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Vegetable fibers as multifunctional materials

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ABSTRACT

Concerns related to the ever-growing use of raw-materials from non-renewable sources by modern society is driving the interest of the academic and scientific sectors for a new concept of material, which takes into account not only mechanical performance, cost and availability, but also environmentally-related issues, such as biodegradability, renewability and energy use, along with the promotion of social and economical development of the economically-challenged segment of the population. Vegetable fibers have been used in many home-made objects, such as ropes and artcraft, for perhaps as long as humanity exists. However, these fibers present a combination of interesting properties which enables their use in a wide variety of sectors. This invited article will review the work recently carried out by the author in collaboration with various researchers from UFRGS, UFPR and UCS, and will be divided into three case studies, focusing on the use of vegetable fibers for oil sorption, as infiltration (flow) medium and as reinforcement for polymer composites, promoting their use in more demanding and rewarding applications.

Keywords: Vegetable fibers, oil sorption, flow enhancement, hybrid composites.

1 INTRODUCTION

Concerns related to the ever-growing use of raw-materials from non-renewable sources by modern society is driving the interest of the academic and scientific sectors for a new concept of material, which takes into account not only mechanical performance, cost and availability, but also environmentally-related issues, such as biodegradability, renewability and energy use, along with the promotion of social and economical development of the economically-challenged segment of the population.

Vegetable fibers have been used in many home-made objects, such as ropes, textiles and artcraft, for perhaps as long as humanity exists. However, these fibers present a combination of interesting properties [1] which enables their use in a wide variety of sectors, among them:

- Twines, ropes, cords [2];
- Textiles, non-woven, cellulose for papers, biomass for energy [3];
- Brooms, fancy articles (lady's bags, purses, table mats), carpets, scouring pads, palm sole, inner soles for shoes, bolters, leather straps, hats, car seats, gardening, mattress/sofa bed, for hammock and fishing lines, floor-furnishing, fertilizers, foot rugs, raw material for the production of plastics [4-5];
- Cones of speakers [6];
- Filler for cementitious composites;
- Filler or reinforcement for polymer composites [7];
- Wood-plastic composites [8];
- Biocomposites [2].

This invited article will revisit the work recently carried out by the author in collaboration with various researchers from UFRGS, UFPR and UCS, and will be divided into three case studies, detailed below.

2 CASE STUDY 1 – SORPTION OF CRUDE OIL [9-11]

Oil spills are a global concern due to their environmental and economical impact, affecting sea life, economy, tourism and leisure activities. Oil spills ruin the beauty of sea and land, the strong odor can be felt miles away and the excessive growth of green algae alters sea color and the landscape.

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Various commercial systems have been developed to control these spills, including the use of fibers as sorbents. Despite the fact that synthetic polymers are sometimes regarded as ideal materials for marine oil-spill recovery due to their low density, low water uptake and excellent physical and chemical resistance, these sorbents are not renewable and biodegradable, becoming themselves a source of environmental impact when discarded after use. On the other hand, vegetable fibers are environmentally friendly materials, with densities close to that of synthetic polymers or even lower, and may show high oil sorption capacity usually at a low cost.

In this work, some vegetable fibers were investigated as sorbent materials for oil. In the sorption experiments carried out, crude oil was poured into a beaker containing deionized water. After that, the fibrous material was gently and evenly placed onto the oil surface (Figure 1a). The material was later removed and placed on a filter paper, being allowed drainage under vacuum for 5 min before weighing. Sorption was calculated as: $(S_t - S_o)/S_o$, where S_o is the dry sorbent mass and S_t is the total mass of the samples.

Other sorption conditions were experimentally simulated: (i) dynamic system (Figure 1b): Tests carried out under constant agitation (approximately 500 rpm); (ii) dry system (Figure 1c): With only oil in the beaker; and (iii) marine conditions: Use of a substitute ocean (salty) water (ASTM D1141) instead of deionized water. Distillation of the sorbent after sorption (ASTM D95) was conducted to evaluate simultaneous water uptake by the fibers. Buoyancy and hidrophilicity were also evaluated.

