OPTIMIZING MECHANICAL BEHAVIOR OF BASALT-NATURAL FIBER HYBRID INJECTION MOLDED COMPOSITES

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Abstract

Environmental consciousness is driving modern research and development in the automotive sector to target the advancement of feasible green materials in automotive applications. Basalt fiber has shown to be a robust competitor against glass and carbon fiber and is more eco-friendly manufacturing processes. Reinforcing polypropylene with basalt fiber and hemp hurd using maleic anhydride-grafted polypropylene (MAPP) as a coupling agent, has shown to contain similar mechanical properties to its competitors. A mixture model was implemented to optimize the mechanical properties of a variation of fiber ratios and MAPP to compare against a controlled GF mixture. Scanning Electron Microscope (SEM) analysis of fracture surfaces show the variation in fiber–matrix adhesion based on addition of MAPP. This study concludes that the addition of MAPP improves the mechanical behaviors of hybrid composites made from basalt fiber and hemp hurd reinforced polypropylene.

Introduction

Polymeric composites are constantly emerging and evolving, especially in industries where weight reduction and enhanced mechanical properties are crucial. Polypropylene (PP) is a widely used polymer in the automotive industry and is one of the few polymers readily recyclable. When reinforced with constituents such as glass fiber (GF), the mechanical properties of the composites are improved. However, the manufacturing process and handling of GFs make them an expensive and an environmentally irresponsible choice [1].

Basalt fiber (BF), a mineral-based natural fiber, is gaining a lot of attention due to its robust mechanical performance and superior environmental qualities [2,3]. BFs are melt processed from hardened magma, and their composition varies slightly based on the region the rock is extracted from; however, these variations do not significantly alter their performance. The composition is primarily made up of SiO_2, Al_2O_3, Fe_2O_3, and CaO with traces of other oxides [4]. It has also been found that typically BFs hold enhanced properties such as strength and tensile modulus to that of GFs and are not as fragile to handle. Additionally, BFs require less resources to produce since the lava rock is naturally rich in minerals, additional elements are not necessary to create the fibers [3].

Likewise, the use of natural lignocellulosic fibers such as hemp hurd (HF) is gaining traction due to their eco-friendly nature, low cost, and low density. Typically, the core of the hemp stalks, hurd, is not used in manufacturing due to its woody pulp like texture and is considered a by-product of the plant. However, when further processed it is possible to obtain useable fiber qualities with a high strength to weight ratio and good damping properties [6].

Adding fibers to a polymer matrix is only beneficial, however, when there is a good interfacial bond between components. A poor interfacial interaction will lead to the composite failing prematurely when strength limits of the matrix are surpassed, and fiber pullout occurs. A strong interfacial bond is critical for the transfer of stress from the polymer to the fiber, the mechanism responsible for maximizing the mechanical performance. To induce this bond, chemical alterations can be made to the surface of the fiber by applying a sizing layer or by modifying the bulk matrix chemistry adding a coupling agent. On the surface of BFs, H-bonded silanol groups act as ideal bonding sites for a silane sizing [2]. These groups also reduce the amount of sizing required compared to that of GF. For the best performance it is important to apply a sizing specified for the polymer matrix. Maleic anhydride g-polypropylene (MAPP) is an effective coupling agent used in BF and HF composites when blended with polypropylene [3,6].

The study of BF-HF hybrid PP composites has not yet been done. Because basalt fibers are relatively new for applications in automotive products, there is a need for data regarding composite materials with basalt fibers blended with other fibers and thermoplastic resins. The purpose of this research is to identify the effects of altering the proportions of BF, HF, and MAPP content on mechanical properties and interfacial bonding. Using this data, optimal fiber-MAPP-matrix ratios tailored to specific parameters can be generated.

Methods and Materials

RheTech (Whitmore Lake, MI, USA) PP (Melt Flow Rate at 230°C/2.16kg of 26 dg/min and density of 0.89 g/cm^3) was reinforced with 3mm-chopped BF (13µm diameter and density of 2.75 g/cm^3) sized with silane and produced by Sudaglass Fiber Technology, Inc. (Houston, TX, USA) and HF (hemp hurd, density of 0.8-1.2 g/cm^3) from Sunstrand (Louisville, KY, USA). The coupling agent, AC 950P MAPP (density of 0.93 g/cm^3) provided by Honeywell (Morristown, NJ, USA) was used to improve the interfacial bond between the matrix and fibers. The D-optimal design of mixture experiment was created with DesignExpert software (StatEase, Inc.) [7] to statistically evaluate and model the effects of component fractions on composite material performance and to numerically optimize the formulation based on a desired criterion. A total of eleven different fiber ratios and MAPP variations were generated, and some mixtures were repeated for value verification purposes, totaling to fourteen mixtures tested. PP was held constant at 65wt%, while the sum of MAPP, BF, and HF made up the remaining 35wt%. The constituent ratios can be found in Table 1. Additionally, pre-made pellets used in industry of 30wt% GF in PP, provided by RheTech, were used as a control mixture to compare mechanical properties to.

