FABRICATION OF BIODEGRADABLE FIBERS USING HDPE/STARCH BLENDS. MORPHOLOGICAL, MECHANICAL AND PROCESSING CHARACTERISTICS.

by

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FABRICATION OF BIODEGRADABLE FIBERS USING HDPE/STARCH BLENDS. MORPHOLOGICAL, MECHANICAL AND PROCESSING CHARACTERISTICS

FAYAZ J ALI

MATERIALS SCIENCE AND ENGINEERING.

ABSTRACT

Products developed from polymeric materials have found a myriad of applications that make life better and more convenient. In many cases, however, plastics end up in landfills after their useful lifetime. The inability of most synthetic plastics to degrade in the landfill presents a challenge to continue to expand their applications in order to minimize their environmental impact. Incorporating natural fibers into synthetic polymers has been investigated recently; however, most of the natural fibers do not have the mechanical properties of their inorganic counterparts. Thus, there is a need for high strength fibers that are degradable. The goal of this research was to develop high strength, ‘green’ fibers based on starch and high density polyethylene (HDPE) using a relatively inexpensive melt spinning process.

Mechanical properties of the blended fibers were examined. It was found that with appropriate processing techniques (i.e. cold drawing) up to 5 wt% TPS could be used as filler without significantly sacrificing the mechanical properties of the blended fibers when compared to their neat counterparts. In some cases, the blended drawn fibers exhibited a 35 fold increase in the mechanical properties when compared to their as-spun counterparts. This result is especially significant when one considers that current HDPE demand exceeds 30 million metric tons.
Wide angle x-ray scattering (WAXS) was used to examine the morphological characteristics of the blended fibers. The WAXS data showed that a very high degree of molecular orientation was achieved in fibers with TPS loadings of up to 5 wt%. The degree of orientation as well as the degrees of crystallinity of the fibers was correlated with the mechanical properties.
DEDICATION

To my parents Feroza and Javed Ali whose love and sacrifice has made this work possible.
ACKNOWLEDGMENTS

I would sincerely like to thank Dr. Derrick Dean for his continued support and guidance which made this research possible. He is and always will be considered as one of the finest mentors and teachers that I have known. I would also like to thank John Tipton for his continued advice, and all the contemporaries in my research group for their input in this work. I would like to thank my parents, Feroza and Javed Ali, for their continued support and sacrifice during my research.

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1. INTRODUCTION

One of the major problems encountered with most synthetic polymers today is their inability to degrade when placed in a landfill [1]. Many of these plastics are reinforced with fibrous fillers. As a result biodegradable reinforcements and fillers are being considered as alternatives to inorganic (i.e. glass) and synthetic fiber reinforcements for various applications, due to their environmental friendliness and relatively high strength. There has been an abundance of research conducted on the use of natural fibers as reinforcements for applications in automotive industry; however due to functional inadequacies of natural fibers their use has been limited [2-3].

There has been little work done on fibers formulated from synthetic and biodegradable polymer blends. Due to growing concerns about the impact of synthetic polymers on the environment, there is demand for inexpensive, functional and green polymers that could also be used as reinforcements. Therefore, this report investigated biocomposite fibers formulated from high density polyethylene (HDPE) and thermoplastic starch (TPS) as a possible material to meet that demand.
1.1. Literature Review

