Processing and Properties of Particulate Reinforced Carbon Matrix Composites

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ABSTRACT

Carbonization of biomass is a type of pyrolysis that allows for the formation of byproducts that have applications in many other industries [1]. In the field of materials science concerned with environmental impact intersecting with desirable material properties and performance, the process of carbonization in particular with commonplace biomass such as food waste is of great interest. In this thesis, pistachio shell was used as the organic biomass of choice for carbonization, and reinforcement was provided by titanium powder. These two materials were milled together at two different compositions and milling times. Experimental conditions consisted of replicates of three bulk samples made from uniaxially pressed powder mixtures heat treated from 800 °C up to 1200 °C in increments of 100 °C. Heat treatment occurred in a tube furnace with a heating rate of 5 °C/min up to the heat treatment temperature, holding the temperature for 1 hour, then ramping back down to room temperature, all in an inert atmosphere. XRD was performed on heat treated samples before polishing, while optical microscopy and SEM were performed after mounting and polishing. TGA was performed on the milled powders, while hardness was performed on the heat treated bulk samples after mounting and polishing. Results obtained suggested that increasing heat treatment temperature and milling time decreased carbon matrix porosity. In addition, greater amounts of titanium seemed to result in increased porosity. However, at increased temperature, more surface cracking was observed, leading to the conclusion that an excessively high temperature is detrimental to mechanical properties. Finally, rutile TiO₂ was formed as a result of the heat treatment process. In considering environmental impact, cost, and mechanical properties, a balance must be maintained between higher temperature processing, duration, milling time, and porosity present due to these factors. Future work includes further investigations into processing parameters and characterization such as XPS and abrasion testing.
Carbonization of organic materials such as wood or nut shells can be explained in short as a decomposition that occurs when those materials are heated up without allowing them access to oxygen as in a normal combustion like a fire. Because of that, carbonization can produce useful products and materials of interest to many. Adding titanium to pistachio shell powder, performing compaction and carbonization, then further heating up those samples, resulted in composite materials consisting of mostly carbon char and particles inside that improve the properties. After testing multiple experimental conditions and analyzing them using equipment such as X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), optical microscopes, Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS), and a hardness tester, some trends in properties and structure were observed. Generally, increasing heat treatment temperature and milling time will reduce porosity in the matrix. On the other hand, decreasing amount of Ti powder added seems to reduce porosity. However, too high of a heat treatment temperature seems to have a detrimental effect on the part manufactured (i.e. surface cracking). In addition, considering processing costs and time costs could discourage one from using a very high temperature to heat treat these samples. Therefore, it is important to balance amount of energy used to heat treat, time spent, and resulting porosity of the final product for its applications. Future work should be done to further determine the effects of processing parameters by making more samples to test the properties of. Other characterization techniques like X-Ray Photoelectron Spectroscopy (XPS) and abrasion testing could be good to determine the exact makeup of the particles in the composite as well as see the sample’s performance in its intended application (i.e. brake pads).
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1. Introduction
Carbonization is a process of interest used to convert readily available biomass into products that can have many different applications. Such products may include liquid compounds that can be used for fuel, but the product of interest in the research conducted in this thesis is the solid carbonaceous material left behind [1]. The solid carbon tends to be very porous but is of interest in the field of materials science as it provides an avenue for generating carbon matrices for carbon composites for applications like brake pads[2]. In addition, carbonization is known to be a carbon-neutral process, making it a more appealing method for producing solid carbon [3].

Pistachio shell is one form of biomass waste produced by the food industry as a by-product of the pistachio nut. Pistachios originate from the Mediterranean region, but the United States produces a large portion of the market for consumption [4, 5]. Iran and Turkey are the largest producers in the Middle East [4]. Over 1 million metric tons of pistachios are produced globally, with global consumption of pistachios at about 850,000 metric tons [4]. Thus, pistachio shell as a biomass material has a lot of potential for reusing or redirecting waste produced by the consumption of the nuts. In view of that, Figure 1 shows the increase in pistachio shell production over the years.

Carbon as a material is also of interest to this research as it has a wide range of appealing properties due to its many forms that make it applicable as a constituent of composite materials. Some
of these properties include high thermal, electrical conductivity, and hardness. Carbon, even in its many different allotropes, has a rather low density. For example, graphite has a density of about 2.2 g/cm\(^3\) and even diamond only has a density of about 3.513 g/cm\(^3\) [7]. When compared with other materials, specifically ones that also display relatively high thermal conductivity such as metals, the density of carbon materials is twice or three times lower [7]. Lower density is desirable because it reduces overall weight of components, which in turn can improve the performance of things such as vehicles that depend on weight for efficiency, or because it makes them easier/cheaper to transport.

Carbon materials also have a relatively high thermal conductivity, at a range of 25 – 470 W/mK [8]. In addition, they are also stable at high temperatures and chemically resistant, making them ideal for applications in extreme environments [8]. By combining carbonaceous material with other desirable materials, a composite can be made with these properties in mind. Applications such as brake pads are of interest to the research being done in this paper, as carbonized material can become very hard, which is then supplemented by the presence of the reinforcement phase to make a more wear-resistant, thermally conductive, thermally stable material.

Overall, with the process of carbonization, carbonaceous materials can be created from organic precursors. In particular, organic biomass that originates as food waste such as pistachio shell can be used in this carbonization process to produce solid carbon. A reinforcement, such as ceramic particles (i.e., TiO\(_2\)), are used to form a composite, thus increasing its thermal and mechanical properties to make a material that has potential in applications such as brake pads.
2. Background and Literature Review

2.1 Carbonization

Carbonization is the foundation upon which the research in this thesis has been conducted. Therefore, it is important to cover this process in-depth in order to provide a base of knowledge and understanding from which good analysis of results can occur. This section of Background and Literature Review will cover information on carbonization relevant to the research conducted.

2.1.1 General Background

Carbonization can essentially be thought of as a subset of pyrolysis. Pyrolysis is the thermal decomposition of a material carried out in an inert atmosphere such as argon or nitrogen gas [1]. What differentiates carbonization from other typical pyrolysis processes is that the material being decomposed is organic in nature. The intent of pyrolyzing organic material (also known as biomass) is that such material by nature contains a large amount of elemental carbon in the compounds present [1]. Biomass contains other elements in the compound structure such as hydrogen or oxygen, but only the carbon is of interest in this situation. Carbonization, as the name suggests, causes the biomass to decompose and leave many waste products, one of which is a solid product known as char that consists of almost entirely elemental carbon [1]. Char typically consists of about 85% carbon in addition to some hydrogen, oxygen, and ash from the starting material [3]. In addition, char tends to have an open porous structure that makes it useful for other applications such as filtering or chemical absorption [3].

Other products than char can be produced with carbonization, such as liquid or gaseous products [1]. Liquid products can consist of condensed vapors called bio-oil, which has its own applications as fuel [1]. Bio-oil is a tar-like fluid that contains about 20% water in addition to many other compounds such as hydroxyaldehydes, phenols, carboxylic acids, hydroxyketones, acetic acid, methanol, etc. [3]. Non-condensable gases are also produced in the carbonization process and typically include CO, CO₂, H₂, methane, ethane, and ethylene [9, 10]. Figure 2 below shows a generic pathway for what happens during carbonization in regard to products produced.
Generally, what was described previously covers the primary decomposition reaction. However, given enough duration secondary reactions can occur with the initial products produced [1]. These secondary reactions consist of polymerization/cracking of some of the initial products, so if those products are not siphoned away after about one second then the secondary reactions tend to occur [1]. In addition, while the original decomposition reactions are endothermic, the secondary ones are exothermic and help to produce more solid product [1].

2.1.2 Factors

Other factors can also affect the carbonization process, including how much of each product is produced. Some are fairly obvious, such as the temperature at which the carbonization is conducted or the heating rate. However, there are less obvious yet important factors to keep in mind such as heat transfer and mass transfer [1].

Since pyrolysis and carbonization are decomposition reactions, temperature plays a significant role in decomposition behavior and the ratio of products produced. Biomass typically contains varying amounts of three main organic compounds: cellulose, lignin, and hemicellulose [1]. The amounts of each are often different depending on the source of the biomass (i.e. different types of wood may contain more cellulose vs. others). In addition other organic compounds may also be present, but the majority contain the three mentioned earlier. Therefore, understanding the decomposition behavior and temperatures at which cellulose, lignin, and hemicellulose break down is important.

Figure 3 below depicts a TGA graph (heating rate of 10 °C/min) demonstrating the different temperatures at which each of the mentioned organic compounds degrade. Cellulose clearly is more thermally stable than the other two, and this is easily explained using structure-property relationships. Cellulose is a polymer with a long linear structure and more crystallinity compared to hemicellulose and...
lignin, which are more branched and amorphous [1]. The structures of cellulose, lignin, and hemicellulose can be seen below in Figure 4.

![Figure 3 – TGA graph of cellulose, lignin, and hemicellulose where dashed lines correspond to the mass loss rate [1].](image)

![Figure 4 – Chemical structures of cellulose, lignin, and hemicellulose [9].](image)

Carbonization carried out at lower temperatures (i.e. < 300 °C) produces waste products from the decomposition of hemicellulose such as formic acid, acetic acid, acetone, and methanol [1]. At higher temperatures closer to 500 °C larger compounds such as hydroxyacetaldehyde or phenols are formed from the decomposition of cellulose and lignin, respectively [1]. Higher temperatures will then aid the secondary cracking/polymerization reactions mentioned earlier to produce more char and non-condensable gases [1]. Char formed from the primary decomposition can continue to break down especially at higher temperatures, so if one is looking to maximize char produced, a lower temperature
for carbonization should be utilized [1]. In addition, if bio-oil is the main product of concern, 500 °C is the temperature at which production is maximized [1].

Heating rate is also important in the carbonization process. The pyrolysis can be classified as slow or fast depending on the heating rate [3]. If the heating rate is faster than the rate of reaction for pyrolysis then it is considered fast pyrolysis, and vice versa for slow pyrolysis, assuming linear heating rates [2]. Slow pyrolysis produces more char and allows those secondary cracking reactions to occur [3]. Fast pyrolysis encourages production of more bio-oil and gaseous products [3]. Therefore, depending on the product desired, processing can be manipulated to allow more of a certain type to be produced. Figure 5 illustrates how different amounts of solid and gaseous products are produced by varying the processing temperature.

![Figure 5 – Product yield with variation in carbonization temperature [3].](image)

A few other factors to keep in mind with carbonization are mass transfer and pressure [9, 12]. In terms of thermodynamics the driving force of the products from the decomposition is the pressure gradient caused by the buildup of said products within the material [1]. Larger particles undergoing carbonization means more distance for bio-oil and gases to travel out, which encourages dwell time and the secondary cracking reactions [1]. Furthermore, increasing the pressure at which the process is conducted increases the rate of reaction since the cracking reactions are vapor-phase reactions [1]. This leads to more char produced under high pressure carbonization [9, 12]. Prior research has been conducted on pressurized carbonization and its influence on the structure and morphology of the carbon produced [10]. Generally, multiple allotropes of carbon can be produced as a mixture with carbonization, but by manipulating pressurization conditions spherical carbon can be synthesized [10].
Overall, to summarize: (1) to increase char a slower heating rate, lower pyrolysis temperature, and long duration should be used; (2) to increase bio-oil production a higher heating rate, moderate pyrolysis temperature and short duration (particularly for the gas produced) should be used; and (3) for more gas a moderate heating rate along with a higher pyrolysis temperature and long duration should be used [3].

