PROCESSING, WEAR, AND MECHANICAL PROPERTIES OF POLYETHYLENE COMPOSITES PREPARED WITH PRISTINE AND ORGANOSILANE-TREATED CARBON NANOFIBERS

By

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Polymers and nanocomposites have been increasingly used for tribological applications over the last few decades. In particular, ultrahigh molecular weight polyethylene (UHMWPE) is a high performance polymer with excellent strength, toughness, and wear resistance. Because of these properties, UHMWPE is an ideal material for a variety of applications including body armor, components of sporting goods such as skis and snowboards, and liners in total joint replacement. Though the toughness and wear resistance far exceed that of most other polymeric materials, there is a high demand for improving the tribological and mechanical properties of UHMWPE for many applications. The approach used in this work for improving such properties is through nanocomposite technology, specifically via the incorporation of carbon nanofibers. In order to obtain the full potential of nanocomposite technology, two critical issues need to be addressed: appropriate interactions between the filler and matrix and proper dispersion of the nano-reinforcement. These critical issues are particularly important for UHMWPE nanocomposites in that UHMWPE is an extremely viscous polymer and thus cannot be processed conventionally, typically resulting in dispersion issues far worse than that of other composite systems. Furthermore, UHMWPE is non-polar, so interactions between filler and matrix will be limited to
Van der Waals forces for untreated nanofillers. Therefore, the research presented aims at solving these issues by using a paraffin-assisted processing method and applying appropriate surface treatment to the carbon nanofibers. Under optimized processing conditions, wear and mechanical properties of UHMWPE composites can be substantially improved.
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CHAPTER 1

BACKGROUND AND OBJECTIVES

1.1 Polymer nanocomposites: overview, tribology, and critical issues

1.1.1 Overview of nanocomposites

Materials can be divided into four very broad categories: polymers, metals, ceramics, and composites. Composites consist of a combination of two or more constituent materials, in which certain properties of the system will generally benefit from each of the materials used [1–3]. Specifically pertaining to the work in this dissertation, polymer composite technology effectively combines properties of the polymer matrix such as toughness and wear resistance with the properties of the filler/reinforcement such as strength and modulus. When put into a polymer matrix, fibers can improve the modulus, strength, and wear properties substantially, among other potential property enhancements. There are various types of conventional composites, including continuously aligned, weaved, short-fiber aligned, and randomly mixed short fiber composites. Nanocomposites, or composites with nanofillers as reinforcement, are typically randomly mixed, though alignment of the polymer chains can yield partial alignment of the nanofibers as well. In order to be considered “nano,” materials must have at least one dimension less than 100nm and this special dimension must substantially enhance the properties of the material in some way. For nanocomposites, this entails fillers/reinforcements with dimensions less than 100nm [4].

There are many advantages of nanoreinforcement compared to conventional composites. For example, as the diameter of the fiber becomes smaller, the number of surface defects decreases, and thus the strength of the fiber can be greatly improved. This concept can be illustrated by the difference in strength between bulk glass and glass in the fibrous form (Figure 1.1).
Figure 1.1 Tensile strength as a function of fiber diameter for glass fibers. As seen from the curve, as the diameter of the glass fiber decreases, the strength of the fiber increases substantially [5].

Figure 1.2. Illustration of micron and nano-sized fillers at 0.1wt% in a 1mm³ cube (representative of: (A) Alumina particle; (B) carbon fiber; (C) graphene nanoplatelet; and (D) carbon nanotube). The figure illustrates the advantage of nanofillers, showing higher contact area with polymer, and thus a better ability to reinforce the matrix (from [10] with permission).

Bulk glass is very brittle and has a relatively low strength. However fiberglass is a very strong material due to the limited amount of defects [5]. In addition to decreasing defects, decreasing the fiber diameter also increases the surface area of the nanofiller (as illustrated in Figure 1.2). This effect potentially improves the interaction between the nanofiller and the matrix, and allows nanofillers to more effectively reinforce the matrix at a lower filler concentration. By reinforcing effectively at a lower concentration, the toughness of the polymer matrix can be maintained, or
in some cases, even improved [6]. Thus, using nanoreinforcement can be effective for improving various mechanical and tribological properties while maintaining toughness [7–9].

1.1.2 Tribological properties of polymer nanocomposites

Tribology is the study of friction (the resistance of lateral motion of two bodies in contact) and wear (the loss of material) as a result of materials sliding against one another [11,12]. Though often stated as material properties, wear and friction are both systemic properties, meaning they depend on the entire system rather than simply the intrinsic materials being used [11,12]. Tribological properties of materials primarily depend on the surface energies of the two articulating components, roughness of each of the surfaces, and mechanical properties (such as strength and toughness), though many other factors can play a role (Figure 1.3). Because of these dependencies, tribological properties vary greatly between the various types materials, whether metallic, ceramic, polymeric, or composite materials.

Figure 1.3 Dependencies of both bulk and surface properties on the wear resistance of materials.
Polymers and polymer composites have been increasingly used for tribological applications over the last few decades, as these materials are typically tough, cheap, and able to develop transfer films onto the articulating surface, thus forming a type of solid lubrication [13–16]. However, polymers also generally have a lower wear resistance compared to metals and ceramics under similar testing conditions [17,18]. In order to improve the wear resistance of polymers, fillers and reinforcements can be added, thus potentially improving both the mechanical and surface properties. In particular, nanofillers have the capability of manipulating both the surface energy of the polymer, as well as the bulk mechanical properties at low filler concentrations. Additionally, nanofillers may allow the toughness of the materials to be maintained. Therefore, polymer nanocomposites are a promising material for next generation tribological applications.

In order to better understand the advantages of nanocomposites for improving wear properties, it is important to understand the basics of tribology. Below is a brief summary of the fundamentals friction and wear.

1.1.2.1 Friction

The coefficient of friction is defined as the frictional force over the normal force applied. Friction can be categorized as static (nonmoving) and kinetic (sliding), though the work in this dissertation is primarily concerned with kinetic friction. The fundamental laws of friction (under dry conditions), which were developed in the 18th century strictly by empirical data, are shown below [19]:

*Amonton’s First law*: kinetic frictional force is proportional to the normal load

*Amonton’s Second law*: frictional forces are not dependant on apparent surface area.
**Coulomb’s Law:** Once sliding, friction is not dependant on sliding speed

These “laws” are largely empirical, and fundamental theories of friction at the molecule level directly oppose these laws. For example, it has been shown that frictional forces are in fact directly dependant on the “actual” surface area, and indirectly dependant on the load \([20–22]\). When two materials come in contact with each other, the “actual” contact at the molecular level is minimal compared to the apparent contact. The higher the applied load, the larger the “actual” contact increases, thus increasing the adhesive frictional forces. However, for a large range of materials, the actual contact area is proportional to the load, and thus the coefficient of friction will not be affected substantially by increasing the normal load or apparent surface area. Though these empirical “Laws” of friction are not consistent with theory, they are still very useful for a wide range of materials, loads, and sliding speeds.

In addition to bulk mechanical properties of the composite, changes in the surface energy with addition of fillers also strongly influences the frictional properties of these materials. Many studies have cited a reduction in coefficient of friction as a mechanism for improvement in the wear properties. This mechanism is particularly important for polymers with high surface energies, such as for polyamides. For polymers with low surface energies such as polyethylene and polytetrafluoroethylene, the coefficients of friction are already relatively low, so adding a nanofiller will generally not significantly reduce the frictional properties, and in some cases may increase the coefficient of friction \([23,24]\). Lastly, the ability of the polymer composite to adhere to the articulating surface (i.e., transfer film) has been shown to improve the tribological properties, as the counterface surface becomes softer, and the coefficient of friction and wear may also be reduced \([13,25–29]\).
1.1.2.2 Wear

Wear is defined as the loss of material associated with sliding against another material. As with friction, wear between two articulating surfaces is very complex and largely empirical, depending on friction, shear strength and toughness of the materials, pressure applied, sliding speed, etc. Nonetheless, there have been attempts to predict the wear properties based on intrinsic material properties. Specifically, Archard’s Equation, which is derived from modeling the elimination of an asperity (a projection from the surface) in contact with an articulating surface, relates hardness of a material to the wear properties, as shown below:

\[ W = \frac{K \cdot L \cdot D}{H} \]  

(1.1)

where \( K \) is a constant, \( L \) is the load, \( D \) is the sliding distance, and \( H \) is the hardness. This relationship works particularly well for pure metals, as shown in Figure 1.4.

![Figure 1.4. Relationship between wear and hardness for pure metals (from [30] with permission).](image-url)
It should be noted that some limiting assumptions are made in the formulation of Archard’s Equation. One of the more questionable assumptions is that an asperity will be removed after sliding. This is considerably problematic for tough polymeric materials in which many asperity passes are needed to remove the material. Nonetheless, this equation demonstrates qualitatively which material will wear more significantly between two articulating surfaces. Furthermore, this equation has been helpful in ranking the wear resistance of various metal and ceramic materials in which the yield strength is similar to the ultimate strength. Certainly in general, the sliding distance is proportional wear rate, and in some instances load is also proportional to the wear rate unless catastrophic wear is realized, as shown by Archard’s Equation. However, using hardness as a predictor of wear properties should be avoided for tough polymeric materials. In another attempt at modeling the tribology of materials, Reye’s Hypothesis states that for a given material wear volume lost is proportional to work done by frictional forces. This hypothesis appears to be more consistent with the wear resistance of tough polymeric materials than Archard’s Equation.

In general, the wear resistance of polymers more strongly correlates with toughness rather than yield strength, though there are certainly deviations from these correlations shown in literature.

Tribology of both unfilled polymers and filled polymer composites has largely been empirical, and very little work has been done on modeling. Polymer tribology is generally more complicated that traditional tribology for metals and ceramics because of its toughness and the ability to create a transfer film are major contributing factors to the wear process.

As mentioned earlier in this section, the wear properties strongly relate to the ability for material to be removed with each asperity pass. This is can be considered to be indirectly related to yield strength, ultimate strength, elongation to break, and toughness. Empirical studies have shown that the wear properties most strongly correlate with a combination of strength and elongation to
break, which may be described as the toughness of the material. This empirical data corresponds well with theoretical work by Reye, as shown by the Ratner-Lancaster correlation (Figure 1.5, [31]).

Figure 1.5. Relationship between wear rate and product of ultimate strength and elongation to break for polymeric materials (from [31] with permission).

As with unfilled polymers, the tribology of polymer nanocomposites is also largely empirical. Research has shown that the wear properties of polymer nanocomposites do in fact strongly depend on the mechanical properties of the material, though polymeric nanocomposite systems are much more complex than unfilled polymer systems. Studies have also shown that the size/morphology of the filler has a strong influence on the wear properties of the composite. This result can be explained largely by the differences in surface area of the between fillers with micron versus nano-sized dimensions. Fillers with higher the surface areas (i.e. smaller dimensions) have potential for better the interactions and thus a better the ability to reinforce the polymer. Typically polymers reinforced with nanofillers need a lower concentration of nanofiller
to show improvement compared to micron-sized fillers. In contrast, composites prepared with micron sized fillers typically have optimized concentrations much higher than nanofillers. For nanofillers, agglomerates will form readily at low concentrations because of the high surface area, yielding a lower optimum concentration than micron-sized fillers. For example, the optimal concentration of CNT nanocomposites typically ranges between 0.5 and 2wt% [32,33], while composites with micron sized fillers have shown improvement of up to 40wt% or more for larger micron-sized carbon fibers [34]. Thus, the size of the filler influences both potential polymer interactions and the formation of agglomerates, resulting in lower optimum concentrations for nanofillers.

1.1.3 Critical issues in nanocomposite tribology

Though nanoreinforcement has much potential to improve tribological properties of polymeric materials, this is largely dependent on the dispersion of the nanofillers. Because of the high surface area of nanofillers in general, agglomerates tend to form and are very difficult to break up. Agglomerates are not only ineffective in reinforcement, but they also tend to act as voids, and thus degrade the properties of the polymer nanocomposite. This is illustrated by such low values in the optimum concentration of nanofillers with regard to mechanical and tribological properties. Furthermore, the sufficient interactions between the filler and the matrix are vital for producing successful nanocomposites. Both dispersion and interaction issues are addressed for ultrahigh molecular weight polyethylene (UHMWPE) composites in Section 1.2 of this chapter.
1.2 UHMWPE and its composites: structure, properties, and processing

1.2.1 Polyethylene structure

Polyethylene is a hydrocarbon polymer consisting of linear chains with repeat unit “-CH₂-”. Both UHMWPE and HDPE have the same chemical structure, differing primarily in molecular weight. UHMWPE has a molecular weight greater than 3.1 million g/mol, whereas the molecular weight of HDPE ranges between 30,000 and 200,000 g/mol [35]. Though the composition of polyethylene is relatively simple compared to other polymers, the microstructure is much more complex, composed of crystalline phases embedded in amorphous domains (Figure 1.6) [36]. For UHMWPE, the chains will fold onto each other in the form lamellar crystals with typical thickness of 10-50 nm and length of 10-50 nm [35]. Amorphous segments can traverse the intercrystalline zone to connect to adjacent crystallites, which can be “tie chains,” “loops,” or “cilia.” The degree of connectivity between neighboring crystallites plays a major role in determining the physical properties of a sample. Because of the high molecular weight and limited chain mobility, UHMWPE generally has a lower crystallinity than HDPE.

![Figure 1.6 Structure of UHMWPE showing semicrystalline characteristics (from [36] with permission).]
1.2.2 UHMWPE Properties and Applications

Non-polarity: The difference in electronegativity between carbon and hydrogen is very small, and thus dipole interactions in the hydrocarbons are limited. Furthermore, the symmetry of the hydrogen bonds on the carbon gives the polymer essentially zero dipole, and thus the polymer is very non-polar. Because of the non-polarity of this polymer, polyethylene has a very low coefficient of friction, generally has a dry coefficient of friction around \( \mu=0.2 \), and is one of the best self lubricating polymers known. The non-polarity of this polymer also gives polyethylene its hydrophobic properties, with water absorption of less than 0.01% [37]. Polyethylene is chemically resistant and biologically inert, making it a great material for biomedical applications such as for liners in total joint replacement.

Table 1.1 Selected properties of HDPE and UHMWPE [38].

<table>
<thead>
<tr>
<th>Property</th>
<th>HDPE</th>
<th>UHMWPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight ( (10^6 \text{ g/mole}) )</td>
<td>0.05–0.25</td>
<td>3.5–7.5</td>
</tr>
<tr>
<td>Melting Temperature ( (°C) )</td>
<td>130–137</td>
<td>132–138</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.40</td>
<td>0.46</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.952–0.965</td>
<td>0.925–0.945</td>
</tr>
<tr>
<td>Tensile Modulus of Elasticity* ( (\text{GPa}) )</td>
<td>0.4–4.0</td>
<td>0.5–0.8</td>
</tr>
<tr>
<td>Tensile Yield Strength* ( (\text{MPa}) )</td>
<td>26–33</td>
<td>21–28</td>
</tr>
<tr>
<td>Tensile Ultimate Strength* ( (\text{MPa}) )</td>
<td>22–31</td>
<td>39–48</td>
</tr>
<tr>
<td>Tensile Ultimate Elongation* ( (%) )</td>
<td>10–1200</td>
<td>350–525</td>
</tr>
<tr>
<td>Impact Strength, Izod* ( (\text{J/m of notch;}) )</td>
<td>21–214</td>
<td>&gt;1070 (No Break)</td>
</tr>
<tr>
<td>3.175 mm thick specimen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Degree of Crystallinity ( (%) )</td>
<td>60–80</td>
<td>39–75</td>
</tr>
</tbody>
</table>
**Mechanical properties:** UHMWPE has an extremely high impact toughness, even at cryogenic temperatures due to the extremely high molecular weight. This material is able to absorb a considerable amount of energy because of the physical entanglement of the polymer chains. Because of these properties, UHMWPE is not only used for tribological applications, but for ballistic applications such as for bullet proof vests and armored vehicles (Figure 1.7). In the fiber form, UHMWPE fiber is one of the strongest commercially available fibers, comparable to Kevlar. Additionally, UHMWPE has a very low density (0.93-0.95 g/cm$^3$), making it the top material in fibrous form in terms of strength to weight ratio. See Table 1.2.1 for detailed mechanical properties.

![Figure 1.7. UHMWPE used for ballistic applications, including bullet proof vests, military helmets, and armored vehicles [39].](image)

**Wear Resistance:** UHMWPE is considered the most wear resistant polymer. The wear resistance of polyethylene increases with increasing molecular weight due to improvement in toughness properties. In addition to the toughness of this material, the low coefficient of friction also contributes to the superior wear properties. Tribological applications include lining for the bulk transport (Figure 1.8), components of sporting goods such as snowmobiles, skis, and snowboards (Figure 1.9), and liners for total joint replacement (Figure 1.10), among other applications.
For bulk material transport, specifically in the mining industry, UHMWPE has been used very effectively in lining dump trucks and bob cat buckets for protection of equipment. Not only do these liners improve the wear and corrosion resistance, but the load of the bed or bucket can be reduced by replacing steel with aluminum. Furthermore, loads to be removed more easily and efficiently as the coefficient of friction of the bed/bucket is reduced. Figure 1.8 shows dump trucks unloading with and without UHMWPE linings, illustrating efficient transfer of load for the truck lined with UHMWPE. Therefore, lining the bucket with UHMWPE can improve the efficiency by potentially reducing the load, allowing material removal to be easier (lower coefficient of friction), improving the wear resistance and thus better maintaining integrity in the equipment. Certainly, more wear resistant liners would further improve the efficiency of bulk transport by reducing maintenance costs and allowing vehicles to be in service longer for longer periods of time.
UHMWPE used for various types of sporting equipment, including snowmobiles, snowboards, and skis [41–43].

UHMWPE is also used as a linear for total joint replacement because of its extremely high wear resistance, toughness, and biocompatibility. Despite its superior properties, UHMWPE is the limiting factor in the lifetime of the total joint prosthesis. The wear debris of this material produces a negative biological response, resulting in osteolysis and loosening of the implant [4, 5]. Because of the unsatisfactory results in vivo for UHMWPE, then it is worthwhile to investigate alternative methods of improving the wear properties of UHMWPE.

Figure 1.10. UHMWPE acetabular cups used for total hip replacement (from [44,45] with permission).

1.2.3 Processing of bulk UHMWPE

Though UHMWPE has many superior properties, processing of this material is a major limiting factor for further potential applications. Processing of polymers is essentially related to the ability of polymer chains to slide past one another [37]. For UHMWPE, the molecular weight of
this polymer limits the ability of polymer chains to slide past one another. Because of these limitations, UHMWPE cannot be extruded or injection molded using conventional processing methods. In the following section, a brief introduction of polyethylene chain mobility and its relation to processability is discussed.

Processing of polymers is strongly dependant on the melt viscosity, or the ability of the polymer to flow in the melted state. There are two general regimes for polymer melt viscosity: below and above the critical molecular weight in which physical entanglements are formed. When in the liquid state, small molecules (low molecular weight) generally diffuse by translation. In contrast, for long polymer chains (high molecular weight), polymer entanglement limits simple translation, and in general, polymers undergo multiple changes in conformation in order for diffusion to occur [37]. The polymer melt viscosity \( n \) dependence of molecular weight \( M_w \) is given by [37]:

\[
\begin{align*}
  n &= K M_w \quad \text{(for } M_w < M_c) \quad \text{(1.2a)} \\
  n &= K M_w^{3.4} \quad \text{(for } M_w > M_c) \quad \text{(1.2b)}
\end{align*}
\]

where \( K \) is a constant and \( M_c \) is the critical molecular weight. Equation 1.2 arises from entanglement and diffusion considerations. Below the critical molecular weight the melt viscosity increases linearly. Whereas above the critical molecular weight significant entanglements occur and the viscosity increases by 3.4 power in relation to molecular weight, as shown in Equation 1.2. As can be seen by equation 1.2, Due to its high molecular weight, UHMWPE has an extremely high melt viscosity compared to other polymers. In fact, it does not regularly flow in the melted state unless under pressure, and its consistency would appear to be as a rubbery solid. As a comparison between HDPE and UHMWPE, a typical average molecular
weight for HDPE is $2 \times 10^5$, whereas a typical average molecular weight for UHMWPE is $2 \times 10^6$. Therefore, using Equation 1.2b, UHMWPE can be over 2000 times more viscous in the melted state than HDPE! Because of this extreme viscosity, UHMWPE cannot be processed by conventional extrusion and injection molding processes, and thus other processing methods must be used in which granules fuse together rather than melt together completely by pressing at elevated temperature, pressure and time.