1.1.1. Thermoplastic Starch

In its raw form, native starch has a very stiff, granular structure that is incapable of flow. Unlike native starch, thermoplastic starch (TPS) is capable of flow; therefore, it can be mixed with other synthetic polymers using processes that are similar to those used for conventional polymer blends [4]. TPS has been studied extensively for use in biological applications as well as for filler in synthetic polymers [3-4]. Introduction of TPS into a HDPE matrix will present an opportunity to replace some of the synthetic polymer with a biodegradable component. TPS fillers have the potential of combining the high strength-to-weight properties of HDPE fibers with biodegradability, while maintaining minimal loss in strain to failure value of neat fibers [4]. This could be a striking mixture of properties especially in the field of general purpose plastics where HDPE is greatly used, and where strength and ductility would be modestly sacrificed in order to achieve biodegradability. However, much of the pioneering work on starch composites describes difficulties in obtaining the correct structure of starch, as well as problems with phase separation when blended with synthetic polymers. Recent research has shown that starch could be plasticized to give a TPS version [4-8].
Native starch is essentially comprised of two molecules: amylose and amylopectin. Amylose (Fig. 1a) has a linear structure whereas amylopectin (Fig. 1b) has a branched structure that gives native starch its brittleness. Essentially, the relative amounts of the above-mentioned molecules will determine the type of starch [9-11]; for example, corn starch has a higher amylopectin content than sweet potato starch [10]. In earlier studies, native starch granules were added to low-density polyethylene (LDPE) [4, 5, 12]. However, these materials have poor mechanical properties including poor tensile strength and significantly lower elongation at break [4]. Due to these results, very few commercial products were developed that used starch as filler, and most of them contain relatively low amounts of starch. The deterioration of mechanical properties of native starch and polymer blends arises from the different polar characteristics of starch and most of the synthetic commodity polymers, which lead to poor interfacial adhesion [13, 14], as well as the branched nature of the native starch structure. The interface is the
region of physical or chemical contact between the reinforcement/filler and the matrix. To increase the interfacial adhesion and further improve the mechanical properties, the structure of starch needs to be modified and plasticized.

1.1.1.1. TPS fabrication methods. One way of modifying the structure of starch is by gelatinization (a process of opening up the amylose and amylopectin chains with water) [4, 8]. In order to further plasticize native starch, one has to eliminate the branched structure, amylopectin, thereby rendering starch thermoplastic with linear amylose molecules. Dean et al. found that by gelatinizing and shearing starch at the same time, one can eliminate the amylopectin molecules and achieve TPS [4,8,10,15,16]. Once gelatinization has been achieved, introducing plasticizers into the water-starch system can further plasticize starch and increase its processability [8-10]. Plasticizers such as glycerol are excellent candidates for starch-based polymers because they maintain biopolymer flexibility relatively independent of the matrix water content [14,15]. It has been shown by Gonzalez and Ramsay that mechanical properties of starch composites can be directly influenced by the amount of plasticizer used [4]. Figure 2 shows SEM images of starch before and after plasticization. It is clearly seen that the plasticization process breaks down the nodular structure of the native starch (Fig. 2a) to yield a more continuous structure (Fig. 2b) which should promote adhesion with the PE. It can be easily inferred from Fig. 2 that TPS would be more a much better option as filler for HDPE fibers than native starch due to the ease of processing.
1.1.2. High Density Polyethylene (HDPE)

High Density Polyethylene (HDPE) is a different form of a simple polyethylene molecule. Because of its versatility polyethylene has many varied forms with different
types and contents of branches such as (a) ultra high density polyethylene (UHDPE); (b) low density polyethylene (LDPE); (c) linear low-density polyethylene (LLDPE); (d) very low-density polyethylene (VLDPE) [17-23]. Polyethylene was first commercialized by the ICI in the 1930s [14]. Polyethylene was found to contain diverse amounts of short chain and long chain branches. Linear polyethylene which had a melting point of 135 °C was first synthesized by Ziegler et al. [19] and by Phillips Petroleum researchers [20] in the 1950s. HDPE is a linear form of polyethylene, because it does not contain a high degree of branching within its structure.

HDPE has relatively high crystallinity when compared to other polymers; this helps to increases HDPE’s mechanical properties. The relatively high amount of crystallinity is due to the symmetry and extremely low amount of branching that exists in HDPE’s structure. The potential to extend PE’s range of applications makes it an ideal candidate for blending with other biodegradable fillers. The difference between an amorphous polymer and a crystalline one is shown in Fig. 3a. As stated earlier, the symmetric structure of PE makes it easy to form highly organized folded structures (Fig. 3a). The folded chains then organize into lamellar crystals, as depicted in Fig. 3b.
Figure 3. The difference between an amorphous polymer chain and a crystalline one (a). The lamellar structure of HDPE (b).

Blending the HDPE with TPS will result in a partially biodegradable blend that retains most of its mechanical properties. Consequently, this blend could result in a “greener” alternative to neat HDPE in many applications.