2.1.3 Kinetics and Chemistry

Understanding the kinetics and chemistry of how pyrolysis and carbonization proceed is important to recognizing factors that affect the process and how to influence them for desired results. Pyrolysis can be thought of as four main thermal processes: (1) drying, which occurs at about 100 °C; (2) initial stage (100-300 °C); (3) intermediate stage (above 200 °C) where primary pyrolysis takes place; and (4) final stage (from about 300-900 °C) where the secondary cracking reactions take place [3].

In the drying stage, any moisture present in the biomass in the form of water is released and evaporated [3]. The initial stage has further dehydration of the biomass take place, where some gaseous products (CO and CO₂) are released in addition to more water [3]. Primary pyrolysis produces most of the products associated with carbonization (char, bio-oil precursors, more gases) [3]. And finally, the secondary reactions occur to produce more char and other products (depending on conditions present) [3].

Although these stages generally describe the process of carbonization/pyrolysis of biomass, it is hard to model or predict kinetics for biomass as a whole since composition and properties can vary from source to source (i.e. different types of wood or plants).

Most kinetics models of pyrolysis consist of: (1) single stage one-step reaction using weight loss; (2) single stage with multiple reactions describing different reactions occurring at the same time; or (3) two stage multi-step reactions not necessarily occurring at the same time [3]. Each of these models has its own assumptions that represent simplification of the experimental conditions and processes. For example, the single stage one-step reaction utilizing weight loss assumes that there is no ash and that moisture stays with the non-char products produced [3]. A simplified general equation of this kind of kinetics model is as follows [3]:

\[ X = 1 - A(e^{-\frac{Et}{RT}}) \]  

(Eq. 1)

Where \( X \) represents the fractional change in biomass, \( A \) is a coefficient dependent on the material, \( E \) is the activation energy, \( R \) is the gas constant, and \( T \) is the temperature. Of course, this represents a very simplistic model of pyrolysis, and thus the models only complicate from here.
Based on the biomass composition and other factors, pyrolysis/carbonization can produce its own heat after a certain amount of time [3]. Several reactions consisting of dehydration, depolymerization, and cracking comprise the majority of the reactions occurring during pyrolysis. Some of these reactions are endothermic while others are exothermic. While pyrolysis of lignin and hemicellulose is known to be entirely exothermic, at lower temperatures pyrolysis of cellulose is actually endothermic; at higher temperatures it is also exothermic [3]. Equations 2 – 5 below show the exothermic reactions which tend to occur at higher temperatures (>450 °C) and overcome the endothermic reactions [3].

\[
\begin{align*}
\text{CO} + 3\text{H}_2 &\rightarrow \text{CH}_4 + \text{H}_2\text{O} - 226 \text{ kJ g}^{-1} \text{mol}^{-1} & \text{(Eq. 2)} \\
\text{CO} + 2\text{H}_2 &\rightarrow \text{CH}_3\text{OH} - 105 \text{ kJ g}^{-1} \text{mol}^{-1} & \text{(Eq. 3)} \\
0.17\text{C}_6\text{H}_{10}\text{O}_5 &\rightarrow \text{C} + 0.85\text{H}_2\text{O} - 80 \text{ kJ g}^{-1} \text{mol}^{-1} & \text{(Eq. 4)} \\
\text{CO} + \text{H}_2\text{O} &\rightarrow \text{CO}_2 + \text{H}_2 - 42 \text{ kJ g}^{-1} \text{mol}^{-1} & \text{(Eq. 5)}
\end{align*}
\]

Heat transfer is also of significance with respect to pyrolysis and carbonization as it is the primary mechanism by which the biomass can reach the temperature at which it starts to decompose. The biomass is heated through radiation and convection from the furnace or heating source, and that heat is then conducted throughout the particle or material through conduction and pore convection [3]. In slow pyrolysis the rate limiting step for heat transfer is usually the secondary transfer from within the particle, and vice versa for fast pyrolysis. This is also aided by the fact that larger particles are typically used in slow pyrolysis. If the particle size varies enough there can be inhomogeneity in the carbonization procession of each particle [1].

2.1.4 Carbon Materials

From a broader perspective, this section will instead cover some of the common allotropes of carbon known. Carbon itself is a very important material for life on earth. In fact, all life on earth is carbon-based, making it an essential element of life. Interestingly, carbon forms many different allotropes of physical structures, despite all being composed of carbon. Many of these allotropes are represented, as seen in Figure 6.
Figure 6 – Different allotropes of elemental carbon [10].

The most well-known allotropes consist of diamond, graphite, carbon nanotubes (CNTs), and fullerenes [10]. The difference in bonding between carbon atoms is what produces some of the differences between allotropes (i.e. diamond vs. graphite) [10]. Other differences come from molecular structure, such as when comparing fullerenes and carbon nanotubes (CNTs). Graphite is one of the most common forms of carbon present and consists of stacked single layers of carbon bonded to each other [10]. Each of these layers is known as graphene, and when stacked together makes graphite. Diamond is another well-known allotrope of carbon formed under high pressures with a crystalline structure where each carbon is bonded to another four carbons, which is different than the atomic bonding of graphite [10].

Carbon can also exist in an amorphous form, where there is no ordered structure to the material. Where diamond carbons are bonded to four other carbons using $sp^3$ bonds only, amorphous carbon can contain both $sp^3$ and $sp^2$ bonds [11]. $sp^2$ comprise all of the bonding in graphite/graphene, as well as fullerenes [10]. Carbons bonded with $sp^3$ orbitals contribute more to the mechanical properties of the resulting material since single covalent bonds are harder to break, while carbons bonded with $sp^2$ orbitals contribute more to optical properties due to the aromaticity and delocalized electrons [11]. This is reflected in the properties of diamond, which is known to be one of the hardest and strongest materials but is generally optically transparent.
2.2 Pistachio shell

Returning to the concept of biomass, these sections will go more in depth with respect to biomass in general and cover some literature involving pistachio shell, the biomass utilized in the research in this thesis. Pistachio shell is a common food waste ingredient generated as part of the pistachio nut on the pistachio tree. The shell is generally rather dense and hard, so there is potential for use in other applications.

A biomass is essentially organic material that has originated from plants and animals, and can be solid, liquid, or gaseous in nature [3]. It is produced through typical interactions between compounds like CO$_2$, sunlight, air, water, etc. that occur during an organism’s life cycle [3]. One important distinction to note is that a biomass is considered greenhouse gas neutral as the carbon and CO$_2$ is utilized throughout the life cycle and itself does not produce any more CO$_2$ [3].

2.2.1 Composition and Structure of Biomasses

There are many different types of biomass, based on the large variety of plant life present on Earth. As mentioned before, the three main components of a biomass are lignin, cellulose, and hemicellulose [3]. These components make up the fibrous/nonstarchy parts of a biomass that are less digestible by humans [3]. Even between different plants and trees, the percentage of lignin to cellulose to hemicellulose can vary a large amount [3]. Other components present in a biomass include extractives (protein, oil, starch, sugar, etc.), the cell wall (carbohydrates, cellulose/hemicellulose/lignin), and ash (inorganic leftovers) [3]. Looking at something like wood, wood is usually made up of long hollow cells parallel to each other [3]. Cellulose, one of the constituents present in the cell wall, is known as the most common organic compound present on Earth [3]. As previously mentioned, cellulose is a very linear long chain polymer with a degree of polymerization greater than 10000 and thus a high molecular weight [3]. It usually makes up 40-44% of wood [3]. The repeating unit of cellulose can be seen in Figure 7.

![Figure 7 – Repeating unit structure of cellulose [3].](image-url)
Hemicellulose, also mentioned previously, is a more branched polymer that exists in an amorphous instead of crystalline structure, lending it less thermal stability than cellulose. Figure 4 in a previous section showed the structures of cellulose compared to hemicellulose and lignin. Hemicellulose produces more gaseous products compared to cellulose, which produces more bio-oil compounds. This is likely due to the fact that during degradation more shorter chain organic compounds are produced in molecular cracking, leading to more volatile compounds. In addition, when compared to cellulose, hemicellulose constitutes 20-30% of most wood [3].

Finally, lignin makes up the last part of the trio of molecules that forms most of the material in the biomass. Lignin is a highly branched polymer and thus degrades more quickly than cellulose. It forms about 20-30% of most woods and acts as a binder for holding cells in the biomass together [3].

2.2.2 Pistachio Shell in Literature

Some research has been conducted investigating pistachio shell and its combustion. One particular paper from the Environmental Science and Pollution Research publication examined the combustion of pistachio shell to determine its composition. In that paper, da Silva et al. used proximate analysis on pistachio shell and determined it to have low moisture and ash (inorganic) present, making it ideal for combustion and pyrolysis. Ultimate analysis identified approximate percentages of C, H, O, N, and S present in pistachio shell with almost equal parts C and O present, at about 45% and 48 respectively. In addition, there were near negligible amounts of S and N, and some H present (5%). Figure 8 shows FTIR conducted on the milled pistachio shell. As can be seen, immediately identifiable peaks include the large broad peak at 3412 cm\(^{-1}\) which corresponds to -OH functional groups, indicative of the hydroxyl groups present in lignin, cellulose, and hemicellulose. At the same time, other peaks demonstrate the presence of bonds expected in pistachio shell based on the structures of lignocellulosic compounds [5].

![Figure 8 – FTIR conducted on pistachio shell [5].](image-url)
Utilizing DTA/TGA (differential thermal analysis/thermogravimetric analysis) up to 1000 °C, the degradation of pistachio shell was observed by da Silva et al. in an inert and oxidative atmosphere. Two main regions of interest in the DTA/TGA plots were present throughout both atmospheres but were located at different temperature ranges depending on the atmosphere. The first region existed around 200-400 °C for both inert and oxidizing atmospheres and likely represents the breakdown of hemicellulose, which was identified to have weak intermolecular forces and a lower thermal stability, as discussed earlier in this thesis [5]. The second region illustrates the degradation of cellulose after 325 °C, while lignin tends to degrade over the entire temperature range [6]. These two ranges were pushed to higher temperatures for DTA/TGA performed in an oxidative atmosphere [5]. These can be seen in Figure 9a-b, seen below:

![Figure 9 – Thermal degradation plots for pistachio shell: (a) TGA, (b) DTA [5].](image)

Another study on pistachio shell by Açkaln et al. investigated the products of this pistachio shell pyrolysis as opposed to combustion and also focused on the byproducts [12]. In this study, it has been confirmed that pyrolysis and combustion are similar, but pyrolysis occurs in an inert atmosphere, which is as has been stated and explained earlier. In general, during the process of pyrolysis and carbonization, several different reactions and processes occur, many of which were covered in the previous section in Equations 2 – 5. However, these pyrolysis and carbonization processes are complex, requiring optimization of many factors to achieve the desired product, such as temperature, heating rate, atmosphere, and initial individual material properties [12]. For example, other studies have shown a maximized bio-oil production at about 500-550 °C with a high heating rate and a lower gas flow rate to flush out gaseous products [12].
This particular study from the Fuel publication, conducted by Açkalı et al., investigated the effect of pyrolysis temperature, reaction time, and flow rate of the gas. It was found that bio-oil production increased from 350 to 500 °C but began to decrease beyond that temperature range. Simultaneously, gaseous production also increased over the same temperature range; however, unlike its liquid counterparts, gas yield continued to increase above 500 °C. In contrast, the solid product yield decreased over the entire temperature range of 350-650 °C [12].

Reaction time did not influence yields by a large amount. Examples of this are that bio-oil production decreased slightly upon increasing reaction time from 10-50 minutes, while gas production increased slightly over the same range of increasing time. On the other hand, solid char production stayed about the same across the time range. Therefore, upon increasing gas flow rate, liquid yield decreased while gas production increased and solid char decreased somewhat [12].

Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) were used to characterize the pyrolyzed pistachio shells and study their structures and properties. Interestingly, SEM conducted on the pyrolyzed pistachio shell found that porosity appeared to increase with pyrolysis temperature. This was likely attributed to the increase in the amounts of liquid/gaseous products exiting each particle during the carbonization process. FTIR demonstrated increasing aromaticity followed by decreasing aromaticity within the temperature range of 350 to 650 °C. The presence of the large broad peak around 3500 cm⁻¹ which is indicative of -OH bonding, was present across all temperature ranges. Based on the information from FTIR, the paper concluded that carbonization had mostly finished by a temperature of 650 °C [12].

2.3 Particle-Reinforced Composites

Composite materials are of interest in many engineering applications due to their unique properties that result from a combination of different types of materials. Generally, a composite can have as little as two different components or phases but can also contain more than that. Due to their desirable properties, composites have been utilized in many different applications, some of which are recognizable by people in their day to day lives. Relevant to the research in this thesis, some particulate composites have been used in brake pads to absorb and convert kinetic energy into heat energy using friction to stop moving systems by utilizing their wear resistance. Typically, graphite, polymers, metals and ceramics can be used in brake pads [13].
Particulate composites (and composites in general), depending on their composition and microstructure, can have properties leaning towards certain constituents compared to others. These properties can also be manipulated by changing their compositions and microstructures [13].

### 2.3.1 Relevant Properties of Particulate Composites

Hardness is one of many other properties of composites that make them useful in certain applications and is also one of the main reasons for the making of composites. Depending on the types of the components or phases and interactions between these components or phases, hardness can follow different models of varying complexity. For example, simple linear volume fraction-based models (i.e., the rule of mixtures) are accurate with composites where no chemical interaction occurs between different components or phases [13]. Equation 6 below demonstrates the linear model, $H_{\text{Composite}}$ [13]:

$$H_{\text{Composite}} = V_1 H_1 + V_2 H_2 \quad \text{(Eq. 6)}$$

Where $V_1$ and $V_2$ represent the volume fractions of each component, and $H_1$ and $H_2$ represent the hardness values of each component, both respectively. However, microstructure can have a large effect on the hardness of the composite [13]. For example, contiguity, which is a measure of the number of grains in contact with other grains composed of the same material, can add an extra parameter to the predicted hardness [13]. Perhaps more well-known is the hardness predicted by the Hall-Petch relation, shown below in Equation 7 [13]:

$$H_{\text{Composite}} = H_0 + \frac{K_G}{\sqrt{G}} \quad \text{(Eq. 7)}$$

Where $H_0$ is the hardness at a large grain size, $K_G$ is the grain size sensitivity parameter, and $G$ is the grain size. It can be seen from Equation 7 that the grain size and microstructure size influence the hardness of the composite. At the same time, other factors like porosity, residual strain, and solubility can also influence hardness, depending on the composite system itself [13].

As mentioned earlier, for the use of particle-reinforced carbon matrix composites in an application like brake pads, thermal conductivity is also an important property of relevance and we should pay a great deal of attention to it, especially when it leads to structural deformation or wear in the brake pad materials which may consist of composites. Generally, thermal conductivity represents the transfer of heat energy over a certain period of time [13]. Therefore, for applications where high thermal conductivity is desired, typically a low coefficient of thermal expansion also applies [13]. Thermal conductivity is typically a function of the properties of each component of the composite (particles and matrix) and the degree of connection between particles, which means that every phase is not continuous. A simplistic linearly related rule of mixtures model can be used to model thermal conductivity as well, but more complicated
models can arise due to microstructural features and interface properties. Porosity generally does not impact thermal conductivity unless there is more than 50% of it, but if so, it will decrease with increasing porosity. This is likely due to the fact that the amount of air present in pores at less than 50% porosity is not enough to change the overall thermal conductivity. In addition, larger grain size is better for conductivity as there will be less changes in grain orientation and thus the directionality of the conduction of heat [13]. In addition, increased interface area will decrease conductivity as more heat ends up dissipated rather than travelling through the material [13].

Finally, one last property or material behavior of importance in particulate composites is deformation and fracture. Often times, the idea behind designing composites is to create materials that have good properties such as toughness and behavior under stress. One factor in determining whether or not the reinforcement will positively influence failure behavior is the nature of the interface between the matrix and particles. A strong interface leads to better load transfer from the matrix to the particle, increasing the toughness as a crack must propagate through both materials. The interface can also influence other mechanical properties like impact strength, fatigue, and strain hardening [13]. Figure 10 demonstrates the various modes by which a crack can interact with a particle in a composite.

![Figure 10 – Crack propagation paths through or around a particle [14].](image)

Thus, it can be concluded that toughness depends very much on the microstructural features and properties of the composite, just as its other mechanical properties do as well. Therefore, large amounts of porosity will decrease toughness, whereas the ideal particle size will maximize toughness [13].
2.3.2 Ceramic Matrix Composites

Ceramic matrix composites (CMCs) are composite materials made with a ceramic as the matrix material. Ceramics have many desirable properties, such as high stiffness/hardness, low density, wear resistance, corrosion resistance, and thermal stability at higher temperatures [14]. However, one well-known and apparent weakness of ceramic materials in general is their low fracture toughness, which naturally makes them very brittle and fragile. Therefore, CMCs aim to adequately address this key issue by typically using reinforcements to increase the toughness of monolithic ceramics.

Ceramics and CMCs by default have a higher durability and stability, particularly in more extreme environments (i.e. high temperatures and chemically corrosive) or when it comes to longevity. Due to their high strength, they are often used in structural applications and buildings (i.e. concrete, or steel bar reinforced concrete) as well as in aerospace applications where they must endure extreme conditions [15]. However, as mentioned, their low fracture toughness which makes them brittle often comes from small critical crack sizes [14]. This means that the size of a flaw necessary to cause catastrophic failure is very low. Typical reinforcement used in CMCs to improve fracture toughness include fibers or whiskers. Often used are also ceramic fibers in a ceramic matrix. In this case, the matrix will actually fail first; proper interfacial bonding is necessary to prevent failure of the reinforcement [15].

Discontinuous reinforcement has also been used with CMCs, and can consist of particles, platelets, or even fibers, as long as there is no particular order or distribution within the matrix. Using discontinuous reinforcement has the benefit of reducing the cost of processing, as it can be manufactured without too much difference compared to monolithic materials. In addition, their properties are isotropic due to the randomness of the orientation of the reinforcement and can have fracture toughness significantly greater than the ceramic material by itself. Particle reinforced CMCs are typically used in applications where high hardness or wear resistance is desired, such as cutting tools or repeated use dies or inserts, bushings, etc. Further, as mentioned earlier, CMCs typically have excellent thermal stability, so any extreme environments that merely require maintenance of properties at high temperatures would be suitable for CMCs [2].

Toughening mechanisms for CMCs include a thermal coefficient mismatch between the matrix and the reinforcement phase. The residual thermal stress that forms from this mismatch comes from the coefficient of thermal expansion (CTE) for the matrix being lower than that of the particle, resulting in shrinkage between the particle and matrix. The shrinkage then causes residual compressive stress around each particle, which discourages crack propagation that usually has tensile stress surrounding it, as demonstrated and shown in Figure 11 [16].
2.3.3 Carbon Matrix Composites

The carbon matrix composites are perhaps most relevant to the research in this work. Most common carbon matrix composites consist of carbon or even ceramic fiber reinforcing a carbon matrix material. These kinds of composites have high mechanical stability even at higher temperatures and have found uses in such environments. However, they tend to be prone to oxidation at a lower temperature (400-500 °C), though in inert atmospheres that oxidation temperature is significantly higher [13, 17]. Since brake pads usually heat up to about 200 °C for normal use, this is typically not a concern; however, for higher performance use (i.e. racing), temperatures can reach past 500 °C [18]. Carbon as a matrix material is known to be brittle and low in strength and stiffness. They also happen to have very low density, making them ideal in applications where weight is a significant factor. In addition, they can have high thermal conductivity as well as low CTE [14]. Often, carbon matrix composites have uses as a brake pad material due to their capability for high energy absorption in addition to lightweight properties [17].

Thermal stability comes from high bond strength, activation energy, heat capacity, and chemical structure features that discourage molecules from moving around too freely. Bond energy, the energy required to break bonds between atoms, represents bond strength; bonds between aromatic carbons and some other atoms are known to have the highest bond energies, making them very strong and stable at higher temperatures. On the other hand, having lower activation energy for certain reactions (i.e., oxidation) can cause a decrease in thermal stability. A similar conclusion can be drawn for heat capacity in terms of storing heat energy where having greater bond energies results in higher heat capacities. Carbon matrix composites are known to have a higher heat capacity than many other materials; graphite has a heat capacity of about 0.71 J/g*K, but diamond has a higher heat capacity despite consisting of the
same elemental carbon. Finally, steric hindrances in the molecule and rigid bonds between atoms also contribute to higher thermal stability by increasing the amount of energy needed to move bonds and atoms around [19].

The manufacturing costs of carbon matrix composites tend to be on the high side just by the nature of producing the material itself. There is generally no “powder” carbon available, at least not in the form required for the composite. Therefore, the carbon needed for the matrix is made by carbonizing a certain precursor with the reinforcement embedded inside, which then produces the carbon matrix [15, 19]. Figure 12 below shows a diagram for how a carbon-carbon composite might be produced. However, as-produced carbon like this invariably tends to be very porous and can be either isotropic or anisotropic in essential nature, typically depending on the exact production methods used. The anisotropic nature of the matrix and reinforcement present may typically lead to microcracking in the matrix as a direct result of CTE mismatch [2].

![Diagram of production of carbon-carbon composites](image)

**Figure 12 – Diagram of production of carbon-carbon composites [2].**

Graphite, one of carbon’s more common allotropes, exhibits a hexagonal crystal structure. With an extraordinary abundance of oxygen present and little to no hydrogen, carbon does not tend to simply produce graphite in its typical hexagonal structure. Regardless of how the carbon forms, in its crystalline form it exhibits anisotropy in its properties. In addition, the presence of large amounts of porosity also influences the final mechanical properties of the composite [20].
2.3.4 Reinforcement Materials

Reinforcement is arguably one of the most important aspects of a composite material. Depending on the material, it can strongly influence the final properties of the composite as a whole. Previous sections described the relevant matrix materials used in composites as it relates to this research. This section will describe reinforcements instead.

Reinforcement phases can be considered continuous or discontinuous. Continuous reinforcement usually consists of material that is aligned in a certain orientation or direction, such as fibers or sheets. Discontinuous reinforcement has no orientation and is usually dispersed randomly within the matrix material, and generally consists of particles, platelets, or even short fibers. Commonly known continuous reinforced composites include fiber reinforced composites or laminar composites. Fiber reinforced composites are anisotropic, just by nature of the alignment of the reinforcement phase. Particulate composites are extremely cheap in comparison and provide their own benefits to the composite itself, despite not being as strong or stiff [17].

2.3.4.1 Titanium Carbide (TiC)

Titanium carbide (TiC) is a well-known carbide that exhibits extremely high hardness and other desirable properties such as thermal and chemical stability. Carbides are typically very hard and thermally stable at higher temperatures [13]. TiC specifically is a refractory material used in cutting tools and other wear resistant applications such as brake pads and abrasives [13]. Table 1 below shows some relevant properties of TiC.