Because UHMWPE is so viscous in the melt state, processing methods are limited to compression molding or ram extrusion rather than melt extrusion or injection molding, after which the materials are machined to the appropriate dimensions. Specific UHMWPE processing problems include: the polymer blocking the die; polymer melt fracture; and barrel slippage due to the low coefficient of friction between the material and the barrel compared to the internal polymer friction/shear stress generated. Therefore, special techniques are needed to process this material.

Four methods are currently used commercially for processing bulk UHMWPE resin [12,19]. The first method is ram extrusion which is essentially a continuous compression machine. The powder is compressed in a heated cylinder by a reciprocating ram, and consolidated by back-pressure from the sizing die through which the rod is extruded. The resin melts from the surface to the center of the die forming a cone of unmelted material that extends into the die. Non-consolidated regions can result in the center of the material if the cone of unmelted material extends beyond the heated zone of the die, or if the pressure is reduced prior to the coiling of the center of the extruded material. Though the quality is poor, it is a relatively cheap process for producing bar stock. Thus, over 90% of UHMWPE for surgical implants on the market today are prepared by this method.
The second method is sheet compression molding developed in the 1950’s, which utilizes large presses with high temperature. Because of the relatively low thermal conductivity of UHMWPE, the duration of the molding cycle will depend on the particular geometry of the press and the size of the sheet to be produced. The long molding time is necessary to maintain the slow, uniform heating and cooling rates throughout the entire sheet during the molding process. An advantage of the sheet molding is that the process allows for greater pressures and results in a more uniform product than ram extrusion. One disadvantage with sheet molding is that there can be areas of varying density and mechanical properties from surface to center of the block formed if improper heat and pressures are applied. Also these materials are heat annealed for dimensional stability which may degrade the material. It is a slow process involving costly capital equipment; hence the material is more expensive than extruded bar.

The third method is hot isostatic molding. This involves cold compaction of powder to form green bars, which are then heated in a foil bag in an inert atmosphere to consolidate under a uniform hydrostatic pressure. Thus, the material is very isotropic and homogenous and may be considered a compression-molded form of the resin, though the batch production process has limited throughout and is expensive.

The last method is direct compression molding (DCM) that is used to make finished parts, with no need for subsequent machining. It is similar in concept to sheet compression molding (also called net shape compression molding), but obviously on a much smaller scale. This enables higher pressures and quicker heat conduction to the center of the molding. One advantage of DCM is the extremely smooth surface finish obtained with a complete absence of machining marks at the articulating surface. From a manufacturability standpoint, the difficulties associated
with process control of DCM has led most implant producers to obtain bulk converted sheet or rod.

1.2.4 Processing of UHMWPE composites

Polymer nanocomposites in bulk form are typically processed by melt extrusion or injection molding. However, as mentioned earlier in this section, UHMWPE composites cannot be processed by such conventional methods because of the extremely high melt viscosity of this polymer. Typical bulk UHMWPE composite processing techniques include dry-mixing, polymer blending, or swelling with a solvent [32,33,46–55]. Below is detailed information for various methods for UHMWPE composite preparation.

Table 1.2 Comparison of UHMWPE composite processing methods

<table>
<thead>
<tr>
<th>UHMWPE Processing method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry mixing</td>
<td>Facile, few steps</td>
<td>Very poor dispersion</td>
</tr>
<tr>
<td>Blending</td>
<td>Relatively easy</td>
<td>Localization of nanofillers, matrix compatibility issues</td>
</tr>
<tr>
<td>Solvent-assisted processing</td>
<td>Generally good dispersion</td>
<td>Typically toxic solvent used, low yield, more difficult to control</td>
</tr>
<tr>
<td>Paraffin-assisted processing</td>
<td>Relatively good dispersion, solvent non-toxic or volatile, can combine extrusion methods with solvent assisted processing methods</td>
<td>Multiple steps, extraction is needed</td>
</tr>
</tbody>
</table>

1.2.4.1 Dry mixing

Dry mixing is a process in which materials are mechanically mixed in the dry state without melting the polymer. This may include mixing by mortar and pestle, or by ball milling. The advantage of this method is that it is very quick and easy. However, there are many
disadvantages of using such a process. One such disadvantage is that the fillers will reside between the UHMWPE granules and thus may limit fusion of the particles. Another disadvantage is simply poor dispersion; fillers will not be able to penetrate into the UHMWPE matrix and reinforce the bulk of the polymer by using the dry mixing preparation.

1.2.4.2 Blending

Another way to process high viscosity polymers is to blend with lower molecular weight polymers. This method has the advantage in that dispersion is much improved compared to dry mixing methods. However, by adding a lower molecular weight polymer, physical properties of the entire system may be compromised. Additionally, the ability for the polymer blends to interdiffuse between each phase may be problematic. This issue may possibly be offset by the positive effects of nanofiller addition.

1.2.4.3 Solvent assisted processing

In order for the solvent system to be effective for polymer processing, there must be dissolution between the polymer and solvent. This criterion can be effectively described using thermodynamic considerations. A polymer will dissolve in a solvent if free energy (ΔG) is released upon mixing. There are two terms to consider in relation to the free energy absorbed or released: enthalpy of the system (ΔH), and the entropy related term (TΔS). The relationship between free energy, enthalpy, and entropy of a system is shown below:

\[ \Delta G = \Delta H - T \Delta S \]  

(1.3)

If the overall free energy is negative, meaning free energy is released, and then the polymer and solvent will dissolve. Otherwise, if ΔG is positive, the polymer and solvent will not dissolve.
unless energy is added to the system. The enthalpy after mixing can be either positive or negative depending on interactions between the solvent and the polymer. If special interactions are present between the solvent and polymer such that they are greater than polymer-polymer interactions, then the enthalpy term will be negative, thus encouraging polymer solubility. The entropy term will always be positive since both absolute temperature and change in entropy are positive values. For polymer solutions, the entropy term is typically very small because of segmental constraints of the polymer chains. This is especially true of higher molecular weight polymers. Therefore in general for polymer systems, the ability of a polymer to dissolve in a solvent depends largely on the enthalpy and less on entropy effects.

For a polyethylene-solvent system, the polymer-polymer interactions are difficult to overcome since polyethylene is a non-polar, semicrystalline polymer. In fact there are no solvents that dissolve polyethylene at room temperature; the temperature needs to be raised above 100°C for polyethylene to be dissolved so that the stability from crystallization is reduced. At room temperature the enthalpy of mixtures for a polyethylene-solvent system is positive because polyethylene crystals stabilize the system. In order for these polymer crystals to dissolve, additional energy needs to be added to the system in the form of heat.

Another important aspect in solution processing is the depression of melting temperature with increasing solvent concentration. Thermodynamics shows that addition of low molecular weight solvent to crystalline polymers results in a melting point depression. With an increase in solvent concentration, the melting temperature of the mixture decreases as shown experimentally and theoretically in literature [56].
For UHMWPE, solvents typically used for solution processing include xylene [57] and decalin [58] in which UHMWPE is boiled in these solvents at over 100°C. Typically such processing methods have the potential to improve the dispersion of the nanofillers substantially. However, the concentration of UHMWPE in these solvents is around 1% to 3%, showing a poor overall yield compared to conventional methods of processing. Additionally, these are toxic solvents, which make them problematic for processing specifically for biomedical applications. Nonetheless, these solvents are used to prepare fibers and films commercially [57]. Processing using paraffin oil solvent which has been much less studied but advantageous in that it has a low toxicity and is very compatible with polyethylene, will be discussed in the following section.

1.2.4.4 Processing using paraffin oil

Paraffin-assisted processing of UHMWPE composites is a relatively new technique that has not been studied extensively [47,50]. Using this method allows for the combination of solvent assistance with conventional melt extrusion methods. Not only can it reduce the viscosity of UHMWPE, but it can also be melt-mixed without the worry of the solvent being evaporated during mixing. Because melt-mixing is possible using paraffin as a processing agent, UHMWPE can be processed at larger viscosities and thus can have a better yield than conventional processing methods used for fibers and films.

The optimal concentration of depends on two competing components: distribution at the macro-scale, and breaking up of agglomerates. For macro-dispersion, it is best if the viscosity of the solution is as low as possible. However, in order to break up agglomerates, large shear forces are needed, which can be generated by reducing the paraffin content (increasing the viscosity). From these two competing factors, it can be seen that there is an optimum viscosity to which the
dispersion of the nanofillers can be improved. Viscosity of UHMWPE gel highly depends on the swelling ratio. The viscosity of UHMWPE gel increases with the concentration by a power law with exponent 3.4 when the polymer concentration is large enough to form a network structure.

In addition to the concentration of paraffin used, the operating variables are vital to the quality of the composite. Parameters for melt mixing using a torque rheometer are mixing time, rotor speed, the volume of material in the chamber, and the temperature [59]. *First*, the optimal mixing time depends on the balance between improving dispersion of the composite and degrading the polymer due to oxidation and chain breakage. *Secondly*, the rotor speed directly affects total shear deformation and thus the shear stresses. A higher mixing speed may result in higher shear and thus may be more helpful in breaking up agglomerates. However, if the rotor speed is too high, there may be damage to the polymer and filler, and the polymer may start slipping against the wall barrel, the reducing the effectiveness of mixing. *Thirdly*, the amount of material in the chamber is important for processing in that it will directly affect the shear forces generated. If the amount of material is too low, shear stresses will not be high enough to properly break up agglomerates. However, if there is too much material, mixing times will need to be longer, and even then there may be portions that are not mixed at all. The optimum batch volume is 70vol%, suggested by torque rheometer manufacturers when using roller rotors is volume. *Lastly*, the choice of temperature is largely a balance between the viscosity of the polymer, which is related to the shear forces generated and the ability of the polymer to wet with the nanofiller, and potential degradation of the polymer. At higher temperatures, the viscosity of the polymer will be reduced. Again, shear forces are needed to break of agglomerates, so the polymer needs to be somewhat viscous in order for this to occur. However, the viscosity also needs to be low enough that the fillers are well distributed. Furthermore, with higher temperatures, the wettability of the
polymer will improve. A balanced temperature will lead to a better dispersed polymer composite with minimal degradation [59].

1.2.5 Effect of processing on wear properties of UHMWPE composites

The method of processing UHMWPE will strongly influence the dispersion of the fillers, and thus the tribological properties of the composite. For dry-mixed UHMWPE composites, the dispersion will typically be very poor. This is especially true for nanocomposites, as there will not be sufficient shear forces to break up agglomerates. Furthermore, if the UHMWPE granules are covered with nanofillers, then UHMWPE will have limited diffusability during compression molding. In contrast, for dry-mixing of micron-sized fillers, dispersion is less of an issue, as the lower surface energy will result in less aggregation. Additionally, since the size of the UHMWPE granules are in the same magnitude as micron-sized fillers, UHMWPE will be able to fuse together more easily. This has been illustrated in literature for dry-mixed UHMWPE composites. For UHMWPE nanocomposites, it is imperative that the fillers are dispersed sufficiently as a result of proper processing in order to yield improved tribological properties.

UHMWPE nanocomposite preparation specifically for tribological applications have included dry-mixing, blending with other polymers, and solution-assisted processing. There limited amount of literature on processing UHMWPE composites by blending with other polymers. Sui et al studied UHMWPE/HDPE/CNF composites with a ratio of 30vol% UHMWPE, 70vol% HDPE, with varying concentrations of CNFs. They found that the addition of CNFs slightly reduced the coefficient of friction. In another study, 80wt% UHMWPE and 20wt% HDPE was mixed with CNTs. Results showed an improvement wear properties with the addition of CNTs.
This processing method was certainly an improved method compared to dry-mixing of UHMWPE nanocomposites. There were some critical issues with this paper. First, the wear testing data was collected using volumetric effects rather than gravimetric. Literature has clearly shown that volumetric wear is difficult to assess because it includes a component of creep due to the viscoelastic properties of polyethylene [46]. Furthermore, the extent of the dispersion state, and the localization of the nanofillers were not studied.

Solvent assisted processing of UHMWPE composites has been a fairly successful method for processing UHMWPE composites for tribological applications, though the quantity of literature on this work has been limited. One such study was performed by Zoo, et al. [33], who showed that the addition of CNTs can improve the wear properties of UHMWPE composites considerably. These composites were processed using toluene as a solvent, which is a carcinogen and should thus be avoided if possible. However, there was no qualitative or quantitative dispersion analysis in this study. Furthermore, there are low yields for composites prepared by solution casting. Nonetheless, there was a substantial improvement in the wear properties.

A specific type of solvent assisted processing, paraffin-assisted processing, has been successfully used to improve tribological properties of composites [47]. In this study, paraffin was used as a means of properties. Wear properties were improved up to a loading of 5wt%. However, there were some minor issues with this work. The main issue with this work was that the concentration of paraffin for processing was not reported, which may significantly affect the melt viscosity during processing. Overall, this method seems to be a good method for processing UHMWPE, as it has been shown that the wear and mechanical properties were improved, the solvent is non-toxic, and very compatible with UHMWPE.
1.2.6 UHMWPE composite limitations

As mentioned in Section 1.1 of this chapter, nanofillers in polymer composites must be dispersed well and have sufficient interactions with the matrix in order for reinforcement to be effective. Because of the extreme viscosity of UHMWPE, this polymer cannot be processed by conventional methods such as extrusion of injection molding, making dispersion issues far worse than other composite systems. Processing thus becomes extremely vital to the properties of UHMWPE composites, as processing will determine the distribution/dispersion of nanofillers which will in turn effect the wear and mechanical properties. Additionally, because polyethylene is non-polar, adhesion and wettability will likely be poor unless sufficient surface treatment of nanofillers is performed. In Section 1.3, carbon nanofibers (the nanofiller predominantly used in this study) are introduced. In Section 1.4, surface treatments specifically designed for improving interactions between fillers/reinforcements and polyethylene are discussed.

1.3 Carbon nanofibers and polymer nanocomposites

1.3.1 Structure, properties and synthesis of CNFs

Carbon nanofibers (CNFs) are a type of graphitic nanofillers composed of conjugated carbon sp² bonds, in which electrons in the pi orbital are able to move freely throughout the resonating structures. Such structure gives this material excellent electrical conductivity, thermal conductivity, and strength within the plane. Graphitic materials have a low coefficient of friction due to the layered structure, in which each layer can slide pass each other. There are numerous types of graphitic nanofillers based on the geometry, including carbon nanotubes (CNTs), graphene, carbon black, and CNFs. There are many advantages and disadvantages of each of
these nanofillers based on the cost, mechanical properties, aspect ratio, conductivity, and reactivity of the surface.

CNTs and CNFs have been subject to much research due to their extremely high strength, aspect ratio, and conductivity. In comparing these two types of nanoreinforcement, CNTs have graphitic tube shaped structure and can be single-walled, double walled, or multiwalled. In contrast, CNFs have a graphitic cup-stacked structure with active edges on the surface (Figure 1.11). CNTs typically have a higher strength and conductivity than CNFs because of the continuity of the rolled graphitic structure of CNTs, though CNFs are much more economical and contain active edges that allow for more facile chemical treatment. Because of the advantages of CNFs compared to other graphitic nanomaterials, these nanofillers were the primary reinforcement used in this research.

![Figure 1.11 Illustration of the structure of a CNF (left) and TEM image of CNF (right). Due to the unique structure of CNFs, active edges are available and more reactive, making surface treatments more facile.](image)

The discovery of CNFs occurred by catalytic conversion of carbon containing gases on the surface of pressure vessels, often damaging the equipment. Because of these problems, the
detailed studies of synthesis and catalysis of these CNFs were performed in hopes of determining how to limit the production of such filaments. Resurgence in interest of CNFs as viable reinforcement came when Iijima “discovered” carbon nanotubes in 1991, in addition to the identification of nanotechnology as a field of its own. Since then, much research on synthesis, structure, and properties of CNFs have been performed, and have yielded fruitful commercialization of the product.

Though other methods of preparing CNFs have been studied, only the chemical vapor deposition method has been successfully utilized commercially. The carbon originates from aliphatic molecules such as methane, ethane, and other hydrocarbons. Under high pressure and temperature the carbon and hydrogen are decomposed, and carbon atoms are absorbed in the catalyst (typically Fe and Cu, among other transition metals) which forms carbides. The carbon then deposits onto the surface of the catalyst, forming sp² hybridized graphitic structures. The shape and diameter of the carbon nanofiber will depend on the shape and chemical structure of the catalyst. For CNFs used in this work, the nanofibers possess cup-stacked structures.

In this thesis, CNFs were supplied by Applied Sciences Inc. The grade of the pristine CNFs used in this work was PR-24-HHT. The PR-24 term is related to the catalyst used for synthesis and yields the smallest diameter of CNFs produced by Applied Sciences Inc., ranging from 60-150 nm in diameter. The term HHT stands for high-heat treatment which is above 3000°C. This procedure is used to eliminate impurities such as chemical vapor deposition layers and the catalyst, as well as to further graphitize the CNFs. PR-24-HHT-ox grade was also used in this study for silane surface treatment of CNFs, as discussed in Chapter 4 of this thesis. The process of oxidation was simply to heating the pristine CNFs to 500°C in air conditions. However, chemical characterization, suspension studies, wear, and mechanical properties of composites did
not show obvious differences between the two grades of pristine and oxidized CNFs. The lack of differences may be due to the high heat treatment process at 3000°C, in which the chemical vapor deposition layer is removed and the CNFs are further graphitized. Thus the surface of the pristine CNFs may be already sufficiently oxidized, and further heat treatment at 500°C may be not fruitful. Nonetheless, oxidized CNFs were used specifically for studying silane surface treatments. Mechanical and geometrical properties of the commercially available pristine CNFs are given in Table 1.3.1, as supplied by Applied Sciences Inc.

Table 1.3 Carbon nanofiber properties [60].

<table>
<thead>
<tr>
<th>Grade of CNFs</th>
<th>Diameter (nm)</th>
<th>Length (microns)</th>
<th>Aspect Ratio</th>
<th>Tensile strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR-24-HHT</td>
<td>60-150</td>
<td>30-100</td>
<td>~200</td>
<td>2.7-7</td>
<td>400-600</td>
</tr>
</tbody>
</table>

1.3.2 Wear and mechanical properties of CNF reinforced composites

The effect of the addition of CNFs on the coefficient of friction has been studied for various polymer systems [51,61–65]. A study on the tribological properties of polystyrene/CNF composites showed a substantial reduction in the coefficient of friction from 0.5 for pure polymer to 0.2 for composites with high concentration of CNFs (50wt%) [63]. In contrast, a study by Sui et al. [51] showed that the coefficient of friction only slightly reduces for polyethylene composites at 3wt% loading. Still another study showed a slight increase in the coefficient of friction with polyphenylene sulfide composites up to 10wt% [61]. Discrepancies in results may be related to the polymer used, articulating surface, concentration of CNFs, and roughness of each surface. Based on literature, the addition of CNFs into a polymer matrix typically do not increase the coefficient substantially, and in most cases, the coefficient of
friction does not change dramatically, but largely depends on the polymer used in addition to other tribological conditions.

The effect of CNFs on the wear properties has also been studied. A study performed by Werner et al. [65] showed that at 10wt% CNFs, wear properties of polyetheretherketone composites could be substantially improved. Unfortunately, wear rates were determined by volumetric wear loss, in which both material loss and viscoelastic properties will influence the result. In another study, Geletz et al. [47] demonstrated the addition of partially dispersed CNFs led to moderate improvements in the mechanical properties of the UHMWPE without significantly changing the overall ductility. They suggested that there was a positive effect on the crack initiation and propagation resistance with the addition of CNFs into UHMWPE. In addition, the wear resistance of the nanocomposite was improved compared to neat UHMWPE. The authors conceded that though improvements were seen, the dispersion of CNFs was unsatisfactory, and could be improved with advanced processing techniques of UHMWPE [47]. Overall the literature on CNF composites is limited and needs to be studied in more detail. Furthermore, there has not been any relevant literature on tribological properties of surface treated CNF-polyethylene composites. Surface treatment of fillers/reinforcement will be discussed in the following section.
1.4 Nanofiller surface treatments

1.4.1 Typical surface treatments

In order to address dispersion and interaction issues between the filler and matrix in polymer nanocomposites, various surface treatments have been applied. The two main types of surface treatments for improving interactions with polymer composites include polymer grafting and silane treatments [10,66,67]. The advantages of silane treatments are that they easily react with oxidized surfaces, they are widely commercially available, and various end groups can be modified to tailor interactions with different types of polymers [66,67]. The follow section describes the basic concepts of silane surface treatments.

