (DC) (75/24/1) and

Flow can have a large affect on the viscoelastic properties of polymer melts filled with anisotropic nanoparticles. The large shear strain from the induced flow can orientate the particles in the direction of flow, subsequently reducing viscosity. The shear thinning observed in DC GnP blends compared to MB blends could be attributed to this phenomenon. The shear thinning observed in DC blends agrees with the observed increase in dispersion in DC blends compared to MB blends. All composite blends showed increased viscosity and decreased MFI compared to the BioPBS matrix, however they are still within acceptable ranges for extrusion and injection molding manufacturing processes.
3.4.4 Thermodimensional Properties

One of the main drawbacks to polymers are their high CLTEs and low HDT which can be undesirable for many applications where materials are exposed to elevated levels of heat\textsuperscript{108}. CLTE ($\alpha$) is a measure of dimensional expansion in response to changes in heat and is calculated by the expanded thickness divided by the initial thickness $\alpha = (\ell - \ell_0)/\ell_0$\textsuperscript{108}, a low CLTE and a high HDT is indicative of greater thermodimensional stability\textsuperscript{131}. Combining polymers with more thermally stable materials has become a common strategy to increase their thermal stability. BC and nanofillers like GnPs have been shown to be effective at reducing thermal expansion\textsuperscript{108,132,133}.

![Figure 13. Thermodimensional properties, specifically, HDT and CLTE (flow direction) of BioPBS composites. Where (A) BioPBS, (B) BioPBS/BC (90/10), (C) BioPBS/BC (85/15), (D) BioPBS/BC (80/20), (E) BioPBS/BC (75/25), (F-G) BioPBS/BC/GnP (MB) (75/24/1) and (75/20/)](image)

The CLTE of all composites were lower than that of the neat BioPBS matrix, Figure 13. However, the most evident reduction (32\%) in CLTE was observed in the blends reinforced with 25\% BC content. Ahmad \textit{et al.}\textsuperscript{134} showed that the shape of silica particles in an epoxy matrix had a slight impact on the CLTE of the composite. Further, angular shapes, containing many sharp edges, and elongated shaped silica particles showed lower CLTE values compared to the same sized cubic particles\textsuperscript{134}. It would follow
then that the irregular shape of BC is an advantageous property in reducing the CLTE of polymer composites.

The HDT is another important thermodimensional property, it is the temperature at which a material deforms by 250 μm under a specific load, ASTM D648. A high HDT is indicative of high thermodimensional stability. Similar to CLTE, the HDT of all composites increased compared to the neat BioPBS matrix, Figure 13. Again, the greatest increase (~12 °C, 11%) was observed in the blends reinforced with 25 wt.% BC content. Improvement in HDT is often attributed to the improved stiffness associated with the reinforced composites 23,135, or improved mechanical stability 132. It was expected that the addition of GnPs would further improve both the HDT and CLTE of the biocomposites 132,133. However, this was not observed in this study. Perhaps higher levels of dispersion and intercalation of GnPs within the matrix would result in further thermodimensional stability.

3.5 Conclusion

BioPBS was successfully combined with BC and GnPs, creating a hybrid nano-biocomposite. These composites had improved thermo-mechanical properties compared to the neat polymer, incorporating BC into a bioplastic composite also increased the value of this co-product. Biocomposites loaded with 25 wt% biocarbon showed 57, 13, and 32% improvements in tensile modulus, heat deflection temperature and thermal expansion. Further improvements were found when GnPs were added to the biocomposite forming a hierarchical hybrid nano-biocomposite. Two processing methods were used to incorporate GnPs in the composites, DC and MB processing techniques. The two methods resulted in different internal morphologies which subsequently impacted the mechanical properties of the composites. However, little change was observed in the thermodimensional properties studied. Composites processed using the direct compounding technique showed the greatest increase in tensile strength and modulus, 17 and 120% respectively. Composites processed using a masterbatch technique had slightly lower strength and modulus but almost twice the impact strength compared DC blends. This masterbatch technique was found to have a superior balance of stiffness and toughness likely due to the presence of superclustered graphene platelets. It is recommended that large scale techniques are used to create these composites to confirm their industrial viability. It would also be interesting to add further toughing agents like bio-based glycerol 136, or study the electrical conductivity of the composites.
Chapter 4.
Electrospinning Process and Structure Relationship of Bio-based Poly(butylene succinate) for Nanoporous Fibers


4.1 Abstract

BioPBS was electrospun to create hierarchical, highly porous fibers. Various grades of BioPBS were dissolved in one of the three solutions: chloroform, a co-solvent system of chloroform/N,N-dimethylformamide (DMF), or chloroform/dimethyl sulfoxide (DMSO). These solutions were then electrospun at room temperature to produce nanoporous micron-sized fibers. The variables investigated were the solvent system used, grade of BioPBS, concentration of BioPBS, applied voltage, and the distance between the electrodes. In determining the optimal solution and electrospinning conditions, it was found that solution properties such as the solvent system, the grade of BioPBS, and the concentration of BioPBS had a significant effect on the fiber morphology. A chloroform/DMSO cosolvent system resulted in less bead defects among fibers compared to those produced from chloroform/DMF systems, regardless of the BioPBS grade. An increase in BioPBS concentration resulted in the reduction of bead defects, which at 15 (% w/v) resulted in bead-free uniform fibers. Increasing BioPBS concentration also increased the porosity of the fibers while reducing the pore size. Dynamic mechanical analysis showed that the reduction of bead defects resulted in increased tensile strength and Young’s modulus of the electrospun fibrous nonwoven mat. The results of this study show that electrospun BioPBS fibers have high porosity at the micro- and nanoscale, resulting in a hierarchical structure that has sufficient mechanical properties for potential applications in wound healing and soft tissue engineering.
4.2 Introduction

Electrospinning has become one of the most popular methods for the preparation of micro- to nano-sized fibrous polymers. However, the electrospinnability of BioPBS and, more importantly, the relationship between process parameters and the resulting morphology and mechanical properties, have not been fully described in previous research.

Nanotechnology is a promising multidisciplinary field that combines state of the art technology with cutting-edge scientific research. Among the many methods utilized to produce materials at this scale, none have seen more widespread use than electrospinning \(^{137}\). Electrospinning is a simplistic, cost effective, and adaptable method that uses an electrically charged jet of polymer solution to produce fibers with diameters ranging from micro- to nanometers \(^{61}\). Electrospinning is capable of producing a wide range of morphologies including hollow tubes, highly aligned fibers, and even 3D shapes \(^{74}\). This is especially advantageous in the production of biomaterials: by adjusting solution properties, electrospinning parameters, or ambient conditions, tailorable hierarchical structures can be produced \(^{138}\). Morphological and mechanical properties can then be matched to the desired biological environment, from advanced wound dressings, \(^{139}\) to load bearing implants that encourage cell growth and osseointegration \(^{140}\).