There are no known reports that exist on fabrication of biodegradable fibers using TPS and HDPE. Since HDPE is a highly versatile polymer and is used extensively in industry, any progress towards its impact on the environment and general biodegradability would be beneficial to the society at large. This research would be
particularly beneficial in the field of general engineering, where HDPE is used extensively in numerous applications. It could also benefit the field of polymer composites, where high-strength PE fibers known as Spectra™, are used as one of the leading high performance reinforcements. The “green” nature of this HDPE/starch fiber could be particularly appealing as an alternative to Kevlar™ [24]. Large amounts of sulfuric acid are required to process Kevlar fibers, posing a potential severe environmental hazard in its handling and disposal of its waste [24]. Ideally, this research may help to replace certain synthetic fibers depending upon the mechanical properties of the blended fibers.

1.1.2.1. HDPE fiber processing methods. Producing a high modulus and high strength fibers from flexible polymers have been one of the challenges in polymer science and technology for a very long time. HDPE fibers with high mechanical properties have been produced by a variety of drawing methods [25]. These include solid state hot drawing [26, 27], solid state extrusion [28,29], free growth [30], surface growth [31], and gel-spinning [24,32]. Prior research has shown that the mechanical properties are proportional to the draw ratio achieved. Because the research is intended to impact the field of general purpose polymers, the melt spinning process was used to fabricate fibers.

Melt spinning is a process by which a polymer is extruded and then is drawn to form fibers. For this process, work done by Ziabicki and Kedzierska in the late 1950’s and early 1960's suggests that molecular orientation is increased as spine line tension, that is the difference between extrusion and take up velocities, is also increased [33-37]. Multiple studies done by Keller [38-44] concluded that the orientation of melt-spun polyethylene relied upon the stress that is subjected to the melt. If the PE is crystallized
under low stress, the lamellae will grow radially outward in the form of twisted ribbons, with their growth axis parallel to the b crystallographic axis [40] (Fig. 4a). Under higher stress, the radially grown lamellae extend directly outward without twisting, (Fig. 4b) [40]. Therefore one can achieve highly aligned HDPE fibers if the proper stress is applied on the melt. For this study, a sophisticated fiber take-up system was not available; therefore, a cold drawing method was applied after the fibers were spun to achieve maximum alignment.

![Figure 4. Difference that take speed and spine stress can have on the structure of PE: (a) the effect of low stress and (b) the effect of high stress.](image)

Although melt spinning is an attractive method, the modulus and strength of melt-spun and hot-drawn fibers obtained are still much lower than that of gel-spun fiber. There are several reasons for this result including the much lower molecular weight of the polymer employed in melt spinning [45, 46], the lower level of chain extension and alignment, and also the formation of various types of defect within the fiber [47– 52]. Most of the research in this field is focused on producing high modulus fiber. However, for use in a general purpose application, strain to failure properties may be more
important. The Young’s Modulus of a highly drawn polyethylene is generally around 1.0–1.3 GPa [39-40, 43-44].

Given what is known about the properties of HDPE and TPS, the goals of this project are to create an inexpensive, highly functional, and partially biodegradable fiber based on HDPE and TPS blends. Another goal of this study is to understand and quantify the morphological, mechanical and processing characteristics of these fibers. By achieving these goals, this report will make a significant contribution to the area of high strength polymers as well as green polymers.
2. EXPERIMENTAL PROCEDURE

2.1. Preparation of the HDPE/TPS blends

The loadings of TPS in the blends were determined by studying the mechanical properties of TPS/HDPE films at different starch loadings. These preliminary findings are presented in Table 1. According to these preliminary results, the mechanical properties deteriorated when the starch loading exceeded 10 wt%. Therefore, it was determined that the TPS loading should not exceed 10 wt% in the fibers. Four TPS loadings were chosen. These loadings were as chosen to be 1wt%, 3wt%, 5wt% and 7wt%.