<table>
<thead>
<tr>
<th>Property</th>
<th>TiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>4.9 - 5.0</td>
</tr>
<tr>
<td>Melting Temperature (°C)</td>
<td>&lt; 3070 °C</td>
</tr>
<tr>
<td>Hardness (HV)</td>
<td>2500 – 3200</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>315 - 440</td>
</tr>
</tbody>
</table>

TiC is most commonly synthesized by reducing TiO₂ with carbon present [20]. This synthesis method produces a lot of TiC powder, but is unable to produce TiC with a submicron particle size [20]. Some research has been conducted in recent years to investigate the formation of TiC powder through the same carbothermal reduction but utilizing carbon coated TiO₂ powder instead to tackle the lower particle size [21]. The chemical equation for the general reduction is seen below [21]:

\[
TiO_2 + 3C \rightarrow TiC + 2CO(g) \quad \text{(Eq. 8)}
\]
Other methods of synthesis include chemical vapor deposition, self propagating high temperature synthesis (multiple avenues), mechanical alloying, and more. TiC has a cubic structure similar to NaCl when crystallized and the carbon atoms will occupy octahedral interstitial sites. The phase diagram for the Ti-C system is shown in Figure 13, and shows multiple phases, including TiC, $\alpha$ – Ti, $\beta$ – Ti, liquid phase, and a graphitic phase [22].

![Phase diagram of Ti-C system](image)

**Figure 13 – Phase diagram of Ti-C system [22].**

At 1 atm and 273 K, also known as standard temperature and pressure (STP), the heat of formation of solid TiC is about -184.10 kJ/mol [23]. In addition, the heat capacity of TiC increases as temperature is increased. Figure 14 demonstrates a model used for heat capacity.

![Heat capacity model plot for TiC](image)

**Figure 14 – Heat capacity model plot for TiC [23].**
2.3.4.2 Titanium Dioxide (TiO$_2$)

Titanium dioxide or TiO$_2$ is another reinforcement material of interest in the research being conducted in this thesis. It is typically white in color and is used in many different applications as a ceramic type material. Part of the reason for its widespread usage is its low cost of production and high thermal stability, a property it shares with TiC [13]. Applications include toothpaste, sunscreen, and insulation material [8]. Some of the relevant properties of TiO$_2$ are listed below in Table 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($g/cm^3$)</td>
<td>4.17</td>
</tr>
<tr>
<td>Melting Temperature ($°C$)</td>
<td>1830 °C</td>
</tr>
<tr>
<td>Hardness (HV)</td>
<td>1000</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>282</td>
</tr>
</tbody>
</table>

When compared to TiC, TiO$_2$ seems to exhibit significantly lower mechanical and thermal properties. TiC has a higher hardness, melting temperature, and elastic modulus. TiO$_2$ exists in three main phases: 1) rutile, 2) anatase, and 3) brookite. Rutile is most common and is what exists at higher temperatures (above 400-600 °C), where a phase transformation into rutile occurs, as seen in Figure 15a. However, anatase is more stable at smaller particle sizes (below 14 nm), so depending on the conditions different phases of TiO$_2$ can form. Brookite is a significantly rare form of TiO$_2$ and thus is not produced or seen in nature as often [24]. The main difference between all three phases are their crystallographic orientations [24]. Figures 15a and 15b below show the phase diagram for a Ti-O system and the stability of different phases of TiO$_2$ at different temperatures and pressures [25, 26].
Figure 15 – Relevant phase diagrams showing: (a) Ti-O system [24], (b) TiO₂ phases pressure vs. temperature diagram [26].

At STP, the enthalpy of formation for rutile and anatase TiO₂ is about -938.72 kJ/mol. Similar to TiC, the heat capacity of TiO₂ also changes with temperature, and Figure 16 shows a plot for the TiO₂ variation in heat capacity [23]. The lower enthalpy of formation for TiO₂ vs. TiC is indicative that at lower temperatures TiO₂ is more likely to form.

Figure 16 - Heat capacity model plot for TiO₂ [23].
3. Experimental

The following sections will detail everything involved with the materials, methods, and experimental design of the research conducted for this thesis.

3.1 Materials

The two main materials used to create each sample was titanium powder and whole pistachio shells. The titanium powder was supplied by Alfa Aesar at 99.5% purity and 325 mesh, yielding a particle size of about 44 microns [26]. The pistachio shells were collected from the food grade pistachios after the nuts were removed and the shells were washed with tap water and air dried.

3.2 High Energy Ball Milling

In order to produce a fine powder from the starting materials, the pistachio shells and titanium powder was milled using high energy ball milling. Due to the oxidative nature of pure titanium powder, a glove box with a vacuum and purge gas was used to handle mass measurements of material. A Labconco Protector Glove Box with argon gas was used to reduce contact of the titanium with atmospheric oxygen. Therefore, the milling container was properly sealed in the glove box to ensure the milling occurred in an inert atmosphere to reduce the risk of a spark of fire from the titanium powder. Another glove box, the MBRAUN LABstar pro, was also used to measure out powder and close off containers for milling. In order to utilize the second glove box, the pistachio shells were further dried overnight using a Thermo Scientific™ Vacuum Oven set to about 60 °C.

A SPEX 8000M Mixer/Mill, as shown in Figure 17, was used to perform the milling with three ½” diameter WC balls, each weighing about 16 g. A total weight of 24.0 g of pistachio shell/titanium was used with the three WC balls, giving it a charge ratio of 2:1 (material to be milled weighs 24 g, total WC balls weigh about 48 g). Tungsten carbide (WC) is a very hard material, allowing it impact and break up the pistachio shell over a certain period of time. Furthermore, it also mills the titanium powder as well as mixes the powder together into a homogeneous mixture. Each composition of pistachio shell/titanium powder was milled for up to 15 hours.
3.3 Sample Pressing

After milling the materials for the appropriate amount of time, the powder was then pressed into small discs using a uniaxial press. No binder or filler was added during this process; only the milled powder of pistachio shell/titanium mixture was used. A uniaxial press with a cylindrical die (Bench Top Manual Press from Carver Inc.), seen below in Figure 18, was used to press the samples. Approximately 0.75 g of each milled powder was compacted in a \( \frac{3}{4} \)" diameter die mold and about 4 mm thick with maximum pressure of about 11 metric tons for 5 minutes. Samples ranged from 3.98-4.24 mm thick. For consistency, anti-rust spray was used to wipe down the die when necessary in between samples. Figure 18 below shows a picture of the press used.

Figure 18 – Carver Inc. Bench Top Manual Press.
3.4 Heat Treatment

After pressing, the samples were then heat treated in a tube furnace at different temperatures. More specifically, samples were carbonized, meaning they were heated to a certain temperature in an inert atmosphere. The temperatures varied from 800 °C to 1200 °C; more details are given in the Section 3.6.2. The inert atmosphere was provided by an influx of argon gas for the duration of the entire heat treatment process. After placing the samples in a crucible, the crucible was placed into the center of the tube and the exit of the tube was sealed. Argon gas was then allowed to flow into the tube until it had displaced all of the atmospheric air. Using a program on the furnace, the sample was then heated up to a certain temperature at 5 °C/min, held at that temperature for 1 hour, then ramped down to room temperature at the same rate. A slower rate of ramp up/down to temperature was utilized to prevent cracking and allow the sample to heat evenly. The heat treatment of the 5 hour milled samples was carried out by a Lindberg/Blue M™ 1500 °C Heavy Duty Tube Furnace.

A different furnace but same model as mentioned above was used to heat treat the 15 hour milled samples due to unavailability of the original furnace. Experimental conditions were kept the same, including use of argon gas, ramp rate, temperature, etc. However, it should be noted that this furnace had a discrepancy between the actual temperature inside the furnace and the temperature shown by the program during heating/cooling. This discrepancy only became significant/apparent once the furnace went above 1000 °C. Therefore, it must be mentioned that all samples labeled as heat treated to 1200 °C averaged about 1150 °C and the samples heat treated to 1100 °C averaged about 1080 °C for the hour.

3.5 Characterization

After milling the pistachio shell and titanium powder together, pressing them into disks, and heat treating those disks, multiple characterization techniques were used to gain information on properties and microstructure. This section details the characterization techniques used and why.

3.5.1 X-Ray Diffraction

X-Ray Diffraction (XRD) is a common characterization technique used to determine crystalline structures present in materials and potentially acquire qualitative information on compounds present for identification and chemical identity. The XRD used in this research was X-Ray Powder Diffraction, done on the heat treated disks, yielding a graph-like image from which the pattern of peaks can be matched to a database to identify compounds present. The graphs for each sample can be found in the appendix but show the angle 2θ on the x-axis and the counts recorded on the y-axis. Wide angle XRD was conducted on
all samples using the Bruker XRD D8 ADVANCE, as shown in Figure 19, with a Cu tube producing x-rays at a wavelength of 1.5418 Å. In this work, a voltage of 40 kV and a current of 40 mA were used to produce the x-rays, and the LYNXEYE 1D detector was used to detect the diffracted rays. In addition, the twin primary slit was set at 1.000 mm and the twin secondary slit was set at 5.000 mm. The scan was set to Coupled Two Theta/Theta and the mode to Continuous PSD fast. Finally, counts were recorded at 0.5 second intervals for about 1000 total counts across the entire scan. Afterwards, the DIFFRAC.EVA software was used to carefully remove the background from the XRD spectra, correctly identify and carefully match the notable peaks to the comprehensive database of essential elements and compounds.

![Figure 19 – Image of XRD system [28.](image)](image)

### 3.5.2 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is another commonly used characterization technique to characterize the thermal properties. TGA allows decomposition and degradation information to be gleaned from the samples tested. It works by recording weight loss vs temperature, then records the data in a curve. Certain curve shapes as well as peaks in the weight loss derivative curves show the onset temperature for a certain reaction that occurs. For the research being conducted in this work, this is of concern as the process of carbonization is used to form a bulk dense char, and carbonization is essentially a decomposition reaction. The samples tested were the milled powder mixtures of pistachio shell and titanium for each composition and milling time. TGA was conducted in a TA TGA 5500, as shown in Figure 20, using a nitrogen atmosphere at a mass flow of 40 mL/min. The running program consisted of a 10-minute isothermal section at room temperature to purge atmospheric gas from the chamber, followed by a ramp section up to 1000 °C at 5 °C/min. Afterwards, the sample was held at 1000 °C for 1 minute then...
ramped back down to room temperature at the same rate as before. Graphs were then analyzed using
TRIOS and onset points of each peak were calculated.

![Image of TGA system](image_url)

**Figure 20 – Image of TGA system [29].**

### 3.5.3 Optical Microscopy

Optical microscopy is a more qualitative characterization technique used to examine the
microstructure and topography present in materials. Many optical microscopes can have extremely high
magnifications, resulting in being able to see detailed microstructural and topographical features.
However, it can only reveal the physical characteristics of the surface of whatever material is being looked
at. Despite this limitation (and others), it is still a useful method for quickly examining materials for further
study and determining what is worth investigating further with other characterization techniques. An
Olympus BH-2 optical microscope was used to look at all the samples with objective magnification ranging
from 5x, 10x, 20x, 50x, and 100x. A polarizing filter was sometimes used to take pictures of the samples
as well and will be labeled as such in any figures.