Many biomedical applications require highly porous materials, which allows for the proper integration of cells and blood vessels, transportation of nutrients and waste, or increased drug loading capacity \(^{141}\). Materials chosen for these applications should mimic the biological environment they are meant to interact with or replace. Biological environments are often complex and hierarchical in nature with different macro-, meso-, and nano-scale structures \(^{142}\). Generally mesopores should be between 100-400 μm but can vary greatly depending on the type of tissue in question \(^{142}\). Nanopores between 10-1000 nm are required to facilitate the transportation of nutrients and metabolic waste \(^{142}\). It is advantageous for a material to match the hierarchical structure of the biological environment it is to be used in, to improve its biocompatibility. The electrospinnability of PBS has been previously investigated \(^{143–147}\). PBS is soluble in various solvents such as: chloroform (CHCl\(_3\)), dichloromethane (DCM), 1,1,1,3,3,3-Hexafluoro-2-propanol, and o-chlorobenzene \(^{18,148,149}\). However, PBS has only been successfully electrospun in CHCl\(_3\) or DCM with the addition of other co-solvents \(^{143–147}\).
As PBS is often in solution in dilute concentrations, the solvent used has a significant influence on the overall solution properties, such as: surface tension, boiling point, conductivity, and permittivity. The resulting morphology of the fibers are subsequently affected by the choice of solvent and ambient conditions. Wannatong et al. investigated the effects of solvent properties on the resulting morphology of electrospun polystyrene fibers. Fiber diameter was found to decrease with increasing boiling points and density of the solvent, while throughput increased with increased dielectric constant and dipole moment. Jeong et al. successfully added various co-solvents like 2-chloroethanol, 3-chloro-1-propanol, and 1-chloro-2-propanol to both CHCl₃ and DCM solvent systems. Klairutsamee et al. electrospun PBS fibers from both DMF and methanol. They also investigated the effects of adding an organic salt alkyl ammonium ethyl sulfate (AAES) on the morphology of PBS fibers. They found that the addition of salts to the solution resulted in thinner fibers, dropping from 503 to 373 nm with the addition of 0.25 to 1 (%w/v) AAES. In fact, the addition of 0.5 (%w/v) AAES to 12 (%w/v) PBS in a CHCl₃ solution caused a drastic change in fiber morphology, changing from highly beaded fibers to smooth and continuous fibers. This improved electrospinnability, evident from the morphological changes, can be attributed to an increase in solution conductivity and charge density at the jet. This ultimately increased the elongation force experienced by the fibers as the excess charge creates self-repulsion within the electric field, suppressing the axial symmetric instability, known as Rayleigh instability.

The morphology of electrospun fibers is a key determinant in both the physical and mechanical properties of the resulting product. Any anomaly or abnormality along the fiber may cause a significant decrease in strength. Much of the electrospinning literature focuses on how various parameters affect fiber morphology. Several factors affect the electrospinning process, which can be broken down into process parameters, solution properties, and ambient conditions. Processing parameters are those that are controlled by the electrohydrodynamic setup, such as the applied electric field, electrode gap, and flow rate. Solution properties include polymer concentration, viscosity, molecular weight, conductivity, and surface tension. Ambient conditions include temperature and humidity.

In this study, electrospun non-woven mats were prepared using two different grades of BioPBS in a single solvent CHCl₃ system, as well as co-solvent systems consisting of CHCl₃ with DMSO and CHCl₃ with DMF. To the best of the authors knowledge, no report has been conducted to demonstrate the effects of DMSO on the electrospinning of BioPBS. The effects of using different solvent systems, BioPBS grades, BioPBS concentrations, applied voltages, and distances between electrodes on the morphological
differences in fiber diameter and diameter distribution of electrospun BioPBS fibers were studied. Various polymer concentrations were prepared to determine the relationship between morphology and subsequent tensile strength and porosity. This study demonstrates the electrospinnability of BioPBS, capable of creating nanoporous fibers that have potential for use in biomedical or tissue engineering applications.

4.3 Experimental

4.3.1 Materials

Two grades (film and injection) of bio-based poly(butylene succinate) (BioPBS), product of PTT MCC BIOCHEM CO., Ltd., Thailand, were obtained from Competitive Green Technologies, Leamington Canada. The film grade (PBS FZ91PM) had a melt flow index (MFI) of 5 g/10 min (at 190°C at 2.16 kg) and the injection grade (PBS FZ71PM) had a MFI of 22 g/10 min under the same conditions. Analytical grade chloroform, DMSO, and DMF were purchased from Sigma-Aldrich and used as received.

4.3.2 Solution Preparation and Characterization

Film grade BioPBS was dissolved in single solvent CHCl₃ systems and co-solvent systems with DMSO and DMF, labelled FC, FO, and FF, respectively. Similarly, injection grade BioPBS was dissolved in the same solvent systems and labelled IC, IO, and IF, respectively. The BioPBS concentration was fixed at 15% (w/v) for initial solvent testing. The ratio of DMSO:CHCl₃ and DMF:CHCl₃ was varied from 10 to 50% (v/v). BioPBS was dissolved in all solvent systems at 50 °C with vigorous stirring. Single solvent systems were mixed for 2.5 h to ensure complete dissolution. Co-solvent systems required BioPBS to be first dissolved in CHCl₃ for 2 h then either DMSO or DMF was added dropwise and continually stirred for an additional 0.5 h. FO solutions were prepared with BioPBS concentrations of 5, 10, and 15% (w/v), labelled FO-5, FO-10, and FO-15 respectively. Solutions were cooled to room temperature prior to characterization and electrospinning. The solution’s complex viscosity was measured using a MCR 302 rheometer (ANTON PARR, Austria) using a shear rate sweep from 100 to 0.01 s⁻¹ at 23 °C. Interfacial surface tension between the prepared solutions and water was measured using the Wilhelmey plate method in a KSV NIMA Langmuir-Blodgett trough (Biolinscientific, Sweden). Solution conductivity was measured using an accumet AP85 pH/conductivity meter (Fisher Scientific), the conductivity meter was not sensitive enough to measure pure CHCl₃ (1.0x10⁻¹⁰ μS/cm). Due to the volatility of CHCl₃, surface
tension was measured with a capping layer of deionized water to prevent evaporation, hence the reported interfacial surface tension reflects the surface tension between the prepared solution and deionized water.

4.3.3 Electrospinning of BioPBS fibers

Electrospinning was conducted using a NANON-01A electrospinning setup (MECC CO., Ltd., Japan). Initial solvent testing was conducted using a solution of 15% (w/v) BioPBS concentration, 15 kV applied voltage, 1.5 mL/h flow rate, 20 cm electrode gap, 18-gauge blunt tipped needle, under ambient conditions (19-21 °C, 55 – 65% relative humidity). A custom made adjustable, flat collector plate was used to achieve a greater electrode gap. Polymer solutions were drawn into a 10 mL glass syringe, where 0.5 mL of each solution was electrospun to determine fiber morphology. 2 mL of each solution was used to create a fibrous non-woven sheet used for tensile testing. Electrospinning time varied depending on cleaning frequency. To maintain a stable Taylor cone, the flow rate was raised proportionately with increasing applied voltage. Electrospun samples were dried at room temperature under a vacuum overnight before subsequent characterization.

4.3.4 Morphology and Structural Characterization

Morphology, specifically fiber diameter, diameter distribution, pore size, and porosity were observed using a Phenom ProX SEM (Phenom-World, The Netherlands) with a 10 kV acceleration voltage. Prior to imaging, samples were gold sputter coated for 5 s using a 108 manual sputter coater (TED PELLA, Inc). The presence of beads, fiber diameter, and diameter distribution was observed at 600X and 2000X magnification, respectively, while pore size analysis was conducted at 25000X magnification. Further analysis was conducted using DiameterJ, a plugin of ImageJ software (National Institutes of Health), where a minimum of two images were taken from random locations and used to calculate both fiber and pore size distributions. Traditional, statistical region merging, and mixed segmentation were used to produce the most accurately segmented image.