1.4.2 Silane treatments

Silane coupling agents typically contain three groups able to react with an oxygen rich surface of an inorganic material, and one group as the coupling agent to improve compatibility/adhesion with organic polymer (Figure 1.12). The general treatment for silanes involve both hydrolysis and condensation reactions (See Equations 1.3, 1.4). The reactive groups, typically chloride or methoxy groups, initially undergo hydrolysis with the addition of water to the reaction forming hydroxyl groups.
Figure 1.12 Silane coupling agent acting as a bridge between the organic polymer and inorganic material. The R-group on the silane is chosen that there is adhesion/wetting between the silane and organic polymer. The methoxy groups on the silane will hydrolyze and then react with the oxidized surface of the inorganic material.

Once hydrolyzed, these silanol groups become very reactive, with the ability to form chemical bonds with oxide groups to the inorganic material upon condensation reactions [66], shown below:

\[
R\text{-Si}(OCH_3)_3 + 3H_2O \rightarrow R\text{-Si}(OH)_3 + CH_3OH \quad (1.3a)
\]

\[
R\text{-Si}(OH)_3 + HO\text{-M} \rightarrow R\text{-Si-O-M} + H_2O \quad (1.3b)
\]

Where M represents the inorganic material. Under both acidic and alkaline conditions, hydrolysis of the reactive groups occurs more rapidly than under neutral conditions. Under acidic conditions the reactive group becomes protonated, forming a better leaving group (i.e., H_2O). In contrast, under basic conditions, hydroxide anions (strong nucleophiles) are prevalent in the solution. These strong nucleophiles result in both increased hydrolysis and condensation reactions. Acidic conditions do not enhance condensation reactions compared to alkaline conditions because of the decreased nucleophilic behavior of protonated groups. A simplified mechanism for the influence of the basic catalyst is shown below:
Thus, hydrolysis and condensation reactions of the silane groups can be controlled by changing the pH value of the solution during reflux [66].

### 1.4.3 Silanes for polyethylene composites

Typical silane coupling agents specifically used for polyethylene include vinyl, methacryloxypropyl, hydrocarbon-tailed silane [68–72]. One advantage of using vinyl or methacryloxypropyl silanes is that chemical bonds can be formed between the filler and polyethylene matrix. However, a free radical initiator such as peroxide is needed in order for the reaction to be completed. The addition of a peroxide initiator may degrade the polymer, and thus effectively reduce the mechanical and tribological properties of the composite.

The effects of vinyl silane treatment on polyethylene composites in relation to mechanical properties have been relatively well studied. In one study [72], methacryloxypropyl trimethoxysilane was applied to hydroxyapatite and then mixed with HDPE. Results showed a slight improvement in both ultimate strength and young’s modulus. In another study [70], vinyl silane was applied to natural henequen fibers and pullout tests, fragmentation tests, and tensile tests were performed. There were mixed results with regards to the fragmentation and pullout tests, though the ultimate strength of the composite did show improvement. However, the use of the vinyl silane in combination with peroxide as an initiator reduced the elongation to break of the composites compared to other untreated composites. Though the mechanical properties have been shown to improve, there is still the issue of the polymer matrix to become more brittle due
to the oxidation from the peroxide, in which the tribological properties could be significantly degraded.

For hydrocarbon tailed silanes, such as octadecyltrimethoxysilane (ODMS), no peroxide is needed and thus polyethylene will not be degraded from such treatment. From such silane treatments, compatibility will likely be improved, and energy dissipation may be improved during mechanical loading. However, one disadvantage of this treatment is that the organosilane cannot form chemical bonding with polyethylene, and thus interactions will be limited to improved van der Waal’s forces unless the silane coating and polyethylene can sufficiently interdiffuse.

In contrast to vinyl silanes, hydrocarbon tailed silanes have been much less studied. In a study by Abdelmouleh et al. [68], a thin coating of hexadecyl silane was applied to cellulose fibers for polyethylene composite systems. Results showed that there was no significant improvement in the mechanical strength. However, only a thin coating was used, and thicker coatings may allow some physical entanglement between the coating and polymer chains. Despite the prevalence of silane treatments, there has been limited amount of studies on the silane treated nanocomposites, which will be further discussed in Chapters 4 through 6.

1.5 Research problems, objectives and organization

1.5.1 Statement of Problems

There is a high demand for improving the wear properties of UHMWPE for various applications. The addition of carbon nanofibers, which have high aspect ratio and strength, are studied in this work for improving such tribological properties. In general, two critical issues need to be addressed in when preparing polymer nanocomposites: proper dispersion of the nano-
reinforcement and appropriate *interactions* between the filler and matrix. These critical issues are especially important for UHMWPE nanocomposites in that UHMWPE is an extremely viscous polymer and thus cannot be processed conventionally, typically resulting in dispersion issues far worse than that of other composite systems. Furthermore, UHMWPE is non-polar, so interactions between filler and matrix will be limited to Van der Waals forces for untreated nanofillers. The research presented aims at solving these issues by using a paraffin-assisted processing method and applying appropriate surface treatment to nanofillers.

### 1.5.2 Research objectives

The overall research objective of this work is to develop novel UHMWPE nanocomposites with enhanced wear resistance for potential use in a variety of tribological applications through various processing techniques and nanofiller surface treatments. The *specific research objectives* are shown below:

**UHMWPE/HDPE/CNF Ternary composites (Chapter 2)**

1. Study the effect of HDPE blend processing on tribological properties of UHMWPE composites
2. Study the effect of CNF concentration on wear properties of UHMWPE/HDPE/CNF composites

**Paraffin-assisted UHMWPE composite processing (Chapter 3)**

3. Compare tribological properties of UHMWPE/CNF composites prepared by dry-mixing and paraffin-assisted processing
4. Study the effect of CNF concentration on wear properties of paraffin-assisted UHMWPE/CNF composites
Silane surface treated CNFs and composites (Chapter 4-6)

(5) Determine the structure of octadecyltrimethoxysilane treated CNFs

(6) Determine the effect of sodium hydroxide concentration on the chemical structure of the polymerized silane coating

(7) Study the effects of the nanofiller surface treatments on the wear and mechanical properties of polyethylene/CNF composites.

1.5.3. Organization

This dissertation is divided into two sections: processing of UHMWPE composites (Chapters 2 and 3), and surface treatments of CNFs specifically designed for polyethylene composites (Chapters 4, 5, and 6). Both processing of UHMWPE composites and surface treatments of CNFs are studied in relation to tribological properties. Figure 1.13 provides an overview for this dissertation.

Figure 1.13 Overview and organization of the dissertation
References:


Image taken from the “Snowmobile” section on Wikipedia.org on June 16th, 2012.


Image taken from “Skiing” section on Wikipedia.org on June 16th, 2012.


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CHAPTER 2

PROCESSING UHMWPE COMPOSITES BY BLENDING WITH HDPE

2.1 Introduction

In Chapter 1, it was illustrated that producing high quality UHMWPE nanocomposites has been very difficult because of the polymer’s extremely high viscosity. In this chapter HDPE is used as a means of processing UHMWPE composites [1]. Methods of processing UHMWPE composites have been limited to dry mixing followed by compression molding [2–5], in situ polymerization [6], swelling with oligomer solvents [7,8], and adding lower viscosity polymers such as high density polyethylene (HDPE) [1,9–12]. Specifically, the incorporation of HDPE into UHMWPE has been shown to improve creep resistance [9], whereas increasing the ratio of UHMWPE to HDPE toughens the composite [11,12]. Xue et al. [9] studied the wear and creep behavior of blended UHMWPE and HDPE composites with carbon nanotubes (CNTs) as fillers. They found that CNTs can reduce the wear compared to UHMWPE/HDPE blends alone. However, UHMWPE/HDPE with CNTs still produced higher wear rates compared to the wear of pure UHMWPE against specific counterface materials.

Phase separation of UHMWPE/HDPE blends has been well documented when processed via melt mixing or extrusion due to the extremely high chain entanglement of UHMWPE, even under relatively high temperatures and prolonged mixing durations [11,12]. Reported amounts of dissolution for UHMWPE/HDPE blends has ranged between 3-6% wt, depending on the ratios of each type of polyethylene in the blend, among other factors [13,14]. Furthermore, adding fillers to an immiscible blend often results in fillers preferentially residing in a specific polymer in the blend. Yui et al. [15] observed that in an immiscible HDPE/polypropylene (PP)/carbon black
composite, carbon black particles mostly resided in the HDPE phase. Similarly UHMWPE/PP/carbon filler systems, a majority of fillers resided in the PP phase [16]. Most pertaining to our study, Thongruang et al. [17] demonstrated that in UHMWPE/HDPE/carbon filler composites, the fillers were predominantly located in the HDPE phase. Note that in this study, the components were only dry-mixed prior to compression molding. However, to the best of the author’s knowledge, no studies have even mentioned phase separation in UHMWPE/HDPE/filler systems for tribological applications. The importance of analyzing the effects of phase separation has been shown for other tribological studies concerning polyolefin blends [18], but essentially ignored for UHMWPE/HDPE/filler systems.

Though localization of fillers in specific phases of partially immiscible polyolefin blends has been reported for studies pertaining to electronic applications [15–17], the heterogeneous nature of UHMWPE/HDPE/filler composites has been neglected for tribological and mechanical studies [9–11]. Furthermore, the influence of the localization of fillers into the lower viscosity polymer on the tribological properties has not been previously realized for UHMWPE/HDPE/CNF composites. Therefore, in this chapter, the phase structure and sliding wear properties of UHMWPE/HDPE blends filled with CNFs is examined [1].

2.2 Experimental

2.2.1 Materials

Grade GUR 1020™ UHMWPE was supplied by Ticona, with an average molecular weight of about 3.5 x 10^6 g/mol. Grade HiD 9018 HDPE was supplied by Bolcof Plastics. The untreated CNFs used in this study were Pyrograf III® carbon nanofibers (CNFs), HHT grade with 60-150 nm diameter and 30-100 µm in length, supplied by Pyrograf Products, OH, USA.
2.2.2 Sample preparation

The polyethylene composites consisted of 60% wt UHMWPE with 40% wt HDPE, reinforced with CNFs. Concentrations of 0.5%, 1%, and 3% CNFs were incorporated into the polyethylene matrix. Composites were processed using a Haake torque rheometer. Nanofillers and UHMWPE powder were first ground with mortar and pestle (see Figure 2.1). Grinding of the nanofiller into UHMWPE allowed the fillers to be slightly dispersed, prior to further dispersion by melt mixing. After pre-dispersion, both UHMWPE/filler and HDPE granules were added to the torque rheometer. A constant pressure was applied to allow for better interdiffusion UHMWPE and HDPE.

![Figure 2.1. UHMWPE granule covered with CNFs (left) and magnified image of UHMWPE mixed with CNFs by mortar and pestle (right).](image-url)
Table 2.1. Summary of sample labels and composition.

<table>
<thead>
<tr>
<th>Label</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>100% GUR 1020</td>
</tr>
<tr>
<td>HDPE</td>
<td>100% Grade HiD 9018</td>
</tr>
<tr>
<td>HDPE +2.5% CNF</td>
<td>Grade HiD 9018 HDPE with 2.5% CNF</td>
</tr>
<tr>
<td>Blend</td>
<td>60%wt UHMPE with 40%wt HDPE</td>
</tr>
<tr>
<td>Blend + 0.5%CNF</td>
<td>60%wt UHMPE with 40%wt HDPE with 0.5% untreated CNF</td>
</tr>
<tr>
<td>Blend + 1.0%CNF</td>
<td>60%wt UHMPE with 40%wt HDPE with 1.0% untreated CNF</td>
</tr>
<tr>
<td>Blend + 3.0%CNF</td>
<td>60%wt UHMPE with 40%wt HDPE with 3.0% untreated CNF</td>
</tr>
</tbody>
</table>

For preparation of all composites, the torque rheometer was set to 30 rpm for 20 min at 190°C. Samples were then compression molded (190°C, 4MPa for 20 minutes), after which the heat was turned off, and samples were allowed to cool to room temperature naturally. Dimensions of the rectangular plates were 50 x 100 mm² with a thickness of approximately 3 mm. As references, HDPE, HDPE with 2.5% wt CNF, and pure UHMWPE were prepared under similar conditions. A concentration of 2.5%wt CNF was incorporated into HDPE corresponding to 1%wt CNF of the total weight in the majority of the 40%wt HDPE phase. Note that UHMWPE was not processed via torque rheometer prior to compression molding because of the extreme viscosity of this material. The composition of the samples prepared in this study is summarized in Table 2.1.

For the rest of the chapter UHMWPE/HDPE blends were labeled Blends, and CNF/UHMWPE/HDPE composites were labeled as Blend nanocomposites for simplicity.

2.2.3 Microscopy

Field emission scanning electron microscope (SEM) images were obtained from cryo-fractured surfaces to determine the dispersion of the CNFs, as well as wear surfaces and debris. SEM images for fractured surfaces were prepared by freezing in liquid nitrogen for 20 minutes prior to fracturing. All sample surfaces were sputter-coated with gold before SEM imaging to reduce
electrostatic charging. Additionally, samples were microtomed to a thickness of 10µm and observed under optical microscope to distinguish between different phases in the composite.

2.2.4 Wear testing

Specific volumetric wear rates were determined using a custom-built pin-on-disk apparatus with a vertical 1020 carbon steel disk under dry testing conditions. Wear testing samples had dimensions of 5mm x 5mm. Wear testing was performed at 180 rpm at 0.408 meters per cycle. Specific wear rates were calculated by the mass loss of the sample being tested, using the following equation:

\[
\text{(2.1)}
\]

Where \( w \) is the wear rate, \( \Delta m \) is the change in mass, \( \rho \) is the density of the material, \( F \) is the normal force, and \( d \) is the linear sliding distance. An Adventurer Pro analytic scale was used to determine mass loss, with a detectable range of 0.1 mg. Wear debris was removed from the disk between mass measurements of each sample. After testing was completed for each sample, the disk surface was cleaned thoroughly with acetone and dried prior to further use. To ensure the correct mass loss during wear testing, measurements were repeated five times, and if any differences were seen, the median value was collected for further analysis.

2.3 Results and Discussion

2.3.1 Processing and morphology

An increasing steady-state torque has been shown to be directly related to an increase in viscosity [19], while differences in viscosity have been used to calculate the amount of
dissolution in UHMWPE/HDPE blends [13,14]. In this study, steady state torque values, obtained from the torque rheometer used for processing, were utilized to compare relative viscosities of the samples. Table 2.2 shows the steady-state torque measurements obtained in this study, revealing two important results. First, the HDPE/2.5 wt % CNF composite had noticeably higher steady-state torque values compared to neat HDPE. Secondly, and more interestingly, the addition of CNFs into 60%wt UHMWPE/ 40% wt HDPE (labeled “Blend”) resulted in a reduction in steady-state torque.

Table 2.2. Steady state torque data from torque rheometer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Steady State Torque</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>.25 Nm</td>
</tr>
<tr>
<td>HDPE + 2.5% CNF</td>
<td>.65 Nm</td>
</tr>
<tr>
<td>Blend</td>
<td>26.7 Nm</td>
</tr>
<tr>
<td>Blend + 0.5% CNF</td>
<td>22.1 Nm</td>
</tr>
<tr>
<td>Blend + 1.0% CNF</td>
<td>23.7 Nm</td>
</tr>
<tr>
<td>Blend + 3.0% CNF</td>
<td>22.1 Nm</td>
</tr>
</tbody>
</table>

The increase in torque in HDPE with the addition of CNFs was specifically attributed to an increased viscosity. Because there was an increase in torque with the addition of CNFs into neat HDPE, it would then also be expected that incorporating CNFs into the Blend would increase the steady state torque compared to the polymer Blend. However, the addition of 1 %wt CNFs into the Blend surprisingly resulted in a reduction in torque, corresponding to a reduction in viscosity. Also, additional amounts of CNFs up to 3 wt% did not show any torque increase accordingly.
Figure 2.2. Optical images of blends filled with 0.5% CNFs (a,b), 1% CNFs (c,d), and 3% CNFs (e,f).
Phase separation can be seen from optical and SEM images. Optical images of the Blends filled with CNFs (Figure 2.2) showed two distinct microstructures. The white (translucent), spherical portions of the image were UHMWPE phases, indicating there were no CNFs in the bulk portion of the UHMWPE phase. The dark, continuous component was a multiphase microstructure containing HDPE and CNFs. Differentiating phases in linear polyethylene blends have previously been shown in literature under polar microscopy [13,14]. Although some polymer blends are immiscible because of a very small entropy of mixing and endothermic nature of the reaction, polymer blends with identical chemical structure only varying in molecular weight, such as UHMWPE and HDPE, may show metastable phase separation as a result of differences in their melt viscosity; UHMWPE and HDPE may not have enough time to homogenize completely during melt mixing [17].

The localization of CNFs into the HDPE phase was attributed to the high viscosity of the dispersed UHMWPE phase. Although UHMWPE melts at elevated temperatures, extreme physical entanglement of the polymer chains inhibited the ability of the CNFs to penetrate into the bulk of the UHMWPE phase during melt mixing. However, there may have been some CNFs residing along the outer portion of the UHMWPE phase. This result was suspected since HDPE likely dissolved into the UHMWPE phase due to the ease of flow of low viscosity HDPE, thus reducing the viscosity along the outer portion of the UHMWPE phase.

Figure 2.3 shows SEM images of the Blends filled with CNFs at varying magnifications. Darker, spherical portions of the image represent the UHMWPE phase of the composite, whereas the much rougher component was the HDPE/CNF microstructure. Such contrasting differences of the cryo-fracture surfaces between HDPE and UHMWPE have been explained by Brough et al. [20], who compared fracture surfaces of neat UHMWPE and neat HDPE.
Figure 2.3. Fracture surfaces of nanocomposites with: 0.5% CNFs (a,b,c); 1% CNFs (d,e,f); 3% CNFs (g,h,i). Scale bars are set to: 100µm (a,d,g); 10µm (b,e,h); and 5µm (c,f,i).
In our study, fractured surfaces of the HDPE phase exhibited small scale necking, such that when broken, there appeared to be rounded knobs (Figure 2.3(c,f,i)), which may have been formed by heating during fracture [20]. In contrast, there was no localized necking phenomenon in the UHMWPE phase. It has been suggested in literature that extremely high molecular weight polymers suppress localized necking, especially under lower temperatures and higher strain rates [20,21]. Thus, the UHMWPE phase consequently had a more smooth fracture surface. Additionally, fracture surfaces showed excellent interfacial interaction between the UHMWPE and HDPE phases. This is suggested by crack propagations running directly through each phase without any sign of unusual deformation at the interface (Figure 2.3a).

The distinct phase morphology of these ternary composites gave insight to the unusual torque rheometer results mentioned earlier. There were two proposed factors that would affect the steady state torque in our study: both an increase in dissolution of UHMWPE into the HDPE phase and the addition of CNFs would result in higher torque values, assuming all other factors are equal. Though adding CNFs into the Blend may increase the viscosity of the HDPE phase, the viscosity of the overall Blend was reduced with the addition of CNFs, which is reflected in Table 2.2. Therefore, it was likely that the overall dissolution between the UHMWPE and HDPE phases was reduced. This was attributed to a decreased mobility of polymer chains at the outer portion of the UHMWPE phase. The interaction between the filler and matrix limited the amount of free polymer chains available to enter dissolution. Thus there was less dissolution between the two phases with the addition of CNFs. Reduced dissolution has also been shown in literature for other types of partially miscible blends with the addition of carbon black.

Other studies have shown phase separation and localization of fillers into the lower viscosity polymer in polyolefin blends [17,18]. For UHMWPE/PP/carbon black systems, a majority of
fillers have been shown to reside in the PP phase [16]. In a UHMWPE/HDPE/carbon filler study [17], fillers were predominantly located in the HDPE phase, but localized at the interface between the two phases. The phase distribution was likely due to the dry-mixing prior to compression molding that led to insufficient time for HDPE to melt together into a continuous phase and inadequate shear stresses to distribute the carbon fillers more homogeneously in the HDPE phase. In contrast, our study showed HDPE was clearly the continuous phase and UHMWPE was the dispersed phase. Furthermore, CNFs in our study appeared to be homogeneously dispersed in the HDPE phase via torque rheometer, rather than localized at the interface.

