Reinforcing Thermoplastics with Natural Fibers Derived from Biofuel Byproducts – Extended Abstract

Michael Fuqua & *Chad A. Ulven, PhD
Department of Mechanical Engineering and Applied Mechanics
North Dakota State University, Fargo, ND 58108
***contact:** chad.ulven@ndsu.edu, 701.231.5641

Increasingly in the last few years, expansion seen in the biofuel sector has managed to dramatically change the dynamic of the United States' agricultural market. Crops traditionally grown as feedstock for consumption have found a lucrative market as fuel stock, which in turn has introduced new questions as to product allocation and usage. This maturing industry has brought with it a new source of lignocellulosic material in the form of biofuel production by-products, such as dried distillers grains with solubles (DDGS) from corn-ethanol. However, these by-products have a rather restricted application as livestock feed, due to their low nutritional value [1,2]. This causes their prices to be low relative to traditional lignocellulosic feed stock, and thus their potential use as reinforcement agents has become an attractive opportunity for production facilities with large quantities of derivative waste. With success being seen in the usage of materials traditionally considered filler agents without reinforcement capabilities, attention has begun to be placed on the usage of micro cellulose based natural fiber sources as well. It is in this pursuit that DDGS fibers have been explored as potential reinforcing fibers within polypropylene (PP).

The polypropylene used in this study was an isotactic PP trade named Formolene® 5100H supplied by the Formosa Plastics Corporation, USA, and the DDGS were supplied by Red Trail Energy, LLC, USA. The DDGS material was mechanically fractionated in a solution of the DDGS and 20 wt% acetone in a Fritsch Pulverisette 6 ball mill. The ball mill was run with 10mm stainless steel balls at 450 rpm for a total of 3 hours. This reduced the fiber size from multiple millimeters to approximately 20 µm colloidal particles.

In this work, PP/DDGS composite materials were explored using 10 wt% DDGS fibers within a PP matrix. Samples were prepared in order to determine the optimal processing methodology based on material performance. Mechanical investigation included both tensile and flexural tests performed according to ASTM standards D638 and D790, respectively. Water absorption tests were performed using a test modeled after ASTM D570. In this test, specimens were soaked in boiling water for 1 hour and tested for water absorption, after which they were tested in flexure to observe the resulting mechanical performance. Dynamic mechanical thermal analysis (DMTA) was also performed to observe changes in the glass transition temperature of the samples and subsequent crystallinity.

The hydrophobic nature of PP poses a potential problem in achieving good fiber/matrix adhesion in these systems however, as cellulose is an inherently hydrophilic polymer because of the numerous hydroxyl groups contained within it. To alleviate this obstacle, chemical compatibilizers have been developed which alter the surface of the hydrophilic cellulose fiber in order to improve interfacial adhesion between the fiber and matrix.

One such compatibilizer is maleic anhydride grafted polypropylene (MAPP), a waxy polymer system that has been proven useful in the processing and production of cellulose reinforced PP composites [3,4]. The MA group of the MAPP is able to react with the hydroxyl groups in cellulose, forming a bond between the MA group's carbon and the oxygen from the cellulose. At the same time, the PP portion of MAPP is able to co-crystallize with the unmodified PP, which allows for the MAPP to act as a bridge between the fiber and matrix [5,6]. MAPP is also able to compensate for insufficient breakup forces during processing, such as low shear stress, by reducing the interfacial tension between PP and the cellulose, which leads to finer dispersion of the fiber throughout the system [7]. MAPP was explored as a compatibilizer in both 5 wt% and 2.5 wt% concentrations with respect to the final composite, using Licomont® AR 504 supplied by Clariant, USA.

Another compatibilizer that was explored is organo-silane ($R\text{-}Si\text{-}(OR')_3$) [4]. Organo-silanes contain alkoxysilane groups which, when hydrolysized, are capable of reacting with surfaces having an abundance of OH molecules. As such, the coupling agent has the ability to close off the polar molecules in the cellulose fibers. This creates a hydrophobic coated fiber with a defined functional R group [8,9,10]. Although the functional group itself can not react with the PP matrix unless grafted during polymerization, the organo-silane does branch out and allows for mechanical interaction with the polymer chains of the matrix. Thus, mechanical interlocking can occur, and an improved fiber/matrix interface is created. In this work, two organo-silanes were used, an Aminopropyltriethoxysilane coupling agent supplied by Dow Corning®, trade name Z-6011 Silane, and an Aminoethylaminopropyltrimethoxysilane coupling agent supplied by Dow Corning®, trade name Z-6020 Silane. The Z-6020 Silane has the same defined functional H_2N group as Z-6011, however it is attached to a larger branched system, which brings with it the potential for better mechanical entanglement and interaction with PP chains.