In order to prepare samples for microscopy (optical and SEM/EDS), the heat treated disks were
cut with a Buehler IsoMet 1000 Precision Saw into small pieces using a LECO 4” diamond blade. These
small pieces were then mounted in a phenolic polymer mounting supplied by Precision Surfaces
International, Inc. using an Allied TechPress 2™ mounting machine. Then, each mounted sample was
grounded using 240, 400, and 600 grit SiC sandpaper on a Buehler Ecomet 3 Variable Speed Grinder-Polisher.
Using the same machine, the samples were then polished with different sizes of high purity alumina
($\text{Al}_2\text{O}_3$) suspension in multiple steps: (1) 5 μm $\text{Al}_2\text{O}_3$ with a nylon cloth; (2) 3 μm $\text{Al}_2\text{O}_3$ with a nylon cloth;
(3) 0.3 μm Al₂O₃ with a suede cloth; and (4) 50 nm colloidal silica with a suede cloth. After each step, prepared samples were rinsed with distilled water and sonicated for three minutes in an ultrasound bath before moving up in grit.

### 3.5.4 Scanning Electron Microscopy/Energy Dispersive Spectroscopy

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) are another set of extremely useful qualitative characterization techniques available. Unfortunately, SEM/EDS can be expensive to use (let alone have the equipment for) and it can often be more time-consuming than optical microscopy. However, the information it yields can be very useful for research being conducted as it can provide qualitative imagery of the surface and just below the surface, depending on the mode used. For example, if backscattered electrons are detected, surface topography is the main output in terms of imaging. As a consequence of different atomic numbers in the sample, secondary electrons can give more information on what is below the surface of the sample as well as show contrast between different phases as a consequence of this. In addition, SEM used in conjunction with EDS can provide even more detailed information regarding the elemental composition present in the material in a quantitative format.

Once samples are mounted and grinded/polished, they were then sputtered using a Cressington 208HR High Resolution Sputter Coater which deposited about 5 nm of Au-Pd atoms on the surface of the samples to make them conductive enough for SEM/EDS. Afterwards, the samples were then loaded into a JEOL IT500 SEM for characterization.

### 3.5.5 Hardness

Hardness is a quantitative characterization technique used to provide information on the mechanical properties of a material. More specifically, the hardness test looks at the ability of the material to resist deformation in response to a given stress. Hardness also relates very closely to strength and stiffness of the material. However, for this research hardness is specifically important to understand the material’s potential for wear/abrasion applications. Vickers hardness was measured using a LECO V-100-A2 Hardness Tester, seen in Figure 21. This microhardness tester utilized a chart for comparison to the measured diagonal values to get the final HV number. A load of 5 kg with a dwell time of about 10 seconds was used. Three tests were performed on the surface of each sample and on the cross section if there were no good locations (i.e. due to a crack or too many previous indentations present in the area).
3.6 Design

Another important aspect of this research is the experimental design. Changing some factors while keeping others constant is essential for understanding how certain things might affect the properties and microstructure of the material. This section details the variables examined and the constants for all the samples created.

3.6.1 Milling Time

Milling time of the powder mixture of pistachio shells and titanium during processing was one variable investigated for this thesis. Although the pistachio shells become crushed into very fine powder rather quickly, choosing to mill the powders for a longer time can eventually make the powder mixture finer and more homogenous. For this research, the mixture was milled for 5 hours and 15 hours to investigate this effect. A reference of pistachio shell powder which contained no titanium was milled for 15 hours.

3.6.2 Temperature

Temperature at which the samples were heated to was another factor investigated. As mentioned previously, temperature for carbonization can greatly influence the products produced as well as the final
structure of the sample. In addition, temperature also influences cost of manufacturing; if a higher temperature is used, that costs more energy. The research conducted investigated carbonization temperatures from 800 °C – 1200 °C in increments of 100 °C, meaning five different temperatures were used. In addition, one sample utilized a lower temperature, 600 °C at a 24-hour duration to see what would happen, though this was not repeated with all the other samples.

3.6 Composition
Composition was the last variable investigated in this thesis. As stated before, the powder mixture consisted of a mixture of pistachio shell and titanium powder. Two different compositions were used: one with 5 wt% titanium powder with the rest of the mass from the pistachio shell, and the other with 10 wt% titanium powder. Varying composition allows one to see how increased or decreased presence of certain elements/compounds may influence the microstructure or compounds formed in the final material.

3.6.4 Constants
Finally, this subsection covers the factors held constant over the entire experiment. All experimental conditions had three replicates of samples, while the reference pistachio shell only sample had two replicates. In addition, for every condition the carbonization temperature was held at a duration of 1 hour before ramping back down to room temperature. The exception to this is a single sample heated to 600 °C for 24 hours. Particle size of the titanium powder as added to the mixture was also another constant in this experiment.
4. Results

This chapter contains results from each of the characterization techniques described in the previous chapter. Experimental conditions for each technique have also been described previously. The characterization was typically done in a certain order. For example, X-Ray Diffraction (XRD) was done before optical microscopy and SEM since XRD is non-destructive and does not require a mounted/polished surface. In addition, TGA was conducted on the milled powder pre-heat treatment so waiting until heat treatment of the samples was completed was not necessary. Optical microscopy was done before SEM to help narrow down features and points of interest to look for. Finally, hardness was completed after all other techniques as it is somewhat destructive and required a polished mounted surface.

The surface of the pressed samples looked smooth and homogeneous with a gray color, as shown in Figure 22a. Meanwhile, the surfaces of the heat treated samples were dark gray or black and smoother at lower heat treatment temperatures, seen in Figure 22b. Higher temperatures exhibited more cracking on the surface and horizontally through the samples. In addition, pressed samples shrunk significantly after heat treatment. Shrinkage increased as temperature increased and is numerically specified by the contents of Tables A and B in the Appendix; though on average samples shrunk about 33% from their original size.

4.1 X-Ray Diffraction (XRD)

XRD conducted on each heat treated sample showed that there was a crystalline material, illustrated by thin sharp peaks in the plot. Comparison plots shown in Figures 23 – 26 show XRD data for each sample, differentiated by milling time and composition. It should be noted that these XRD plots have had the background subtracted and flattened to make the pattern more apparent.
Figure 23 – XRD patterns of 5h milled heat-treated samples containing 5 wt.% Ti.

Figure 24 - XRD patterns of 5h milled and compacted heat-treated samples containing 10 wt.% Ti.
In general, all plots showed extremely similar if not the same peaks present at the same locations. This was true even across different compositions and milling times. Figures 25 - 26 show the XRD patterns for the 15h milled samples, again separated by composition.

Figure 25 - XRD patterns of 15h milled and compacted heat-treated samples containing 5 wt.% Ti.

Figure 26 - XRD patterns of 15h milled and compacted heat-treated samples containing 10 wt.% Ti.
Intensities for each peak present appear very similar or at least in the same range as each other sample, even across compositions, temperatures, and milling times.

4.2 Thermogravimetric Analysis (TGA)

TGA was conducted on all milled sample powders before they were pressed and heat treated. Experimental conditions for the TGA conducted are given in the previous section. Figures 27 and 28 show combined weight loss and derivative weight loss with respect to increasing temperature for the 5 hour milled powders for compositions of 5 and 10 wt.% Ti.

Figure 27 – TGA weight loss and derivative weight loss curves of a 5 wt.% Ti – Pistachio powder, milled for 5 hours.
In some of the TGA plots a large amount of background noise is apparent particularly with the derivative weight loss curves. The 5 hour milled samples shared many features, including significant weight loss occurring after 200 °C and 300 °C, as well as an increase in weight percent after 600 °C. The peaks in the derivative weight loss curve corroborate this since they occur at approximately the same locations on both plots in Figures 27 and 28.

On the other hand, there are some slight differences in the 15 hour milled samples containing titanium, as seen in Figures 29 and 30. Similar features to their 5 hour milled counterparts include the occurrence of significant weight loss at two temperatures, above 200 °C and 400 °C. The main notable difference with the 15 hour milled powder is that the increase in weight percent occurs above 700 °C instead of 600 °C. Otherwise, Figures 29 and 30 show similarity in derivative weight loss peak location to Figures 27 and 28.
Figure 29 - TGA weight loss and derivative weight loss curves of a 5 wt.% Ti – Pistachio powder, milled for 15 hours.

Figure 30 - TGA weight loss and derivative weight loss curves of a 10 wt.% Ti – Pistachio powder, milled for 15 hours.

Figure 31 shows a TGA plot for milled pistachio powder, taken as a reference powder with no titanium added. Again, similar features are present as in the other sample powders, most notably the weight loss above 200 °C and 400 °C. However, it differs from the other powders in that there is no weight
percent increase above 600 °C. The leftover weight drops to near zero at that temperature and nothing more occurs until the end of the test.

Figure 31 – TGA weight loss and derivative weight loss curves of pure pistachio shell powder, milled for 15 hours.

4.3 Optical Microscopy

Several optical micrographs were taken of all the heat treated composites after they were mounted and polished. Figure 32 shows micrographs for 5 hour milled samples heat treated at 800 °C. It should be noted that the images represent the cross section of their respective samples. It can be clearly noted that from Figure 32, the microstructures are typical composite microstructures. However, the similarities include a large amount of porosity within the matrix material (carbon) and the presence of brightly colored particles (from the titanium powder) as the reinforcement phase. These particles are similarly shaped across compositions, and even across different temperatures, as seen in Figure 33. Particle shapes vary from spherical, needle like, large, small, and even some irregular shapes. However, their distribution is random and homogenous across both compositions and temperatures.
The main difference between compositions is that the 10 wt.% Ti samples had a larger amount of reinforcement particles present. Of course, this is a logical explanation, as there is simply more reinforcement material added at the beginning. The more interesting differences in the microstructures of the samples come from changes in temperature, as seen in Figures 32 and 33. When comparing these two figures, a difference in the amount of porosity is observed. Figure 33 shows the heat treatment that occurred at 1200 °C, which has considerably less porosity in the matrix of the composite as compared with the samples that were treated at 800 °C. However, the pores on the high temperature heat treated samples present appear to be smaller in size. Furthermore, the reinforcement particles in the sample that were heat treated at higher temperatures display some porosity within their bulk themselves, whereas lower temperatures have almost no particles with porosity inside, as seen in Figures 32 and 33.
Figure 33 - Optical micrographs of a 5h milled sample cross section heat treated at 1200 °C for (a) 5 wt.% Ti photomicrograph at 10x, (b) 5 wt.% Ti photomicrograph at 50x, (c) 10 wt.% Ti photomicrograph at 10x, and (d) 10 wt.% Ti photomicrograph at 50x.

When comparing the 5 hour milled samples to the 15 hour milled samples, similar features were found between the two. Particle distribution, shape, and coloring were the same across milling times. The differences in porosity of the matrix within were more difficult to determine, though it appeared for the most part that porosity was reduced in the 15 hour milled samples, as seen in Figures 34 and 35. As can be seen from the Figures, similar trends in microfeatures as seen within the 5 hour milled samples across temperatures were present within the 15 hour milled samples. All particles were less than 50 μm long, and lengths and widths varied within a range of less than 20 μm to greater than 40 μm. Pores were also significantly smaller than 20 μm though large-scale cracks that were sometimes visible to the human eye were present as well. More macro-sized cracks were present in the 15 hour samples in comparison to the 5 hour milled samples, as shown in Figures 34 and 35.
Figure 34 - Optical micrographs of a 15h milled sample cross section heat treated at 800 °C for (a) 5 wt.% Ti photomicrograph at 5x, (b) 5 wt.% Ti photomicrograph at 50x, (c) 10 wt.% Ti photomicrograph at 5x, and (d) 10 wt.% Ti photomicrograph at 50x.
Figure 35 - Optical micrographs of a 15h milled sample cross section heat treated at 1200 °C for 
(a) 5 wt.% Ti photomicrograph at 5x, (b) 5 wt.% Ti photomicrograph at 50x, (c) 10 wt.% Ti 
photomicrograph at 5x, and (d) 10 wt.% Ti photomicrograph at 50x.