Tensile yield strength and Young’s modulus of fibrous non-woven mats were measured using a Q800 DMA (TA instruments). Rectangular, non-woven fibrous mats with average dimensions of 15, 5, 0.15 mm (length, width, thickness) were loaded into the DMA using tension film clamps. An isothermal stress-strain, displacement ramp test was conducted at 23 °C, with a 0.001 N preload, 0.1% initial strain, and a 1 mm/m ramp rate.
4.4 Results & Discussion

4.4.1 Solution Properties

4.4.1.1 Solvent System

Under ambient conditions (19-21 °C, 55–65% relative humidity) BioPBS was not electrospinnable in CHCl₃. The low boiling point of CHCl₃ compared to other solvents (Table 4) resulted in rapid evaporation of the solvent at the tip of the needle. This evaporation prevented the formation of a Taylor cone (circled in Figure 14a), and eventually led to a build-up of BioPBS at the tip of the needle, circled in Figure 14b. Although the electrospinning process can be conducted without the formation of a Taylor cone, a Taylor cone is required to produce continuous defect free fibers. To reduce the evaporation rate of the solution, solvents with lower vapor pressures and high boiling points were added to CHCl₃ to form a co-solvent system. DMSO and DMF were chosen as co-solvents because both possess high boiling points and low vapor pressures compared to CHCl₃, as seen in Table 4. However, BioPBS is insoluble in both DMSO and DMF, which can be attributed to the differences in Hansen solubility parameters between BioPBS and DMSO or DMF. The total Hansen solubility parameters given in Table 4 are based on three bond energies: dispersion, polar, and hydrogen bonds, which contain information about the intermolecular interactions of the solution. These three parameters can be used as coordinates for a point in three-dimensional space, known as Hansen space. The closer the substances are to each other in Hansen space, the more likely they are to dissolve each other. This is an approximation only, and there are limitations to using this method such as: not accounting for parameters varying with temperature, molecular bonding being more complicated than three parameters, molecular size and shape, and dipole, electrostatic, and metallic interactions.
Table 4. Physical properties of solvents (reported at 20 °C) used in this study.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Boiling Point (°C)</th>
<th>Surface Tension (mN/m)</th>
<th>Viscosity (mPa/s)(^a)</th>
<th>Vapor Pressure (MPa)</th>
<th>Hansen solubility parameter (MPa(^{1/2}))(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_3)</td>
<td>4.8</td>
<td>61.0</td>
<td>27.16</td>
<td>0.57</td>
<td>22.26</td>
<td>19.0</td>
</tr>
<tr>
<td>DMSO</td>
<td>46.6</td>
<td>189.0</td>
<td>43.7</td>
<td>2.0</td>
<td>0.093</td>
<td>26.7</td>
</tr>
<tr>
<td>DMF</td>
<td>36.7</td>
<td>153.0</td>
<td>35.0</td>
<td>0.82</td>
<td>0.507</td>
<td>24.9</td>
</tr>
</tbody>
</table>

\(a\) reported at 25 °C

Hansen solubility parameter of PBS = 20.3 (MPa\(^ {1/2}\))\(^b\)

As PBS is not soluble in either DMSO or DMF, an optimized co-solvent system needed to be established. When more than 10% of DMF (results not shown) or DMSO was added to both grades of BioPBS dissolved in CHCl\(_3\), gelation rapidly occurred as the solution cooled to room temperature. Figure 15 shows the gelation of BioPBS in different fractions of DMSO:CHCl\(_3\) as the solution was cooled to room temperature. Solutions of 30, 40, and 50% DMSO:CHCl\(_3\) and DMF:CHCl\(_3\) solidified before the solution could return to room temperature. 20% co-solvent systems returned to room temperature as a liquid but solidified shortly after, restricting the time available for electrospinning to approximately one hour. This limitation in processing time would severely hinder the solution’s practical and industrial potential. Incredibly large throughputs would be needed to produce macroscale products. Conversely, a continuous production method could be utilized instead of a batch process to overcome this limitation. However, 20% co-solvent systems were not used further in this study. Both 10% DMSO:CHCl\(_3\) and DMF:CHCl\(_3\) sufficiently reduced the evaporation rate of the solution, allowing the formation of a Taylor cone.

![Figure 14](image1.png)

Figure 14. a) Evaporation of CHCl\(_3\) preventing the formation of a Taylor cone, leading to b) Build up BioPBS at the tip of the needle.
With the amount of co-solvent optimized at 10%, both the solvent system and BioPBS grade that resulted in the best morphology could be selected. Both DMSO and DMF co-solvent systems showed an outward effect on morphology regardless of which BioPBS grade was used. Figure 16 shows a drastic change in morphology from beaded fibers to continuous smooth fibers between film grade solutions FF (Figure 16a) and FO (Figure 16b). A similar, but less drastic change can be seen in injection grade solutions where a transition from beaded to non-beaded fibers was not observed. However, the frequency of beads was drastically decreased in IO (Figure 16c) compared to IF (Figure 16d). This morphological change can be attributed to the changes in surface tension and conductivity of solutions between DMF and DMSO co-solvent systems. Table 5 summarizes solution properties measured in this study for single-solvent CHCl₃ solutions, co-solvent systems, as well as FO solutions at 5, 10, and 15 (%w/v) BioPBS concentration. The conductivity of both film and injection grade BioPBS increased when DMSO was used compared to DMF (Figure 16c), which could partially explain the improved morphology observed in DMSO solvent systems compared to DMF. More importantly, the differences in surface tension observed between DMF and DMSO were more profound in film grade solutions (11.9 mN/m) compared to injection grade solutions (5.13 mN/m). This further explains why a more drastic change in morphology was observed in DMSO co-solvent systems compared to DMF. Surface tension is a function of the polymer solution, including the solvent. Various solvents can be used to adjust the surface tension of the solution. In general, low surface tension encourages the electrospinning process to occur in lower electric fields, which is advantageous for many reasons including the reduction of processing costs.
Table 5. Solution properties (complex viscosity, conductivity, and surface tension) of various solutions, measured at 23 °C, prepared for electrospinning.

<table>
<thead>
<tr>
<th>Grade-solvent</th>
<th>Complex Viscosity (Pa·s)</th>
<th>Conductivity (μS/cm)</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat CHCl₃</td>
<td>5.732x10⁻⁴ ± 2.83x10⁻⁵</td>
<td>(&lt;1.0 x 10⁻¹⁰)</td>
<td>30.55 ± 0.414</td>
</tr>
<tr>
<td>FF</td>
<td>0.213 ± 4.5x10⁻³</td>
<td>0.0275 ± 5x10⁻³</td>
<td>7.200 ± 0.887</td>
</tr>
<tr>
<td>FO</td>
<td>0.229 ± 0.0115</td>
<td>0.0475 ± 9.6x10⁻³</td>
<td>19.10 ± 2.21</td>
</tr>
<tr>
<td>FC</td>
<td>0.256 ± 0.0114</td>
<td>0.0003 ± 5x10⁻⁴</td>
<td>28.88 ± 2.15</td>
</tr>
<tr>
<td>IF</td>
<td>0.138 ± 1.2x10⁻³</td>
<td>0.0475 ± 9.6x10⁻³</td>
<td>11.86 ± 1.67</td>
</tr>
<tr>
<td>IO</td>
<td>0.156 ± 2.7x10⁻³</td>
<td>0.07 ± 0.018</td>
<td>16.99 ± 0.68</td>
</tr>
<tr>
<td>IC</td>
<td>0.178 ± 0.0104</td>
<td>0.0003 ± 5x10⁻⁴</td>
<td>28.61 ± 1.87</td>
</tr>
<tr>
<td>FO-15</td>
<td>0.229 ± 0.0135</td>
<td>0.0475 ± 9.6x10⁻³</td>
<td>19.10 ± 2.22</td>
</tr>
<tr>
<td>FO-10</td>
<td>0.075 ± 1.75x10⁻³</td>
<td>0.19 ± 0.02</td>
<td>15.32 ± 2.32</td>
</tr>
<tr>
<td>FO-5</td>
<td>0.0170 ± 1.06x10⁻³</td>
<td>0.41 ± 0.01</td>
<td>5.892 ± 1.87</td>
</tr>
</tbody>
</table>

*FF-film in DMF, FO-film in DMSO, FC-film in CHCl₃, IF-injection in DMF, IO-injection in DMSO, IC-injection in CHCl₃, FO-15 film in DMSO with a BioPBS concentration of 15%*