Before blending, native corn starch had to be gelatinized to form TPS. Corn starch was used due to its low cost and availability. According to Dean et al., native starch could be gelatinized by boiling it in water for approximately 45 minutes [8]. Also, most
literature sources report that gelatinization and the subsequent removal of amylopectin occurs via heating and shearing the native starch at the same time in an extruder [8]. Native corn starch was gelatinized by boiling it in water and shearing with a magnetic stirrer. Glycerol was then added to further plasticize the starch. A total of 20wt% of glycerol was added for each blend. After the modification process was completed, TPS was blended with HDPE in a HAAKE PolyLab torque rheometer (Fig. 5) at 8rpm and at a temperature of 150 °C. The blend was recovered from the mixer and used to spin fibers from the melt.

Figure 5. HAAKE polyLab torque rheometer.
2.2 Spinning of Fibers

Fibers were drawn from the blends using a ThermoHaake TM Minilab co-rotating twin-screw extruder located at Auburn University. Fibers were extruded at a rate of 5 rpm and a temperature of 150 °C from a die with a diameter of 5 mm. The take-up speed was maintained constant to obtain a uniform diameter. However, the fibers still had a diameter in the range 0.15-0.30. The blended fibers were also cold drawn using a MINIMAT tensile tester at a rate of 5mm per minute at room temperature. The draw ratio was determined by the strain-to-failure results of the as spun fibers. The cold drawing process would serve to further increase the fiber’s crystallinity and mechanical properties.

2.3. Mechanical Characterization of the fibers

Tensile properties of the fibers were analyzed using the MINIMAT tensile tester at a rate of 5mm per minute at room temperature (Figure 6). These continuous fibers were cut into 30mm long fibers and each individual fiber was attached to a test stub. Ten tests were conducted on each type of fiber and the five best results were chosen for this report. The fibers, both as-spun and drawn, were tested using the same instrument and the same methodology.
2.4. Morphological Characterization of the fibers

Wide angle x-ray scattering (WAXS) at Air force Research lab in Dayton, Ohio, was used to characterize the morphology of the fibers. A Rigaku RU200 rotating anode generator equipped with a Statton camera was used to acquire 2-D WAXS patterns. Nickel filtered CuKα radiation was used at an accelerating voltage of 50 kV/170 mA. The data were collected on phosphor image plates and digitized using a Molecular Dynamics scanner.

2.5. Thermal Characterization of the fibers

Thermogravimetric analysis (TGA) was used to measure the degradation temperature of the blends. For TGA measurements, air was used as the medium and the temperature was ramped up at a rate of 10°C per minute. The degree of crystallinity, DOC, in the fibers was characterized by using the DSC. A differential scanning calorimeter (TA Instrument DSC Q100) was used to study the melting behavior of the nano fibers. The sample was ramped at 10°C/min from room temperature to 250°C under...
a nitrogen atmosphere. The enthalpies of fusion were used to calculate the degree of
Crystallinity. The equation for calculation of DOC is as follows;

\[ \text{DOC} = \frac{\text{Heat of fusion}}{\text{Heat of fusion}} \]

, where \( \text{Heat of fusion} \).
3.0. RESULTS AND DISCUSSIONS

3.1. Processing Characteristics

In order to determine the proper processing window for these blends, it was important to understand the thermal stability of each individual component in it as well as the thermal stability of the blends. The TGA results (Fig.7) show that neat HDPE has a degradation temperature of approximately 450 °C; whereas, native starch exhibits a weight loss near 100 °C, which is presumably due to loss of water, and a degradation temperature of about 360 °C (Fig. 8). TGA analysis was attempted on TPS; however, the high moisture content of TPS as a result of the plasticization process caused the results to become noisy at approximately 90 °C; therefore, it is not presented.

The TGA results of a blend of 50wt% TPS and HDPE are presented in Fig. 9 and they show that the composite fibers exhibit three onsets of degradation. These temperatures are as follows: approximately 155 °C; approximately 310 °C; and approximately 370 °C. Charring of the blends was also noticed visually when they were processed at approximately 160 °C, suggestive of significant degradation occurring. Apparently, the addition of the glycerol and its subsequent interaction with the constituents lead to an overall lowering of the thermal stability of the blend. Based on the TGA studies and observations during the blending process, the upper limit for processing these blends was determined to be approximately 160 °C.
Figure 7. TGA results of neat HDPE.