Table 1: Mixture model varying basalt and hemp fiber content and MAPP.

Run	Basalt (wt%)	Hemp (wt%)	MAPP (wt%)	PP (wt%)
1	25	10	00	65
2	10	20	05	65
3	00	32	03	65
4	35	00	00	65
5	00	32	03	65
6	32	00	03	65
7	25	08	02	65
8	17	17	01	65
9	00	35	00	65
10	32	00	03	65
11	12	23	00	65
12	20	10	05	65
13	08	23	04	65
14	17	17	01	65

First, HF was hammer milled to 680 µm and sieved through 25 to 50 mesh pans for fifteen minutes. Particles that passed through the 50-mesh pan (< 297µm) were collected and used in the composite mixtures. HF was dried at 100°C for 24 hours before processing. 300 g of each mixture was extruded using a Leistritz 18mm twin-screw extruder maintaining 180°C in each chamber and a screw speed of 40 rpm. The extruded filament was cooled in a water bath then pelletized. Pellets were dried for 24 hours at 100°C, then injection molded into a standard dog bone and bending specimens at 180°C in a Sumitomo injector under 700 kgf/cc and a mold temperature of 100°C. A minimum of five replicates for each mixture were used for testing. GF pellets were injection molded under the same conditions.

Tensile and flexural tests were performed following ASTM standards D638 and D790, respectively. A 2-kip Instron was used to carry out both tensile and flexural tests. Tensile tests were completed with a crosshead speed of 5mm/min using a two-inch MTS extensometer to measure strain. During bending tests, the crosshead displacement was used to measure deflection of the specimen and verified using a LE-05 Laser Extensometer.

The fractured surfaces of tensile specimen were imaged using a Tescan scanning electron microscope (SEM). The specimens were sectioned, mounted vertically on the sample holder keeping the cross-section of the sample perpendicular to the electron beam, and Au-sputter coated. Preliminary work is being done using ImageJ to quantify area fractions across the fracture surface of each constituent, as well as the void area to measure the matrix-fiber interaction. The software uses a color threshold manipulation to isolate each constituent on the fracture surface and determine an area fraction based on the pixel count.

All mechanical behavior values were statistically analyzed using StatEase and GraphPad Prism. An Analysis of Variance (ANOVA) was performed for each property to contrast the mean values for each mixture. Finally, StatEase software was used to optimize constituent ratios based on desired parameters. An optimal formulation maximizing strength was generated and will be used in future research.

Results & Discussion

Mechanical testing was performed on the composite mixtures to determine the tensile and flexural response to altering fiber and MAPP content. Figure 1 shows box and whisker plots of the Ultimate Tensile Strength (UTS) data. An ANOVA analysis was completed comparing the mean value of each mixture to one another to determine if any statistical trends exist. The same letter represents a non-statistical significance and different letters represent a statistical significance. A statistically significant difference exists between two composites when $\alpha < 0.05$.

It can be observed that the UTS does not vary significantly between fiber variations with 0wt% MAPP. The addition of MAPP, even with only 1wt%, significantly increases the UTS for all fiber ratios. The greatest improvement of UTS from the addition of MAPP is found in the BF only composites; 3wt% MAPP and 32wt% BF specimen have the best strength performance of the eleven mixtures. A significant increase in UTS is observed for the HF only composites when incorporating MAPP; however, it is the lowest mean UTS of all mixtures with MAPP. The hybrid composites with both HF and BF variations do not vary significantly when altering the fiber content or MAPP except the 10BF/20HF/5MAPP mixture which has the second highest UTS of the eleven combinations. The GF specimen yielded significantly higher UTS than all other composite variations.

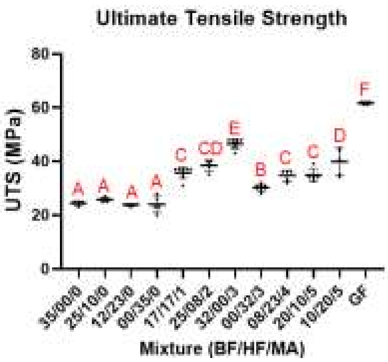

Figure 1: UTS values for all composite mixtures with MAPP increasing to the right on the x-axis.