Many researchers have investigated how choice of solvent impacts on the resulting fiber morphology, specifically its dielectric constant and boiling point \(^{152,162,163}\). Wannatong *et al* \(^{152}\) investigated several different solvents with various properties such as density, dielectric constant, and boiling point, and their affect on electrospun polystyrene fibers. They measured the productivity of fiber production (number of fibers per square meter per time) and found that fiber productivity increased as the dielectric constant of the solvent increased. It was also found that as the boiling point of the solvent increased the diameter of fibers decreased \(^{152}\). Casasola *et al* \(^{162}\) found a similar relationship between the fiber diameter of electrospun PLA fibers and the boiling point of the co-solvent in a two solvent system; as the boiling point of the co-solvent increased, fiber diameter decreased. DMSO has a higher boiling point relative to DMF (Table 4), using solvents with higher boiling points results in lower rates of evaporation. This allows the polymer jet to retain its viscoelastic properties longer, resulting in longer exposure to stretching forces, producing smaller diameter fibers \(^{162}\). This further explains the improved morphology observed when electrospun from DMSO co-solvent systems compared to DMF.
Figure 16. SEM images (magnification of 600X) of electrospun BioPBS fibers produced from 15 (w/v%) BioPBS at 15 kV, 1.5 mL/h flow rate, 20 cm electrode gap. a) FF - film grade, 10% DMF b) FO - film grade, 10% DMSO c) IF - injection grade, 10% DMF d) IO - injection grade, 10% DMSO.

The dielectric constant (ε) of the solvent system also affects the resultant fiber morphology. Both co-solvents used in this study have a higher ε relative to CHCl₃ which could explain the improved electrospinnability observed by the addition of either DMF or DMSO. Furthermore, DMSO has a higher ε relative to DMF, which could also explain the differences in morphology observed in Figure 16. An increase in ε results in an increase in solution conductivity, this results in more self-repelling
charges on the surface of the polymer jet, increasing the Coulombic stretching force resulting in a stronger elongation force\textsuperscript{143}. A decrease in solution conductivity will result in insufficient elongation of the Taylor cone resulting in the formation of undesirable beads\textsuperscript{78}. An increase in solution conductivity can considerably decrease fiber diameter, and the availability of ionic salts can also create smaller diameter fibers\textsuperscript{72}. This increased charge density suppresses the Rayleigh instability experienced by the polymer jet, increasing the bending instability experienced by the electrospun fiber. The subsequent change in fiber morphology observed between DMSO and DMF co-solvent systems suggests a strong correlation between the aforementioned solvent properties and morphology\textsuperscript{143,164}.

4.4.1.2 BioPBS Grade

The major difference between the two grades of BioPBS is the reported MFI, 5g/10 min and 22g/10 min, for film and injection grade, respectively\textsuperscript{106}. Bremner \textit{et al}\textsuperscript{165} established a relationship between MFI and molecular weight distribution (MWD) using both viscosity average molecular weight $M_v$ and weight average molecular weight $M_w$. The most practical MWD to measure is $M_v$ by solution rheology and obtains a good correlation coefficient ($R^2 = 0.93$) by a linear least squares fit with the natural log of MFI\textsuperscript{165}. It is important to note that if a solvent is used in rheological analysis, then $M_v$ will be a function of both the properties of the solvent and the polymer’s inherent molecular weight\textsuperscript{165}. Systems involving highly branched polymers or non-Newtonian polymer solutions are more complicated and require full rheological characterization of the polymer\textsuperscript{165}. The lower MFI of film grade BioPBS could be an indicator of higher MWD, which explains the improved electrospinnability of the film grade compared to the injection grade observed in Figure 16. Research suggests that the molecular weight of the polymer plays a significant role in its ability to be electrospun into defect-free fibers\textsuperscript{60,70,137,151,166}. This is due to its significant effect on solution properties such as: viscosity, conductivity, and surface tension\textsuperscript{166}. Koski \textit{et al}\textsuperscript{166} varied the molecular weight of poly(vinyl alcohol) from 9000 to 50000 g/mol and observed a drastic change in fiber morphology. Polymers with lower molecular weights (9000-10000 g/mol) produced beaded fibers, whereas polymers with molecular weights between 13000 and 23000 g/mol produced defect-free fibers. Further increases in molecular weight (from 31000 – 50000 g/mol) resulted in flattened fibers. If the difference in MFI of the BioPBS is inversely proportional to the molecular weight of the BioPBS as Bremner \textit{et al}\textsuperscript{165} reported, than the improved electrospinnability of film grade BioPBS relative to injection grade can be attributed to an increase in molecular weight between film and injection grade BioPBS.
4.4.1.3 BioPBS Concentration and Solution Viscosity

The same trend seen in the MFI of film and injection grade BioPBS was observed in the solution’s complex viscosities, shown in Figure 17a. Regardless of solvent used film grade BioPBS have higher complex viscosities compared to injection grade BioPBS. Further, an increase in BioPBS concentration resulted in an increase in the viscosity of that solution, due to an increase in polymer chain entanglements and molecular cohesion. A polymer solution has to have an optimal concentration, too high a concentration can prevent polymer motion, too low and it will inhibit the appropriate polymer entanglements required to create fibers. Polymer concentration is one of the most crucial variables in the electrospinning process, a minimum concentration is necessary to produce fibers, while a higher concentration is necessary to produce bead free fibers, as lower concentration solutions are prone to unwanted droplets forming throughout the fiber due to the unbalanced effects of viscosity and the Coulombic stretching force. This morphology is observed in FO-5 (Figure 18a) and to a lesser degree in FO-10, seen in Figure 18b. In FO-5, the viscosity is significantly lower than the FO-10 or FO-15 solutions, thus the Coulombic stretching force is far greater than the solution’s viscosity and causes the jet to break-up into spherical droplets (roundness = 0.70 ± 0.17) held by surface tension. In FO-10, the solution has sufficient viscosity to maintain fibrous form. However, the Coulombic stretching force is still imbalanced with respect to solution properties such as surface tension and viscosity. The Rayleigh instability is still prominent compared to the bending instability, which resulted in elongated beads (roundness = 0.55 ± 0.15). Bead-free fibers were observed in FO-15 solutions, as seen in Figure 18c. This is likely due to the further increase in viscosity, and limited increase in surface tension illustrated in Figure 18a and Figure 18b, respectively. The larger increase in viscosity relative to surface tension suppressed the Rayleigh instability in favor of the bending instability, which resulted in increased elongation forces, resulting in defect-free fibers. The concentration of the solution to be spun was found to have the greatest effect on fiber properties. When a solutions concentration is low, there is not enough molecular cohesion to stabilize the jet required to produce fibers, hence destabilization of the jet occurs, resulting in the production of fine spherical particles. The charged droplets naturally resist agglomeration and coagulation because of electrostatic repulsion, resulting in particles with very small diameters, smaller than a conventional mechanical atomizer. When the molecular cohesion in the solution is high enough, a stable jet can be produced from the Taylor cone, resulting in the production of a continuous fiber, observed in Figure 18c.
Figure 17. a) Complex viscosity  b) Interfacial surface tension, between the solution and water  
c) Conductivity of BioPBS solutions prepared for electrospinning. Conductivity of Neat CHCl₃ from ⁴³. All data taken at 23 °C.
Figure 18. SEM images (magnification of 2000X) of BioPBS fiber morphology electrospun at 15 kV, flow rate of 1.5 mL/h, 20 cm electrode gap with various polymer concentrations. a) 5 (% w/v) b) 10 (% w/v) and c) 15 (% w/v).
Viscosity is dependent on the polymer being used, as different polymer solutions have different viscoelastic properties. However, regardless of the type of polymer used, a minimum viscosity is essential to produce smooth and bead-free nanofibers. To electrospin neat, defect-free fibers, the polymer concentration must be at least twice the entanglement concentration (EC). The EC is a boundary between an unentangled and entangled solution. In an unentangled solution, the polymer chains overlap but do not entangle, whereas in an entangled solution, polymer chains overlap and entangle, constraining each other’s movement. The EC of BioPBS in DMSO/CHCl₃ was found to be approximately 7.5 (%w/v). The frequency of beads amongst the fibers was calculated for BioPBS solutions ranging from 5 to 15 (%w/v) concentration, where beaded morphology was present up until 15 (%w/v). The number of beads per 100 μm² decreased with increasing BioPBS concentration, as seen in Figure 19b. At significantly lower viscosities, surface tension is the primary effect on fiber morphology, and below a critical concentration, electrospayed drops form instead of electrospun fibers, seen in Figure 18a. Too high of a viscosity, and the polymer will not form fibers at all, as jet formation is difficult at high viscosities.