In general, there appeared to be good interfacial bonding between the particles and the matrix, 
represented by no gap present between particles and the matrix (Figure 33b). The good bonding is 
contrasted by the large amounts of porosity present in the matrix, which instead caused a poor interface 
between the reinforcement and the matrix. Due to these properties of the composite, some particles 
appear to be well bonded while others appear to be poorly bonded, as seen in Figure 35d.

The more notable features in some of these optical micrographs within the selected samples is 
the presence of a secondary interface phase. For example, on the right side of Figure 34b a differently 
colored gray phase surrounds the white phase. This interfacial phase is not present in all of the 
composites; in fact, it seems to be more present at lower temperatures. In addition, this secondary 
interfacial phase also is present in larger quantities closer to all surfaces of the composite. Figure 36a
shows the presence of the secondary phase as the location varies from the surface to the inside of the cross section. The top of Figure 36a represents the edge of the composite, and as the location changes from the edge to further within the composite, the presence of the gray colored particles decreases, and the white phase appears at about 500 µm into the composite. Figure 36b shows a micrograph of the surface, where this gray phase can be seen as the reinforcement instead of the expected white phase. The gray phase particles are also evenly dispersed and are about the same size as the particles consisting of the white phase, though they appear less needle-like in shape and tend to be wider if not more spherical in shape. They also are present across all temperatures and for both milling times and compositions. However, it should be noted that the presence of the gray phase as an interfacial material decreased as the temperature increased. The gray phase still appeared at the surface but did not surround the white phase particle reinforcement as they did at lower temperatures, meaning they existed as single phase particles. This gray phase is distinguished from the matrix and pores present by its color with respect to the matrix and pores. For example, pores are seen as close to a black color, while the matrix is a darker shade of gray than the secondary phase mentioned, which in turn is darker than the white colored phase.

![Figure 36](image_url)

Figure 36 – Optical micrographs of a 10 wt.% Ti sample milled for 15h and heat treated at 800 °C for (a) a cross section photomicrograph at 10x, showing the sample edge, and (b) a surface photomicrograph at 50x, showing the particles present.

Figure 37 shows the difference in the structure between the white phase and the gray phase. Figure 37a and 37c show that the images were taken without a polarized light filter, whereas Figure 37b and 37d have a polarized light filter on both. Therefore, the polarized light filter shows the presence of grains in the white reinforcement particle that are not present in the gray phase. The grain size varies largely even within each particle let alone across particles (Figure 37b).
4.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM was performed after optical microscopy for further investigating and analyzing the structure of the samples. Optical microscopy identified points of interest to be carefully looked into, so using SEM/EDS became necessary because they typically provide higher clarity and resolution with more detail on chemical analysis.
Figure 38 shows SEM images of cross-section samples of various compositions milled for 5 hours and heat treated at 800 °C, whereas Figure 39 shows SEM images of samples milled for 5 hours and heat treated at 1200 °C. It can be seen from the SEM images that many of the microstructural features and their trends across milling time, temperature, and composition are clearly observed in their respective SEM images. Thus, this section will not detail those features and trends but instead confirm their presence and note anything new. The 15 hour milled samples are shown below in Figures 40 and 41 and confirm many of the features already observed previously. For example, the decreasing porosity with increasing temperature and milling time as well as the larger amounts of reinforcement material with an increasing weight percent of Ti added. In addition, the general sizing of the particles and other microstructural features like porosity are about the same as observed with optical microscopy.

Figure 38 – SEM images of cross-section samples of various compositions milled for 5 hours and heat treated at 800 °C. (a) 5 wt.% Ti, photomicrograph at 100x; (b) 5 wt.% Ti, photomicrograph at 500x; (c) 10 wt.% Ti, photomicrograph at 100x; (d) 10 wt.% Ti, photomicrograph at 500x.
Figure 39 - SEM images of cross-section samples of various compositions milled for 5 hours and heat treated at 1200 °C. (a) 5 wt.% Ti, photomicrograph at 100x; (b) 5 wt.% Ti, photomicrograph at 500x; (c) 10 wt.% Ti, photomicrograph at 100x; (d) 10 wt.% Ti, photomicrograph at 500x.
Figure 40 - SEM images of cross-section samples of various compositions milled for 15 hours and heat treated at 800 °C. (a) 5 wt.% Ti, photomicrograph at 100x; (b) 5 wt.% Ti, photomicrograph at 500x; (c) 10 wt.% Ti, photomicrograph at 100x; (d) 10 wt.% Ti, photomicrograph at 500x.
Figure 41 - SEM images of cross-section samples of various compositions milled for 15 hours and heat treated at 1200 °C. (a) 5 wt.% Ti, photomicrograph at 100x; (b) 5 wt.% Ti, photomicrograph at 500x; (c) 10 wt.% Ti, photomicrograph at 100x; (d) 10 wt.% Ti, photomicrograph at 500x.

The SEM images provided more clarity of what was seen in optical microscopy rather than having completely different findings. In SEM images, for example, the difference in porosity becomes more nuanced; however, samples with a composition of 10 wt.% Ti appear to have more porosity than samples with a composition of 5 wt.% Ti. In addition, most, if not all, samples display the interfacial layer on the
reinforcement particle. Figure 40b represents the most conspicuous instance of the presence of these two phases within a single particle. However, it appeared that this interfacial layer was less visible in the samples with a composition of 10 wt.% Ti, or perhaps there were fewer layers of interfacial around the particles. Figure 42 shows a more clear image of the two different materials in the same particle.

Figure 42 – SEM image of a 5 wt.% Ti cross-section milled for 15 hours and heat treated at 800 °C with a photomicrograph at 1500x.

Figure 43 depicts surface SEM images for various compositions of pistachio shell- 5 and 10 wt.% Ti milled for 15 hours and heat treated at 1100 °C. As seen in optical microscopy (Figures 36b, 37c, and 37d), the particles seen on the surface tend to be more spherical or wider in comparison to the more needle-like shapes of the reinforcement seen in the cross section. The 10 wt.% Ti samples seem to have significantly more of the reinforcement particles on their surface, and they tend to be less clean and precise, as shown in Figure 43. This therefore means that compared to the 5 wt.% Ti samples, the reinforcement particles on the surface appear to smear or bleed into the matrix more, as shown in Figure 43.
Figure 43 - SEM images of the surface of various compositions samples milled for 15 hours and heat treated at 1000 °C. (a) 5 wt.% Ti, photomicrograph at 100x; (b) 5 wt.% Ti, photomicrograph at 500x; (c) 10 wt.% Ti, photomicrograph at 100x; (d) 10 wt.% Ti, photomicrograph at 500x.

In addition to SEM, EDS was also performed to gain some insight into the chemical composition of the matrix and reinforcement particles present in each sample. Figure 44 shows the locations of the EDS analyses that were used to reveal the elemental composition of the matrix and reinforcement particles. Based on these elemental composition results, the amount of titanium present seems to be greater within the reinforcement particles as opposed to the edge. However, this is only applicable where the particle is not homogenous throughout. Therefore, it was found that the center of the reinforcement...
particle is titanium-rich in the range of 50–60 at.%, which represents the brighter portion of the particle, whereas the oxygen makes up about 30–35 at.% and the remaining carbon fills up about 15 at.% . In contrast, the outer portion of the reinforcement particle consists of high oxygen content, consistently close to about 60 at.%, with titanium making up about 25–30 at.% and carbon having similar leftover percentages of about 15 at.%.

Figure 44 – EDS element analysis spectra for pistachio shell-5 at% Ti composite bulk milled for 15 hours and heat treated at 800 °C includes (a) SEM images with analysis locations, (b) location 6, (c) location 7, and (d) location 8.

Figure 45 depicts the EDS element analysis spectra for the surface of the pistachio shell-5 at% Ti composite bulk milled for 15h and heat treated at 1100 °C. However, these EDS element analysis spectra results show that the matrix composite consists mostly of carbon with some residual elements present such as silicon and titanium. The results showed that the particles had a high atomic percentage of oxygen content, followed by titanium and carbon, as seen in Figure 45. However, these percentages are similar to what is seen in Figure 44c, with oxygen having close to 60 at.%, titanium having close to 30 at.%, and
carbon taking up the leftovers with about 15 at.%. Therefore, this ratio is very similar to the ones observed in Figure 45b and 45d below.

Figure 45 – EDS element analysis spectra for pistachio shell-5 at% Ti composite bulk milled for 15 hours and heat treated at 1100 °C includes (a) SEM images with analysis locations, (b) location 1, (c) location 3, and (d) location 4.

4.5 Hardness

The micro or macro hardness measurement of the composites has been carried out to know the effect of reinforced particulates on the mechanical behavior of the composites. However, the averages of the hardness measurement results were recorded in Table 3 and plotted in Figure 46. In general, the 10 wt.% Ti composite samples showed a higher hardness than the 5 wt.% Ti samples. However, other trends were hard to specify, as hardness values would increase or decrease only with respect to one group, as
opposed to the overall set of data. As seen in Figure 46, the trends across single groups can be noticeable, but when looking at larger data sets, they seem to contradict each other.

Table 3 – Averages of Vickers micro or macro hardness measurements on composite samples milled for (a) 5 hours and (b) 15 hours.

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<th>10 wt% Ti</th>
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Figure 46 – Plot of average Vickers micro or macrohardness values for all experimental conditions.
5. Discussion

This chapter will cover more analysis and discussions involving the results given in the previous chapter. The analysis includes possible explanations for the results and data observed, supported by reports and published results of previous research into similar areas.

An explanation for the darker color of the 15 hour milled powder Ti and pistachio shell mixture could be that some of the pistachio shell carbonized at points of contact between the WC balls, which during impact can reach very high temperatures. Thus, with a longer milling time, more of the powder comes in between the balls during milling, leading to more point carbonization.

5.1 XRD

The XRD patterns for all the samples, as shown in Figures 23–26, showed extremely similar, if not the exact same, peaks patterns, including the 2θ location and relative intensity, which are mostly representative of a rutile TiO\textsubscript{2} pattern and some of TiC and WC. For example, Figure 47 depicts the XRD patterns for the 5 wt.% Ti, milled for 5h, heat treated at 800 °C, where it showed a good match with the rutile TiO\textsubscript{2} patterns as well as Tic and WC, which was confirmed by the database of the International Center for Diffraction Data (ICDD). For clarity of the overall pattern, (hkl) values were omitted for the peaks located at the black circles in Figure 47, but Table C in the Appendix displays the full list of 2θ angles, d-spacings, and relative intensities of the reference peaks for TiO\textsubscript{2}.

![Figure 47 – The XRD pattern of a 5% Ti sample milled for 5 hours and heated treated at 800 °C shows the majority of the major peak data and planes for TiO\textsubscript{2}.](image-url)
However, it is very clear that the peaks within all the samples match those of rutile TiO$_2$, which obviously confirms that the rutile TiO$_2$ was formed after heat treatment. In order to confirm these results and to obtain more accuracy in the results, the XRD patterns of anatase TiO$_2$, TiC, and WC were extracted from the database of the International Center for Diffraction Data (ICDD), as seen in Figure 48, and compared with the XRD patterns of the samples to identify and confirm the possible presence or lack of these compounds in the samples. Although it is unlikely that anatase TiO$_2$ would form, especially at higher temperatures, it is still a common phase of TiO$_2$. A full list of peaks and $2\theta$ values for the reference patterns can be seen in Tables D, E, and F in the Appendix. The TiC had the potential to form due to the carbonization of the pistachio shell, resulting in high amounts of carbon which could have reacted with the titanium to form TiC. If there was a very small amount of TiC present in this samples, it could have been relegated to background noise due to the large amounts of TiO$_2$ present which result in very high intensity peaks. Some of the TiC peak locations in the reference pattern also coincide with TiO$_2$ peak locations, which may also hide their presence. Although there is a possibility of TiC being present in the sample, it is more likely that there is not a significant amount if any at all. Furthermore, the temperature at which these samples were heat treated was likely not high enough to form TiC. However, to truly confirm whether or not TiC exists in these samples, further characterization is needed.