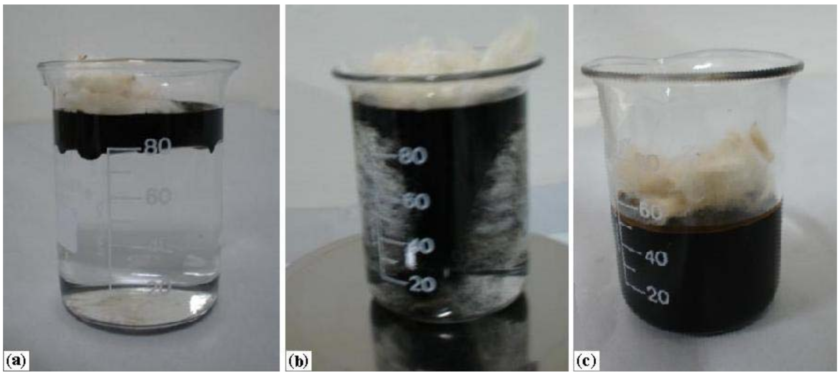

Figure 1: Different sorption experiments just after fiber placement on the oil surface: (a) Static system, (b) Dynamic system, and (c) Dry system [9].

The results of the various sorption tests showed the following general trends: (i) Higher sorption for all fibers as the sorption time increased; (ii) Sorption capacity of the fibers followed: Silk-floss > Sisal > Sawdust > Coir fiber > Sponge gourd > Leaves residues (Figure 2), and (iii) A much larger sorption for the silk-floss.

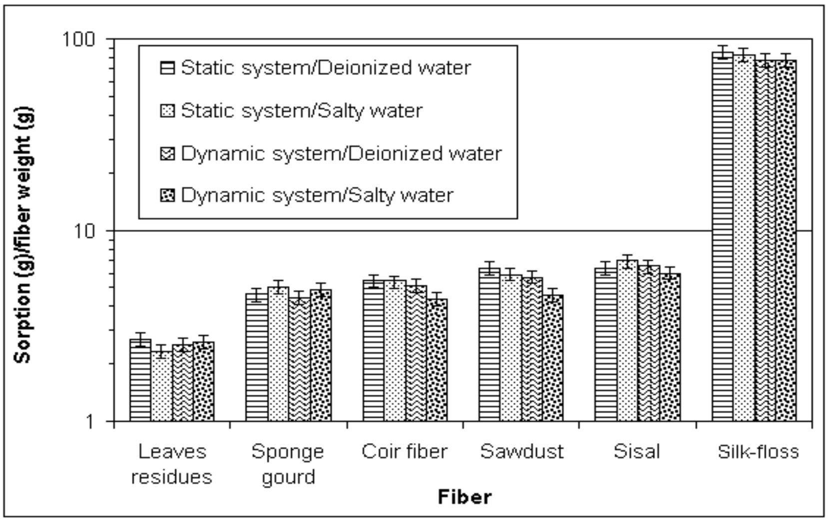

Figure 2: Sorption of the different fibers for a 60-minute sorption period under various conditions [9].

Not all weight gain shown in Figure 2 refers to oil sorption, since water is also sorbed by the fibers to an extent dependent on the particular fiber. Water uptake (Tab. 1) was higher for sponge gourd and coir fibers, whereas sisal, leaves residues and sawdust showed intermediate values, and silk floss sorbed little water.

Buoyancy of the fibers in the dynamic system was higher than in the static system (Table 1) and all fibers showed higher buoyancy under marine conditions. The silk-floss reached around 98% hydrophobicity (Table 1) and 100% buoyancy in the simulated experimental conditions. Several of the investigated low-cost vegetable fibers may be used in a dry environment, with variable sorption capacity. But, sisal, sponge gourd, sawdust and even coir were considered not adequate to water oil-spill conditions.

Table 1: Water uptake, degree of hydrophobicity and buoyancy under different conditions for the various fibers.

Fiber	Water uptake (%)	Hydrophobicity - Deionized water (%)	Buoyancy - Static system - Deionized water (%)
Leaves residues	23-33	86.9	65.5
Sponge gourd	50-51	0.0	3.4
Coir fiber	42-45	38.6	20.6
Sawdust	21-27	56.5	12.4
Sisal	27-31	0.0	0.0
Silk-floss	3 - 5	97.6	100.0

Irrespective of the sorption conditions, the 24-hour oil sorption of the silk-floss reached approximately 85 g of oil/g sorbent. This sorption capacity is much higher than those reported in the literature for other vegetable fibers. In order to ratify these results, two commercial vegetable sorbents of peat sorb were analyzed following the same methodology (using dry system, 20 °C, 60 min) yielding between 4.8 and 9.8 g oil/g sorbent only. Indeed, the value found for silk-floss is even comparable to those of synthetic materials. Witka-Jezewska [12] reported sorption values of 30 g oil/g viscose rayon and 40 g oil/g polypropylene, being the highest a polyurethane foam, that reached 100 g oil/g sorbent.