Figure 8. TGA results of native starch.
3.2. Mechanical Results

3.2.1. As-spun Fibers

Figure 10 shows the average yield stress of the as-spun fibers vs. wt% starch. The figure shows predictable results: as the percentage of starch increases, the average yield stress decreases. The highest yield stress, 23 MPa, was attributed to the neat fiber. The 1% starch sample has an average value of 22.5 MPa, while the 3% and 5% starch fibers showed a discernible decrease in the yield stress with values of roughly 17 and 16 MPa, respectively. This represents an approximately 70-75% retention of the yield stress of the neat sample. It is possible that with the appropriate strengthening techniques the yield stress of the 3% and 5% samples could approach that of the neat sample.

All of the as-spun samples, except the 7 wt%, exhibit very high levels of extensibility, with strains well above 500%. The 7 wt% sample also had the lowest yield stress value of approximately 13 MPa. The drop in yield stress with increasing starch...
content is presumably due to an increase in immiscibility between the starch and the HDPE matrix [3, 6, 8, 48].

![Graph showing Average Y.S vs wt% TPS](image)

Figure 10. Yield stress values vs. wt% TPS for the as-spun fibers.

Figure 11 compares the Young’s modulus of the as-spun samples vs. wt% starch. As the figure shows, the Young’s modulus decreases drastically as the amount of starch is increased to 1 wt%. The neat sample has an E value of approximately 550 MPa; whereas, the 1% sample has a value of roughly 260 MPa. The 3 wt% sample has a value of 160 MPa, and the 5 and 7 wt% samples have approximately the same value of 140 MPa. Traditionally speaking, if starch is used as filler, it tends to stiffen the polymer blend [48-51]; however, the figure shows the exact opposite. There are several reasons for such results to occur.

Since this report investigated the fabrication of HDPE melt spun fibers, a higher than normal amount of glycerol was used. This fact, combined with the results discussed
in the earlier paragraph, suggest that glycerol may play the dominant role in such a drastic decrease in stiffness of the as-spun samples as the wt% of starch was increased.

A drop in Young’s modulus of a polymer could also be attributed to a decrease in the crystallinity of that polymer. Therefore, one can presume form Fig.11 that there is a drastic decrease in the % crystallinity from the neat to the 7 wt% sample. Morphological data will be used to confirm this suspicion.

![E vs wt% TPS](image)

Figure 11. Young’s modulus as wt% TPS of as-spun samples.

3.2.2. Drawn Fibers

When compared with the as-spun fibers, the drawn fibers showed a remarkable increase in their mechanical properties. As shown by Fig. 12, the neat fiber exhibited a yield stress of approximately 500 MPa as compared to 23 MPa of the as-spun samples. This is an approximately 20-fold increase. The 1 and 3 wt% samples exhibit approximate yield stresses of 470 and 480 MPa, respectively, representing an increase of
approximately 30-fold. These are encouraging results since they prove that with the appropriate processing techniques, up to 3% of synthetic HDPE could be replaced by biodegradable starch for high strength applications. When considering that the current demand for HDPE for general purpose applications is 30 million metric tons, a 3% synthetic polymer replacement becomes significant.

The 5 wt% sample showed the lowest yield stress value of approximately 250 MPa. Although this value was the lowest of the drawn samples, it was still significantly higher than the value for the as-spun 5 wt% sample. The 7% sample was not tested since it could not be drawn to the specified ratio of 5.

![Figure 12. Yield stress values for the drawn fibers.](image)

The average strain-to-failure values of the drawn fibers are shown in Table 2. The average strain-to-failure values of the 5 wt% sample was about 25% less than the neat
sample. Such a result, combined with the fact that the 5wt% sample also had a drastic
decrease in its yield stress value, raises the question of whether there is less than desirable
miscibility in the 5 wt% sample and/or whether there are micro defects developing in the
structure of the fibers. According to Table 2 the strain to failure of neat is 65.6%; 1 wt% is 51.1%; 3 wt% is 67.6%; and 5 wt% is 49.2%.

