EFFECT OF ADDITIVES ON THE STRUCTURE AND PROPERTIES OF WHEAT STRAW-POLYPROPYLENE COMPOSITES

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Abstract

Natural fibers from agricultural activities have been emerged as alternative fillers in the thermoplastic industry. Crops such as wheat straw are renewable and low cost materials that, combined with thermoplastics such as polypropylene, provide engineering products with unique characteristics. Due to the wide range of thermoplastics and potential agricultural fillers, the influence of additives in the systems is one of the points yet to be determined for different combinations of matrix and filler. In this study composites containing 30 wt-% of wheat straw (WS) fibers and polypropylene (PP) were prepared in a batch mixer. The individual effects of two coupling agents and a lubricant in the composites were investigated. Scanning electron microscopy (SEM) was used to examine the morphology of wheat straw particles and composites. The water absorption behavior and mechanical properties were assessed for those composites prepared. Results showed a strong interaction between filler and matrix in compositions containing coupling agent; differences were observed in the performance of the two coupling agents tested. Furthermore, the lubricant used contributed to the water absorption of the composites.

Literature Review

Natural fibers (NF) present some advantages over inorganic fillers, such as low specific gravity, high specific properties, they are easily recycled and have low cost compared to the resins [Johnson, 1999]. Nevertheless, NF composites present some drawbacks such as moisture uptake and weak surface adhesion to hydrophobic matrices (non-polar polymers). Plenty of publications describe the chemical modification by coupling method as a very efficient treatment to improve adhesion forces between matrix and filler. The mechanism involves a chemical reaction between the fibers surface and the coupling agent, promoting covalent bonds between filler and matrix. Maleic anhydride (MA) has been used for this purpose by several research groups [Avella, 1995; Gassan and Bledzki, 2000; Caufield, 1999; Sanadi, 2001; Rowell, 1999; Pickering and Lee, 2006; Mi, 1997].

In addition to the surface adhesion improvements, coupling agents are suggested to be also capable of influencing filler distribution in the matrix [Chen, 1998] and mechanical properties [Marcovich, 1998]. The good adhesion between matrix and filler is likely to modify the mechanical properties of the composite as well as the water absorption behavior. However, the effect of coupling agents can be beneficial, prejudicial or none, depending on the final property evaluated [Rijsdijk, 1993]. Moreover, the molecular weight [Denault, 2006] and the amount of coupling agent used can also have influence in the mechanical properties of the composites; for example, the optimum dose for 2 different coupling agents tested by Arbelaiz et al. [Arbelaiz, 2005] was 5 or 10%, depending on the structure of the compound. In the reaction between maleic anhydride and fibers, polar carboxylic groups of the maleic acid firmly bond to OH groups present in the fibers' surface, thus reducing the hygroscopicity of the composites [Marcovich, 1998].

Agricultural crop materials are usually hydrophilic, opposite to the majority of thermoplastic materials, which are hydrophobic; therefore, natural fibers are likely to absorb water. When high water contents are absorbed by NF composites the dimensional stability of the final product is usually compromised, narrowing the field of application of those composites.

The effect of coupling agents on NF composites has been reported in the literature with special attention to obtain information about the long-term water absorption and the influence of water absorption in thermoplastic composites [Tajvidi, 2006]. However, there is a general lack of information available about the conversion of agricultural by-products (wheat straw for example) into novel materials. In order to develop economically competitive bio-composites it is necessary to understand the structural properties of filler, matrix and composite of different combinations of materials.

Wheat Straw Polypropylene Composites

Agricultural crops such as wheat straw are renewable and low cost materials that, combined with thermoplastics such as polypropylene, provide engineering products with unique characteristics. For a nominal fiber loading of 25% by weight the measured density of wheat straw-polypropylene composites was about 998.8 $kg.m^{-3}$ [Hornsby,1997]. The market advantage is usually based on elements such as availability, price of the crop and performance of the final product.

The opposite surface properties of wheat straw and polypropylene result in difficulties to achieving good dispersion of the filler (WS). Furthermore, an increase in the composite moisture content may cause swelling and diminish the adhesion forces between filler and matrix, decreasing final mechanical properties of the composite [Johnson, 1999; Caulfield, 1999] and compromising the original shape of the product. Lubricants can be introduced in the system to diminish the attrition forces acting on the fibers. Lubricants usually decrease the friction coefficient of the system, either acting internally (on matrix-matrix friction) or externally (on matrix-processing recipient friction).