For tribological studies, there has been no discussion of any phase separation at the microscopic level for UHMWPE/HDPE/filler systems. Therefore, in the following sections we relate this phase separation phenomenon to the wear properties of the composite.

2.3.2 Wear properties

The specific wear rates for the CNF/UHMWPE/HDPE composites were obtained by measuring the mass loss after pin-on-disk testing. Figure 2.4 shows the effect of CNF concentration on the wear rate of the Blend nanocomposites with CNFs. As the concentration of the CNF content increased, the steady-state wear rate decreased (Figure 2.4). The Blend nanocomposite with 3 wt% CNFs exhibited the highest wear resistance of all the Blend nanocomposites, with a 56% reduction in the wear rate compared to that of the polyethylene Blend. Multiple mechanisms have been suggested for the reduction in wear rate with the addition of CNFs. First, CNFs have the ability to contribute some load-bearing capacity, reducing the stresses applied to the polyethylene matrix and improving the shear strength of the composite [8,22]. Additionally,
CNFs may have acted as lubrication, given the graphitic structure of these fillers [8]. Because CNFs have been shown to clearly improve the thermal conductivity of polyethylene composites [10], then localized heat caused by friction can be dissipated more easily, reducing negative effects of thermal softening on the plastically induced damage layer [10]. Lastly, CNFs may reinforce polymer films adhered to the articulating wear testing disk, which would reduce the friction, and ultimately wear rate during testing [23]. Mechanisms for reduced wear with the addition of CNFs were further discussed in Chapter 4.

Figure 2.4. Wear rate of Blend and nanocomposites with different concentrations of at steady state wear.
A comparison of wear properties of Blends and its components was made. Figure 2.5 shows that HDPE had a very high wear rate under the conditions of this study, about an order of magnitude higher than that of the Blend. Furthermore, the polyethylene Blend had a wear rate of about an order of magnitude higher than UHMWPE. These results have been attributed to differences in molecular weight. It has been well established that the higher the molecular weight of a polymer, the better the wear resistance, assuming all other factors are equal [24]. Briefly, this is due to increased physical entanglement with increasing molecular weight, thus improving the toughness of the polymer. When comparing the effects of CNFs on the wear properties of Blends and HDPE, wear testing results (Figure 2.5) showed that the addition of CNFs into neat HDPE resulted in a 10% reduction in the wear rate. In contrast, the Blend nanocomposite with 1 wt % CNFs had about 42% reduction in wear rate. Therefore, in terms of relative changes in the wear rate, the addition of CNFs had a more pronounced effect on the wear properties of the Blend rather than neat HDPE, and UHMWPE was shown to have a greater contribution to the reduction of wear resistance of the system. This result suggests that the combination of HDPE, UHMWPE
and CNFs induce a synergistic effect on the wear properties of the Blend nanocomposites. From the morphology of the Blend nanocomposites, it was shown that the majority of CNFs were located in the HDPE phase. Accordingly, CNFs had little or no influence on the bulk portion of the UHMWPE phase. Therefore, in order for a synergistic effect to take place, UHMWPE may have had an influence on the HDPE-CNf phase. The influence of the UHMWPE phase on the HDPE phase was broken down into multiple: the dissolution of UHMWPE chains into the bulk HDPE phase, and dispersion of CNFs in the HDPE.

The amount of dissolution between UHMWPE and HDPE phases would seem to have competing influences on the wear rate of the Blend. First, higher amounts of dissolution of UHMWPE into HDPE would result in a higher wear resistant HDPE phase. In contrast, a higher dissolution of HDPE into UHMWPE would produce a less wear resistant UHMWPE phase. In order to explain which phase was most influenced (in terms of wear resistance) by changes in dissolution, a model was introduced in which the wear rate is inversely proportional to the molecular weight [24]. Because UHMWPE and HDPE have identical chemical structure, with only varying molecular weight, it may be appropriate to use this relationship to discuss the wear rates related to the amount of dissolution between the UHMWPE and HDPE. For a given polymer, the lower the molecular weight, the stronger the effect of any incremental changes in $M_w$ on the wear rate. This suggests that wear resistance of the HDPE phase was more strongly influenced than the UHMWPE phase by changes in molecular weight (which can be caused by changes in dissolution). As mentioned earlier, a decrease in dissolution of UHMWPE into HDPE should result in a less wear resistant, relatively lower molecular weight HDPE phase, while also maintaining a more wear resistant UHMWPE phase. Because the wear resistance of the HDPE phase is more strongly influenced by changes in dissolution, the overall wear resistance of the
Blend system would be expected to decrease with a reduced dissolution between the two phases, considering all other factors equal.

Though the decreased dissolution would seem to reduce the wear resistance of the Blend nanocomposites, the addition of CNFs both improved the wear resistance and reduced the dissolution of the Blend nanocomposites. Because of the phase separation, it is unlikely that the “synergistic effect” of UHMWPE and CNFs on the wear properties described earlier influenced the bulk portion of the HDPE phase by changes in dissolution. Rather, this synergistic effect may have been related to dispersion of CNFs by increasing shear stresses during mixing. However, due to the complexities of wear mechanisms, generally depending non-linearly with load, sliding speed, and counterface roughness, further research is needed for verification of this mechanism.

2.3.3 Wear surfaces and debris

Wear surfaces of the Blend and its constituents are shown in Figure 2.6. Due to the phase structure, the Blend and its nanocomposites were initially hypothesized to have much rougher wear surfaces than that of neat HDPE and UHMWPE. In the Blends, we suspected that the HDPE phase was removed first from the surface due to the lower wear rate of the HDPE phase, leaving elevated asperities of the UHMWPE phase. The UHMWPE phase would then be cyclically deformed under higher contact stresses, resulting in the formation of delaminated wear debris. For the neat HDPE and UHMWPE samples, we hypothesized that these wear surfaces would be much smoother than the Blends with and without CNFs due to the formation of UHMWPE asperities in the Blends. However, from wear surface images obtained (Figure 2.6), it was difficult to make any certain conclusions pertaining to the model that was proposed, as all samples had some asperities on the wear surface. UHMWPE showed the smoothest wear surface,
though there was still some roughness on the surface of this sample (Figure 2.6d). The size of the asperities in the Blends appeared to be much smaller than the size of the dispersed UHMWPE phase observed in optical images and fracture surfaces (which were generally around 100 microns in diameter). Thus, it was unlikely that these asperities were concealing any observations of the UHMWPE phase at the 100 micron size range of the Blends.

![Figure 2.6. Wear surfaces of (a) HDPE, (b) Blend, (c) nanocomposite with 1%wt CNF, (d) UHMWPE. Scale bar is set to 500 microns.](image)

In contrast to the results from our study, observation of phase separation of PP/UHMWPE blends has been clearly shown in literature on the wear surfaces under SEM [18]. These contrasting results can be attributed to a limited compatibility between PP and UHMWPE compared to the
UHMWPE/HDPE Blends in our study; UHMWPE and HDPE have essentially identical structure, with only varying chain length differences, thus there was superior inter-diffusion between the two phases. The enhanced dissolution in UHMWPE/HDPE blend compared to UHMWPE/PP systems increases the interfacial interaction between the two phases, making any distinction between the two phases on wear surfaces more difficult to observe. Moreover, any phase differences would be much less pronounced on wear surfaces than on fracture surfaces due to any melting that occurred during wear testing. In sum, there was no distinction between the HDPE and UHMWPE phases on the wear surfaces in our study.

For the debris, there were also no major differences among HDPE and the Blends with and without CNFs, as shown in Figure 2.7. The wear debris of HDPE and the Blend had comparable form, as small flakes with larger aggregates, though the wear debris of HDPE appeared to be smaller than that of the Blend. Similar morphology has been reported in literature for polyethylene wear debris [25] The wear debris of the Blend and its nanocomposites were very similar, having a large size distribution of wear debris ranging between 20-200µm. Additionally, no CNFs were found in the wear debris of the Blend nanocomposites. This suggests that the CNFs were exfoliated due to shear stresses during wear testing, resulting in minimal third body abrasive wear caused by the filler particles. The smaller, flake-like debris indicated adhesive wear, as the plastically deformed surface of the sample adhered to the counterface material. The HDPE phase of the Blends had the ability to flow under elevated temperatures (caused by friction between the counterface and the sample) such that when heated to sufficient levels, the strength of the adhesive bonds between the counterface metal and the contact surfaces were great enough to overcome the strength of the surface layer [26]. Therefore, adhesive wear of the HDPE phase due to thermal softening outweighed any abrasive wear mechanisms.
Figure 2.7. Typical wear debris of HDPE (a,b), Blend/nanocomposite (c,d), and UHMWPE (e,f).
Though no major differences were seen in the wear surfaces or debris between the Blend and Blend nanocomposites, there was an obvious reduction in the wear rate by adding CNFs. Since wear mechanisms of the Blend and nanocomposites appeared to be predominately adhesive, it is likely that the addition of CNFs into the Blend reduced the adhesive wear of the composite. Both decreasing the coefficient of friction and improving thermal conductivity (which has been clearly shown in literature for this ternary composite by increasing the concentration of CNFs [10]) would reduce any negative thermal softening effects on the wear rate. A reduction in thermal softening would allow the surface layer of the sample to maintain strength, while reduced friction would weaken adhesive bonds between the counterface metal and the contact surface of the sample. Therefore, reduced adhesive wear may have contributed significantly to the decrease in the overall wear rate of the composites with the incorporation of CNFs.

Figure 2.7 (e) and (f) shows the wear debris of pure UHMWPE, indicating a completely different distribution and morphology from that of Blend/Blend nanocomposites. The shape of the UHMWPE debris consisted of extremely long ribbons with widths between 50 and 200µm and some apparent fiber shapes (Figure 2.7e). A more detailed image shows that these “fibers” actually have a furled ribbon structure (Figure 2.7f). The long ribbon shape has been observed in other studies, where the formation of these ribbons has been shown to mostly depend on the roughness of the counterface metal [27,28]. These longer ribbon-shaped wear debris indicate a predominantly abrasive wear mechanism [28], in which counterface asperities plow the surface of the sample under repeated deformation.
2.4 Conclusions

The microstructure and wear properties of UHMWPE/HDPE/CNF composites were investigated in this chapter. Morphological results indicated two distinct UHMWPE and HDPE phases with CNFs preferentially residing in the HDPE phase. The addition of CNFs into both HDPE and the Blend reduced both the run-in and steady state wear rate of the material considerably, with an increasing concentration of CNFs resulting in lower wear rates. Though no major differences were seen among the wear surfaces or the debris of the Blend and Blend nanocomposites, there was an obvious reduction in the wear rate by adding CNFs. Interestingly, no CNFs were observed in either the wear surface or debris for the nanocomposite wear samples.

Though improvements in the wear properties were seen with the addition of CNFs, there are limitations of using HDPE for processing. First, CNFs do not reinforce the bulk portion of the UHMWPE, but rather the HDPE phase. Additionally, the incorporation of HDPE lowered the wear rate of the overall composite considerably. Therefore, in the sense of reinforcing the UHMWPE phase or improving the tribological properties of a UHMWPE composite, HDPE may not be appropriate for processing. Nonetheless, the synergistic effect of this ternary composite via the addition of CNFs may help satisfy specific demands where higher loadings of fillers are needed. Therefore, CNFs should be considered to be used to improve the wear resistance of UHMWPE materials through other processing methods, such as paraffin-assisted processing, which will be discussed in Chapter 3.
References:


CHAPTER 3

PROCESSING UHMWPE COMPOSITES USING PARAFFIN OIL

3.1 Introduction

In chapter 2, it was shown that adding HDPE can be used as a means to melt-mixing UHMWPE-CNFs composites. However, CNFs will be distributed exclusively in the HDPE phase, and tribological properties of these composites are inferior to pure UHMWPE. Therefore, for specific interest in tribological applications, it is necessary to for the matrix to be entirely composed of entirely UHMWPE. As mentioned in Chapter 2, proper dispersion of UHMWPE nanocomposites has been shown to be very difficult due to the exceptionally melt viscosity of this polymer. In this chapter, paraffin is used as a means of processing UHMWPE nanocomposites [1].

Processing of bulk UHMWPE composites is generally limited to dry mixing prior to compression molding due to the extremely high viscosity of this polymer [2–5]. However, this processing method results in very poor dispersion, leaving fillers trapped at the grain boundary between the granules. Agglomerates located at this interface may limit fusion between the UHMWPE granules, thus potentially degrading any performance enhancement. Other well-developed method for processing UHMWPE composites are through solution casting and gel spinning, though the UHMWPE must be extremely diluted (generally 1-3% UHMWPE) [6–10], yielding very small amounts of composite fibers and films with respect to original composition. Additionally, toxic solvents, such as xylene, are often used during processing [9,11], thus making this technique inappropriate for biomedical applications.

A bulk processing method that allows for improved dispersion of UHMWPE has recently been developed using paraffin oil to reduce the viscosity of this polymer during melt-mixing [12,13]. This processing method allows for improved dispersion compared to conventional dry-mixing...
methods, higher yield than solution casting and gel-spinning methods, and maintained tribological properties compared to polyethylene blending methods. In the paraffin-assisted melt-mixing method, UHMWPE is first dry-mixed with filler and then swelled with small oligomers (paraffin oil) to create more mobile UHMWPE chains and thus reduce the viscosity and allow penetration of the fillers into the UHMWPE grains. The composition is then melt-mixed to improve the dispersion using conventional extrusion mixing methods, after which the paraffin oil is extracted to limit any degradation in the mechanical and wear properties. The solvent used for extraction is generally hexane, which is also used in the food industry for extraction of various vegetable oils [14]. Though this method for processing UHMWPE appears to have great potential, combining high yield and improved dispersion, there has been only very few reports on this composite processing technique [12,13]. Furthermore, these studies have used higher concentrations of fillers, up to between 10 and 50 wt%. In order to maintain ductility and toughness, lower concentrations are desirable. Lastly, in these studies, there was no attempt at optimization of processing parameters reported, and relatively low concentrations of UHMWPE to paraffin oil were used.

In this chapter, we build upon those previous results for processing of UHMWPE-CNCF composites using paraffin oil, attempting to optimize important processing parameters such as UHMWPE/paraffin ratio. Additionally, we use low loadings (0.5 to 3 wt%) so that ductility and toughness of the UHMWPE composites are maintained. Wear and mechanical properties were determined to assess the effect of CNF concentration and processing parameters on property enhancement.
3.2 Experimental

3.2.1 Materials

Grade GUR 1020™ UHMWPE was kindly supplied by Ticona, with an average molecular weight of about $3.5 \times 10^6$ g/mol. CNFs were grade Pyrograf III®, HHT grade with 60-150 nm diameter and 30-100 µm in length, supplied by Pyrograf Products, OH, USA. Pharmaceutical grade Paraffin oil (Equaline) was used for processing. Hexanes (95% n-hexane, purchased from J.T. Baker) was used as the extraction solvent.

3.2.2 Processing methods

Composites with varying concentrations of CNFs were prepared as follows (Figure 3.1): UHMWPE and CNFs were first ground with mortar and pestle at concentrations of 0.5, 1, and 3 wt% CNFs. As a reference, neat UHMWPE was processed under similar conditions. Paraffin was then added to the composition at 7 vol% UHMWPE to paraffin oil. The slurry was then suspended by hot plate and magnetic stir bar for 1 hr at 145°C to ensure UHMWPE did not settle to the bottom during swelling. A temperature of 145°C was chosen so that the temperature was sufficiently past melting point, but not high enough to significantly degrade the UHMWPE and paraffin. Throughout this step the CNFs were bound to the UHMWPE, and excess paraffin oil remained clear. Once suspended, the composition was sealed to limit oxidation and was further swelled in an oven at 145°C for 3 hrs. The swelled composition was then cooled and cut into small pieces. Samples were melt-mixed in a Haake torque rheometer at 30 rpm, 145°C for 6 minutes until the samples appeared to be melted and homogenous, then the rpm was increased to 80 and samples were mixed for 9 more minutes. After mixing, samples were squeezed by compression molding at 100°C to eliminate a majority of the paraffin oil (yielding about a one-to-one ratio of UHMWPE to paraffin oil). Samples were then shredded to increase the surface
area and allow for paraffin oil to be extracted. Next, the remaining paraffin was removed using a soxhlet extractor for 24 hrs using hexane as a solvent. Extracted samples were then dried in a hood for at least 12 hours to eliminate the volatile hexane. Samples were compression molded at 180°C with a pressure of 4MPa and allowed to cool naturally to room temperature. For comparison with conventional processing methods, a dry-mixed UHMWPE 1 wt% CNF composite was prepared by mixing the polymer matrix and CNFs together in a mortar and pestle, after which the mixture was compression molded under the same conditions as above.

![Figure 3.1. Paraffin-assisted processing methods showing: dry-mixing, swelling, melt-mixing, initial reduction in paraffin, soxhlet extraction, and final compression molding.](image)

To improve dispersion of the CNFs in UHMWPE, various adjustments were made to the experimental above. First, before the swelling step, varying ratios of paraffin oil to UHMWPE were prepared (7 vol%, 35 vol%, and 50 vol% UHMWPE). Additionally, two samples were prepared with additional dispersion techniques prior to swelling: 1hr low-powered bath
sonification and 1hr high-powered ultrasonification. These samples were prepared in a similar manner as the samples initially prepared.

3.2.3 Thermogravimetric analysis

A thermogravimetric analyzer (TGA, SDT Q600) was used to determine the relative amount of any residual paraffin oil residue after each step of processing. Samples were heated from 50°C to 450°C at a rate of 10°C/min. TGA was performed at each stage of processing UHMWPE with paraffin oil.

3.2.4 Microscopy

Optical images (Olympus BX51TRF, Camera-U-CMAD) were obtained from microtomed composite samples (20µm thick). Field emission scanning electron microscopy (SEM, Quanta 200F) was used to observe fractured surfaces of samples. Fractured surfaces were prepared by freezing in liquid nitrogen for 15 minutes prior to fracture. All samples prepared for SEM were gold coated prior to imaging to limit static charging.

3.2.5 Wear testing

Wear testing was performed on a custom-built vertical pin-on-disk apparatus with a 1020 carbon steel disk, with surface roughness of Ra=0.21µm. Wear samples had dimensions of 5x5mm², and were mounted to SEM stubs prior to wear testing. The pin-on-disk wear tester was set to an effective sliding speed of 1.23 m/s with a normal force of 57 N, and wear tests were run for 72 hours. Specific wear rates were determined using the equation 3.1 discussed in Chapter 2:

\[ w = \frac{\Delta m}{\rho F d} \]  (3.1)
Between each wear test, wear debris were removed and the disk was cleaned thoroughly with acetone and dried before further use. Wear surfaces and debris were analyzed using SEM.

3.2.6 Punch testing

Mechanical testing was performed on a miniature punch tester according to ASTM F 2183 standards. Punch testing samples were prepared with a thickness of 0.5mm (+/-0.01mm) and diameter of 6.4mm. The diameter of the punch head was 2.54mm, with a die clearance of 3.8mm in diameter. The displacement rate was set to 0.5mm/min. A total of 10 punch testing specimens were tested for each sample.

3.3 Results for paraffin-assisted torque rheometer processing

3.3.1 Processing and morphology

In this study, paraffin oil was used as a plasticizer to improve processability of UHMWPE by reducing the entanglement of polymers and allowing fillers to enter into the granules during melt-mixing. Processing using paraffin oil involved many steps, including mechanically dry mixing constituents, swelling, melt-mixing, squeezing, and extracting paraffin with hexane. In order to maintain mechanical and wear properties, the paraffin oil needed to be extracted thoroughly.
Figure 3.2. Thermogravimetric analysis results for each stage of UHMWPE processing with paraffin oil for: (a) weight loss and (b) derivative of weight loss.

Thermogravimetric analysis (TGA) was used to determine if there was any residual paraffin oil in the processed UHMWPE after extraction, and tests were performed at each stage in processing (Figure 3.2). TGA curves were nearly identical between the neat UHMWPE and the control processed with paraffin oil, indicating that paraffin oil was extracted completely from the matrix during processing, within experimental error (Figure 3.2a). Figure 3.2b shows the derivative of the TGA curves for each stage of processing. The peak at around 350°C for UHMWPE at each stage before extraction is attributed to degradation of paraffin oil. After extraction, this peak is completely eliminated, further indicating satisfactory extraction of the plasticizer.

