TORREIFIED BIOMASS REINFORCED HIGH TEMPERATURE THERMOPLASTICS

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Abstract
In higher melting temperature thermoplastics, such as polyamides, the increased processing temperatures hinder the incorporation of biomass fillers during composite production. By employing a process commonly used in energy production, torrefaction, a biomass able to survive the increased temperatures of engineering thermoplastics was produced. Torrefied flax shive was incorporated into a polyamide-6 matrix at various filler loadings and evaluated for mechanical performance. These polyamide biocomposites show great promise as viable replacements for common industrial applications such as under the hood components in the automotive industry.

1 Introduction
Biobased fillers in thermoplastics have seen a remarkable increase in usage over the last several years. The increased usage of biobased fillers follows the ever-increasing thrust to reduce petroleum and synthetic petrochemical product consumption. The automotive industry, which is the single largest consumer of polyamides, is becoming a proponent of greater utilization of biobased materials. This opportunity makes the addition of biobased fillers to engineering thermoplastics attractive for under-the-hood applications. However, the increased processing temperatures of engineering thermoplastics present challenges. For lower melting temperature thermoplastics such as polyolefins, biobased fillers cause increases in elastic modulus over the neat polymer albeit with moderate changes in tensile strength [1, 2]. Incorporation of biomass in engineering thermoplastics is a challenge since the increased processing temperatures lead to filler degradation, which often decreases the mechanical performance. Torrefaction has been identified as an effective means of preparing the biomass for introduction into engineering thermoplastics such as polyamides. Polyamide biocomposites were produced and shown to have comparable mechanical properties to the neat matrix. The objective of this work was to evaluate the effectiveness of flax shive as filler in polyamide-6 by applying preprocessing to the filler to mitigate the effects of increased processing temperatures. Mechanical performance comparable to the unfilled matrix was successfully achieved using torrefaction.

2 EXPERIMENTAL PROCEDURES
Torrefaction is a method to prepare biomass for energy production commonly conducted in the temperature range of 220-300 °C. The process decomposes hemicellulose, fats, waxes, and other constituents yielding a biomass consisting of cellulose, degrading between 300-375
°C, and lignin, degrading slowly over 250-500 °C [3, 4]. The cellulose remaining acts as the reinforcing agent in the biocomposites. In this study, flax shive (the woody core of flax stalk) was torrefied at 300 °C for 6 hours in an inert atmosphere of argon.

To prepare the biocomposites, polyamide was blended with the torrefied flax shive (TFS) using a co-rotating twin-screw extruder. This study investigated four grades of the biocomposite; neat polyamide-6, 10 wt% filler, 20 wt% filler, and 30 wt% filler loadings. The compounded biocomposites were pelletized, dried, and injection molded into test specimens. Mechanical testing was performed on the specimens and correlations between biomass input and loading were drawn.

Tensile testing was performed on the four grades of biocomposites according to ASTM standard D638. Five specimens of each biocomposite grade were tested. Flexural testing was performed according to ASTM standard D790 using five specimens. Notched Izod Impact testing was performed according to ASTM standard D256 with six specimens for each grade. Immersion density was performed using isopropyl alcohol. The moisture uptake was analyzed using 24 and 72 hour soaks in distilled water.

3 Results and Discussion
The first step in this research was to determine the effectiveness of torrefaction in preparing the biomass for exposure to temperatures beyond its degradation point. Two biocomposites were tested, one using untorrefied biomass filler and the other using torrefied biomass filler. Figure 1 shows the results of tensile testing for these two composites. It can be seen in the figure that the torrefaction lead to higher mechanical properties compared to the untorrefied filler. During processing the torrefied filler also showed to increase the melt strength of the polymer stream. There was a noticeable difference in odor during processing as well. The untorrefied filler had the distinct odor of biomass degrading due to excess heat, while the torrefied filler displayed no noticeable odor.

![Figure 1. Tensile comparison between torrefied and untorrefied 20 wt% filled polyamide biocomposites.](image-url)
Tensile, flexural, and impact property results from the PA6/TFS biocomposites can be seen in Figures 2-4. The elastic modulus improved with added filler while the tensile strength saw small decreases with increased filler loadings. The flexural modulus and strength displayed similar trends. The impact toughness of shows a decreasing trend with increased filler loadings.

**Figure 2.** Tensile properties for torrefied flax shive reinforced polyamide-6 biocomposites.

**Figure 3.** Flexural properties for torrefied flax shive reinforced polyamide-6 biocomposites.
Fillers can be considered imperfections within biocomposites due to poor interfacial bonds between filler and matrix. The poor interfacial bond stems from the differences in polarity between the fiber and matrix. In polyamide torrefied biocomposites, the fiber is more hydrophobic than hydrophilic and the matrix is hydrophilic. Although the polarity difference in polyamide biocomposites is present, the difference is not as great as that in polyolefin biocomposites. As the polarities are more similar in polyamide biocomposites, the interaction between matrix and fiber is stronger than those present in polyolefin biocomposites without the need of an added compatibilizer. These imperfections which hinder the ability of polymer chains to move freely aid in increasing the elastic modulus. The transferring of load from matrix to filler comes at the cost of lower tensile strengths. These imperfections also cause increased flexural performance and decreased impact resistance.

Density and moisture uptake results can be seen in Figure 5 and 6. The density results show as filler loading is increased the density also increases, with the exception of 30 wt% loading. The decrease at 30 wt% loading could be due to voids in the molded specimens or a loading less than 30 wt%. Some further investigation is needed to explain this phenomena.

Figure 4. Impact toughness of torrefied flax shive reinforced polyamide-6 biocomposites.
Figure 5. Density comparison of torrefied flax shive reinforced polyamide-6 biocomposites.

Figure 6. Moisture uptake of torrefied flax shive reinforced polyamide-6 biocomposites at 24 and 72 hour soaks.
During the torrefaction process, the hydroxyl groups of the cellulose monomers are decomposed which increases the hydrophobic nature of the torrefied biomass [5]. The addition of this more hydrophobic filler to a hydrophilic matrix is hypothesized to decrease the moisture absorption. This effect can be seen in the testing results with the biocomposites absorbing on average 2% less moisture than the neat matrix at 24 hours and 6% less moisture at 72 hours.

4 Conclusions
Torrefied flax shive was shown to increase the modulus of the neat polyamide-6, while maintaining the tensile strength similar to that of the neat polymer. The flexural properties showed similar trends while showing a decrease in impact toughness compared to the neat matrix. The addition of torrefied flax shive also showed to decrease the moisture absorption of polyamide-6 biocomposites over the neat polymer in both 24 and 72 hour soaks. An investigation into other matrices and biomass feed stocks would be beneficial in furthering the promising results already seen in this work. The dynamic-mechanical and thermo-mechanical properties are also of interest in future study.

References