As for the Young's modulus, an apparent trend is not present due to altering MAPP content alone (Figure 2). However, change in BF wt% on Young's modulus is very apparent (Figure 3), significantly reducing in a linear manner with decreasing BF content. Similar to UTS, the GF control group has a higher mean E than any of the BF-HF composites.

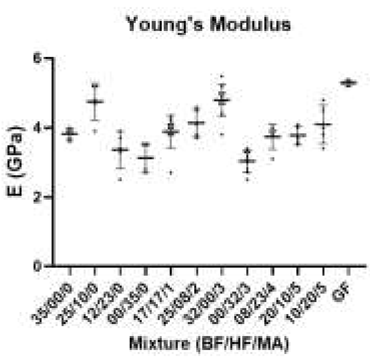

Figure 2: Young's modulus values plotted against varying MAPP content.

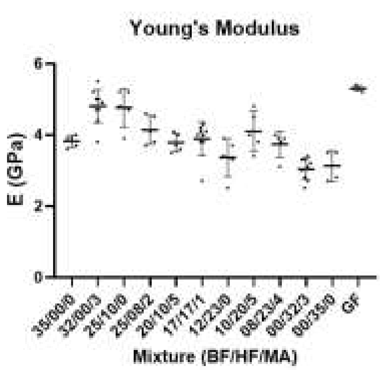

Figure 3: Young's Modulus values plotted against varying fiber content.

Using StatEase, contour plots were created for both UTS and Young's modulus to display trends in how each property changes when altering each constituent amount. The red coloring represents maximum values and transitions to dark blue as the values decrease. Both plots shown in Figure 4 reiterate the trends found from the ANOVA tests discussed previously.

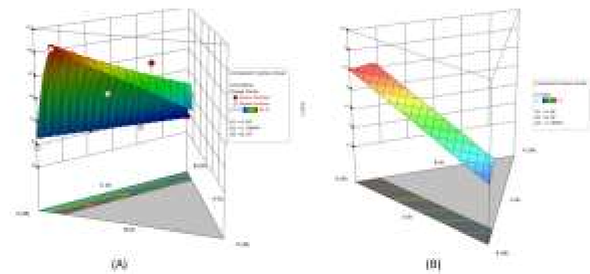

Figure 4: Contour plots created based on the data collected for a) UTS and b) Young's Modulus

Flexural strength can be seen in Figure 5, and results show a similar trend to that of the tensile strength. The addition of MAPP increases the flexural strength and has the greatest impact at 32wt% BF 3wt% MAPP. Figure 6 displays flexural modulus vs. decreasing BF content. Though not as apparent as tensile modulus, a decreasing linear trend exists with decreasing BF.

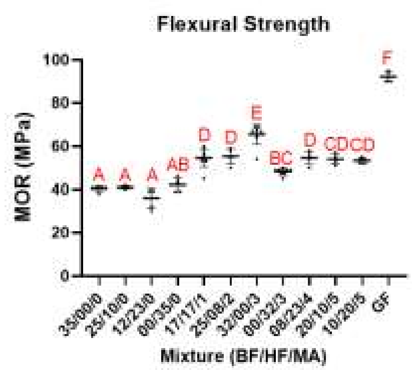

Figure 5: Flexural strength data plotted against increasing MAPP content.

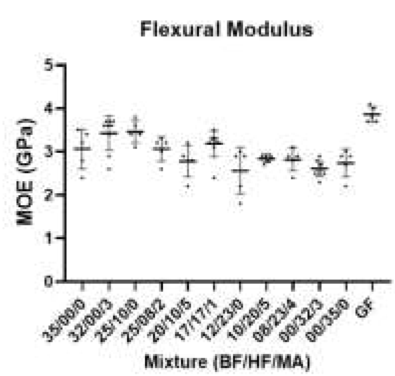

Figure 6: Flexural modulus data plotted against decreasing BF content.

These results were used to determine optimal fiber-MAPP-matrix ratios depending on set criteria for performance of the composite material. Table 2 displays some examples of how a numerical optimization tool can be implemented based on the desired performance requirements in the end product. When all mechanical properties (strength and stiffness in tension and bending) are maximized the ideal composite mixture would consist of 32wt% BF 3wt% MAPP.

Table 2: Examples of optimization criteria and the generated formulation to reach optimal parameters.