For both the compatibilized and non-compatibilized fiber/PP blends, composite samples were produced by means of melt blending with a lab scale co-rotating twin screw extruder (Leistritz Micro-18/GL-40D). The screw rotation rate was set at 350 rpm and the temperature profile from hopper to die was as follows: 177°C, 182°C, 185°C, 189°C, 195°C, 195°C, and 195°C. This yielded a dwell time of approximately 30-40 seconds for the fiber/polymer system, minimizing prolonged exposure to degradation temperatures. Upon extrusion from the die, the extruded composite sample was quenched and pelletized. Sample pellets were then molded to shape for tensile and flexural specimens using injection molding. In this method, the composite pellets were injection molded into dog-bone tensile and flexural specimens using a Technoplas, Inc. SIM 5080 injection molder. The temperature profile from hopper to nozzle tip was as follows: 193°C, 204°C, 210°C, 216°C, and 204°C.

Mechanical testing demonstrated the importance of proper compatibilizer usage in obtaining optimal performance out of the DDGS fibers. As shown in Table 1, compatibilizer usage has significant trends on both tensile and flexural strength. First examining tensile strength, it is noted that the addition of 10wt% untreated DDGS caused a decrease in the tensile strength, and that this was not alleviated by treatment with either organo-silane treatment. However, both 2.5 and 5 wt% MAPP additions were shown to be beneficial in raising the tensile performance back to the base PP. Flexural strength performance shows a similar trend, with the MAPP compatibilization yielding improved strength results in comparison to neat fiber or silane treated.

From a polarity standpoint, all three compatibilizers should have performed similarly, since the MA group in the MAPP and the hydrolysised alkoxysilane in the organo-silanes are both acting as a bridge to de-polarize the hydroxyl groups in the cellulose components of the fibers. However, since chain entanglement of the PP and MAPP is virtually impossible [11], better fiber distribution is achievable in these composites than in the organo-silane treated ones. This in turn increases the likelihood of the fibers to carry load and improve the strength of the composites.

It was suspected that the lack of chain entanglement between PP and MAPP would cause fairly significant variation between the 2.5 wt% and 5 wt% MAPP concentrations. This is because if one concentration was in excess, the MAPP would be detrimental to adhesion because of the inability for entanglement between the modifier and neat PP. However, a concentration starved of enough groups to fully bridge the fibers would also perform poorly as part of the system would act as untreated fibers. Ultimately both loadings examined appeared to be within a window of optimal usage, in which there is not an extraneous excess of MAPP, but there is enough to create sufficient bridging between the DDGS and neat PP chains.

Table 1: Mechanical Properties of DDGS Reinforced Polypropylene Samples

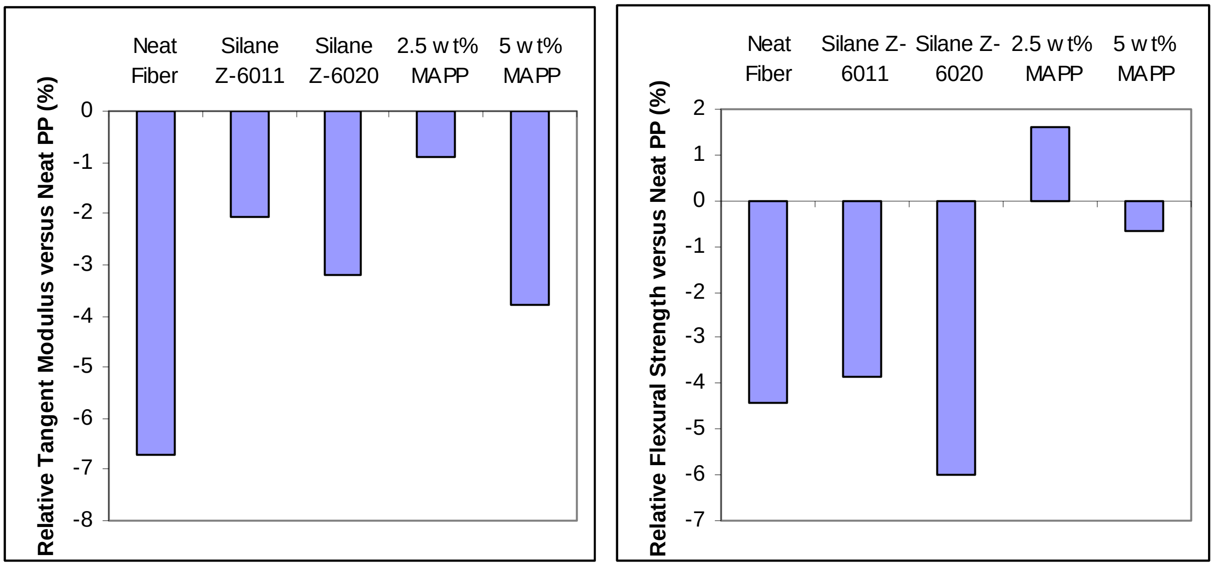
Sample Type	Fiber Treatment	Elastic Modulus (GPa)	Tensile Strength (MPa)	Tangent Modulus (GPa)	Flexural Strength (MPa)
Neat PP	---	1.57 ± 0.09	27.6 ± 0.1	1.13 ± 0.04	37.3 ± 1.1
DDGS	Neat Fiber	1.66 ± 0.10	25.3 ± 0.2	1.30 ± 0.03	39.7 ± 0.3
	Silane Z-6011	1.55 ± 0.03	24.8 ± 0.1	1.30 ± 0.02	39.1 ± 0.4
	Silane Z-6020	1.59 ± 0.07	24.9 ± 0.1	1.29 ± 0.04	38.6 ± 0.7
	2.5 wt% MAPP	1.60 ± 0.03	27.9 ± 0.2	1.33 ± 0.03	41.6 ± 0.8
	5 wt% MAPP	1.59 ± 0.06	27.9 ± 0.2	1.34 ± 0.03	42.4 ± 0.6