The objective of this study was to investigate the influence of additives on the final properties of wheat straw-polypropylene composites. For this purpose wheat straw and polypropylene were compounded and the individual effects of two coupling agents and a lubricant on some of the final properties of the composites were inspected.

Materials

Wheat straw (WS) was obtained from the region of Ontario, Canada. The base resin used was isotactic polypropylene (PP) (supplied by A. Schulman Inc.), with density 0.9g/cc and melt flow rate 1.5 g/10min, according to the supplier. Antioxidant Irganox 1010 (Ciba Inc.) was added to all formulations prepared on a 0.5 wt-% based on polymer weight. The base resin and antioxidant were used as supplied. Two coupling agents were tested in this study from (supplied by DuPont): maleic anhydride modified polypropylene (MAPP) and maleic acid ethylene copolymer (MAET). A commercial amine based lubricant Glycolube WP 2200 (supplied by Lonza Inc.) was also tested in these experiments.

Compounding and Analysis Methods

Prior to compounding the wheat straw was passed through a stainless steel rotary cutter (Thomas-Wiley Laboratory Mill Model 4). The ground material was dried in an air circulating oven at 110°C during 10 hours. The WS fibers were compounded with polypropylene in a batch mixer (Haake Fisons Rheocord 90) at speed of 40 rpm. Every 200g batch contained 30 wt-% of WS fibers and was conducted in the same way: first PP was fed into the mixer and melted, after that the antioxidant was added, followed by the WS fibers. All composites were prepared at 190°C.

Morphology of the WS fibers and composites were observed through a scanning electron microscope (SEM) in fracture surfaces obtained by immersing the samples in liquid nitrogen. The fracture surfaces were gold coated previous to observation. Water absorption test was carried out based on ASTM D570-98 specification. The composites were molded in bars 76.2 mm long, 25.4 mm wide and 3.2 mm thick (approximately) and dried in an air circulating oven during 1 hour at 108± 2°C °C. Flexural tests based on ASTM D790-03 (procedure A) were performed on the pure polypropylene and composite materials in a miniature materials tester – MiniMat 2000. Specimens were conditioned at 23 ± 2°C and 50 ± 5% of relative humidity for at least 48 hours before testing, as suggested in the standard specification.

Results and Discussion

Morphology of WS fibers and wheat straw-PP composites were analyzed by scanning electron microscopy (SEM). Electron micrographs revealed changes in the wheat straw surface structure due to processing and the surface interaction between filler and matrix. Figure 1 shows the damage in the fiber's surface, probably caused by shear forces during processing the mixture of 30 wt-% WS fibers in PP at 190°C. In this image, some parts of the structural walls of the wheat straw were peeled off, revealing the modifications that the filler undergoes during the melt-mixing process.

The surface interaction between filler and matrix in the composite containing coupling agent MAPP can be observed in Figure 2. The micrograph of a freeze fracture surface shows that there is good interaction between the two phases. Furthermore, it can be pointed that forces between the WS and matrix were stronger than the ones along the wheat straw structure, so that when the fracture surface was originated the fiber was broken instead of the being pulled out of the polymeric phase. Strong forces between surfaces can promote the strength of the material, which becomes more suitable for engineering applications. There was no clear evidence of fiber-matrix bonding in the composite sample prepared without additives.

Figure 1: Fracture surface of WS-PP composite: wheat straw particle damage after compounding at 190ºC. Mag. (x500)