UTS	E	MOR	MOE	Optimal Formulation (wt%) BF:HF:MAPP
Maximize	In Range	In Range	In Range	30:1:4
Maximize	In Range	Maximize	In Range	29:3:3
In Range	Maximize	In Range	Maximize	31:0:4
Maximize	Maximize	Maximize	Maximize	32:0:3

As noted previously, GF/PP formulation considered as an industry standard outperformed all BF/HF formulations. This is because of premature failures at the interface between the matrix and BF and/or HF fibers due to poor interaction. SEM analysis was done on the fracture surfaces of tensile specimen to gain insight on the interaction between the fibers and matrix. A visual increase of interfacial bonding between the fiber and matrix is present when adding MAPP. Small holes, or dark circles, show fiber pullout from the matrix indicating poor interfacial bonding. Gaps in the matrix around the fibers can also be seen when poor adhesion is present.

Figure 7 shows the comparison of basalt fiber only composites (a) without MAPP and (b) with 3wt% MAPP. In both mixtures, there is a uniform distribution of fibers throughout the matrix, with a majority of fiber aligned in the flow direction. However, in (a) there is a large amount of fiber pullout present and large gaps between the fibers and matrix. Though there are some areas without interaction, micrographs of (b) show a decrease in fiber pullout and better interfacial bonding. When comparing these micrographs to the mechanical data collected, (b) resulted in a higher UTS than (a) did; this is likely due to the increased interfacial bonding that is observed. However, this interaction can be further improved.

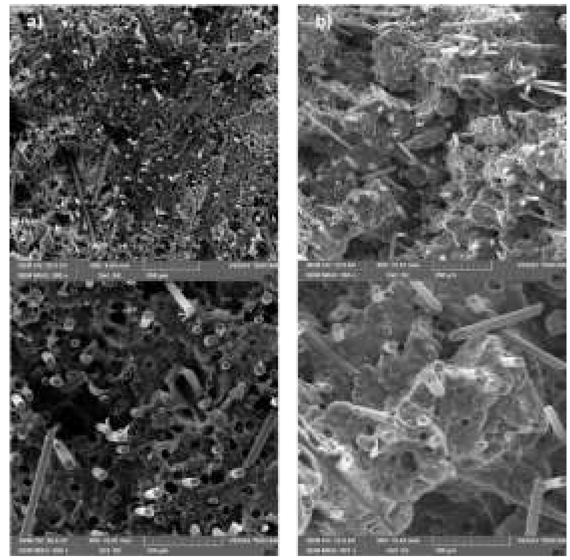

Figure 7: a) Basalt only composite without added MAPP at two different magnifications. b) Basalt only composite with 3wt% MAPP at two different magnifications.

When analyzing hemp only mixtures, (a) without MAPP and (b) with 3wt% MAPP, similar trends were present and can be seen in Figure 8.

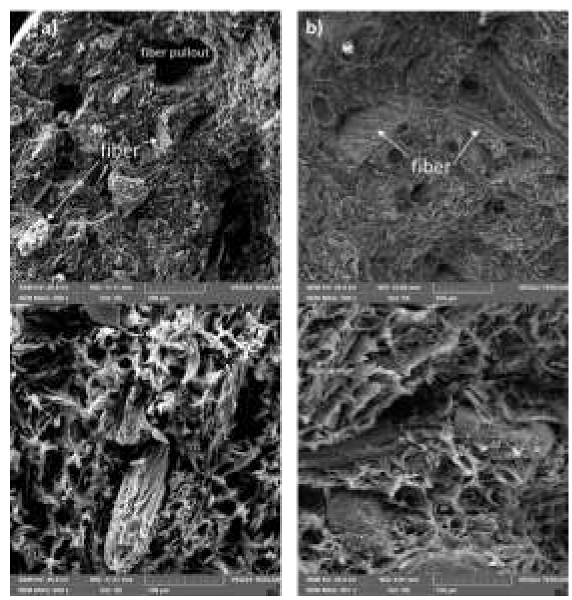

Figure 8: a) Hemp only composite without MAPP at two different magnifications b) Hemp only composite with 3wt% MAPP at two different magnifications.

In Figure 9a of hybrid mixture, 17BF/17HF/1MAPP, there appear to be regions of good interfacial bonding present even with minimal MAPP content. However, there is still a large area across the surface that does not exhibit good interaction. Figure 9b is a magnified view displaying the vast size and texture difference between HF and BF.