Figure 19. a) Tensile strength and Young’s modulus against BioPBS concentration of non-woven electrospun mats done using a DMA, 15, 5, 0.15 mm (length, width, thickness). Isothermal stress-strain, displacement ramp test conducted at 23 °C, with a 0.001 N preload, 0.1% initial strain, and a 1 mm/m ramp rate. b) Fiber porosity (SEM image analysis, 25000X magnification) and frequency of beads among fibers (SEM image analysis, 25000X magnification) against BioPBS concentration.
4.4.2 Process Parameters

4.4.2.1 Voltage

The impact voltage has on morphology is still controversial among researchers. With increasing voltage, researchers have observed smaller fibers, larger fibers, or observed negligible effects on morphology. The rationale for how an increase in voltage results in smaller diameter is as follows: an increased voltage exposes the polymer jet to a greater electric field. This increases the elongation forces applied to the polymer, due to higher Coulombic charges on the surface of the polymer. Mo et al. found that increasing the voltage from 9 to 15 kV resulted in a small decrease in fiber diameter, from roughly 0.75 to 0.5 μm. Polymer concentration was found to have a much greater effect on fiber diameter, a small change in concentration (7 to 9% w/v) resulted in an increase in fiber diameter from 0.8 to 1.5 μm, respectively. Lee et al. observed a similarly small reduction in fiber diameter, where the fiber diameter decreased from approximately 325 to 260 nm when the voltage was increased from 10 to 25 kV.

Conversely, a higher applied voltage could result in larger fibers because a higher build-up of charge at the needle causes the polymer jet to accelerate faster, resulting in more solution being ejected from the needle. Greater amounts of polymer in the electrospinning jet results in a larger fiber. Zhao et al. showed that a smaller voltage reduces the acceleration of the jet due to a weaker electric field, thereby increasing the amount of time the fiber is exposed to the electric field before reaching the collector, resulting in a thinner fiber. This suggests that a voltage approaching the minimum critical voltage could be effective at producing thin fibers. Furthermore, increasing the voltage, and hence the electric field, creates a larger charge formed at the tip that can create droplets or beads. Bead formation could be due to the increased instability of the jets as the Taylor cone disappears. Voltage was found to have a smaller effect in fiber morphology when compared to other variables such as concentration, choice of solvents, and distance to collector. The results shown in Figure 20a-c suggest that with increasing voltage, both fiber diameter and diameter distribution increase. Smaller diameter fibers and distributions are observed in electrospun fibers at 15 kV, while at 22.5 and 30 kV, larger diameter fibers and distributions are observed. Such large distributions observed in both 22.5 and 30 kV suggest that a voltage close to the critical voltage should be used to produce smaller fibers with a narrower distribution. These results are in accordance with the results presented by Demir et al. and Zhao et al.
strengthens the rationale that increasing the applied voltage will increase the diameter of the resultant fibers.\textsuperscript{171,172}

![Figure 20](image)

**Figure 20.** SEM images (magnification of 2000X) and corresponding histograms of BioPBS fiber morphology electrospun at: (a-c) 20 cm electrode gap a) 15 kV, 1.5 mL/h b) 22.5 kV, 3.0 mL/h c) 30 kV, 4.5 mL/h. (d-e) 15 kV, 1.5 mL/h d) 20 cm e) 25 cm f) 30 cm.

### 4.4.2.2 Distance Between Electrodes

Varying the distance between the electrodes, the electrode gap (EG), alters the time the fiber is exposed to the electric field between the electrodes. Shortening the EG increases the electric field gradient and the jet’s acceleration, hence reducing the time available for evaporation. Lengthening the distance generally results in thinner fibers.\textsuperscript{72,176} SEM images and the corresponding histograms (Figure 20d-f) show a clear left shift towards smaller diameter fibers. Buchko et al\textsuperscript{82} showed that when the EG was
sufficiently small, an interconnected fibrous mesh formed on the collector due to the inability to remove the solvent in time. A larger EG, thus a longer period for the solvent to evaporate, allows the fiber to continue to elongate before solidifying. Conversely, too large a distance will create beaded fibers. Fiber diameter and jet current both decrease with increasing EG, this is because the flight time is increased, allowing more time for elongation, resulting in thinner fibers. The collector is commonly made from a conductive material and is grounded to form a stable electric field. Non-conducting materials result in a lower packing density. However, in some cases, like three dimensional nanofibrous scaffolds, it is advantageous to allow the fibers to amass in a lower packing density, resulting in a more porous material. To this end, the EG of the electrospinning process must be optimized in terms of morphology with careful consideration given to the interaction effects between EG, flow rate and solvent used.

4.4.3 Physical and Mechanical Properties

4.4.3.1 Porosity

As previously mentioned, porosity is a crucial parameter for many biomedical applications and can be easily controlled by adjusting the type and concentration of the polymer, solvent system, or humidity. The volatility of CHCl₃ creates pores as the solvent evaporates. Areas with relatively higher solvent content evaporate more rapidly compared to the more homogeneous regions resulting in voids or pores forming along the fiber in these areas. Megelski et al. investigated the effects of solvent volatility on the porosity of the resulting fiber: they varied the ratio of relatively volatile tetrahydrofuran (THF) with DMF, a less volatile solvent. As the ratio of THF:DMF changed from 10:0 to 0:10, fiber morphology subsequently changed from highly porous in pure THF, to less porous structures in 3:1 THF:DMF, to completely nonporous fibers in pure DMF. Humidity was found to have a similar effect on fiber porosity as solvent volatility: as the relative humidity increased from 20 to 50%, fiber morphology changed from smooth non-porous fibers, to highly porous fibers, respectively. In a humid environment, moisture can condense on the relatively cold surface of a fiber, water vapor interacts with the solvent, and as they both evaporate, a pore is formed. Porosity is also dependent on the polymer chosen to electrospin. Wagner et al. showed that with increasing fractions of PLA in a PLA:PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) blend, that fiber porosity increased while bead formation decreased.
Figure 21. a) 15% BioPBS concentration creates porous, hierarchical electrospun fibers. b) 5% BioPBS concentration creates electrospayed droplets connected by nanofibers (SEM images at 5000x, 10000x, and 25000x). c) High magnification image of porous fibers.
Porosity was found to increase while pore size was found to decrease with increases in BioPBS concentration, as shown in Table 6. Pores were observed regardless of solvent system or grade of BioPBS selected. However, FO-5 solutions did not have any pores along the surface, likely due to the disproportionately high surface tension compared to viscosity. In solutions with significantly low viscosity, solvent molecules agglomerate together due to the influence of surface tension. Furthermore, elongated pores (43 – 67% roundness) formed with the long axis of the pores aligned with the direction of the fiber, seen in Figure 21a. This orientation was likely due to the elongation forces present during the electrospinning process. Electrospinning took place in humidity’s as high as 65% using a known volatile solvent. It is likely that a combination of high humidity and volatility contributed to the formation of pores on the surface of the fibers, although it is unclear which had a more significant effect on fiber porosity. Solution properties and ambient conditions, specifically humidity, have a considerable influence on pore size and porosity of electrospun fibers.