Table 2: Comparison of mechanical properties of the as-spun and drawn fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Y.S (a.s)</th>
<th>Y.S (Drawn)</th>
<th>S-F (Drawn)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td>MPa</td>
<td>%</td>
</tr>
<tr>
<td>NEAT</td>
<td>23.0</td>
<td>500</td>
<td>65.6</td>
</tr>
<tr>
<td>1 wt%</td>
<td>22.5</td>
<td>470</td>
<td>51.1</td>
</tr>
<tr>
<td>3 wt%</td>
<td>17.0</td>
<td>480</td>
<td>67.6</td>
</tr>
<tr>
<td>5 wt%</td>
<td>16.0</td>
<td>250</td>
<td>49.2</td>
</tr>
</tbody>
</table>

* = The as-spun fibers did not exhibit a failure strain before exceeding the travel limit of the test frame.

When compared to their as-spun counterparts, the drawn fibers also showed a
dramatic increase in their Young’s modulus. As shown in Figure 13, the modulus value
(E) of the drawn neat fiber increased to 4800 MPa when compared to 550 MPa of the as-
spun neat fiber. Table 3 shows the comparison of E values of the as-spun samples and the
drawn samples. According to Table 3, the E value of 1 wt% sample increases to 5200
MPa as opposed to 260 MPa of the as-spun sample, a 20-fold increase; the value of 3
wt% sample increased to 5600 MPa as opposed to 160 MPa of the as-spun sample, a 35-fold increase; and the value of 5wt% sample increased to approximately 3900 MPa as opposed to 140 MPa of the as-spun sample, a 28-fold increase. The data for the 1 and 3 wt% samples follows the expected trend of increasing the modulus as a function of starch addition as discussed earlier.

The drawn samples do not exhibit the extreme loss in modulus as was observed for the as-spun samples. These fibers showed the traditional increase in stiffness as the wt% of starch was increased except for the 5 wt% sample. This result raises the question of whether or not immiscibility and a loss of crystallinity play a role in the decrease in the stiffness value of the 5 wt% sample. Again the morphological results should shed some light on this question.

Figure 13. Values of the Young's modulus of drawn samples.
Table 3. Comparison of the Young’s modulus of as-spun fibers and drawn fibers.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>E (Drawn )</th>
<th></th>
<th>E (As-spun)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td></td>
<td>MPa</td>
<td></td>
</tr>
<tr>
<td>NEAT</td>
<td>4800</td>
<td>1.00</td>
<td>550</td>
<td>8.72</td>
</tr>
<tr>
<td>1 wt% STARCH</td>
<td>5200</td>
<td>1.08</td>
<td>260</td>
<td>20.0</td>
</tr>
<tr>
<td>3 wt% STARCH</td>
<td>5600</td>
<td>1.16</td>
<td>160</td>
<td>35.0</td>
</tr>
<tr>
<td>5 wt% STARCH</td>
<td>3900</td>
<td>0.81</td>
<td>140</td>
<td>27.85</td>
</tr>
</tbody>
</table>

The above-mentioned results also show that when appropriate processing techniques are applied, up to 3 wt% of synthetic HDPE could be replaced by TPS with minimal loss of tensile properties. Furthermore, the 5 wt% sample only exhibits an 18%, loss of stiffness when compared to the neat drawn sample. This may still be acceptable for some applications. The results shown above also suggest that further optimization of the ratio of glycerin used could result in more property improvements.

3.3. Morphological Results.

Films of the blends were made to evaluate the miscibility by SEM. Films were easier to study in this respect than fibers. Once the fibers are formed, they consist of smaller fibrillar and microfibrillar structures which would be difficult to characterize for phase separation. The blends exhibit a small degree of miscibility at low concentrations of starch but become immiscible as the starch loading increases. Films of higher wt% TPS to HDPE loadings were studied since they show this effect more clearly. Figure 14 shows the effect of morphology of a blend containing 10 (Fig.14a) and 20 wt% starch.
(Fig. 14b). The image shows that as the wt% of TPS is increased the amount of spherical particles in the blend increase, indicating that the starch phases separates into distinct domains. The same trend is shown in Figure 15 for 30 wt% (Fig. 15a) and 40 wt% (Fig. 15b) samples. This result could explain why the 7 wt% as-spun and 5 wt% drawn samples have a drastic decrease in their yield stresses. The onset of spherical particles may begin in 5 wt% blends and increase in 7wt% blends. WAXS calculation of % crystallinity will also be used to corroborate this result since a decrease in the E value could also be caused by a decrease in the % crystallinity of the samples.