To ensure that processing of UHMWPE with paraffin oil is in fact a superior method in relation to conventional dry-mixing methods, a direct comparison was made between composites prepared by first swelling with paraffin oil and composites prepared by dry mixing with mortar and pestle. Optical images were obtained for a comparison of the distributions between samples at the microscopic scale (Figure 3.3a,b). Figure 3.3a showed a homogeneous distribution in the microscopic range for the 1 wt% CNF composite prepared by swelling with paraffin oil.
compared to the dry-mixed composite. In the dry-mixed composite, CNFs were distributed at the boundary of the UHMWPE grains (Figure 3.3b). Obviously, the composite processed with paraffin oil showed much improved homogeneous distribution at the microscopic scale compared to conventional bulk processing methods of UHMWPE.

Figure 3.3. (a,b) Optical images and (c,d) fracture surfaces (SEM) of composites prepared with paraffin oil (a,c) and dry-mixing (b,d) prior to compression molding.
Figure 3.3c and 3.3d show SEM images of fracture surfaces of 1 wt% CNF/UHMWPE composites processed with paraffin oil and dry-mixed, respectively. Fracture surfaces of samples processed with paraffin oil showed no obvious granule boundaries. In contrast, in the dry-mixed composite, there were obvious cracks between granule boundaries after fracture, likely due to limited fusion between the grains from CNF agglomerates at the grain boundaries. It should be noted that the fusion between granules may be improved by increasing the temperature and pressure during compression molding. However, the compression molding parameters were chosen in order to reduce degradation of the polymer and limit the adhesion to mold, while also yielding sufficient fusion of neat UHMWPE and composites processed with paraffin oil. Though fusion of the dry-mixed composite could be improved with different compression molded parameters, the fracture surfaces of the dry-mixed composite clearly demonstrated that fusion between UHMWPE granules was strongly affected by CNF agglomerates at the granule boundaries. Overall, fracture surfaces indicated that processing with paraffin oil allowed the CNFs to penetrate into the UHMWPE matrix resulting in a microscopically homogeneous distribution, while sufficiently eliminating granule boundaries.

Despite the availability of alternate processing of UHMWPE that can improve the distribution of fillers in UHMWPE, many recent reports continue to use dry-mixing as a means of processing UHMWPE [2–4]. The continued use of dry-mixing as a means of UHMWPE processing is due to its simplicity and 100% composite yield compared to solvent-assisted processing. In other processing methods, such as with the use of paraffin oil, there are multiple steps that can be time consuming. Therefore, further studies should work to make the paraffin-assisted method more time and cost effective while further improving property enhancement, which will be discussed in the melt extrusion section.
3.3.2 Wear testing

To further show the enhancement using paraffin-assisted UHMWPE processing and to determine the effect of concentration on tribological properties, wear testing was performed on these composites. Wear resistance of the UHMWPE composites were determined on a pin-on-disk apparatus. First, a comparison was made between the wear resistance of the composite processed with paraffin oil and the dry-mixed composite (Figure 3.4). Results showed an obvious improvement in the wear resistance of the composite processed with paraffin oil compared to the dry-mixed composite at 1 wt% CNF concentration. This property enhancement is attributed to improved dispersion and distribution of CNFs in composites processed with paraffin oil, as shown in the optical images, further illustrating the importance for improving bulk processing of UHMWPE composites. Next, the effect of CNF concentration on the wear rate of paraffin-assisted, melt-mixed UHMWPE composites was determined (Figure 3.4). A low loading of 0.5 wt% CNFs showed improved wear resistance compared to that of the UHMWPE control. However, with a higher concentration of CNFs, wear rates increased. It was hypothesized that the tendency for wear rates to increase at higher concentrations of CNFs was due to a larger number of agglomerates. This explanation was analyzed in further detail.
Figure 3.4. Influence of carbon nanofiber (CNF) concentration and distribution on the wear properties of UHMWPE composites. Inset optical images show the microscopic distribution of composites prepared by both dry-mixing and swelling with paraffin oil.

To verify the presence of agglomerates, we observed SEM images of fracture surfaces (Figure 3.5). From these SEM images, we found agglomerates in all samples, with the tendency for composites with higher loadings of CNFs to have an increased number of agglomerates. Therefore, the higher concentrations of agglomerates in the higher loadings may have accelerated the wear rate of the composites, as has been shown with other composite systems [13,15].
SEM images of wear debris and surfaces were obtained to further analyze mechanisms for the wear testing tendencies (Figure 3.6). From these images, the wear debris of both the UHMWPE control (Figure 3.6a) and UHMWPE composite (Figure 3.6b showed a similar ribbon-like morphology. This result suggests that the main mechanism for wear loss was through abrasive wear [16]. Furthermore, wear surfaces of the UHMWPE control (Figure 3.6c) and its composite (Figure 3.6d) show plowing of the plasticity-induced damage layer, as well as large grooves due to asperities on the articulating disk surface, both indicating abrasive wear mechanisms. Though there was a tendency for an increase in the wear rate with increasing concentration of CNFs, the composite prepared with 0.5 wt% CNFS showed an improved wear resistance compared to the UHMWPE control. Improved wear properties at such low loadings is important in that there are fewer chances to create defects, while ductility and toughness of the matrix can also potentially be maintained.
Figure 3.5. SEM images of fracture surfaces for (a) UHMWPE control, (b) UHMWPE-0.5 wt% CNFs, (c) UHMWPE-1 wt% CNFs, and (d) UHMWPE-3 wt% CNFs.
3.3.3 Punch testing

To determine the mechanical properties of the composites and ensure that the toughness of the material was maintained, punch testing was performed (Table 2). Punch testing was chosen as a means of determining the mechanical properties as it has been validated for use on UHMWPE and only small amounts of material are needed to perform testing [17]. The addition of CNFs in
UHMWPE resulted in moderately improved mechanical properties, with a tendency for strength and area under the load-displacement curve (toughness) to increase with increasing concentration of CNFs (Table 2). These results are very promising given that there was likely a high concentration of agglomerates at higher loadings. The mechanism for the improved energy dissipation is likely from fiber pull-out, in which nanofibers bridge the gap between microcracks. Long fiber pull-out was shown in fracture surfaces (Figure 3.5d). The stiffness of the material, determined by the initial slope of the load displacement curve, slightly increased upon loading of CNFs (Table 2). However, higher loadings up to 3 wt% did not show further increase in the stiffness properties. This nonlinear stiffness response may be partly due to CNF agglomerates at higher concentrations.

Table 3.1. Punch testing of UHMWPE and composites with varying concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stiffness (N/mm)</th>
<th>max load (N)</th>
<th>Ultimate load (N)</th>
<th>Ultimate displacement (mm)</th>
<th>Area under curve (N*mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE Control</td>
<td>40.3 (3.9)</td>
<td>86.4 (6.9)</td>
<td>65.3 (9.0)</td>
<td>4.15 (.22)</td>
<td>259.2 (32.1)</td>
</tr>
<tr>
<td>UHMWPE + 0.5 wt% CNFs</td>
<td>43.9 (1.8)</td>
<td>88.5 (11.9)</td>
<td>58.1 (11.5)</td>
<td>3.95 (.29)</td>
<td>246.7 (34.1)</td>
</tr>
<tr>
<td>UHMWPE + 1 wt% CNFs</td>
<td>43.6 (2.3)</td>
<td>89.8 (7.8)</td>
<td>69.9 (8.0)</td>
<td>4.09 (.14)</td>
<td>271.31 (27.8)</td>
</tr>
<tr>
<td>UHMWPE + 3 wt% CNFs</td>
<td>43.7 (3.3)</td>
<td>95.7 (6.4)</td>
<td>71.7 (6.89)</td>
<td>4.15 (.19)</td>
<td>286.4 (25.2)</td>
</tr>
</tbody>
</table>

The improvement in toughness from the nanocomposites prepared in our study is in direct contrast to the previously commercially produced carbon fiber-reinforced UHMWPE, under the trade name of Poly II, which had a much higher stiffness and much lower ductility than that of
neat UHMWPE. The increased contact stresses and decreased ductility resulted in failure in the form of delamination and fracture [18]. From the composites prepared in our study, the increase in stiffness was only moderate. Therefore, contact stresses between the composite and articulating metal surface during wear testing were not significantly increased at higher CNF loadings. Additionally the area under the load-displacement curve increased moderately, indicating slightly improved toughness of these nanocomposites. The punch testing results in this study are comparable to another study by Galetz et al. [13], who also showed that the toughness of UHMWPE-CNf composites prepared by paraffin-assisted extrusion tended to increase with additional loadings of CNFs. Though toughness of the nanocomposites prepared in our study was maintained, further improvement in the dispersion nanocomposites is needed in order to realize full potential, as indicated by wear testing and fracture surfaces. Thus, processing parameters were further optimized to enhance the dispersion of the nanocomposites.

3.3.4 Further optimization of processing parameters

Because of the obvious need to improve the dispersion of the CNFs in the prepared composites, indicated by the increased wear rate at higher loadings of CNFs, additional procedures were applied during processing. First, the composites were prepared with varying concentrations of paraffin oil prior to swelling. It was hypothesized that there was an optimal amount of paraffin oil to which the dispersion of the carbon nanofibers could be improved: higher concentrations of paraffin oil would allow fillers to enter into the UHMWPE granules more easily, and thus improve the distribution of CNFs. In contrast, lower concentrations of paraffin oil would induce higher shear stresses on the agglomerates, allowing the agglomerates to be broken up more
readily, given that friction between the barrel and polymer matrix was greater than the internal friction of the composite during mixing. Wear testing was used to evaluate the effect of changing paraffin concentrations during processing, as wear testing results were shown to be sensitive to the dispersion in composites with varying concentrations of UHMWPE (7, 35, and 50 vol%). A high concentration of 35 vol% UHMWPE for composite processing resulted in the most reduced wear rate, while UHMWPE concentration of 50 vol% for composite processing resulted in the highest wear rate.

![Figure 3.7](image)

Figure 3.7. Relative wear rate of UHMWPE-1 wt% CNF composites prepared with varying concentration of paraffin during processing.

3.3.5 Discussion

Wear testing results suggested that there was in fact an optimal concentration of paraffin oil used during processing at about 35 vol% UHMWPE to paraffin oil in which wear properties of the nanocomposites were enhanced (Figure 3.7). The existence of an optimum concentration of UHMWPE/paraffin oil for processing can be explained by contributions between the distribution and dispersion of the CNFs. Processing with low concentrations of UHMWPE allows sufficient
distribution of CNFs throughout the UHMWPE matrix. However, the shear forces generated will be low, and thus fewer agglomerates may be broken up. At higher concentrations of UHMWPE, the shear forces will generally be much greater, though the homogeneous distribution may be affected because of the difficulties in fillers penetrating into the matrix. Lastly, the viscosity of the melt-mixed composition cannot be so great as to overcome the shear forces between the wall of the mixing barrel/rotor and the melted composition. This would potentially result in slipping, resulting in both inferior distribution and dispersion of fillers. In addition to optimizing the concentration of paraffin oil used during processing, both low-power bath-sonification and high-power ultrasonification were implemented into the processing (Figure 3.7). Both bath sonification and high powered ultrasonification reduced the wear rate of the composites by also breaking up agglomerates, with high-powered ultrasonification showing the largest improvement in wear resistance. Further optimization of processing parameters should be implemented by combining sonification and paraffin oil parameters while simultaneously optimizing mixing speed and temperature, as these parameters may be coupled due to stick-slip processes and shear-induced phase separation [19].

Processing with higher concentrations of UHMWPE not only enhanced the physical properties of the composites, which was attributed to improved dispersion, but it also dramatically improved the yield of the final product compared to other UHMWPE composite processing methods found in literature. To the best of the authors’ knowledge, there are only a few studies that have used paraffin-assisted extrusion for bulk processing of UHMWPE composites [12,13]. Of these few studies, only one actually reported the concentration of UHMWPE in paraffin oil used for mixing (15 vol%) [12]; however, no optimization of the UHMWPE concentration was attempted or determined. In the present study, our expanded processing evaluation determined an optimal
concentration of UHMWPE to be about 35 vol%, more than twice the concentration of that used previously [12], and thus more than twice the yield of the final composite product. Furthermore, for studies related to processing of UHMWPE composite films and fibers, this polymer is generally diluted to around 1-3 vol% UHMWPE [6,8,11], resulting in a very poor final product yield, about ten times lower than the optimal concentration determined in the current study (35 vol%). The choice of using such a low concentration of UHMWPE was likely based on processing of UHMWPE fibers without any fillers, in which the primary concern would be to align polymer chains rather than break up agglomerates during mixing. However, a higher concentration of UHMWPE can be more beneficial, not only by generating shear stresses during mixing that will be helpful to break up agglomerates, but also improving the yield of the final composite product.

These results may have implications for processing of UHMWPE composites in industry by allowing preparation to be more time and cost efficient, in which the paraffin-assisted melt-mixing/extrusion could be made into a continuous process. Additionally, by using paraffin oil as a means of processing, volatile and toxic solvents are not needed for swelling of the polymer. Volatile solvents make melt-mixing virtually impossible, as the solvent will evaporate during mixing. Furthermore, toxic solvents, which are often used for processing of UHMWPE films and fibers, should be avoided when possible, especially if the composite is intended for biomedical applications. Using paraffin oil to assist in melt-mixing eliminates any of these concerns, while also improving the yield of the final composite product. Though improvement in wear properties were seen with optimization of processing parameters, there is still dramatic potential for further improvement using this processing technique. In particular, a more detailed analysis should look to eliminate stick-slip processes, which is a major issue for paraffin-assisted mixing because
paraffin oil has the ability to act as a lubricant between screw/barrel of the mixer and the material. By further adjusting the temperature, mixing speed, and paraffin content, the shear forces between the screw/barrel and material, and thus the dispersion of the fillers, can be further enhanced.

3.4 Paraffin-assisted twin-screw extrusion

In this section, previous paraffin-assisted processing results are expanded upon by mixing with a high-powered twin-screw extruder instead of a torque rheometer, allowing for a higher volume of composites to be processed and potentially higher shear stresses to be generated. Furthermore, tedious processing steps, such as swelling and manually cutting samples before and after melt mixing were eliminated to improve efficiency. Again, various concentrations of paraffin were used for processing. Wear and mechanical properties of these composites were studied.

3.4.1 Processing methods

Twin-screw extruded UHMWPE composites were prepared as follows (Figure 3.8): First, UHMWPE was dry-mixed with 1wt% pristine CNFs by mortar and pestle, and then further mixed with paraffin into a slurry with varying UHMWPE/paraffin ratios at 400ml volume total. However, due to the consistency of the 100g/300ml UHMWPE/paraffin samples, this ratio was not further processed using the twin-screw extrusion method. All other samples were processed using the twin-screw extruder. The temperature profile of the extruder was 150°C throughout.
Figure 3.8. Methods for twin-screw extrusion of UHMWPE CNF composite processing. Note that fewer processing steps were needed using this method.

After mixing, paraffin was extracted to ensure that mechanical properties are not degraded. Paraffin was squeezed out of the composition using a hot press at 100°C. See the methods section of this chapter for more details. A soxhlet extractor was used for extraction, with hexane as the solvent of choice. Extraction was performed for 24 hrs. For this extraction, 80ml thimbles and 250ml of hexane were used for this extraction process. Because of the differences in extraction techniques between twin-screw and torque rheometer batches, TGA was again performed to ensure adequate extraction of the paraffin.

3.4.2 Characterization methods

TGA was used to determine if there was any residual oil present in the nanocomposites after extraction. Figure 3.9 shows that extraction was complete within the sensitivity of TGA. After extraction, composites were reconsolidated using a hot press under identical conditions to previously prepared UHMWPE composites, as described in the Section 3.2.2 of this chapter.
3.4.3 Results and discussion

For initial qualitative purposes, optical images were observed for each of the composite samples. Samples were sectioned at 10 microns and were observed at 5x and 100x magnification (Figure 3.19). Results showed that though composites were essentially homogeneously dispersed at the macroscopic level, agglomerates were widely seen microscopically, indicated further improvement in dispersion is needed.
Tensile tests were performed on UHMWPE composites prepared by twin-screw extrusion under varying concentrations of paraffin oil (Figure 3.11). Though the modulus and yield strength showed only marginal differences between UHMWPE and 1wt% CNF composites, there was an obvious increase in ultimate strength and elongation to break. From this data, it appeared that CNFs were effectively reinforcing the UHMWPE matrix. Though there was an improvement in ultimate strength and elongation to break, there did not appear to be a strong effect of processing conditions on the mechanical properties.
Figure 3.11. Mechanical properties of UHMWPE/1wt% CNF composites prepared by twin-screw extrusion: (a) yield strength, (b) modulus, (c) ultimate strength and (d) strain at break.

Figure 3.12. Wear rates of UHMWPE and 1wt% CNF composite prepared by twin-screw extrusion with 37.5vol% UHMWPE in paraffin.
In addition to mechanical testing, wear testing was performed on twin-screw extruded samples prepared with 37.5vol% UHMWPE (Figure 3.12). Thus far, only a comparison was made between 37.5vol% UHMWPE and 1wt% CNF composites, and wear testing of other samples prepared with other UHMWPE concentrations are still under way. Wear testing results showed that the wear resistance of UHMWPE and its 1wt% CNF composite were very similar to each other, comparable to the results shown in Figure 3.4. When evaluating the mechanical and wear properties for all of the samples, there appeared to be no correlation between mechanical properties, such as ultimate strength, elongation to break, and area under the stress-strain curve, in relation to the wear properties. Because wear testing involves repeatedly applied loads, mechanical properties pertaining to fatigue may correlate better with wear properties [20,21].

Though no substantial differences were seen between various paraffin-assisted processing conditions and wear properties of composites, the twin-screw extrusion method allowed for more material to be processed and fewer steps to be needed for full production of the composites compared to the torque rheometer processing method. Given the wear and mechanical testing results, further work needs to be performed for improving the dispersion of these composites. The inconsistencies in the dispersion, wear, and mechanical properties are likely caused by differences in the processing techniques between the samples mixed by torque rheometer and twin-screw extrusion. Most obviously, the shear stresses generated between the two mixing techniques will be much different. Generally, the shear stresses generated by twin-screw extrusion will be larger than by the torque rheometer. However, if the melt viscosity is too high compared to the friction between the material and barrel, slippage between the material and mixing barrel may occur. Another difference between the two processing methods was that samples prepared by twin-screw extrusion were not swelled prior to mixing, which may have
further affected slipping against the barrel wall. Obviously a quantitative dispersion study should be performed between the two different types of processed materials prepared. Further work should also look at differences between pre-swelled and un-swelled samples in relation to dispersion, wear, and mechanical properties. Lastly further wear testing of composites prepared with an initial volume 43.25 and 50\text{vol}\% \text{UHMWPE} need to be performed in order to determine the true effect of paraffin concentration on the wear properties. Though optical images show satisfactory dispersion at the macroscopic scale, dispersion at the microscopic scale, mechanical testing, and wear testing indicate a need for continued improvement in the dispersion.

3.5 Conclusions

In this study, a comparison was made between composites prepared with a new paraffin-assisted melt-mixing method and a conventional dry-mixing method. Results showed that processing with paraffin oil prior to melt-mixing resulted in a dramatically improved distribution of the CNFs at the microscopic scale. Additionally, it was illustrated that both the wear resistance and mechanical properties can be enhanced at low concentrations of CNFs using our paraffin-assisted processing technique, in which composites prepared with lower concentrations maintained ductile and toughness properties of the matrix. Previous studies that utilized a paraffin oil method made no attempts at optimization of processing parameters, and relatively low concentrations of UHMWPE in paraffin oil were used. In this current research, we built upon those previous results, attempting to optimize critically important processing parameters such as the UHMWPE/paraffin ratio. The optimal concentration of UHMWPE in paraffin oil was found at 35\text{vol}\% for samples mixed by a torque rheometer, resulting in a final composite yield substantially greater than what has been previously reported under similar processing methods.
Thus, not only can the property enhancement be more substantial, but also the efficiency of composite preparation.