<table>
<thead>
<tr>
<th>Grade-Solvent</th>
<th>Pore diameter (nm) Major/Minor</th>
<th>Pore Size (μm²)</th>
<th>Roundness (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IO</td>
<td>226±136 119±48</td>
<td>0.12 ± 0.12</td>
<td>63 ± 16</td>
<td>20.44 ± 1.08</td>
</tr>
<tr>
<td>FO-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FO-10</td>
<td>655±412 275±98</td>
<td>0.16 ± 0.15</td>
<td>49 ± 19</td>
<td>30.74 ± 2.55</td>
</tr>
<tr>
<td>FO-12.5</td>
<td>599±211 242±82</td>
<td>0.12 ± 0.07</td>
<td>43 ± 13</td>
<td>35.97 ± 2.60</td>
</tr>
<tr>
<td>FO-15</td>
<td>481±218 192±85</td>
<td>0.08 ± 0.07</td>
<td>43 ± 16</td>
<td>41.84 ± 2.18</td>
</tr>
</tbody>
</table>

4.4.3.2 Tensile Strength

Similar to porosity, BioPBS concentration has a large effect on the subsequent mechanical properties of the BioPBS non-woven fibrous mats. Adjusting BioPBS concentration results in prominent changes in morphology, such as, frequency of defects, fiber diameter, and fiber porosity. These nano- and microsized morphological changes affect the mechanical properties of the macrostructure, the non-woven fibrous mat. Tensile properties of the BioPBS non-woven mat such as tensile strength and Young’s
modulus were found to increase with increasing concentrations. As BioPBS concentration increased the frequency of beads along the fibers decreased, Figure 19b. The reduction of these defects resulted in an increase in tensile properties, Figure 19a. Beaded electrospun fibers can find applications in air filtration, where uniform diameters, narrow diameter distributions, and strength are less crucial \(^{178}\), as increased bead size and frequency contribute to low pressure drops and increased filtration efficiency \(^{178}\).

Vautard et al.\(^ {156}\) used three different techniques to induce surface defects on PAN based carbon fibers. Showing that the frequency of defects predominately controlled the resulting strength of the fiber, an increase in the frequency of defects results in a decrease in fiber strength \(^ {156}\). In this study, beaded fibers acted as defects within the non-woven fibrous mat. A decrease in the frequency of beads resulted in an increase in tensile properties. It is also well known that an increase in porosity is linearly associated with a decrease in the Young’s modulus of that material \(^ {179}\). However, it was found that the presence of bead defects predominately affected the mechanical properties, irrespective of porosity. The tensile values reported in this study are within the range of those reported for skin (1-20 MPa) or cardiac tissue (0.3-0.8 MPa), but are far too weak for structural tissues like bone, tendon, or ligament (50 – 100 MPa) \(^ {34,142,180}\). It is recommended that further tensile testing should be conducted at 37 °C in simulated bodily fluid to get a better understanding of how these fibers would perform within a human body.

4.4.3.2.1 Statistical analysis

In order to determine if there was a significant difference between the fibrous mats mechanical properties created from different polymer concentrations (10, 12.5, and 15\%) a single factor ANOVA test was performed. A summary of the analysis can be seen in Table 7, Full ANOVA results can be seen in Tables 12 and 13 in the supporting information. P-values for both Young’s modulus and tensile strength are much lower than the alpha value = 0.05 therefore, we reject the null hypothesis that the means of the groups (polymer concentrations) are equal for both Young’s modulus and tensile strength. Meaning there is a significant difference observed between the means of the groups.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Young’s Modulus</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>P-value</td>
</tr>
<tr>
<td>Polymer Concentration</td>
<td>52.07321</td>
<td>1.22E-06</td>
</tr>
</tbody>
</table>
4.5 Conclusion

In this study, solution properties such as BioPBS concentration, type of solvent system, and grade of BioPBS had a greater effect on fiber morphology than process parameters, specifically the applied voltage and the distance between electrodes. Co-solvent systems were optimized to 10% DMSO:CHCl₃ and 10% DMF:CHCl₃. DMSO:CHCl₃ co-solvent systems produced fibers with less bead defects compared to DMF:CHCl₃, regardless of the BioPBS grade used. It was found that increasing BioPBS concentration yielded fibers with fewer bead defects, which at 15 (%w/v) resulted in bead-free uniform fibers. Furthermore, increasing the BioPBS concentration was found to increase the porosity of the fibers while simultaneously reducing its pore size. Dynamic mechanical analysis showed that the reduction of bead defects resulted in a stronger non-woven fibrous mat. It was determined that electrospun BioPBS fibrous non-woven mats possess a high degree of porosity at the micro- and nano-scales, resulting in a hierarchical structure that has sufficient mechanical properties for applications in wound healing and soft tissue engineering.
Chapter 5.
Significance and Overall Conclusions

5.1 Significance

The current methods used to produce the extensive amounts of plastic necessary to meet consumers’ demand is having a significant effect on the health of our planet \(^1\)\(^,\)\(^11\). Almost 50% of all polyolefins produced in the United States are derived from petroleum feedstocks and the remainder from natural gas feedstocks, our carbon cycle is suffering tremendously \(^4\). Unfortunately, the low costs associated with processing and manufacturing make plastics a very attractive option when comparing them to other materials, such as glass and metal, that have significantly greater costs associated with their processing and manufacturing. No doubt materials created from fossil fuels have increased the quality of life for billions of people all over the world. However, there is increasing evidence and commentary on the acute effect of human impacts on the natural carbon cycle \(^181\),\(^182\). In order to disrupt the fossil fuel industry, a viable economic alternative is required, as well as a focus on a particular part of the industry. Disrupting the chemicals and materials sector is a strategic option as it accounts for over 40% of fossil fuel revenues \(^10\). Bio-based and compostable plastics have incredible potential to replace petroleum-based plastics, although further research is required to maximize this potential.

BioPBS has similar properties to petroleum-based plastics and could substitute them as commodity plastics, utilized in advanced composites, and used as a biomaterial. BioPBS is an ideal candidate for displacing current materials in these applications, particularly in the medical field, due to its biodegradability, biocompatibility and high capacity for drug loading \(^28\). This thesis successfully demonstrated that BioPBS could be used in a wide variety of applications, specifically the three mentioned above. Some of the current limitations to bio-plastics were overcome by blending with high strength BC and GnPs, simultaneously lowering the cost, making bioplastics more competitive with petroleum-based material counterparts. The use of BioPBS in high value medical application furthers the goal of adopting bio-based materials into all aspects of life.
5.2 Conclusions

BioPBS was combined with pyrolyzed miscanthus microparticles to create biocomposites and graphene nanplatelets to create a hybrid nano-biocomposite. BC was incorporated into BioPBS to improve the thermo-mechanical properties of the bioplastic while simultaneously increasing the value of this co-product. Biocomposites loaded with 25 wt% biocarbon showed 57, 13, and 32% improvements in tensile modulus, HDT and CLTE, seen in Figure 22. Further improvements were found when GnPs were added to the biocomposite forming a hierarchical hybrid nano-biocomposite. Two processing methods were used to incorporate GnPs into the composites, MC and DC processing methods. The two methods resulted in different internal morphologies which subsequently impacted the mechanical properties of the composites, little change was observed in the thermal properties studied, Figure 22. Composites processed using the DC technique showed the greatest increase in tensile strength and modulus, 17 and 120% respectively. Composites processed using the MB technique had slightly lower strength and modulus but almost twice the impact strength compared the direct compounding method. The MB technique was found to have a superior balance of stiffness and toughness likely due to the presence of superclustered graphene platelets.