![SEM images of 10 wt% TPS (a) and 20 wt% (b) TPS films](image)

Figure 14. SEM images of 10 wt% TPS (a) and 20 wt% (b) TPS films
3.3.1. Wide Angle X-ray Scattering (WAXS) Results

Wide angle x-ray scattering (WAXS) was used to characterize the morphology of the fibers. WAXS can be used to determine the crystalline structure of polymers (eg., unit cell dimensions, degree of crystallinity, crystal size and orientation). In this study, we are most interested in characterizing the degree of orientation of the fibers as well as the degree of crystallinity. These parameters can both be correlated with the processing and properties. A highly oriented fiber consists of a large number of crystallites, which all have one particular crystallographic direction typically designated the c-axis, oriented in the direction of the fiber axis. When the incident x-ray beam is normal to the fiber axis, the resulting diffraction is essentially the same as that obtained from a single crystal that is rotated continuously around the fiber axis during exposure to the x-rays. In an ideal highly oriented fiber, the c-axes of all the crystallites are parallel to the fiber axis, as illustrated in Figure 16 which depicts scattering from such a fiber. The large dots

Figure 15. The immiscibility of 30 wt% TPS blend (a) and 40 wt% TPS blend (b).
represent a column of unit cells separated by a distance c along the fiber axis. Strong scattering will be observed at the angle \( \Phi \) shown when

\[ c \sin = l\Phi \] (where \( l \) is an integer and \( \Phi \) is wavelength of x-rays) [53].

The diffraction spots, or reflections, intersect the detector on specific lines known as layer lines, as shown in Fig. 17. These occur when the path difference for scattering from adjacent unit cells equals an integral number of wavelengths, which are denoted by \( l \). When \( l=0 \), the layer line is known as the equator. The normal through this point where the x-ray beam would strike the detector is known as the meridian. In contrast to the fiber diffraction pattern, a pattern for an unoriented sample would consist of a series of rings. As the orientation of a sample increases, the rings become arcs; and ultimately at high degrees of orientation, they become spots.
Diffraction data similar to that shown in Fig. 17 can be used to quantify the amount of orientation in a sample by analyzing the intensity of the meridional reflections as a function of azimuthal breadth, as depicted in Fig. 18. The intensity of the selected reflections, which correspond to planes, is scanned as a function of radial angle, $\Phi$. The resulting plot will show two peaks as a function of radial angle, reflecting the two normals to the diffraction plane relative to the fiber axis direction [51-52].

The degree of orientation of the fibers can be quantified by the Herman’s orientation constant, $f$, which is defined as:

$$f = \frac{1}{2}[3\cos^2\Phi - 1]$$
Where $\Phi$ is the angle between the polymer chain axis and $\cos^2 \Phi$ is the average over all the polymer chains around the solid angle. When all the chains are parallel to the fiber axis, $f=0$ and $f=1$ and when chains are perpendicular to the fiber axis $\Phi$ is $90^\circ$ and $f = 0.5$ [53-54].

Figure 19 shows 2-D scans for the as-spun samples. The predominant pattern is a series of rings. The two prominent inner rings can be indexed as reflections from the (200) and (110) planes of HDPE, respectively. The presence of the rings indicate that little to no orientation is present. Further analysis of the data showed that generally the (200) peaks were meridional and the (110) peaks were off-axis, indicating the a-axis was parallel to the fiber axis and the b- and c-axes perpendicular, Fig. 19.

![Figure 19. 2D x-ray scans of the as-spun neat (a), 1% (b) and 3% (c) samples. The 5wt% and 7wt% samples showed similar results.](image)

This is confirmed by the azimuthal scans of the intensity of the (110) and (200) reflections, shown in Fig. 20. The broadness of the peaks confirm the very low level of orientation. The one exception to this orientation was the 5% starch sample whose orientation was reversed. The (200) peaks were equatorial and (110) peaks off-axis. This
indicates the b-axis was parallel to the strand axis instead of the a-axis. Then the 7% returned to the original orientation. There are no known reasons for such a result to occur.