On the other hand, the WC could also have been present, which may have transferred from the grinding media (vial and balls) to the system. Depending on the amount of material used and the length of the milling, the WC balls used could have begun to contaminate the sample. However, based on the software used to match the peak patterns and the reference pattern below it is unlikely that an observable amount of WC was present in the sample, indicating that contamination was negligible. In addition, a specific mass charge ratio of 2:1 for material to WC was used to mill the material, reducing the likelihood of the balls impacting each other during milling. It is possible that there could still be WC contamination as the intensities of the TiO$_2$ peak patterns may have overshadowed any peaks for WC. However, the lack of observable contamination is also supported by the EDS results, all of which did not show a match for W as one of the elements detected (Figure 45).
Figure 48 – Reference XRD patterns for: (a) COD 1010942 TiO₂ Anatase, (b) COD 5910091 TiC and (c) COD 2100639 WC.

Other relevant XRD peak patterns to compare these results to include pure titanium and pistachio shell. Figure 49a shows the XRD peak pattern for pure titanium and 49b shows the XRD pattern for raw pistachio shell, labeled as PS in the literature reference from which it was performed. Key features in both patterns (Ti and pistachio shell) are missing from the sample XRD pattern results. For example, there is no broadening for any of the peaks in the sample XRD pattern, and most if not all of the peaks in the pistachio shell pattern are missing as well. In comparing the titanium peak pattern to the sample XRD pattern, some
of the peaks are missing as well, though others may be overshadowed by the TiO₂ peaks. With this, there is likely a negligible amount of Ti left in the sample.

Figure 49 – Literature peak patterns including: (a) XRD pattern of pure Ti [31] and (b) XRD pattern for raw pistachio shell, labeled as PS [32].

5.2 TGA

First, it should be noted that the large amounts of variation and fluctuation in the derivative weight loss curves seen in Figures 27 – 31 can likely be attributed to background noise. TGA is dependent on the changes in the pan weight and sample weight over time and temperature, which makes it very sensitive to the changes in the weight. Therefore, spikes in measurements can occur when the machine or the table it is resting on is hit by either another person or an item being placed down forcefully. Second, the scaling used for the derivative weight loss is mostly arbitrary especially when compared between each of the plots. The purpose of the scaling was to make the derivative weight loss curve and its features visible for further analysis.

It was noted earlier in the results that there were some differences in the TGA plots for the powder mixture milled for 5 hours vs. the mixture milled for 15 hours. The likely explanation for that difference is that the mixture milled for 15 hours had the pistachio shell oven dried overnight before milling, resulting in there being less moisture left in the biomass prior to carbonization. As a result, less mass was lost early in the TGA test.

There were several decomposition reactions occurring from room temperature up until about 600 °C. The first ‘reaction’, represented by the first small peak in the derivative curve around 60 °C, was likely due to drying of the powder, especially since it occurred at lower temperatures and did not result in a large weight loss. Therefore, this small peak that occurred at lower temperatures is present in all the
tested powders, as seen in the TGA curves, which makes sense because all powders contain a large amount of milled pistachio shell powder, which is most likely where the moisture was evaporated from.

The next area of interest in all the TGA plots concerns the region between 200 °C and just above 300 °C. Although the weight loss percent curve looks fairly smooth throughout this region, upon closer inspection a change in slope can be observed. This is supported by the derivative weight loss curve which clearly shows two peaks present across this temperature range. This indicates the presence of two decomposition reactions that are occurring. However, these peaks occur across all the TGA plots of the samples as well as the reference samples (pure pistachio shell milled powders), suggesting that reactions from decomposition in the pistachio shell are what is causing the weight loss. In addition, when comparing the reference TGA plot (Figure 31) to TGA conducted on pistachio shell from previous research papers (Figure 9), the literature plot shows the same two peaks on its derivative curve [5]. According to da Silva et al.'s work [5], the first region on the TGA curves of the pistachio shell powders, and particularly the first peak that occurs between 200 °C and 325 °C, is likely a result of the decomposition of hemicellulose. As mentioned in Chapter 2, hemicellulose is one of the more structurally branched molecules that comprise biomass. Thus, it is logical to conclude that the earliest significant decomposition reaction after the drying of water would involve hemicellulose. As has been explained in the literature section, the TGA plot of the pure pistachio shell powder, as seen in Figure 3, shows the decomposition behavior of all three molecular components of biomass: (1) cellulose, (2) lignin, and (3) hemicellulose [1]. However, this TGA plot for the pure pistachio shell powder shows the derivative weight loss peaks, with a first peak appearing between 200 °C and 300 °C, which results from the hemicellulose decomposition, whereas the second peak, from about 300 °C to 400 °C, represents the cellulose decomposition. Indeed, the agreement between the traces of the TGA plot of the pure pistachio shell powder and the traces of the TGA plot in this work is systematically and qualitatively good. Although the temperatures are slightly different, these two peaks (pure pistachio shell powder) are easily comparable to the two peaks seen in the TGA plots given in the results. Therefore, the second peak most likely belongs to the decomposition of cellulose, based on Figure 3 [1]. However, this conclusion is corroborated by the analysis made by da Silva et al. in their study on the combustion of pistachio shell [5] in which the second peak in the derivative weight loss curve is also discussed.

On the other hand, another significant amount of weight loss occurs in the range of just over 300 to 600 °C, albeit at a much slower rate than in the previous section. The inflection point occurs at about 300 – 320 °C (Figures 27 – 31). This section is characterized by a less steep weight loss curve which suggests that the rate of decomposition has slowed down significantly compared to before. One possible
explanation is the onset of secondary decomposition reactions during pyrolysis, mentioned previously in
the literature review in Chapter 2 of this thesis. These secondary reactions utilize the initial products made
by the primary decomposition reactions as driving forces to start the reactions, resulting in the formation
of more char in addition to what has already been formed [1]. Thus, these secondary reactions could lead
to a weight percent increase, though perhaps the net effect is still a weight loss. However, it would explain
the reduced rate of weight loss during this period.

The final area of interest on the TGA curves occurs in the temperature range of 600–1000 °C. Figures 28 – 31 show this area with an increase in weight percent as the temperature increased. The reference pistachio shell TGA plot (Figure 32) is lacking this weight percent increase after 600 °C, indicating that the presence of the added titanium within the powder has led to an increase in mass in this region. This is also supplemented by the fact that Figures 27 and 29, which show the TGA plots for powders containing 5 wt.% titanium, have a smaller amount of weight percent increase compared to Figures 28 and 30, which show plots for 10 wt.% powders. The amount of weight percent increase for 10 wt.% Ti powders appears to be almost twice as much as for the 5 wt.% Ti powders. The most likely explanation for this phenomenon is the occurrence of atmospheric reactions. Other reactions seem to have taken place since the nitrogen gas was the purge gas used for all these TGA runs and is meant to be an inert alternative to atmospheric air, which contains oxygen. However, at higher temperatures and with the right reactants, the nitrogen gas may end up reacting with the samples producing products such as TiN, leading to a mass increase. The lack of nitrogen detected with EDS also rules out the formation of TiN while heat treating in an argon atmosphere.

5.3 Microscopy

This section will cover the analysis and discussions of optical microscopy and SEM/EDS, as these
two characterization techniques specialize in characterization of the structures of the samples, and in the
meantime, their results complement each other, and it would be better if they were explained alongside
each other.

As has been seen in the optical micrographs as well as SEM images and as noted in the results
chapter previously, there appeared to be a trend in porosity with temperature and milling time. An
increase in heat treatment temperature results in less porosity and a denser matrix substrate. Similarly,
the increase in milling time also resulted in less porosity in the matrix substance, as seen in the 15-hour
milled samples. One explanation for the trend with temperature is that higher temperatures may
encourage more secondary decomposition reactions in the pistachio shell, as mentioned earlier in the
TGA section. These secondary decomposition reactions often result in more char forming after the initial pyrolysis, but ultimately the end result is the exodus of more byproduct from the sample, leading to densification of the matrix material. A more fundamental explanation of this is through diffusion; diffusivity increases at higher temperatures, which again allows these decomposition byproducts to exit the sample more quickly. Thus, the increased diffusivity allows the leftover matrix material to possibly migrate more easily to fill those open gaps, leading to less porosity in the final matrix and a denser sample. Another factor in this densification process is the presence of a pressure gradient caused by the formation of volatile gaseous byproducts within the matrix, which also facilitates diffusivity of these byproducts out from within the material [1].

The effect of milling time on the porosity of the matrix material in the samples is not as clear as the effect of temperature, though it was still observable based on optical microscopy and SEM imaging. Compared to micrographs of bulk composite samples milled with different milling times and the same heat treated conditions, 15 hour milled samples appeared to have less porosity. However, this difference was not as significant as the difference between samples heat treated at 800 °C and 1200 °C. It is likely that the increase in milling time led to a finer powder mixture (i.e., finer particles), which in turn led to a higher particle packing arrangement and resulted in a denser sample when pressed, which means that the sample was denser at the start of the heat treatment process. Thus, it is very probable that this led to a denser matrix as the gaps where porosity would have existed previously were filled with the finer powder mixture. Another observation on changes in the amount of porosity came with weight composition differences. The samples containing 10 wt.% Ti appeared to have a more porous matrix than those with 5 wt.% Ti. This can likely be attributed to the presence of more reinforcements, which may trap some reaction products (gases) and prevent them from escaping, leaving more pores behind. The gases trying to escape from the center of the sample may run into more obstacles along its path in the form of reinforcement particles with the samples containing more weight percent Ti added, which slows down their movement through the matrix, resulting in more porosity compared to the samples containing less reinforcement particles.

The presence of large macroscopic cracks on the surface of some samples is easily explained. These large surface cracks typically only occurred with samples heat treated at higher temperatures (i.e. above 1000 °C, though mostly only seen with 1100 °C and 1200 °C samples). The higher temperatures, as mentioned before, lead to more waste products from the decomposition; the consequence of this is that the byproducts need to exit the sample, even from the center of the sample. At higher temperatures, this rate of escape increases, perhaps leading to large cracks forming near the surface as the stress of trapped
gases and liquids increased. Another explanation is the less consistent heating rate of the heat treatment for the 15 hour milled samples due to using a different oven. This uneven heating rate could have added extra thermal stress to the surface of the samples, leading to cracking.