![Figure 22](image_url)

Figure 22. A radar plot summarizing the improvements in thermo-mechanical properties when BioPBS (black) is compounded with 25% BC (red), 20% BC and 5% GnP through a masterbatch technique (green), and 20% BC and 5% GnP through a direct compounding technique (blue).
BioPBS was electrospun to create hierarchical, highly porous fibers. Various grades of BioPBS were dissolved in one of three solutions: CHCL₃, CHCL₃/DMF, CHCL₃/DMSO. CHCL₃/DMSO (90/10) produced uniform bead-free fibers with a high level of porosity, ~42%. In determining the optimal solution and electrospinning conditions, it was found that solution properties such as the solvent system, the grade of BioPBS, and the concentration of BioPBS had a significant effect on fiber morphology. An increase in BioPBS concentration resulted in the reduction of bead defects, which at 15 (%w/v) resulted in bead-free uniform fibers. Increasing BioPBS concentration also increased the porosity of the fibers while reducing pore size. DMA showed that the reduction of bead defects resulted in increased tensile strength and Young’s modulus of the electrospun fibrous non-woven mat. The results of this study show that electrospun BioPBS fibers have high porosity at the micro- and nano-scale resulting in a hierarchical structure that has sufficient mechanical properties for potential applications in wound healing and soft tissue engineering.

Figure 23. Electrospun BioPBS from a CHCL₃/DMSO (90/10) solvent system producing highly nano-porous microfibers.
5.3 Future work

It is suggested that for BioPBS composites to be adopted in commercial markets large scale experiments be conducted to replicate the properties observed in micro compounding techniques. It would also be interesting to add further toughing agents like bio-based glycerol\textsuperscript{136}, or perhaps use a PBS grade with higher impact strength, such as BIONOLLE PBS 1001 higher impact\textsuperscript{116}. As GnPs are known to effect electrical conductors it would be interesting to see if these properties are present in their composites with BioPBS. It could also be possible to utilize electrospinning as a method to improve the dispersion of GnPs in BioPBS. By mixing GnPs into the solvent system used to electrospin BioPBS, then collecting them to be compounded into the final composites. The electrical forces during the electrospinning process could have interesting effects on the orientation and distribution of the GnPs. Further the increased conductivity due to the presence of the GNP could also improve the electrospinning process. To further investigate the morphology of the graphene composites, higher magnification analysis will need to be conducted, such as transmission electron microscopy or atomic force microscopy. Long term studies such as heat aging experiments and confirmation of the blends compostability is also suggested.

If the BioPBS fibers are intended to be used in medical applications, it is suggested that further investigation into biocompatibility, biodegradability, and mechanical properties under \textit{in vitro} conditions be done to better predict the fiber’s performance in environments that more closely mimic those found within the human body. If used in an advanced wound dressing application then cytotoxicity, skin irritation, and drug loading studies should be conducted. Further pore analysis will need to be conducted to determine the volume of the pores.
Supporting Information

Table 8. Supporting thermal data.

<table>
<thead>
<tr>
<th>Blend</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BioPBS</td>
<td>115.7 ± 0.03</td>
<td>70.45 ± 1.63</td>
<td>91.20 ± 0.05</td>
<td>69.20 ± 0.43</td>
<td>34.60</td>
</tr>
<tr>
<td>BioPBS/10BC</td>
<td>115.21 ± 0.16</td>
<td>57.48 ± 0.44</td>
<td>89.41 ± 0.05</td>
<td>62.79 ± 0.24</td>
<td>28.26</td>
</tr>
<tr>
<td>BioPBS/15BC</td>
<td>115.75 ± 0.007</td>
<td>50.85 ± 0.39</td>
<td>89.81 ± 0.20</td>
<td>55.545 ± 0.76</td>
<td>23.61</td>
</tr>
<tr>
<td>BioPBS/20BC</td>
<td>115.5 ± 0.25</td>
<td>48.07 ± 0.54</td>
<td>88.39 ± 0.22</td>
<td>52.07 ± 0.87</td>
<td>20.83</td>
</tr>
<tr>
<td>BioPBS/25BC</td>
<td>115.57 ± 0.40</td>
<td>43.96 ± 0.08</td>
<td>87.97 ± 0.29</td>
<td>48.61 ± 1.0</td>
<td>18.23</td>
</tr>
<tr>
<td>BioPBS/24BC/1GnP - masterbatch -</td>
<td>114.77 ± 0.57</td>
<td>54.33 ± 3.27</td>
<td>96.43 ± 0.11</td>
<td>51.06 ±1.1</td>
<td>19.15</td>
</tr>
<tr>
<td>BioPBS/20BC/5GnP - masterbatch -</td>
<td>114.01 ± 0.29</td>
<td>54.32 ± 1.53</td>
<td>98.78 ± 0.12</td>
<td>49.49 ± 0.5</td>
<td>18.56</td>
</tr>
<tr>
<td>BioPBS/24BC/1GnP - direct -</td>
<td>114.93 ± 0.04</td>
<td>51.22 ± 0.08</td>
<td>95.87 ± 0.11</td>
<td>50.62 ± 0.76</td>
<td>18.98</td>
</tr>
<tr>
<td>BioPBS/20BC/5GnP - direct -</td>
<td>115.31 ± 0.85</td>
<td>52.38 ± 0.55</td>
<td>98.24 ± 0.14</td>
<td>51.38 ± 1.3</td>
<td>19.27</td>
</tr>
<tr>
<td>BioPBS/25GnP - masterbatch -</td>
<td>114.6 ± 1.00</td>
<td>51.86 ± 0.47</td>
<td>99.3 ± 0.33</td>
<td>52.02 ± 0.24</td>
<td>19.51</td>
</tr>
</tbody>
</table>