For the drawn samples, the (110) and (200) peaks in the x-ray diffraction pattern are visible as two strong reflections on the equator (Fig. 21). This means the c-axis or chain axis is oriented parallel to the fiber axis. Figure 22 shows azimuthal plots of the

Figure 20. Azimuthal scans of intensity for the (110) reflection (a) and (200) reflection (b).
intensities of the 110 and 200 reflections, respectively. The width of these peaks at half maximum was used to compute the orientation constant. The narrower the peak, the higher the degree of orientation. Both reflections exhibited peak widths of 6-7°. A Hermans’ orientation factor of ~0.99 was calculated for all of the samples. This value indicates that there is near maximum orientation with drawn samples. This result is also confirmed by the 2D x-ray plots of the drawn samples, (Fig. 21). The result corroborates the significant increase in mechanical properties as the fibers were drawn.

![Figure 21. 2D x-ray scans of the drawn neat (a), 1% (b) and 3% (c) samples.](image)
Figure 22. Normalized intensities versus angle from the equator for the drawn samples.

The degree of crystallinity as measured by WAXS varied between 51% to 46% (Fig. 23) in the as-spun samples. There is a small trend to lower degrees of crystallinity at the higher starch levels; however, this decrease is within the margin of error of the measurements, ±3%. The results shown in Fig. 23 confirmed a presumption that was
made about the drop of E values of 1 wt%–7 wt% as-spun samples. It was presumed that the drop in modulus values was due to the increased addition of glycerol and/or a general decrease in the amount of crystallinity of the as-spun samples. However, according to Fig. 23, there is not a significant change in the degree of crystallinity for the samples. This result suggests that the loss of moduli suffered by the 1 wt% to 7 wt% as-spun samples was due to the addition of glycerol.

Figure 24 shows the % crystallinity values of the drawn samples. The figure also provides an insight as to why the 5% drawn sample has a discernible decrease in its modulus values when compared to the neat drawn sample. The amount of crystallinity is related to the overall stiffness of the blends. As Fig. 24 shows, there is a 10% decrease in the percent crystallinity as one goes from the neat drawn sample to 5 wt% drawn sample; and according to Fig. 12 the modulus value of the 5 wt% sample drops to 3900 MPa from 4800 MPa of the neat drawn sample. Therefore, this result confirms the fact that a noticeable loss in percent crystallinity and an overall decrease in the miscibility of the blends is responsible for the drop in mechanical properties of fibers with TPS loadings greater than or equal to 5 wt%.
Figure 23. Degree of crystallinity versus wt% TPS via WAXS for the as-spun samples.

Figure 24. Degree of crystallinity of the drawn samples via WAXS.
4.0. CONCLUSIONS

The objective of this project was to create highly functional polymer fibers that were partially biodegradable. Melt spinning was successfully employed to create these fibers. The mechanical properties of the drawn blended fibers showed that with appropriate processing techniques (i.e. cold drawing), up to 5 wt% TPS could be used as filler without significantly sacrificing the mechanical properties of the neat fiber. In some cases, the blended drawn fibers exhibited a 35-fold increase in the mechanical properties when compared to their as-spun counterparts. This result was especially significant when one considers that current HDPE demand exceeds 30 million metric tons.

The 7 wt% as-spun sample and the 5 wt% drawn sample showed a discernible decrease in their yield stress and modulus when compared to their neat counterparts. The WAXS data showed this decrease in the modulus value of the 5 wt% drawn and the 7 wt% as-spun samples was due to a general decrease in the miscibility of the blends as well as a decrease in their % crystallinity.

WAXS was also used to examine the morphological characteristics of the blended fibers. The results showed that addition of up to 3 wt% starch did not adversely affect the morphology of the fibers. Almost perfect alignment was achieved in fibers with TPS loadings of up to 5 wt%; however, crystallinity decreased when TPS loadings reached 5wt%.
These results combined with mechanical results show that with appropriate processing techniques, up to 5 wt% TPS, could be used as biological filler in an HDPE matrix for applications requiring a high strength fiber.
LIST OF REFERENCES


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