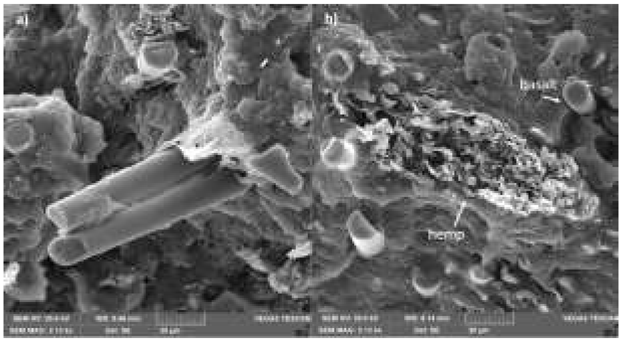

Figure 9: Hybrid composite mixture 17/17/1 a) Display of good interfacial bonding between components. Matrix can be seen bonded on tips of basalt fibers. b) Cross-sectional image displaying major differences between hemp (center fiber) and basalt fibers.

Typically, SEM micrographs are qualitatively analyzed to detect the extent of interfacial bonding and fiber distribution. Using ImageJ software, preliminary quantitative analysis of seven mixtures has been done. By calculating the area fraction of voids, one can determine the amount of fiber pullout present, including gaps between the fibers and matrix. Figure 10 shows an example of how the software separates components. The results for seven of the composites can be found in Table 3. The preliminary results suggest that there is a prominent decrease in void area when HF is present as opposed to BF only composites. Note that these values are based solely on one image for each mixture; quantitative analysis of images to better relate the influence of coupling agent and fiber sizing is ongoing. Once sufficient data is generated, relationships between structure and composite material performance can be established.

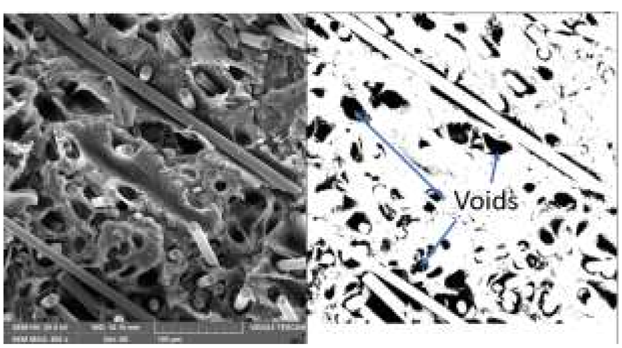

Figure 10: SEM micrograph of 35wt% BF 0wt% MAPP composite showing threshold manipulation to isolate void space from other constituents.

Table 3: Area percentage for each constituent in the analyzed micrographs.

	35BF 0MAPP	32BF 3MAPP	35HF 0MAPP	32HF 3MAPP	20BF 10HF 5MAPP	17BF 17HF 1MAPP	10BF 20HF 5MAPP
VOIDS AREA	22.84	23.86	10.41	0.00	2.66	1.18	0.38
BF AREA	16.44	21.84	0.00	0.00	4.05	3.24	1.73
HF AREA	0.00	0.00	26.25	26.51	5.33	10.80	24.60
PP AREA	60.71	54.30	63.34	73.49	87.96	84.77	73.29

Conclusion

Through mechanical testing, it was found that the incorporation of MAPP, with all variations of fiber, improves strength and moduli. The highest performing composite mixture was 32wt% BF and 3wt% MAPP; however, the mechanical properties of this mixture did not surpass that of the control GF mixture. When analyzing the SEM micrographs, the presence of interfacial bonding was directly correlated to the improved mechanical performance, reiterating the importance of good interfacial bonding between fibers and matrices. The image analysis completed through ImageJ, helped further quantify the interfacial interactions present, showing a significant decrease in void area in HF only and hybrid composites.

Future Work

As the mechanical data shows, it is necessary to continue to improve the BF-HF composites to compete with the GF alternative. Focus will be on maximizing the interfacial bonding between fibers and matrix to reach full performance potential from these materials. Different sizing layers will be applied to the BFs and HFs, then analyzed through mechanical testing and SEM micrographs. Additional work needs to be done to establish proper techniques in ImageJ quantifying the traits within SEM micrographs. This advancement will be crucial to better understand the fiber-matrix interactions.

Using the optimization tool, a new experimental model will be used to understand the effects of MAPP and fiber type at constant fiber content. Rotational and capillary rheometer testing will be done in addition to mechanical testing to understand the processing variables for these materials. Recycling is another important component in industry and will be analyzed to understand how the performance will be altered as the specimen are reprocessed.

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