Figure 24. Stress-strain curves for Neat BioPBS.
Table 9. Summary of Chapter 3 data.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Elongation at yield (%)</th>
<th>Elongation at break (%)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Izod Notched Impact Strength (J/m)</th>
<th>HDT (°C)</th>
<th>CLTE 90°C</th>
<th>MFI 190°F/2.16 (g/10min)</th>
<th>Zero Shear Viscosity (Kpa*s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BioPBS FZ71PM</td>
<td>41.5 ± 0.72</td>
<td>814 ± 66.79</td>
<td>15.90 ± 0.42</td>
<td>135.15 ± 8.5</td>
<td>34.15 ± 0.47</td>
<td>783 ± 14.38</td>
<td>19.55 ± 0.83</td>
<td>91.60 ± 0.98</td>
<td>255.8 ± 7.50</td>
<td>243.35 ± 25.67</td>
<td>13.2 ± 0.57</td>
</tr>
<tr>
<td>PBS/10BC</td>
<td>42.3 ± 0.75</td>
<td>1086.2 ± 65.88</td>
<td>14.61 ± 0.9</td>
<td>15.12 ± 1.13</td>
<td>40.97 ± 0.59</td>
<td>980 ± 16.85</td>
<td>29.58 ± 2.16</td>
<td>93.24 ± 0.71</td>
<td>250.6 ± 1.83</td>
<td>218.5 ± 10.74</td>
<td>18.8 ± 0.72</td>
</tr>
<tr>
<td>PBS/15BC</td>
<td>42.3 ± 0.57</td>
<td>1182.4 ± 66.33</td>
<td>10.40 ± 0.34</td>
<td>10.75 ± 0.44</td>
<td>45.36 ± 0.60</td>
<td>1073 ± 16.97</td>
<td>27.76 ± 0.85</td>
<td>96.68 ± 0.26</td>
<td>203.95 ± 1.20</td>
<td>194.65 ± 3.04</td>
<td>16.32 ± 1.03</td>
</tr>
<tr>
<td>PBS/20BC</td>
<td>42.8 ± 0.38</td>
<td>1224 ± 60.43</td>
<td>8.02 ± 0.4</td>
<td>8.18 ± 0.28</td>
<td>48.44 ± 1.84</td>
<td>1144 ± 51.81</td>
<td>27.73 ± 1.13</td>
<td>97.33 ± 0.40</td>
<td>194.6 ± 7.25</td>
<td>178.7 ± 7.50</td>
<td>13.37 ± 0.63</td>
</tr>
<tr>
<td>PBS/25BC</td>
<td>43.2 ± 0.47</td>
<td>1288 ± 61.32</td>
<td>7.35 ± 0.45</td>
<td>7.45 ± 0.45</td>
<td>52.22 ± 1.65</td>
<td>1321 ± 42.56</td>
<td>16.77 ± 1.51</td>
<td>103.02 ± 0.61</td>
<td>173.7 ± 4.03</td>
<td>173.0 ± 4.81</td>
<td>10.54 ± 0.23</td>
</tr>
<tr>
<td>PBS/24BC/1GnP masterbatch -</td>
<td>45.9 ± 0.61</td>
<td>1293.2 ± 66.35</td>
<td>7.84 ± 1.0</td>
<td>7.88 ± 1.04</td>
<td>56.43 ± 0.17</td>
<td>1404.25 ± 7.04</td>
<td>26.06 ± 0.79</td>
<td>99.28 ± 0.89</td>
<td>199.1 ± 1.70</td>
<td>177.9 ± 4.60</td>
<td>10.97 ± 0.51</td>
</tr>
<tr>
<td>PBS/24BC/5GnP masterbatch -</td>
<td>47.2 ± 0.93</td>
<td>1655.75 ± 88.11</td>
<td>6.78 ± 0.71</td>
<td>6.8 ± 0.72</td>
<td>60.06 ± 0.67</td>
<td>1653.5 ± 33.48</td>
<td>57.70 ± 1.93</td>
<td>59.45 ± 0.47</td>
<td>202.85 ± 6.62</td>
<td>166.25 ± 8.50</td>
<td>7.65 ± 0.27</td>
</tr>
<tr>
<td>PBS/24BC/1GnP direct -</td>
<td>46.9 ± 0.85</td>
<td>1436.2 ± 92.56</td>
<td>7.56 ± 0.58</td>
<td>7.76 ± 0.65</td>
<td>58.01 ± 0.53</td>
<td>1055 ± 20.24</td>
<td>19.12 ± 0.77</td>
<td>98.86 ± 0.14</td>
<td>198.82 ± 3.28</td>
<td>176.85 ± 4.60</td>
<td>11.29 ± 0.95</td>
</tr>
<tr>
<td>PBS/24BC/5GnP direct -</td>
<td>48.5 ± 0.96</td>
<td>1786.4 ± 44.52</td>
<td>7.75 ± 0.78</td>
<td>7.66 ± 0.64</td>
<td>61.52 ± 0.72</td>
<td>1769.8 ± 54.04</td>
<td>21.09 ± 1.19</td>
<td>57.61 ± 0.24</td>
<td>200.2 ± 2.76</td>
<td>177.25 ± 4.26</td>
<td>5.62 ± 0.22</td>
</tr>
<tr>
<td>8.34ABS 1150EM</td>
<td>41.7 ± 0.47</td>
<td>1896 ± 82</td>
<td>3.63 ± 0.4</td>
<td>29.82 ± 3.99</td>
<td>66.05 ± 0.23</td>
<td>2036 ± 10.45</td>
<td>438.50 ± 3.91</td>
<td>104.15 ± 0.66</td>
<td>116.75 ± 3.32</td>
<td>106.55 ± 2.62</td>
<td>0.98 ± 0.12</td>
</tr>
</tbody>
</table>

PBS – Injection grade FZ71PM, GnP – graphene nanoplatelet, BC – Miscanthus biocarbon 500 °C, 1/64 sifted, 1-hour ball milled, ABS – 1150EM
a) ASTM D638 type IV samples, baseline conducted at 50 mm/min (failure between 95-120 s), composites conducted at 5 mm/min (failure between 75-90 s)
b) ASTM D790 Procedure A, three-point bending, 14 mm/min.
c) ASTM D256, samples were notched 24 hours after processing, testing occurred 48 hours after that.
d) DMA 3-point bending, -50 °C, ramp 2 °C/min to 180 °C, abort at displacement ≥ 300 μm

e) Load: 0.05N, Range: -30 -100 °C, Rate: 5 °C/min, Size: 3-6 mm
f) ASTM D1238, procedure A, 4-8g samples, residence time 7 min, time interval of 15 s at 190 °C under 2.16 kg, ABS - 230 °C under 3.8 kg
g) Frequency sweep 500 – 0.1 rads/s at 150 °C, zero shear obtained using a Carreau regression
Figure 25. Stress-strain curves for BioPBS/BC (90/10).

Figure 26. Stress-strain curves for BioPBS/BC (85/15).
Figure 27. Stress-strain curves for BioPBS/BC (80/20).

Figure 28. Stress-strain curves for BioPBS/BC (75/25).
Figure 29. Stress-strain curves for BioPBS/BC/GnP (75/24/1) DC.

Figure 30. Stress-strain curves for BioPBS/BC/GnP (75/20/5) DC.
Figure 31. Stress-strain curves for BioPBS/BC/GnP (75/24/1) MB.

Figure 32. Stress-strain curves for BioPBS/BC/GnP (75/20/5) MB.
Table 10. $2^2$ analysis of variance of impact strength on GnP content and processing methods, alpha - 0.05.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process method</td>
<td>415.9637</td>
<td>1</td>
<td>415.9637</td>
<td>255.9819</td>
<td>2.33E-07</td>
<td>5.317655</td>
</tr>
<tr>
<td>Amount of GnP</td>
<td>123.7198</td>
<td>1</td>
<td>123.7198</td>
<td>76.13656</td>
<td>2.33E-05</td>
<td>5.317655</td>
</tr>
<tr>
<td>Interaction</td>
<td>70.15585</td>
<td>1</td>
<td>70.15585</td>
<td>43.17356</td>
<td>0.000175</td>
<td>5.317655</td>
</tr>
<tr>
<td>Within</td>
<td>12.99785</td>
<td>8</td>
<td>1.624973</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>622.8391</strong></td>
<td>11</td>
<td></td>
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</tr>
</tbody>
</table>

Table 11. $2^2$ analysis of variance of tensile strength on GnP content and processing methods, alpha - 0.05.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process method</td>
<td>11.1005</td>
<td>1</td>
<td>11.1005</td>
<td>11.17031</td>
<td>0.004135</td>
<td>4.493998</td>
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<tr>
<td>Amount of GnP</td>
<td>11.7045</td>
<td>1</td>
<td>11.7045</td>
<td>11.77811</td>
<td>0.003422</td>
<td>4.493998</td>
</tr>
<tr>
<td>Interaction</td>
<td>0.0405</td>
<td>1</td>
<td>0.0405</td>
<td>0.040755</td>
<td>0.842557</td>
<td>4.493998</td>
</tr>
<tr>
<td>Within</td>
<td>15.9</td>
<td>16</td>
<td>0.99375</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>38.7455</strong></td>
<td>19</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 12. Single factor analysis of variance of Young’s modulus on polymer concentration, alpha - 0.05.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Concentration</td>
<td>42.84509</td>
<td>2</td>
<td>21.42255</td>
<td>52.07321</td>
<td>1.22E-06</td>
<td>3.885294</td>
</tr>
<tr>
<td>Within Groups</td>
<td>4.936714</td>
<td>12</td>
<td>0.411393</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>47.7818</strong></td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 13. Single factor analysis of variance of tensile strength on polymer concentration, alpha - 0.05.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Concentration</td>
<td>2.63933</td>
<td>2</td>
<td>1.319665</td>
<td>89.40329</td>
<td>6.19E-08</td>
<td>3.885294</td>
</tr>
<tr>
<td>Within Groups</td>
<td>0.17713</td>
<td>12</td>
<td>0.014761</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2.816459</strong></td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 33. Segmentation process for fiber diameter and pore size analysis.
References

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