Another feature of interest noted in both optical microscopy and SEM was the presence of what appeared to be different phases of structure with regards to the reinforcement particles. These two phases consist of one which appears to be a darker gray in both optical and SEM (distinguished from the composite matrix, which was even darker in color), and the other significantly lighter gray (almost white) in both optical and SEM. The dark gray phase was more prevalent in and around the sample’s surface up to a depth of about 500 μm, and it also appeared as an outer layer of the particle in some samples, similar to an interfacial material. On the other hand, the lighter phase is characteristically seen internally in the sample (i.e., the cross section), though rarely some particles show this phase on the surface. It is also possible that while grinding/polishing samples enough material was taken off the surface to expose more particles that displayed this lighter color phase. The fact that some particles existed as this dual-layered phase with an outer layer and inner layer suggests that some kind of transformation or reaction was occurring from the outside of the particle toward the inside of the particle. This is supported by the fact that the outer layer of the sample up to a depth of about 500 μm showed homogeneous particles consisting of only the dark gray phase. Based on this observation, it is likely that the transformation was occurring from the surface towards the inside of both the matrix and the particles. Perhaps with more time held at the heat treatment temperature the particles would have homogenized throughout the sample, not just at the surface. Optical micrographs taken of the particles displaying the lighter phase vs. the darker phase show not just a clear difference in color, but also structure. For example, in Figures 37b and 37d a polarizing lens was used to capture images of their corresponding locations. In these polarized light micrographs (Figure 37b, specifically), grains are very clearly seen within the particles containing the lighter phase, with the grains showing up as multiple different colors. Grains are only seen in crystalline materials, suggesting that this lighter phase is crystalline in nature. The presence of a crystalline phase has also been confirmed by the observed XRD patterns, which show thin, sharp peaks indicating the presence of a crystalline phase. However, these sharp peaks very closely match those of the TiO₂ that were found in the database, and this confirms the presence of a crystalline phase of TiO₂. Along a similar vein, polarized light micrographs were taken of the surface particles containing the dark gray phase (see Figure 37d). These dark gray phase surface particles did not display the same multi-colored grains as the light gray phase, and instead seemed homogenous with the polarized light. Despite this result, one cannot conclude that this dark gray phase is amorphous, as the grains may not be visible even through a polarized
light lens. Further processing and characterization are necessary to determine the true structure of both
the light and dark gray particle phases seen in optical microscopy and SEM.

The reinforcement particles were also observed to have generally good adhesion to the matrix, as well as
having some variation in shapes and sizes. Apart from where porosity might result in poor surface adhesion,
most reinforcement particles displayed no gap between their edges and the matrix. This demonstrates good
adhesion between the matrix of the composite and the outer layer of the reinforcement particles. Most variation
in particle size and shape likely comes from the distribution in the manufactured titanium powder. Reinforcement
particles in the center of the sample tend to have a higher aspect ratio with more needle like shapes, while the
reinforcement particles on the surface appear to be more spherical or at least have a lower aspect ratio. In addition,
circular particles seen in micrographs could actually be needle shaped particles cut at a cross section, revealing
a two-dimensional circle. As was previously stated, this variation in the shape of the reinforcement particles
could result from the particle distribution of the original titanium powder, but it is unlikely that this can explain
why the shape of the reinforcement particles in the center of the sample is different compared to those at the surface.
A possible explanation for this variance is connected to the earlier proposal that there is a phase transformation
or chemical reaction occurring within the particle from the outside in.

Another possible explanation for variation in particle sizes and shapes is due to agglomeration of
the Ti particles. Based on information from the manufacturer the Ti powder was processed through 325
mesh, resulting in particles about 44 µm in diameter or length. Possible agglomeration can be seen in
Figure 40b, where the particle on the left about 30 µm long appears to have two particles bonded
together. In addition, what might have been perceived as porosity within particles (Figure 33b) could
potentially be agglomerations. Given that there are particles present that are significantly smaller than 44
µm, it is possible that some of the larger particles seen in the matrix are agglomerations. Furthermore,
bail milling of the Ti and pistachio shell powder mixture may also cause agglomeration of particulates prior
to heat treatment. Similarly, darker spots seen within particles may be carbonized mass that was trapped
inside via the milling process.

Finally, one of the more interesting phenomena observed in the results was the discovery with
EDS that the lighter phase within the particles contained more titanium and less oxygen compared to the
darker gray phase (Figures 44 and 45). The outer dark gray phase had an approximate atomic ratio
between oxygen and titanium of 2:1 (about 60 at.% to about 30 at.%). From this result, it can logically be
concluded that the likely compound present in this phase is mostly TiO₂. Meanwhile, the light gray phase
has significantly more titanium present, even more than oxygen (~53 at.% titanium compared to ~33 at.%
oxygen). One possible explanation is that there does happen to be crystalline rutile TiO₂ present in the inner light gray phase, but instead there is significantly more unreacted pure titanium. When comparing the sample plots to a literature XRD plot of a metallic titanium sample (Figure 49a), the peaks do not match, suggesting that there is a negligible amount of pure titanium on the surface of the samples. However, when considering penetration depth of XRD, it is possible that the X-Rays are not reaching the center of the sample. In that case, it is possible that pure titanium peaks would then appear in the XRD pattern.

Although there is evidence that TiO₂ is present in the samples, it is not clear what form of TiO₂ is present, and where precisely it is located within the reinforcement phase. Some results demonstrate the presence of crystalline rutile TiO₂, while others suggest TiO₂ may exist in an amorphous form. Amorphous TiO₂ (am-TiO₂) has been observed before, but more extensive research has been conducted on crystalline forms of TiO₂ due to its abundant nature and common applications [33]. am-TiO₂ can be synthesized in many ways, including hydrolysis, sol-gel, precipitation, electrodeposition, and more [33]. However, most of the am-TiO₂ investigated in the review by Sun et al. takes the form of nanotubes, thin films, or irregular nanoparticle dispersions, and other nano-sized forms, rather than a bulk form [33]. Due to the disorder present in the structure of am-TiO₂, depending on the actual structure am-TiO₂ may phase transform into rutile TiO₂ during heat treatment [33]. In general, since am-TiO₂ is a metastable phase, it will transform into crystalline TiO₂ (anatase and eventually rutile) at higher temperatures. There is no definitive explanation for what the exact structure of the TiO₂ in these particles is (amorphous or crystalline), but one may imagine that during heat treatment any am-TiO₂ that was present may have undergone phase transformation into crystalline rutile TiO₂. Further experimentation, including more samples as well as more characterization techniques, is needed to confirm or disprove any possible explanations.

5.4 Hardness

Composite hardness was hard to measure due to the nature of the material being quite brittle. This made it hard to take even measurements due to the presence of cracking around each indent. Taking multiple measurements helped to mitigate this, however the variation was still present after averaging out the measurements. Figure 46 shows a plot of each subset of hardness measurements to help identify any possible trend. However, there don’t appear to be any significant obvious trends. The hardness for 10 wt.% Ti samples tended to be higher than the 5 wt.% samples, though this was less true for the 5 hour milled samples. The 15 hour milled samples followed this trend across all temperatures. It is likely that the higher hardness measurements can be explained by the nature of the presence of a greater quantity
of reinforcement particles with higher hardness than the existing weaker carbon matrix. Meanwhile, some trends only exist in each specific subset, and don't apply for other subsets. For example, 5 hour milled samples with 5 wt% Ti added show an overall decrease in hardness as heat treatment temperature increased. However, this trend is not observed at all with the 5 wt.% Ti samples milled for up to 15 hours, which instead shows a general increase in hardness. Despite these subset-specific trends, some other notable common points are that hardness seems to average higher for 900 °C and 1100 °C samples across all subsets. However, due to the random nature of these trends and their inability to be definitively applied to all samples, it is hard to label this as anything beyond speculation or variation due to the brittleness of materials. However, it should be noted that higher temperatures for heat treatment resulted in more surface cracks on samples, so that could be followed to a logical conclusion of increased brittleness with higher heat treatments.
6. Conclusions and Future Work

Based on the research conducted in this thesis, from research, sample preparation, processing, and ultimately characterization, some conclusions can be drawn from the results. However, there is some uncertainty about certain results and by which mechanism they occurred. Thus, future work should be conducted to determine more conclusively the nature of what happened and why.

Qualitative analysis of microscopy results showed a strong correlation between heat treatment temperature and porosity of the carbon matrix. Higher heat treatment temperatures resulted in less porosity, which implies better mechanical properties. Similarly, samples using powder mixtures milled for a longer period of time (15 hours vs. 5 hours) also showed a decrease in porosity across all heat treatment temperatures, though the difference was not as noticeable as across temperatures. Although hardness testing was inconclusive, based on observations in microscopy and results from XRD, a higher temperature with higher milling time will lead to better mechanical properties. However, there is clearly a point where the higher temperature starts to affect the integrity of the carbon matrix, as demonstrated by noticeable macro cracks on the surface of the material. TGA results suggest that the majority of carbonization reactions finish by about 600 °C, and the literature review states that excessively high temperature may degrade the already formed solid carbon char from which comprises the matrix material. In addition, another factor to keep in mind is the processing cost; higher temperatures and durations means more energy required to power furnaces, and longer manufacturing time to make the product. A balance must be struck between temperature and duration of heat treatment to achieve a sample that is less prone to cracking but has desirable mechanical properties.

To that end, further work should be conducted to better define the limits of the processing used to create the samples and define an explanation for the occurrence of observed phenomena. More samples should be created to test out different processing parameters such as: different milling times, different heat treatment temperatures (increase up to 1600 °C), changing duration of heat treatment to greater than 1 hour.

Other work that can be done to help clarify results could be looking at the pure titanium powder under optical microscopy or SEM to see the shape of the particles and compare that to the particles present in the final samples. Also, to perhaps encourage the formation of TiC, a much more desirable reinforcement material, the pistachio shell could be carbonized by itself first then ground into powder that is then mixed with the pure titanium powder. The powder then follows the same procedure until a final heat treated sample is produced. Characterization could then be conducted to see what is produced. Finally, different characterization techniques could be used to provide more insight on the composition.
of some materials in the particles, as well as into practical applications. For example, abrasion or wear testing of the samples could also provide information on the long term practical properties of these samples in their particular predicted application of something like brake pads.

X-Ray Photoelectron Spectroscopy (XPS) has the potential to identify actual molecular compounds of materials, unlike EDS which just provides elemental composition. This could help confirm or deny the hypothesis of whether the inner light gray material is TiO$_2$ or not, and same to the outer material. XRD of the cross section could also assist in this endeavor. In addition, TEM should also be performed to determine the structure of the phases in the samples. If the sample is nanocrystalline or truly amorphous, conducting TEM can confirm that. Another less labor intensive method of investigating whether or not grains (and therefore crystallinity) exists in each phase is to etch the sample to reveal the microstructure and make it more visible in optical microscopy. Finally, testing to determine thermal conductivity can also be important for determining the performance of this material since a high thermal conductivity is a desirable property in brake pads.
References


# Appendix A

Table A.1 – Dimensions before and after heat treatment for 5 hour milled samples.

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<td>~35% shrinkage</td>
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<td>Temp (°C)</td>
<td>Diameter (mm)</td>
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<td>900</td>
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Table A.2 – Dimensions before and after heat treatment for 15 hour milled samples.

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| 10 wt   | ~34% shrinkage | 10 wt   | ~29% shrinkage |
| Temp (°C) | Diameter (mm) | Thickness (mm) | Temp (°C) | Diameter (mm) | Thickness (mm) |
| 800     | 12.7 | 3.98 | 800     | 8.25 | 2.85 |
| 900     | 12.7 | 3.98 | 900     | 8.2  | 2.87 |
| 1000    | 12.7 | 3.98 | 1000    | 8.15 | 2.86 |
| 1100    | 12.7 | 3.98 | 1100    | 8.07 | 2.84 |
| 1200    | 12.7 | 3.98 | 1200    | 8.01 | 2.79 |
Table A.3 – XRD database reference values for rutile TiO$_2$.

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Table A.4 – XRD Database reference values for anatase TiO₂.

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Table A.5 – XRD Database reference values for TiC.

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Table A.6 – XRD Database reference for WC.

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