Composites samples were also prepared by paraffin-assisted twin-screw extrusion in order to prepare more material for further mechanical testing, potentially generate higher shear forces, and reduce tedious steps such as swelling and manually cutting samples before and after melt-mixing. Certainly, much more material can easily be processed, and the processing steps were substantially reduced by using the twin-screw extrusion process. However, both mechanical and wear properties were not satisfactory, suggesting that there was poor dispersion within the composites. Further work is needed in order to study mechanisms for contrasting results and improved dispersion of the melt-mixing methods.
References:


CHAPTER 4
SYNTHESIS AND CHARACTERIZATION OF OCTADECYLTRIMETHOXYSILANE-
TREATED CARBON NANOFIBERs

4.1 Introduction
In Chapters 2 and 3, processing of UHMWPE nanocomposites was discussed extensively, which will have a direct impact on the dispersion of the nanocomposites. However, an important aspect of nanotechnology that has not yet been discussed thoroughly is improving interactions between the nanofiller and polymer matrix. Interactions are particularly important for nonpolar matrices, such as polyethylene, as interactions are generally limited Van der Waals forces unless special treatments are made. In this chapter, non-polar silane coupling agents are applied to the surface of CNFs to improve such interactions. Specifically, this chapter illustrates the effect of using NaOH as a catalyst on the coating thickness of octadecyl trimethoxysilane treated CNFs, and the effect of such treatments on the potential for improved compatibility with non-polar matrices [1].

4.1.1 Surface treatment of nanofillers
Uniform dispersion of nanofillers and strong interaction between polymer matrix and the fillers are critical for the development of high performance nanocomposites. Therefore, in the past various treatment approaches for the nanofillers have been applied. Generally, for development of polar polymer nanocomposites, the treatments of the nanofillers can be more facile, as even simple oxidation can work well to enhance the load transfer and the dispersion of nanofillers within polymer matrices, due to the polar interactions [2,3]. However, for non-polar polymer matrices such as polyethylene, the approaches to obtain advanced nanocomposites in volume production have been more challenging. To improve the compatibility of the reinforcements with a non-polar matrix, reinforcements can be functionalized with various hydrophobic and vinyl
moieties similar to the polymer matrix being used [4,5]. An effective approach to obtaining functionalized nanofillers is to provide a coating to form a bridge layer between nanofillers and the polymer matrix. When coatings are applied to the fillers in various composite systems, the coating thickness may have a dramatic influence on the overall properties of the composite [6,7]. This may be particularly important for composite systems with non-polar polymer matrices, as interactions between non-polar coatings and polymer matrices are limited to weak van der Waals forces. Much stronger physical entanglement interactions may be realized by applying thicker coating layers.

4.1.2 Silane treatments

Silanization is a very popular method used to improve dispersion and load transfer in polymer composites. Silane coupling-agents have many advantages, including: widespread commercial availability, capability of readily reacting with oxide-rich surfaces, and extensive variety of end groups that can be chosen based on the polymer matrix being used [4]. Thus, by selecting the appropriate silane end groups, the compatibility and interaction between the filler and the polymer matrix can be improved. Silane coupling agents have been applied to natural fibers [4], titanium oxide particles [5], clay nanoparticles [8], oxidized carbon nanofibers [9], and oxidized carbon nanotubes [10–12]. For polyethylene composites, generally two types of silane treatments have been used: vinyl silanes and long hydrocarbon-tailed silanes [4,5,13]. The advantage of using long-hydrocarbon tailed silane treatments is that additional free radical reactions are not needed to complete the treatment. In a study using a composite system with a long hydrocarbon-tailed coating, the effect of hexadecyltrimethoxysilane (HDMS) on cellulose fiber reinforced polyethylene composites was reported [4]. More recently, Barus et al. also applied an HDMS treatment to nanosilica reinforced HDPE composites [13]. However, in those studies, only thin
coatings were applied, so the HDMS coatings likely were not thick enough to induce physical entanglement between the coating and matrix, resulting in only marginal improvement in mechanical properties of the composites with hydrocarbon-tailed silane treated fillers. To the best knowledge of the authors, thus far, there has been no reported work on the synthesis of thicker silane coatings on nanofillers or studies on effects of silane coating thickness of nanofillers for nanocomposite applications. It was hypothesized that thicker coatings would yield much improved mechanical properties compared to thin-layered organosilane treatment in polyethylene composites.

![Diagram of silane coupling agent reaction onto CNFs](attachment:Scheme4.1.png)

Scheme 4.1. Reaction of silane coupling agent onto CNFs.

In this chapter, octadecyltrimethoxysilane (ODMS) was chosen as an organosilane coupling agent. ODMS has long non-polar hydrocarbon chains to improve the compatibility between the CNFs and polyethylene matrix (the structure shown in Scheme 1). CNFs with both thin and thick
coatings were synthesized for reinforcement of the nanocomposites. The coating thickness was adjusted by altering the amount of water present during hydrolysis and using a basic catalyst (NaOH) to enhance the condensation reaction during synthesis of the coating, which has not been used for any reported work for silane coating onto nanofillers. It is shown here that such treatments show improved suspension in paraffin oil, thus indicating improved compatibility with nonpolar matrices.

4.2 Experimental

4.2.1 Materials
Pristine and oxidized CNFs (PR-24-HHT, and PR-24-HHT-OX grade, respectively) were obtained from Applied Sciences Inc. The diameter of the carbon nanofibers were approximately 60 to 150nm in diameter and 30 to 100 microns in length. HDPE (LB010000) was purchased from Equistar, with flow momentum index of 0.5g/10min (at 190°C) and density of 0.953g/cm³. Octadecyltrimethoxysilane (ODMS) (90% technical grade) was supplied by Sigma Aldrich. Acetone was obtained from J.T. Baker. Ethanol was purchased from Decon Laboratories Inc.

4.2.2 Silane treatment of CNFs
A typical reaction was as follows: oxidized carbon nanofibers (Ox-CNFs) were first bath sonified (Branson Sonifier 1510) in ethanol in a three-neck round bottom flask for 1 hour. ODMS was diluted in 10ml of ethanol, and the ODMS-ethanol solution was added to the Ox-CNF suspension slowly in 0.5ml increments after the suspension started to reflux. The reaction was under reflux for five hours. The silane-treated CNFs were then vacuum dried, washed with ethanol and acetone to remove any unreacted coupling agent, then left in the hood over night,
after which the treated CNFs were dried in an oven at 100°C for 12 hours. Reactions varied
based on the amount of CNFs treated, amount of ODMS used, water added to increase
hydrolysis (ranging between 0% and 20%), the amount of solution present, and the addition of
NaOH as a catalyst. Details of each treatment are shown in Table 4.1. For all treatments using
NaOH as a catalyst, effectively $5 \times 10^{-4}$ mol/L was added to the suspension prior to the addition of
diluted ODMS, resulting in a pH of about 10. Three treatments were selected for further analysis.
For these three samples, ~1g of CNFs were treated with 3ml ODMS in 80ml of ethanol solution
($8.8 \times 10^{-2}$ mol/L). For Treatment 1 (Table 4.1), 95% (v/v) H$_2$O/ethanol was used as solvent for the
reaction, and NaOH was added prior to reflux. For Treatment 2, pure ethanol was used and
nitrogen gas was added prior to reflux to reduce the amount absorption of moisture from the air.
Finally, for Treatment 3, 95% (v/v) H$_2$O/ethanol was used as a solvent. Experimental setup is
shown in Figure 4.1.

Figure 4.1. Experimental setup for synthesis of octadecyl trimethoxysilane treated CNFs.
4.2.3 Characterization

A Thermogravimetric Analysizer (TGA, SDT Q600) was used to determine the wt% of coating on the CNFs with each type of treatment. TGA was also used to screen treatments for further analysis. The temperature range for TGA testing was from ambient temperature to 600°C, with a heating rate of 20°C/min in an N₂ environment and flow rate of 100ml/min. Approximately 2mg of CNFs were tested for each sample. Fourier transform infrared microscopy (FTIR, Nexus 670 ESP) was used to characterize the functional groups of the ODMS treatment on the CNFs. Diluted CNFs (~0.01mg) were mixed with 10 mg of potassium bromide (KBr) to prepare KBr disks of 0.5mm in thickness. A JEOL-EX transmission electron microscope (TEM) was used to observe the morphology of the treated and untreated CNFs. For TEM sample preparation, CNFs were suspended in ethanol. After settling, the top layer was collected and dispersed onto a 300 mesh copper TEM grid. To determine the effect of treatment on the dispersion of CNFs in paraffin oil, 1 mg of CNFs were suspended in 10ml of paraffin oil by agitation. Additionally, to further suspend the CNFs, bath sonification was performed and was allowed to settle for one week. Images were taken after initial agitation, directly after bath sonification, and one week after sonification.

4.3 Results and Discussion

4.3.1 Thermogravimetric analysis

Because of the high thermal stability of CNFs and relatively low degradation temperatures of organic coatings, thermogravimetric analysis (TGA) was used to screen silane-treated CNFs for further testing by determining the wt% of the coatings [14]. Preliminary treated CNF samples were prepared by adjusting the pH (adding a basic NaOH-ethanol solution, ~10 pH), as well as
altering the concentration of water and silane in the solution. The general reaction between the silane coupling agent and the filler is as follows: first, the trialkoxy groups on the silicon are hydrolyzed by either moisture on the filler or by water in the solvent. Once hydrolyzed, these silanol groups become very reactive, forming chemical bonds to hydroxyl groups on the CNFs [11], as shown in Scheme 1.

This mechanism shows that increasing the concentration of water and silane will drive the reaction toward silane-treated CNFs. However, from initial TGA results, the concentration of water and silane had a very small effect on the weight loss of the silane coating compared to the effects of the catalyst (Table 4.1). Increasing the concentration of water from 5% to 20% (by volume) only increased the coating weight by about 2wt%, while doubling the concentration of the silane yielded an increase in coating weight ranging between <1wt% to 5wt%, depending on other conditions of the treatment. In contrast, the weight loss of catalyzed silane-treated CNFs upon TGA dramatically increased (>50wt%) compared to all other treatments.
Scheme 4.2. Simplified mechanism for influence of basic catalyst on the silane treatment of CNFs.

Hydrolysis and condensation reactions of the silane groups can be controlled by changing the pH value of the solution during reflux [15]. Both low and high pH values result in increased hydrolysis compared to neutral conditions. However, acidic solutions stabilize hydrolyzed silane molecules, while basic solutions enhance condensation reactions [16]. Under acidic conditions, the alkoxy-groups of the silane are protonated, forming leaving groups and thus increasing the rate of the hydrolysis reaction, while also creating some stability against further condensation reactions [16]. In contrast, under alkaline conditions very strong nucleophiles are formed, enhancing both hydrolysis and condensation reactions. Therefore, the coating thickness can be increased by increasing the pH of the solution during reflux. A simplified mechanism for the
influence of the catalyst is shown in Scheme 4.2. The selection of treated CNFs for further analysis was chosen based on the strong influence of the catalysis on the thickness of the coating. Treatments 1, 2, and 3 (shown in Table 4.1) were selected for further analysis.

Table 4.1. Detailed conditions for each carbon nanofiber treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grams of CNF</th>
<th>Volume of ODMS(ml)</th>
<th>H2O added</th>
<th>Volume of solution</th>
<th>Catalyst</th>
<th>Wt% (TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>.17g</td>
<td>.75ml</td>
<td>5%</td>
<td>150ml</td>
<td>None</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>(b)</td>
<td>.17g</td>
<td>.75ml</td>
<td>20%</td>
<td>150ml</td>
<td>None</td>
<td>~3%</td>
</tr>
<tr>
<td>(c)</td>
<td>.05g</td>
<td>.25ml</td>
<td>5%</td>
<td>150ml</td>
<td>None</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>(d)</td>
<td>.05g</td>
<td>.25ml</td>
<td>5%</td>
<td>80ml</td>
<td>None</td>
<td>~6%</td>
</tr>
<tr>
<td>(e)</td>
<td>.05g</td>
<td>.25ml</td>
<td>5%</td>
<td>80ml</td>
<td>NaOH</td>
<td>~60%</td>
</tr>
<tr>
<td>(f)</td>
<td>.11g</td>
<td>.5ml</td>
<td>5%</td>
<td>80ml</td>
<td>NaOH</td>
<td>~60%</td>
</tr>
<tr>
<td>Treatment 1</td>
<td>~1g</td>
<td>3ml</td>
<td>5%</td>
<td>80ml</td>
<td>NaOH</td>
<td>~55%</td>
</tr>
<tr>
<td>Treatment 2</td>
<td>~1g</td>
<td>3ml</td>
<td>none</td>
<td>80ml</td>
<td>None</td>
<td>~2%</td>
</tr>
<tr>
<td>Treatment 3</td>
<td>~1g</td>
<td>3ml</td>
<td>5%</td>
<td>80ml</td>
<td>None</td>
<td>~5%</td>
</tr>
</tbody>
</table>

According to TGA results, Treatment 1 yielded approximately 60 wt% coating, treatment 2 yielded approximately 2 wt% coating, and Treatment 3 yielded approximately 5 wt% (Figure 4.2). Changes in the weight percent of the silane coating with different treatments can be attributed to differences in reactivity, influenced by the catalyst and concentration of H2O in solution. For Treatment 1, a basic catalyst was used to increase both hydrolysis and condensation by enhancing the nucleophilic properties of the reactive portion of the silane groups [16]. For Treatment 2, pure ethanol was used for both dilution and reflux, so hydrolysis of the ODMS was limited to the effect of moisture absorbed in the CNFs and impurities in ethanol,
resulting the thinnest coating. Lastly, for Treatment 3, 5vol% water was present in the solution, so hydrolysis was more prevalent resulting in more reactive silane groups than Treatment 2, though much less than Treatment 1 due to the effects of the catalyst.

Figure 4.2. (a) TGA curve for ODMS, Ox-CNFs, and Ox-CNFs with various treatments. (b) Detailed curve for Ox-CNFs, Treatment 2, and Treatment 3

Not only can TGA results quantify the amount of silane coating, but it can also give information about the chemical structures of the coating based on the weight loss temperature [13,17,18]. For ODMS, weight loss initiated at about 200°C, corresponding to the boiling point of ODMS (170°C). In contrast, there was no mass loss of the silane near 200°C, and all of the silane-treated CNFs showed accelerated mass loss at approximately 450°C, in the temperature range of hydrocarbon chain scission [13,19]. (Figure 4.2). These TGA results give evidence for two important properties concerning the chemical nature of the treatment. First, the lack of any measured weight loss of the silane-treated CNFs near 200°C indicated that ODMS molecules
have been completely reacted or have been washed thoroughly, within experimental sensitivity of the TGA. Secondly, the acceleration of weight loss of silane-treated CNFs in the temperature range of hydrocarbon chain scission indicated that the silane coating had been effectively condensed [20].

4.3.2 Fourier transform infrared spectroscopy

Figure 4.3 shows FTIR data of silane-treated CNFs and its constituents. For ODMS, the peaks at 2920 and 2850 cm$^{-1}$ were assigned to C-H anti-symmetric and symmetric stretching bands, respectively [21,22]. The peak at 820 cm$^{-1}$ was assigned to the methyl rocking mode in SiO-CH$_3$ bonding [12,23], and the peak at 1191 cm$^{-1}$ was assigned to Si-O-CH$_3$ bending [24]. Lastly, the peak at 1089 cm$^{-1}$ was assigned to Si-O stretching [25].

For silane-treated CNFs, the peaks at 2920 and 2850 cm$^{-1}$ were present, but especially emphasized for Treatment 1. These peaks confirm the presence of C-H sp$_3$ bonding, indicating hydrocarbon chains on the surface of CNFs prepared with Treatment 1 [20,21]. The disappearance of peaks at 820 and 1191 cm$^{-1}$ upon CNF treatment, shown in Figure 4.3b,
indicated the methyl group of the Si-O-CH$_3$ in ODMS is no longer present upon treatment of CNFs. Additionally, the peak at 1089 cm$^{-1}$ was broadened upon treatment of OX-CNFS treatment, with additional peaks formed at 1026 and 1115 cm$^{-1}$. This result indicated there may have been Si-O-Si bonding formed during treatment [21]. FTIR results confirm the presence the silane coating, and there is strong evidence for a change in the chemical structure of the coupling agent from SiOCH$_3$ to Si-O-Si and potentially Si-O-CNFS for Treatment 1. This change in chemical structure allows for a crosslinking network of the silane coating to be formed [21]. Thus for Treatment 1, a slightly basic solution appeared to be sufficient to induce condensation of the modified ODMS onto the CNFs. For Treatments 2 and 3, confirmation of the silane treatment was less noticeable, and further analysis was needed.

4.3.3 Transmission electron microscopy

To confirm the relative coating thickness of each treatment, and to verify that the silane treatment was indeed coated onto the CNFs, transmission electron microscopy images were prepared for treated CNFs (Figure 4.4). Figure 4.4a shows Ox-CNFS without silane, showing very distinct edges of the cup-stacked CNF structure. Note that there are outer portions with long edges of the CNFs that are darker than other areas. These darker outer portions served as an indicator for the location of the interface between the CNFs and the silane coating for Treatments 1, 2, and 3. Figure 4.4b shows a very clear heavy coating on Treatment 1, with a distinct interface between the CNFs and silane coating. An Additional image of Treatment 1 is shown in Figure 4.5, clearly showing a silane coating on the CNFs. Treatments 2 and 3 appeared to have much less noticeable coatings, though rough edges were no longer visible, in contrast to images of Ox-CNFS without silane treatment. Additionally, for both Treatments 2 and 3, there was material extended past the
darker outer portions of the CNFs, indicating potentially thin coatings on the surface of these fillers.

![Figure 4.4. TEM images of (a) Ox-CNF, (b) CNF with Treatment 1, (c) Treatment 2, and (d) Treatment 3](image)

Table 4.2. Calculated coating thickness from each treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>% wt (from TGA curves)</th>
<th>% Volume of silane coating</th>
<th>Calculated coating thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>77</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4.4</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>10.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

In order to make a direct comparison between TEM and TGA results, the average coating thickness was calculated based the wt% loss for each treatment obtained from TGA. Assuming
that the Ox-CNFS and ODMS have a density of 1.95g/ml and .88g/ml, respectively, the volume fraction of CNFs for each treatment was calculated (Table 4.2). Additionally, a cylindrical shape of the CNFs and silane coatings was assumed. Under this assumption, the volume of each CNF and silane coating must be proportional to the cross-sectional area. Therefore, the average coating thickness was calculated for each of the treatments based on the following equation:

\[ \pi r^2 x_v \pi (r + \tau)^2 \]  

where \( r \) is the radius of the CNF, \( x_v \) is the volume fraction of CNFs, \( \tau \) is the thickness of the coating. Simplifying and solving for \( \tau \), we get:

\[ \tau = (1 - x_v^{1/2}) r / x_v^{1/2} \]  

From Equation (2), an estimated average thickness was calculated using TGA data, assuming an average CNF diameter of 100nm.

Figure 4.5. TEM image of individual CNF treated with ODMS under alkaline conditions.

The calculated thickness according to the TGA results was completely congruent with TEM images. The Average coating thickness for Treatments 1, 2, and 3, was 46nm 1.2nm, and 2.8nm,
respectively (Table 4.2). The coating thickness of Treatments 2 and 3 are comparable to that found in literature for silane-treated fillers [26]. However, Treatment 1 yields a much thicker coating for a typical silane treatment on fillers, as the NaOH catalyst used for this treatment enhanced the condensation reaction, thus increasing the crosslinking network structure between silane groups.