Water absorption testing was performed in order to examine potential weatherability issues with the polymer systems while using the natural fiber reinforcement. As seen in Table 2, after one hour of immersion in boiling distilled water, the DDGS reinforced systems did not undergo significant changes in water weight absorption compared to neat PP. Previous research into water absorption of natural fiber reinforced polypropylene composites has demonstrated that significant absorption occurs over extended immersion [3]. However, this work has shown that under low immersion, mass gain from water absorption is not a significant factor.

Table 2: Water Absorption Results After 1 Hour Immersed in Boiling Water

Sample Type	Fiber Treatment	Weight Gain (%)
Neat PP	---	1.78 ± 0.34
DDGS	Neat Fiber	1.09 ± 0.42
	Silane Z-6011	1.50 ± 0.67
	Silane Z-6020	1.07 ± 0.72
	2.5 wt% MAPP	2.05 ± 1.05
	5 wt% MAPP	1.17 ± 0.63

Although there was a minimal observed change in water absorption by mass, the examination of the resultant flexural properties of the immersed composite samples demonstrates that water absorption did play a role on mechanical performance. Examining the flexural modulus, it can be seen in Figure 1a that water absorption caused a decrease in the tangential modulus of the yielded composites. However, it is worth noting that the samples which had been compatibilized saw a lessened degree of tangent modulus loss, indicating that the closing of the hydroxyl groups of the DDGS did play a role in preventing excessive water absorption. Flexural strength data, shown in Figure 1b, has a slightly different trend, in which MAPP usage showed to significantly prevent strength loss due to water absorption, while the organo-silanes and neat fiber did not. This would indicate that the MAPP creates more bonding with the open hydroxyl groups in the DDGS cellulose than the organo-silanes, a trend which is mirrored in the basic mechanical testing data.



(a) (b)

Figure 1: Relative Flexural Properties of DDGS Reinforced PP after Boiling Water Immersion

DMA work was performed using a TA Q800 DMA, operated at a frequency of 1 Hz, an amplitude of 20 μm, and a temperature ramp of 3°C/min. From this, analysis of the α-transition of the tan δ curve can be made, corresponding to the glass transition temperature (T_g) of the material as well as the crystallinity change in the specimens. As shown in Table 3, the addition of DDGS was found to decrease the glass transition temperature of the neat PP slightly. This indicates that DDGS fibers are being introduced between the polymer chains, increasing the spacing and free volume of the PP. However, such an interaction should also change the magnitude of the tan δ peak at T_g, which does not occur as shown in Table 3. As such, it is difficult to ascertain the level of polymer relaxation that was initiated due to the fibers. Previous work with natural fiber reinforced polypropylene has concluded that lignocellulosic natural fibers are too large to obstruct the mobilization of the PP macromolecular chains, and thus there is nothing to prevent the macromolecular segment from obtaining ordered alignment of the crystal lattice [12]. This would in turn prevent a crystallinity change, which falls in agreement with the tan δ peak value not changing.

Table 3: DMA Results

Sample Type	Fiber Treatment	T_g (°C)	tan δ
Neat PP	---	15.34	0.0575
DDGS	Neat Fiber	8.51	0.0592
	Silane Z-6011	10.10	0.0575
	Silane Z-6020	11.11	0.0570
	2.5 wt% MAPP	8.15	0.0575
	5 wt% MAPP	7.80	0.0600

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