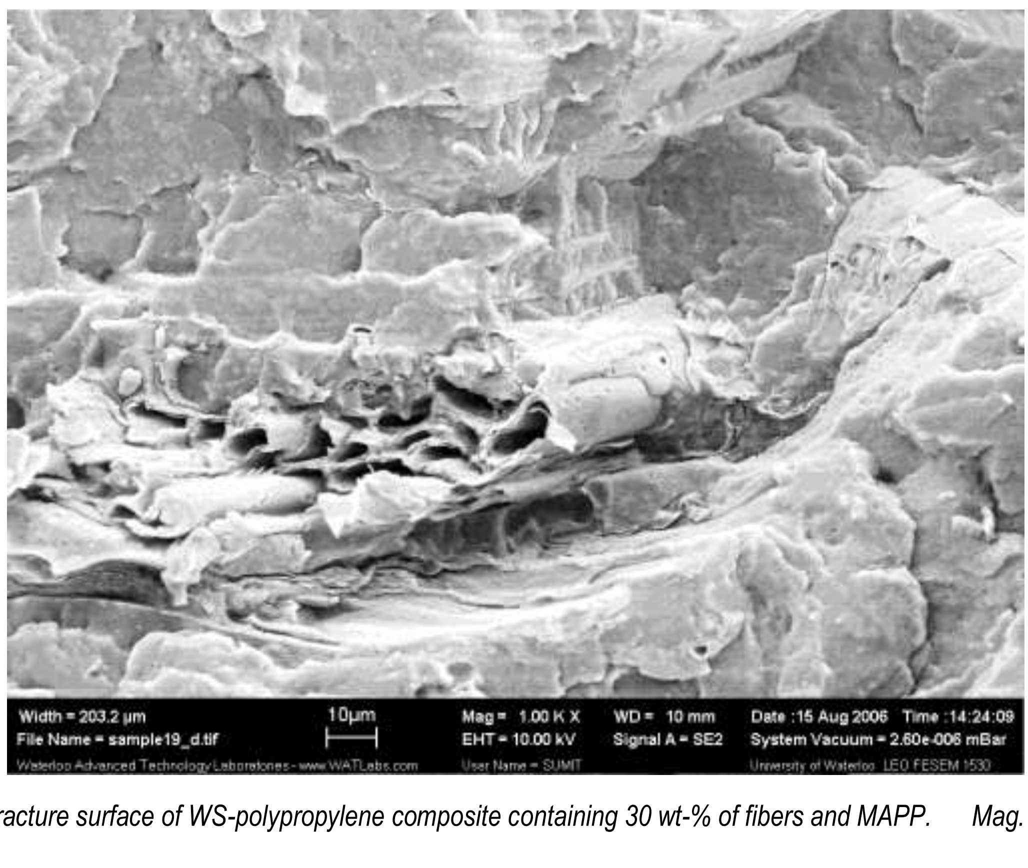

Figure 2: Fracture surface of WS-polypropylene composite containing 30 wt-% of fibers and MAPP. Mag. (x1000)

Strong interaction between WS fibers and polypropylene was also observed in torque curves recorded during the compounding process. Torque values were slightly higher for those samples containing coupling agent (MAPP or MAET) when compared to the sample without any additive. Furthermore, the composite containing lubricant presented the lowest torque, thus confirming the positive effect of decreasing the friction coefficient between filler and matrix during processing.

Flexural modulus of polypropylene and wheat straw-polypropylene composites was measured in the three point loading mode. The effect of additives in the flexural modulus of PP and 30 wt-% WS-PP composites is shown in Table I. Wheat straw composites present higher flexural modulus than pure PP. Introduction of coupling agent based on PP increased the flexural modulus of the composite system while the introduction of coupling agent based on ethylene or addition of lubricant did not change significantly flexural modulus values in relation to the formulation without additives. In agreement, Arbelaiz et al. [Arbelaiz, 2005] reported that the modulus of flax fiber-polypropylene composites slightly increased with addition of maleic anhydride (MA) based coupling agent. Tensile properties such as tensile strength were also observed to increase with addition of MAPP to hemp reinforced polypropylene composites [Beckermann, 2006]. Unlike those results, Hornsby et al. [Hornsby, 1997] reported no significant alteration on flexural modulus values with addition of MAPP in 25 wt-% flax straw filled composites. Flax straw-polypropylene composites studied by that same group presented equivalent flexural modulus results between samples grafted and ungrafted with MA as well. On the same track, uncoupled PP/kenaf systems presented higher flexural moduli than coupled systems [Sanadi, 1999].

The increase in flexural modulus of the MAPP coupled system observed in the present work can be attributed to the better interaction between filler and matrix promoted by the additive. When higher bonding forces act between matrix and filler the transfer of the load applied to the composite material is well transferred between the phases, thus allowing the material to perform elastic deformation.

Table I: Flexural modulus of polypropylene and wheat straw-polypropylene (30 wt-%) composites containing different additives.