4.3.4 Suspension Studies
Suspension studies give an idea of the dispersion and compatibility between the treated filler and solvent, which in turn relates to the interactions between fillers and polymer matrices with similar structure to the solvent. Paraffin oil was chosen as the medium for suspension testing, as paraffin oil is composed of linear hydrocarbon chains analogous to HDPE. Figure 4.6 shows images of the suspension of untreated and treated CNFs in paraffin oil. Both pristine and Ox-CNFs showed poor suspension in the paraffin oil after initial agitating. Additionally, Treatment 1 did not disperse well upon initial agitation, likely due to CNFs being loosely bound together from the coating. On the contrary, Treatments 2 and 3 had an improved suspension, with 2 having the most improved suspension properties. The relationship between the initial suspensions of Treatments 1, 2, and 3 correlate well with the thickness of the coating. At low coating thickness, the interaction between the CNFs and paraffin oil is improved. However, with increasing coating thickness, the CNFs may have been loosely bound together and simple agitating could not break up these lightly attached CNFs so bath sonification was used to further suspend CNFs in paraffin oil.
Upon bath sonification, all CNFs initially suspended in the paraffin medium (Figure 4.6). This indicates that low power bath sonification was able to break up the lightly bound CNFs prepared with Treatment 1. One week after bath sonification, pristine and Ox-CNFs, as well as CNFs prepared with Treatments 2 and 3, fell out of suspension at similar rates. In contrast, CNFs prepared by Treatment 1 stayed suspended very well. Once agglomerates were broken up by low-powered sonification, the thicker coating on CNFs prepared with treatment 1 may have allowed for paraffin molecules to absorb on the surface more readily, thus resulting in a more stable solution compared to CNFs prepared with Treatments 2 and 3. The improved suspension with Treatment 1 is very promising for using silane-treated CNFs as fillers for hydrophobic
polymers. Specifically, the results from suspension seem to be very beneficial for processing of ultrahigh molecular weight polyethylene (UHMWPE) composites, in which paraffin oil has been used to improve the processability of UHMWPE for preparation of nanocomposites [19].

Results obtained from the suspension studies can give us an indicator about the influence of the coating thickness on the compatibility and interaction between the CNFs and the polyethylene matrix. According to the suspension results, there would appear to be an optimal coating thickness for tailoring to the dispersion and mechanical properties. A very thin coating resulted good initial dispersion upon simple agitation. However, for thin non-polar coatings, there may not be sufficient enough thickness to create physical entanglement between the coating and the polymer matrix. Additionally Simple van der Walls interactions between filler and matrix may not be enough to induce an adequate load transfer. In contrast, a thick coating may allow for hydrophobic polymer chains to entangle into the silane coating, thus improving the load transfer between the filler and the matrix. Additionally, the suspension results suggest that the dispersion of CNFs into a non-polar polymer matrix can be improved upon thicker silane treatments given that there are sufficient shear stresses to break up loosely-bound agglomerates.

4.4 Conclusions

In this chapter, both thin and thick organosilane coatings were successfully applied to carbon nanofibers. The thickness of the coating was increased considerably by using a novel nanofiller treatment with NaOH as a catalyst. TGA, TEM, and FTIR clearly showed a thick coating for the treatment using NaOH as catalyst with hydrocarbon chains applied to the surface of CNFs. Suspension studies showed that the thick silane-coated CNFs had a stronger ability to thoroughly
disperse in a non-polar solvent analogous to polyethylene, indicating improved compatibility. In the following chapters, further research is performed on these silane treatments. Specifically, in Chapter 5, further chemical characterization of silane treated CNFs was determined, and the effect of catalyst concentration on the structure of the silane treatment was determined. Additionally in Chapter 6, mechanical and tribological properties of polyethylene/silane-treated CNFs are discussed.
References:


CHAPTER 5

CHEMICAL CHARACTERIZATION OF ODMS-TREATED CNFS PREPARED UNDER VARIOUS ALKALINE CONDITIONS

5.1 Introduction

In Chapter 4, a novel organosilane treatment of CNFs in which NaOH was used as a catalyst to increase the thickness of the coating. Suspension studies indicated that this thick organosilane coating could improve the compatibility between CNFs and nonpolar matrices, which may have implications on wear and mechanical properties in polyethylene composites (discussed in Chapter 6). In this chapter, polymerized ODMS coatings were applied to the surface of oxidized CNFs, pristine CNFs, and oxidized CNTs by refluxing ODMS and nanofillers under various concentrations of NaOH in aqueous/alkaline ethanol solution. Modifications to the structure of the coatings were made by adjusting the alkalinity of the solution during treatment. Interestingly, only under highly alkaline conditions were shish-kebab structures formed onto the CNFs.

Literature has shown that the self-assembly of amphiphilic octadecyl silane molecules has been used to build highly-ordered inorganic–organic polymer hybrids with nanolayered features [1]. In polymerized octadecylsiloxanes (PODS), the hydrophobic tails can yield well-organized bilayers due to Van der Waals forces and steric hindrances in the hydrocarbon chains [2–6]. An important aspect of these hybrids is that they contain both siloxane and hydrocarbon groups, thus having properties intermediate of that between inorganic and organic materials [1] which may useful for nanocomposite applications. Furthermore, in contrast to other polymers that have been decorated onto nanomaterials, these trifunctional organosilanes can chemically bond to oxidized inorganic surfaces. Though there have been many recent studies on the synthesis of PODS [2–4], there has been no research on the shish-kebab decoration of PODS coatings applied onto nanoreinforcement.
In this work, chemical characterization of the polymeric shish-kebab structure was performed using Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), and nuclear magnetic resonance (NMR). Results indicated that silane treatment yielded aligned hydrocarbon chains with frequent crosslinking of the siloxane groups. For the siloxane polymer with the distinctive shish-kebab forming structure, NMR results showed that there was an incomplete reaction of siloxane groups, which may have facilitated heterogeneous crystallization of the polymer onto the Ox-CNFs. Further detailed chemical and structural characterization was also performed. Results showed that a unique method was established for patterning polymerized ODMS shish-kebabs onto the CNFs, which was attained only under highly alkaline conditions.

5.2 Experimental

5.2.1 Materials

CNFs (PR-24-HHT, both pristine and oxidized) were obtained from Applied Sciences Inc. The dimensions of the carbon nanofibers were approximately 60 to 150nm in diameter and 30 to 100 microns in length. Oxidized multi-walled carbon nanotubes (10-20nm diameter) were purchased from Cheap Tubes, Inc. Octadecyltrimethoxysilane (ODMS) (90% technical grade) was supplied by Sigma Aldrich. Acetone was obtained from J.T. Baker. Ethanol was purchased from Decon Laboratories Inc. Sodium hydroxide was obtained from Alfa Aesar.

5.2.2 Various Silane Treatments

Typical synthesis procedures for the ODMS treated nanomaterials were as follows: 0.1g of graphitic nanomaterials (Ox-CNFs and oxidized CNTs) was first mixed in 70ml alkaline 95vol% aqueous ethanol solution and bath sonified in a round bottom flask for 1 hour. ODMS (0.3ml, 0.7mmol) was diluted in 10ml of ethanol, and then added drop-wise to the nanofiller suspension
under reflux. After 5 hrs of reflux to ensure complete reaction, the suspension was removed from
the heat and allowed to cool to room temperature. The ODMS-treated nanomaterials were then
vacuum dried, washed with ethanol and acetone to remove any unreacted material, left in the
hood over night, and then dried in an oven at 70°C for 24 hours. Reactions varied based on the
type of nanofiller used and the concentration of NaOH used as a catalyst during each treatment.

5.2.3 Characterization

Scanning electron microscopy (SEM, FEI 200F) was used at an acceleration voltage of 30 kV to
determine the morphology of ODMS treated CNFs. Samples were gold coating before imaging
to ensure sufficient conductivity. Fourier transform infrared microscopy (FTIR, Nexus 670 ESP)
was used to characterize the functional groups of the ODMS treatment on the CNFs. Diluted
CNFs (~0.01mg) were mixed with 10 mg of potassium bromide (KBr) to prepare KBr disks of
0.5mm in thickness. Differential scanning calorimetry (DSC, TA 822 Mettler-Toledo, Inc.) was
performed in an aluminum holder at a heating rate of 10°C from 25°C to 125°C, held at 125°C of
2 minutes, then back to 25°C at the same rate. $^{29}$Si cross polarization magic angle spinning (CP-
MAS) spectra were acquired on a Bruker DRX-400 solid state nuclear magnetic resonance
spectrometer (NMR) with a Chemagnetics 5 mm MAS probe spinning at 6KHz. For cross
polarization, the Hartman-Hahn matching condition was used, with a contact time of 2 ms. The
$^{29}$Si chemical shifts were referenced to tetramethyldisilane (TMS). It should be noted that CP-MAS
$^{29}$Si NMR was applied to PODS rather than coated nanofillers, as the nanofillers were
conductive, and thus matching could not be performed effectively. A Siemens D-500 X-ray
powder Diffractometer (Cu Kα$_1$ radiation, $\lambda$=0.154059nm, with graphite diffracted beam
monochromator, scintillation detector, and aluminum cavity mount) was used to determine
crystalline structure of PODS modified CNFs.
5.3 Characterization Results

5.3.1 Thermogravimetric analysis

In order to perform an initial screening of the various silane treatments prepared with different NaOH concentrations, thermal gravimetric analysis was performed on the samples (Figure 5.1). Results very surprisingly showed that treatments with the highest concentrations of NaOH prepared degraded the most quickly. This could possibly be due to differences in molecular weight, chemical structure, or surface area of each of the coatings. More specifically, the higher the surface area of the sample, the quicker the sample will burn on. In order to explore this potential explanation, SEM images of the surface treatments were collected to show the morphology of these treatments.

![Graphs showing weight loss and derivative of weight loss as a function of temperature for different NaOH concentrations.]

Figure 5.1. Thermogravimetric analysis of octadecyltrimethoxysilane treated CNFs prepared with varying concentrations of CNFs.

5.3.2 Scanning electron microscopy

Figure 5.2 shows scanning electron microscopy (SEM) images of ODMS-treated Ox-CNFS prepared with 0.1M and 0.01M NaOH. Images show that ODMS-treated CNFs prepared in a
0.1M NaOH solution yielded very interesting shish-kebab structures consisting of central CNF cores and lamellar coatings (Figure 5.2a). In contrast to CNFs treated in 0.1M NaOH, ODMS treatment of Ox-CNFs prepared in 0.01M NaOH were unevenly distributed onto the nanofillers, with no shish kebab structures forming onto the CNFs (Figure 5.2b). Detailed images show portions of the 0.1M NaOH treated CNFs with very large, highly organized shish kebabs of CNFs and PODS (Figure 5.3). It can be observed that the lamellar PODS coatings were attached epitaxially and perpendicular to the fiber axis.

Figure 5.2. SEM image of ODMS treated Ox-CNFs prepared in aqueous-95vol% ethanol solution containing (a) 0.1M NaOH and (b) 0.01M NaOH. ODMS treatment of Ox-CNFs prepared in 0.1M NaOH showed shish kebabs of CNFs and PODs. However, samples prepared in 0.01M NaOH showed unevenly distributed coatings, with no shish kebab structures surrounding the CNFs.

To ensure that the shish-kebab structure was strictly dependant on the pH during treatment rather than the melting point of the coatings formed, ODMS-treated Ox-CNFs in 0.01M NaOH solution and air-dried (rather than oven dried) to make certain that the coating did not melt during the drying process. The shish-kebab morphology was not readily formed on the ODMS-treated Ox-CNFs prepared in 0.01M NaOH solution and air dried, demonstrating that the distinct shish-
kebab morphology was unique to the treatment prepared with 0.1M NaOH solution. In contrast to treatment of Ox-CNFs, ODMS-treated Ox-CNTs in 0.1M NaOH solution did not show such shish-kebab structure. However nucleation did occur on agglomerates of CNTs rather than individual tubes (Figure 5.4). These results suggest that nucleation of the coating depended strongly on the size of the nanofiber/nanotube. Because such drastic differences in the nucleation of PODS onto CNFs were observed in treatments prepared with varying concentrations of NaOH, detailed structural characterization was performed.

Figure 5.3. SEM images of ODMS-treated Ox-CNFs prepared in an aqueous 95vol% ethanol solution with 0.1M NaOH, showing large shish kebabs of polymerized octadecylsiloxane (PODS) decorated onto CNFs. A detailed image of PODS disks and CNFs is shown on the right.
5.3.3 Fourier transform infrared spectroscopy

FTIR results showed Si-O-Si bonding was formed during treatment. For silane-treated CNFs, the C-H peaks were present at 2919 and 2850cm\(^{-1}\), showing narrowing and shifting of the silane treated CNFs compared to pure ODMS. The inset in Figure 5.5a shows small ripple peaks between 1150 and 1300cm\(^{-1}\), due to CH\(_2\) wag mode vibrations of the alkyl chain. Both these results show that alkyl chains are predominantly in the trans conformation, indicative of crystallinity of the coating [3,7].
Figure 5.5. (a) FTIR and XRD (b) of ODMS-treated CNFs prepared under varying concentrations of NaOH. Inset of (a) shows C-H wag modes, indicative of hydrocarbon chain alignment.

5.3.4 X-ray diffraction

X-ray diffraction (XRD) peaks confirmed crystallinity in the coatings (Figure 5.5b). XRD results show a peak near 2θ=21.4°C, indicating a d-spacing of about 0.415 nm, similar to spacing between aligned hydrocarbon chains of polymerized octadecylsiloxane reported in literature [3,2,4,8]. Results from this study clearly show that highly organized hydrocarbon chain alignment was formed during treatment, indicating that the hydrocarbon chains have the ability to self organize even after polymerization via condensation reactions in solution.

Differential scanning calorimetry results (Figure 5.6) showed peaks at about 60°C for all of the ODMS coated CNFs. For ODMS-treated CNFs prepared in 0.1 M NaOH, Additional peaks at 100°C are seen, possibly due to multiple compositions/phases in the coating. However, these samples did not actually melt above 100°C, indicating crosslinking in the coatings.
5.3.5 Solid State NMR

Cross polarization magic angle spinning $^{29}$Si nuclear magnetic resonance (CP-MAS $^{29}$Si NMR) spectroscopy was used to determine chemical states of the siloxane groups in the PODS coatings. Because of difficulties in performing solid state $^{29}$Si NMR on conductive materials such as CNFs, PODS samples (without CNFs) were prepared under identical conditions as ODMS treated Ox-CNFS prepared in 0.1M and 0.01M NaOH. In the $^{29}$Si NMR spectrum, the signals from trifunctional alkoxysilanes are designated as $T^n$ (n=0-3), where n represents the number of siloxane bonds. For the PODS samples, $^{29}$Si peak resonances were observed at -54.9 and -69.6 ppm (Figure 5.7), which can be associated with the structures (HO)(R)Si(OSi)$_2$ [$T^2$], and (R)Si(OSi)$_3$ [$T^3$], where R represents the octadecyl group [3,8]. The peak corresponding to $T^2$ (-54.9 ppm) is slightly shifted to a lower field, which may indicate the formation of some cyclic...
species [9]. From the integrated peak ratios, the $T^3/T^2$ percentages were determined to be (59.8%/40.2%) for the 0.1M treatment.

We hypothesized that the sample prepared with 0.1M NaOH has a linear siloxane structure with frequent crosslinking (Scheme 5.1). This PODS structure has been studied in literature previously, though generally prepared by much different synthesis routes [3,8]. Literature of PODS generally shows a mixture of $T^2$ and $T^3$ Si-O-Si bonding, indicating a linear siloxane portion with crosslinked portions from condensation reactions of –OH groups. Results from this study match most closely to that of Shimojima et al., [9] who showed similar $T^3/T^2$ ratios and DSC peaks (~100°C) upon thorough drying and condensation reactions. Therefore, based on FTIR, XRD, $^{29}$Si NMR, and previous reports [3,2,4,8,9] there is ample evidence to suggest that samples prepared with 0.1M NaOH have structures consisting of trans hydrocarbons attached to frequently crosslinked siloxanes.

Figure 5.7. Solid state $^{29}$Si NMR of PODS (without nanofillers). Samples were prepared by polymerizing ODMS via reflux in an aqueous 95% ethanol solution with 0.1M and 0.01M NaOH.

Figure 5.7. Solid state $^{29}$Si NMR of PODS (without nanofillers). Samples were prepared by polymerizing ODMS via reflux in an aqueous 95% ethanol solution with 0.1M and 0.01M NaOH.
Scheme 5.1. An idealized representation of PODS shish-kebab crystals forming onto CNFs under highly alkaline conditions. The chemical structure shows the linear portion of siloxane groups. Note that $^{29}$Si-NMR Results show that there are crosslinked portions in addition to the linear siloxane segments.

5.4 Discussion

The PODS prepared with 0.01M NaOH had nearly all Si-OH groups reacted ($T^3$) indicating either nearly complete crosslinking or a caged structure was formed. Given that the melting temperature is relatively low at ~60°C, (i.e., low molecular weight) it is likely that samples prepared in 0.01M had PODS with a siloxane caged structure (highly crosslinked structures do not truly melt, especially at such low temperatures). Of the common caged siloxane structures ($T_6$, $T_8$, $T_{10}$, $T_{12}$) only the $T_8$ polyoctahedral silsesquioxane (POSS) will pack nicely and allow hydrocarbon chains to stay in the trans conformation. Furthermore, the melting point of the ODMS coating prepared with 0.01M NaOH (~60°C) corresponds well with the melting points of alkyl substituted POSS.\textsuperscript{27} Therefore, the PODS coating on ox-CNFs prepared in 0.01M NaOH may have a predominantly $T_8$ POSS structure, though further study is needed to determine unequivocally. Typical synthesis routs for octadecyl POSS generally start with hydrogen substituted POSS reacting with octadecene [10], which is much more complicated than the synthesis conditions in our study. The crystalline structure of the sample prepared with 0.01M
NaOH is likely similar to that of the fluorocarbon substituted POSS shown described in literature [11]. Such POSS structures are relevant in superhydrophobicity and tribological applications.

Differences in the chemical structures between samples prepared with 0.1M and 0.01M NaOH can be explained by reaction rates and reactivity. For typical hydrolysis and condensation reactions, NaOH acts as a catalyst so that the overall chemistry of the final product is unchanged. However, ODMS has three reactive groups, so the rate at which each condensation reaction occurs will have an effect on the overall structure of the coating. The faster the reaction rate, the less time the reaction has to form the most stable structure. Other metastable structures may form as a result of the rate at which crosslinking occurs between siloxane groups, with steric effects limiting complete condensation reactions in the case of samples prepared with 0.1M NaOH.

Furthermore, differences in the nucleation between samples may be attributed to changes in CNF wetting between the samples, which is directly related to structural differences in the coatings. Nucleation occurs when the free volume energy released is greater than the surface energy needed to create the new interface between the crystal and surroundings. In order for heterogeneous nucleation to occur, as is the case in this study, there must be sufficient wetting between the nucleation site and the crystal being formed. If there is sufficient wetting, then the surface free energy barrier is diminished, allowing crystals to grow on the heterogeneous surface. For samples prepared with 0.1M NaOH, CNFs were clearly acting as nucleation sites of the polymerized ODMS. From Si$^{29}$-NMR, samples prepared with 0.1M NaOH showed a high proportion of unreacted siloxane groups. These Si-OH groups may have improved the wettability between the siloxane polymer and oxidized CNFs, and thus improved the ability for the CNFs to act as a nucleating agent for crystallization of the polymer coating. However, further work is needed to identify mechanisms for such drastic differences in heterogeneous nucleation.

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Patterned decoration of nanofillers has drawn much interest as hierarchal structures for nanodevice and nanocomposite applications [12–21]. Among the various studies, Li’s group has led the field in this research [16–21], with much of their work focusing on periodic decoration of polyethylene shish-kebabs onto CNTs. However, regarding studies of ordered decoration for carbon nanofibers (CNFs), there have been very few reports, showing randomly oriented coatings formed onto the CNFs rather than patterned shish-kebabs [17,21].

It has been suggested in literature that periodically formed lamellar crystals may help prevent aggregation by acting as spacers between nanotubes [19]; the shish kebabs can be used as a template for decorating other materials on the interval regions [18]; and the disk morphology can be controlled by changing the coating concentration and crystallization parameters [16,20]. By manipulating these nanofillers in such a way, this type of decorating may prove to be useful in nanodevice applications[16,20]. However, most related research has been focused mainly on non-covalent decorations of polyethylene onto CNTs, which will have limited interactions, and thus poor bonding between the decorated polymer and CNTs.

The shish-kebab treatments onto CNFs is of great interest for a host of different applications. Periodic functionalization of one-dimensional nanofillers allows researchers to make ordered structures that can be tailored for specific electrical, optical, and mechanical properties. With regards to nanocomposite applications, the periodically ordered hydrophobic coatings may allow for better wetting in nanocomposites with non-polar matrices such as polyethylene. Furthermore, the unique disk structure seen in the samples prepared with 0.1M NaOH may help prevent aggregation by acting as spacers between nanofillers and also yield a high degree of mechanical interlocking in such nanocomposites due to the kebab portion of the treated nanofiber. However, further work needs to be performed to optimize synthesis conditions and to ensure effectiveness
of the disk-like coating in improving the mechanical properties of nanocomposites with non-polar matrices.

5.5 Conclusions

This chapter describes the periodic decoration of a polymerized organosiloxane onto nano-reinforcement. Polymerized organosiloxane patterned shish-kebab structures were generated onto carbon nanofibers, which interestingly could only be achieved in highly alkaline solutions. Detailed characterization of the chemical structure and morphology of the hybrids was performed. For the siloxane polymer with the distinctive shish-kebab forming structure, NMR results showed that there was incomplete reaction of siloxane groups, which may have facilitated heterogeneous crystallization of the polymer onto the Ox-CNFs. This polymer has the potential to chemically bond to the nanofibers, thus forming much more durable hybrid nanomaterials than shown in literature. Both FTIR, XRD and morphology results confirm that this patterned polymer contains highly-ordered inorganic–organic hybrids. Such hierarchical structures may have potential for nanodevice and nanocomposite applications.
References:


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CHAPTER 6
WEAR AND MECHANICAL PROPERTIES OF SILANE TREATED
POLYETHYLENE/CNF COMPOSITES

6.1 Introduction

In Chapters 2 and 3, the wear and mechanical properties of UHMWPE and its CNF composites were studied in detail. In Chapters 4 and 5, novel organosilane treatments were applied to CNFs for improving compatibility and interactions with the polyethylene matrix. Results in Chapter 4 concerning suspension studies indicated that the organosilane surface treatment may produce improved interactions and compatibility with nonpolar matrices. In this chapter, the effects of octadecylsilane treatment on the wear and mechanical properties of polyethylene/CNF composites are studied. Results showed that applying the silane surface treatment to the CNFs improved the wear resistance of the composite, though the mechanical properties were not improved. Possible mechanisms for improvement in the wear resistance were studied.

6.2 Experimental

In Chapter 4, three different methods of octadecyl trimethoxysilane (ODMS) treatments were studied: preparation in 100% ethanol (labeled Treatment 2), 5% aqueous ethanol solution (labeled Treatment 3), and NaOH as a catalyst in 5% aqueous ethanol solution (Treatment 1). See Chapter 4 for details of each of these treatments. The selected organosilane-treated CNFs were added to polyethylene in order to study the effect of surface treatments on wear and mechanical properties of the composites. Because of the difficulties in processing UHMWPE composites, HDPE was used for initial tribological experiments. The grade of HDPE used was Bamberger HP54-60 flake. The HDPE control and its composites were melt-mixed in a Haake torque rheometer at 70 rpm and 180°C for 15 minutes. The samples were then compression
molded at 180°C, after which the samples were allowed to be cooled naturally to room
temperature. Specific volumetric wear rates were determined using a custom-built pin-on-disk
apparatus with a vertical 1020 carbon steel disk under dry testing conditions. Wear testing
samples had dimensions of 5x5 mm$^2$. Wear testing was performed at 180 rpm, with an effective
disk radius of 6.5 cm, or 0.408 m per cycle. The disk surface was polished with 600-grid sand
paper and cleaned thoroughly with acetone and dried prior to each use. In order to study transfer
films, a reciprocating ball on flat apparatus was used. A carbon steel ball was used to match the
original wear testing disk. The sliding distance varied between 12m and 500m at 20mm per cycle
and 1Hz. Tensile tests were performed according to ASTM D638 for nonrigid Type IV materials
[1]. To determine the Young’s modulus, an initial strain rate of 0.1 (mm/mm)/min was applied
until the material was strained to 1%. After the initial determination of the Young’s modulus, the
strain rate was increased to 1(mm/mm)/min until fracture. Tensile tests were performed using
20kN load cell and 1” strain gauge on an Instron frame. Differential scanning calorimetry (DSC)
was performed at a heating rate of 10°C from 30°C to 180°C. To observe the microscopic
dispersion of composites and to detect the presence of any large agglomerates, samples were
microtomed to 10µm and observed under optical microscopy. Ten images were analyzed at 5
times magnification for each sample. Dispersion analysis was performed using custom built
software to analyze agglomerate size and frequency (See www.mme.wsu.edu/~qsma/index.html
for the details of the program).
6.3 Results and Discussion

6.3.1 Initial screening of composite samples

Of the silane treatments prepared in Chapter 4, an initial screening was used to determine which PE/CNF composites would be studied in further detail with regards to wear, mechanical, and dispersion properties. Figure 6.1 shows that the silane treatment prepared with NaOH as a catalyst had the lowest wear rate of all the composites, and was therefore studied in more detail.

Figure 6.1. Initial screening of HDPE/CNF composites. Sil(NaOH) represents the treatment with 5% aqueous ethanol solution and NaOH used as a catalyst, Sil(ETOH) represents the silane treatment with 100% ethanol as solution, and Sil(aq. ETOH) indicating the silane treatment using 5% aqueous ethanol solution. Results show that the treatment with the NaOH catalyst yielded the most improved wear resistance, and was thus studied further.
Table 6.1. Crystallinity of HDPE and its composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Crystallinity</th>
<th>Peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>64.1</td>
<td>136.5</td>
</tr>
<tr>
<td>PE-CNFs</td>
<td>66.4</td>
<td>137.5</td>
</tr>
<tr>
<td>Sil(NaOH)-CNF</td>
<td>65.5</td>
<td>135.5</td>
</tr>
<tr>
<td>Sil(ETOH)-CNF</td>
<td>65.4</td>
<td>136.7</td>
</tr>
<tr>
<td>Sil(aq. ETOH)-CNF</td>
<td>67.8</td>
<td>135</td>
</tr>
</tbody>
</table>

In our work, DSC results showed only marginal to no change in the degree of crystallinity or crystalline size. Therefore, for our study, it is unlikely that the changes in the crystallinity had any substantial effect on the wear properties. Furthermore, for the pin-on-disk wear testing, the wear conditions were very harsh with a relatively high speed. At higher sliding speed conditions, the surface of the polymer generally melts. Therefore, changes in crystallinity will not likely contribute substantially to changes in the wear properties for this particular system studied.

6.3.2 Wear Testing of selected composites

Figure 6.2 shows wear testing results of HDPE and composites prepared with untreated CNFs and selected surface-treated CNFs with varying concentrations. Wear testing results showed that the addition of CNFs resulted in improved wear resistance for composites with lower loadings (0.5, 1wt%) compared to neat HDPE. Many modes have been demonstrated showing the effect of CNFs on the wear rate of composite systems. First, CNFs have the ability to contribute some load-bearing capacity, potentially improving the overall strength of the composite [2–5]. Secondly, CNFs may reinforce transfer films that adhere to the articulating surface, i.e., reducing the effects of hard/sharp asperities, and thus reducing the wear rate of the system [6–10]. Figure
6.2(b) shows optimal CNF loading between 0.5wt% and 1wt%. The optimal CNF loading at lower concentrations is likely due to better dispersion at lower loadings, whereas at higher concentrations agglomerates are much more prevalent. This trend was also seen for UHMWPE/CNF composites processed with paraffin oil (See Chapter 3 for details).

In addition to the improvement in wear properties in composites compared to neat HDPE, wear testing results showed further improvement with silane-treated CNFs with a thick coating. Improvement of wear properties upon silane treatment has also been shown in literature for PTFE composites [11–13]. The friction coefficient of HDPE, CNF-PE composites, and silane-treated CNF/PE composites with varying concentration are shown in Figure 6.2. Results suggested that the coefficient of friction was nearly constant for HDPE and its composites, though for composites with higher concentrations of CNFs, some small differences were seen. These small differences in friction were not likely enough to cause such drastic changes in the wear rate of the samples. Therefore, other potential influences were studied.
Figure 6.2. Wear rate of HDPE and composites prepared with untreated CNFs and silane-treated CNFs with varying concentrations. The articulating disk was polished after each use to remove transfer films.

6.3.3 Mechanical properties

The effect of the coating on the wear properties is a complicated process, and may affect many of other properties of the composite and tribological system. For example, the thick coatings may have improved the mechanical properties of the composite due to improved load transfer between CNFs and polyethylene which may result in a reduced shear deformation, thus improved wear resistance [14]. In order to see which concentrations of CNFs will show differences in mechanical properties, HDPE-CN F composites were prepared at various concentrations up to 5wt%, and tensile testing was performed on these samples at a strain rate of 10%/min. Preliminary results showed that at 3wt%, both strength and modulus could be improved considerably. Therefore, further tensile testing was then performed on HDPE, pristine CNF composites, and silane-treated CNF composites at 3wt% filler loadings.
To determine the effect of the silane treatment on the mechanical properties, HDPE and 3wt% samples were again prepared and tested under a strain rate of 100%/min (according to ASTM standard D638) in order to observe area under the curve in addition to tensile strength. Results showed surprisingly that the strength of the silane treated CNF composites were reduced compared to both HDPE and PE-CNf composites. An explanation for the poor mechanical properties may be that though the compatibility between treated CNFs and nonpolar matrices were superior to that of untreated CNFs, actual physical bonding/entanglement (mechanism for interactions) may have been limited. First, the molecular weight of the coatings may have been too small to induce physical entanglement. Secondly, the crystallinity of the coating may have limited interactions (unless extensive co-crystallization could occur). Based on the previous chemical and crystallinity characterization results, there may have actually been poor physical entanglement between the coating and polyethylene despite indications of improved compatibility. Comparing these values to the wear testing results suggest that difference in the wear rate between the untreated and silane-treated CNFs were not due to changes in the observed mechanical properties. Thus, other mechanisms for improvement in the wear properties are likely to be present.
6.3.4 Dispersion analysis

Though tensile tests suggested that there was limited physical entanglement (and thus secondary bonding) between the silane coating and polyethylene, previous work suggested that compatibility between the silane coating and nonpolar matrix could be improved. It seems very plausible that the silane treatment may have acted as a dispersing agent during mixing rather than a coupling agent. To test this hypothesis, samples were microtomed at 10 microns and optical images were observed. Results indicated that silane treated CNFs had a smaller amount of large agglomerates than untreated CNF composites (Figure 6.4).

![Figure 6.4](image)

In order to better understand the effect of the dispersion on the wear properties, samples were prepared by different mixing times to induce varying dispersion states. 0.5wt% CNF-HDPE composite samples were melt-mixed in a torque rheometer for various mixing times (2, 5, 15, and 30 minutes). Both wear rate and dispersion analysis were tested on these samples (Figure 6.5). Figure 6.6 shows optical images of 0.5wt% CNF composites mixed for 2 minutes and 30
minutes via torque rheometer. These images clearly show a much improved dispersion state for the samples mixed for 30 minutes compared to the samples mixed for 2 minutes, coinciding well the quantitative dispersion analysis data. Thus the desired effect of various dispersion states was obtained. Figure 6.5 clearly shows that there was a strong relationship between the mixing time and the wear rate of these samples. These samples were then compared with the batch of silane treated CNF composites (Figure 6.7). In comparing the dispersion between untreated and silane treated composites, the silane treated sample did in fact show improved dispersion when comparing larger agglomerates, and there was a reasonable correlation relating dispersion and wear properties. These results suggest that the silane treatment may in fact have acted as a dispersing agent for the carbon nanofibers. However, it should be noted that both wear testing and dispersion analysis between the silane-treated and samples prepared with varying mixing times were not tested together, so further work should include a new batch of samples in which sample preparation, wear testing, and dispersion analysis are all performed concurrently. Here, the results indicate that the silane-treatment may have helped improve dispersion, though further work is needed to verify these results by using a new batch of samples. Furthermore, higher optical magnifications should be observed to better distinguish between each of the dispersive states.
Figure 6.5. Dispersion (left) and wear rate (right) of 0.5wt\% pristine CNF-HDPE composites prepared by various mixing times under torque rheometer.

Figure 6.6. Typical optical images for 0.5wt\% CNF samples prepared by torque rheometer mixing for 2 minutes (left) and 30 minutes (right).
In all the polyethylene composites tested, wear rates appeared to be more sensitive to presence of agglomerates than tensile and punch testing results. This may be explained in that wear of the specimen undergoes cyclic loading and the fatigue, and thus fatigue properties will strongly be related to wear properties [15–17]. It has been well demonstrated that fatigue properties are strongly related to the defects (i.e. agglomerates) [18–21]. Since wear testing undergoes cyclic fatigue, this type of test may be more sensitive to defects more so than simple tensile tests. What is unusual about these results is that the mechanical properties were not improved compared to pristine CNF composites, accept for a small increase in the strain to break. However, the improved dispersion of the carbon nanofiber composites may improve fatigue properties by reducing the amount of micron-sized defects, and thus the wear properties of the composite. These results may suggest that the improvement in wear properties of silane treated composites may have been from improved dispersion, though more detailed analysis needs to be performed.
at higher magnifications. Fatigue properties should be examined to determine if such an effect is taking place, which should be much more sensitive to the dispersion of the sample.

6.3.5 Transfer films

Another possible mechanism for the decrease in wear rate upon silane treatment of CNFs is due to the generation of improved transfer films onto the articulating metal disk. Transfer films have been shown to have a dramatic effect the wear properties of polymeric materials [6-10]. Transfer films may soften the effects of rubbing against hard and sharp asperities of the metal surface. Furthermore, in some instances, transfer films can reduce the coefficient of friction. Because the original wear tester has a disk that is permanently mounted to a motor, the study of transfer films was not possible for this set-up. In order to study the transfer films of PE composite materials, a reciprocating ball-on-plate wear testing configuration was used, so that the metal surface could be observed. It should be noted that care should be taken when comparing results pertaining to these transfer films with previously collected wear testing data, as there were some considerable changes in the pin-on-disk testing compared to reciprocating ball-on-plate testing. Nonetheless, images of transfer films are helpful in obtaining preliminary results for further studies.

Figure 6.8. Transfer films developed after sliding a distance of 12m for HDPE (a), 0.5wt% CNF-HDPE composites (b), and 0.5wt% silane-treated CNF composite (c).
To study the effect of the silane treatment on the formation of transfer films, HDPE and its composites were mated against carbon steel balls and wear testing was performed at various sliding distances (12, 25, 50, 100, 200, and 500m) on a reciprocating ball-on-flat apparatus. The transfer films formed were observed under SEM. Microscopy results showed that relatively thick transfer films were observed at a sliding distance of 12m (Figure 6.8). Transfer films for HDPE appeared to be the same for all sliding distances, indicating that the transfer film formation may not have been the primary cause for the differences in the wear rates between composite samples. After the initial run in wear scars were formed, any additional wear was negligible and could not be determined by the width of the wear scar. The similarities between the transfer films of HDPE, p-CNf composites, and silane-treated CNF composites may imply that transfer film formation was not a significant factor in the mechanism for improved wear properties of the silane-treated CNFs, though further quantitative studies are needed.

**Conclusions:**

- Wear testing results showed that the addition of CNFs resulted in improved wear resistance for composites with lower loadings (0.5, 1wt%) compared to neat HDPE. Furthermore, wear testing results also showed further improvement with silane-treated CNFs with NaOH as catalyst for all concentrations studied. This improvement may have been due to improved dispersion of the composites, though further studies are warranted.

- There was little difference between the transfer films of HDPE, pristine CNF composites, and silane treated CNF composites. This may imply that the formation of transfer films was not a significant factor in the mechanism for improved wear properties of the silane-treated CNFs.
References:


CHAPTER 7
SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 Summary

A general summary of this research is shown below:

- For UHMWPE/HDPE/CNF composites, morphological results indicated two distinct UHMWPE and HDPE phases with CNFs preferentially residing in the HDPE phase. This result has essentially been ignored for literature on tribology of ternary UHMWPE/HDPE/filler systems.

- For UHMWPE/HDPE/CNF composites systems, the addition of CNFs into the blend reduced both the run-in and steady state wear rate of the material considerably, with an increasing concentration of CNFs up to 3wt% CNFs resulting in lower wear rates compared to the control.

- For paraffin-processed UHMWPE composites, processing with paraffin oil prior to melt-mixing resulted in a dramatically improved distribution of the CNFs at the microscopic scale compared to dry-mixing methods.

- For paraffin-processed UHMWPE composites, the wear resistance and mechanical properties can be enhanced at low concentrations of CNFs. Interestingly, polymerized organosiloxane patterned shish-kebab structures were generated onto carbon nanofibers under highly alkaline solutions.

- For HDPE-CNF composites, wear testing results showed that the addition of CNFs resulted in improved wear resistance for composites with lower loadings (0.5, 1wt%) compared to neat HDPE. Furthermore, wear testing results also showed further improvement with silane-treated
CNFs with NaOH as catalyst for all concentrations studied. This improvement may have been due to improved dispersion of the composites, though further studies are warranted.

-There was little difference between the transfer films of HDPE, pristine CNF composites, and silane treated CNF composites. This may imply that the formation of transfer films was not a significant factor relating to the improvement in wear properties of the silane-treated CNFs.

-Further studies are needed to determine the mechanism for improved wear resistance in silane treated composites.

A very persistent theme throughout this work was the importance of dispersion in relation to wear properties. In observing both negative effects in higher concentrations of CNFs, and the improvements in dispersion from the silane treatment, it appears that dispersion issues are very important for wear testing and should be one of the first properties to be considered when preparing nanocomposites for tribological applications. The relationship between the volume fraction of agglomerates and wear rate may be strongly related in that the wear process has a strong fatigue component associated with it. Fatigue properties of nanocomposites are strongly negatively affected by agglomerates because these agglomerates may act as defects and cause stress concentrations, and thus may allow for cracks to grow out of these defects due to repeated normal and lateral loading. In addition to more detailed dispersion analysis at the micron and nanoscale, correlation between dispersion, fatigue and wear properties should be studied more thoroughly.


7.2 Suggestions for future work

*Combined wear testing results:* For both UHMWPE and HDPE composites a CNF concentration of 3wt% was detrimental to the wear properties of the composites. This was likely due to an increase in the number of agglomerates, which will strongly affect the fatigue properties of the composite. However, for the UHMWPE/HDPE/CNF composites, there was an obvious improvement at 3wt%, suggesting that the dispersion of the composite was improved compared to the UHMWPE and HDPE composites. Though there were slight differences in the processing parameters, the major difference between these composites was simply that UHMWPE and HDPE were blended. The higher shear forces during mixing may have allowed the CNFs to be broken up more readily, allowing the CNFs to better reinforce the polymer matrix without allowing the agglomerates to deteriorate the wear resistance of the composite. Future work should be performed on dispersion analysis of UHMWPE, UHMWPE/HDPE, and HDPE composites to determine if there is such a synergistic effect on the dispersion of such composites.

*Silane treatment characterization:* A critical issue that has yet to be resolved is whether or not chemical bonding between CNFs and the Polymerized ODMS has been sufficiently formed. Difficulties in characterization arise in that the coating prepared is very thick, and thus bonding between PODS dominates the spectral data, making it difficult for the interface between CNFs and the silane coating to be studied. Furthermore, NMR of CNFs cannot be obtained because of the conductivity of CNFs, and FTIR does not yield any fruitful results because of the resonance of sp² graphitic bonds in CNFs. One experiment that may show some evidence towards chemical bonding is through XPS. These experiments are currently under way. Other experiments that should be performed are to test the durability of the polymerized ODMS onto CNFs by performing ultrasonification onto these materials and then observing the CNF surface.
**PODS-CNFS composites:** For studies on HDPE, pristine CNF composites, and silane treated CNF composites, dispersion analysis was limited in that only large agglomerates above 15µm were included. Obviously dispersion at the nanoscale will also have an impact on both wear and mechanical properties, and should thus be observed in further detail. Furthermore, studies on transfer films should be developed further. Only a very preliminary qualitative study was shown for HDPE, pristine-CNF and silane treated CNF composites, which did not show any substantial differences in the transfer film. Further work should combine qualitative SEM images with more quantitative chemical analysis. In addition to PODS-CNFS composites, wear properties of PODS-PE (without CNFs) should be studied. A comparison between wear testing of PE-PODS and PE-PODS-CNFS composites would help determine what type effects the silane treatment is having on the wear properties of the composites.
APPENDIX A: List of Publications

PEER-REVIEWED JOURNAL PUBLICATIONS

- **Wood W., Liu T., Zhong W.H. (2012)**, Synthesis and characterization of polyoctadecylsiloxane-decorated carbon nanofibers with unique shish-kebab architectures (Submitted to Polymer)

PEER-REVIEWED CONFERENCE PAPERS AND ABSTRACTS