Sample #	Additive	Flexural Modulus (MPa)
PP	none	531
1	none	691
2	Lubricant	674
3	MAET	710
4	MAPP	961

Figure 3 shows the increase in weight of PP and WS-PP composites with 30 wt-% of WS fibers containing different additives. It can be clearly seen that the sample containing lubricant exhibits the highest increase in weight (around 34.3%), while the smallest amount of water absorbed was observed for the sample containing coupling MAPP. Low water uptake of systems with coupling agents was also noticed in previous works [Hornsby, 1997; Mishra and Verma, 2006], which reported lower water pick up for system with MA based coupling agents.

The system containing MAET exhibited larger weight increase than the composite without additives. It can be inferred that the efficiency of the ethylene based coupling agent (MAET) is lower than the efficiency of the PP based one (MAPP). Indeed, the presence of a second polymer in the composite introduces a new factor to the system: the interaction between the two types of polyolefin. It is possible that the interaction between molecules of polypropylene and molecules of polyethylene, due to structural reasons, were not able to entangle or mix, thus creating irregularities in the matrix and therefore interfering on the wettability of the matrix.

It is well known that natural fibers are the main responsible for the composite moisture absorption; however, according to Chow et al. the weight gain characteristics also depend on the matrix polymers [Chow, 2007]. To avoid water absorption natural fibers must be well wetted by the matrix so that the polymer will encapsulate the fibers, keeping them away from moisture present in the environment. The ability to encapsulate the fibers can vary from polymer to polymer.

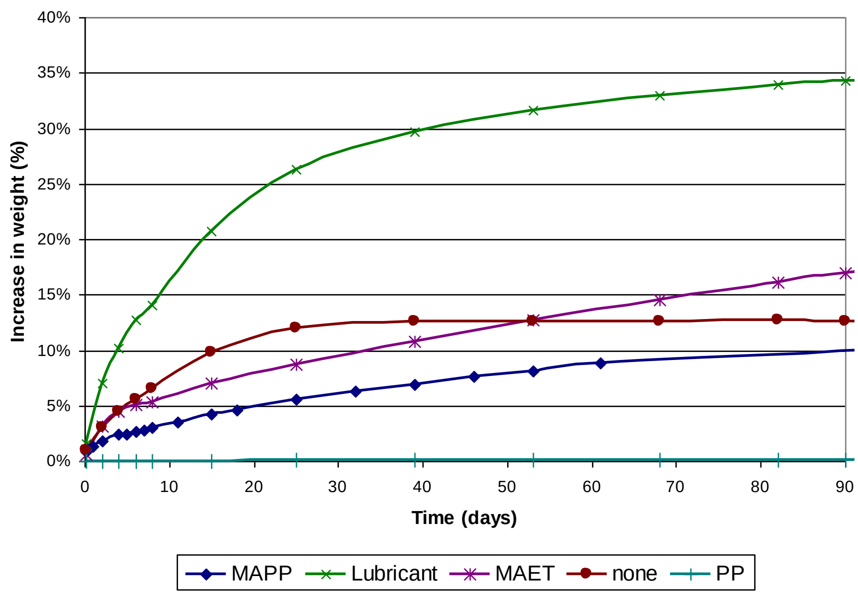

Figure 3: Weight of water absorbed with time by pure polypropylene and wheat straw-PP composites containing MAPP or MAET or lubricant or no additives.

After 90 days immersed in water all composites presented more visible fibers at the surface than previous to the test, probably due to swelling of the fibers. Swelling of the composite caused by moisture absorption can lead to dimensional stability problems in lignocellulosic fiber composites [Rowell, 1999]. Dimensional changes were markedly observed in composite samples containing lubricant or containing MAET. In those three samples, the average thickness after immersion in water was around 3.80mm, representing 15% of increase in this dimension. Changes in the other dimensions were negligible. The composite specimen containing MAET presented also some sort of waves (elevations) on the surface after immersion in water. Although noticeable, the elevations on the surface were relatively small. According to Espert et al. [Espert, 2004], dimensional stability problems can be caused by processes such as chain reorientation and shrinkage after water absorption

From the curves of water absorption as a function of time the water diffusion coefficients were calculated for each specimen. The Boltzmann's form of Fick's general diffusion equation used in this work is given in Equation (1). In this equation D is the water diffusivity (mm^2s^{-1}), M_∞ is mass uptake value at equilibrium time, M_1 and M_2 (gr) are two mass uptake values corresponding with t_1 and t_2 (h) is the sample thickness, w is the sample width and l is the sample length (mm). Water diffusion coefficients were calculated for each composite formulation; the results are presented in Table II, as well as the value considered as water uptake at equilibrium time for the calculations.

$$D = \pi \cdot \left(\frac{h}{4M_\infty} \right)^2 \cdot \left(\frac{M_2 - M_1}{\sqrt{t_2 - \sqrt{t_1}}} \right)^2 \cdot \left(1 + \frac{h}{w} + \frac{h}{l} \right)^{-2} \quad (1)$$

Table II: Water diffusion coefficients calculated for pure PP and WS-polypropylene composites containing Lubricant or MAET or MAPP or no additives.

Sample #	Additive	D (mm^2s^{-1})	M_∞ (%)
PP	none	8.9029E-09	0.15
1	none	4.0531E-07	12.61
2	Lubricant	2.7666E-07	34.34
3	MAET	2.2534E-07	16.91
4	MAPP	1.4613E-07	10.50

Diffusion coefficients have been reported in the literature for polypropylene containing different natural fibers such as kenaf or rice hulls; results demonstrated dependence of water diffusion on the type of fiber and formulation of the composite [Tajvidi, 2006]. The diffusion coefficient calculated for wheat straw-PP composites (Table II) is about 2 orders of magnitude higher than pure polypropylene, which differs in one order from results reported for natural fiber composites and PP in a previous work [Tajvidi, 2006]. All composite samples in Table II presented diffusivity values in the same order of magnitude. Comparison among them reveals that addition of coupling agent decreased the diffusivity; those results agree with the fact that samples containing MAPP or MAET absorbed lower amount of water than samples without additives during the same period of time. Similarly, slightly reduced equilibrium water uptake and remarkable reduction in water uptake rate were denoted for MAPP-modified samples of short flax fiber-PP composites [Arbelaiz, 2005].

The specimen containing lubricant presented the highest increase in weight but did not present the highest diffusion coefficient. As expected, the neat PP was the one presenting the minimum value of diffusivity among the all samples. Among the composites, the lowest value of diffusivity was observed for the composition containing MAPP (1.4613E-07 mm^2s^{-1}). The inconsistency between diffusivity values and final weight increase in the composites can lead to the conclusion that water diffusion into WS-PP composites does not completely follow the Fickian relationship with time, i.e., there is a small deviation from Fick's law. In the present experiment, after 90 days not all samples had reached a saturated moisture level.

Summary and Next Steps

Wheat straw-polypropylene composites containing 30 wt-% of fibers were prepared at 190ºC; three additives were tested: two coupling agents, MAPP and MAET, and one lubricant. Some of the final properties of the composites were evaluated.

Freeze fracture surface images evidenced the good interaction between natural fibers and polypropylene in composites containing MAET or MAPP. Torque measurements confirmed the poor interaction between filler and matrix when lubricant is added to the system; the lack of adhesion between the components was the mainly responsible for the large amounts of water uptake.

The diffusion coefficient of wheat straw-PP composites is about 2 orders of magnitude higher than pure polypropylene. There is deviation from Fick's law on water diffusion into wheat straw-polypropylene, voids and other structure issues are likely to be the main responsible for that.

Water uptake can be a severe problem on natural fiber composites leading to dimension instability and significant weight gains. Those issues can be minimized with the introduction of coupling agents in the composites. Coupling agents promote better interaction between filler and matrix in natural fiber composites studied here. Among the composites, the lowest value of diffusivity was observed for the composition containing MAPP (1.4613E-07 mm^2s^{-1}). The most pronounced enhancement of mechanical properties was also detected in the sample grafted with MAPP.

The success of natural fiber composites in the thermoplastic composite industry is dependent on the understanding of the system components on the final properties. There is definitively room for improvement on the study of the effects of filler loading processing conditions of WS-PP composites. Future work including mechanical tests such as tensile and impact could give extra information on the mechanical behavior of wheat straw-polypropylene composites. Continuation of this project would consider other processing techniques such as extrusion or injection molding. Those techniques would take the production of wheat straw-polypropylene composites to a next level, closer to the industry and therefore to the commercialization of the composites.

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