In all, the potential of silk-floss to be used as sorbent was evidenced by its rapid oil sorption and very high sorption capacity of approximately 85 g oil/g sorbent (in 24 h), high degree of hydrophobicity and buoyancy and low water uptake. The sorption capacity was around 8.5 - 12 times that of two commercial products composed of peat sorb. The silk floss tree is abundant in various states of Brazil and the estimated cost of R$ 60.00/kg is approximately half that of the commercial product used for this aim. Mats and barriers produced with silk floss also showed a performance similar to those commercial products under controlled conditions and this has led the authors to deposit a patent [13].

3 CASE STUDY 2 - INFILTRATION (FLOW) MEDIUM FOR RESIN TRANSFER MOLDING [14]

Resin transfer molding (RTM) is a process that is being increasingly used to manufacture fiber reinforced polymeric composites, including high-performance parts, such as automotive and aerospace structural components. RTM has many advantages over other manufacturing processes, including lower labor cost, shorter cycle time, fabrication of large and complex structures with lower environmental impact, and production of parts with finished surfaces on both sides.

The RTM process involves the injection of a liquid resin into a closed mould cavity containing the fiber reinforcement and subsequent resin curing, producing a rigid composite part. Flow during RTM is usually modeled with Darcy's law, that dictates that the velocity of a fluid through a porous medium is proportional to the pressure gradient and inversely proportional to the fluid viscosity. The coefficient of proportionality, i.e. permeability (K), is the key property that determines how easy it is for a fluid to flow through the open pores.

Parts with large in-plane dimensions and/or with high fiber content can be more rapidly infused when a high-permeability distribution medium, also called flow-enhancement fabric or flow media, is integrated into the reinforcement. Commercially available flow media exhibit good permeability mainly due to the low fiber content of this layer and the particular fibrous architecture, being typically produced with low mechanical performance synthetic fibers, e.g. polypropylene. In this work, the use of natural fiber mats as flow media to decrease filling time was evaluated. Besides, the mechanical properties of the produced composites were compared with those of hybrid composites with commercial flow media.

The following materials were used: Commercial soybean oil; ortophthalic polyester resin UC 2080 (Elekeiroz) and P-MEK; E-glass fiber mat - 300 g/m^2 (Owens Corning); polypropylene non-woven commercial flow medium - 200-250 g/m^2. Sisal fibers were chopped (40 mm) from commercial sisal ropes, washed with distilled water for 1 h and dried in an air-circulating oven at 105˚C for 30 min under low pressure to produce sisal mats. The total fiber volume fraction (%V_f = 20.2%) used was selected based on commercial reinforcements available for usual RTM light applications.

- The porous systems studied were:
- 6-7 glass mats (called GLASS);
- PP core (called PP CORE);
- Sisal mats (called SISAL);
- (4 glass mats/PP core) hybrid reinforcement (13.7 and 6.5%, respectively), called GGPGG, where "G" represents a glass layer and "P" a PP layer;

(4 glass mats/sisal mat) hybrid reinforcement (13.7 and 6.5%, respectively), called GGSGG, where "S" represents a sisal layer.

Soybean oil was injected at constant pre-set pressure (10 kPa) into the different dry porous systems in rectilinear (unidirectional) RTM flow experiments carried out at 19-21°C. Photographs of the position (X_{ff}) of the fluid flow-front, taken at regular periods, along with synchronized pressure readings were employed to determine permeability (K).

In addition, polyester was mixed with P-MEK (1% v/v), degassed via sonication for 3 min and then injected into the mould with the hybrid reinforcement stack (GGSGG or GGPGG). The plates were cured for 30 min at room temperature. The rigid composites were demoulded and cut for testing. Tensile (ASTM D3039), three-point bending (ASTM D790) and short-beam (ASTM D2344) tests were carried out using an Emic DL2000 universal testing machine. Izod impact tests (ASTM D256) on unnotched specimens were performed using a Ceast impactometer (5.5 J hammer).

Table 2 shows the estimated permeability values of all studied reinforcements. It may be readily seen that $K_{SISAL} > K_{PP\ CORE} > K_{GLASS}$. The PP CORE presented permeability 46% higher than that of the GLASS mat, with a 40% reduction in filling time. For the SISAL mat, the permeability was even higher, three-fold that of GLASS, with a 70% reduction in filling time, i.e. sisal allows a faster impregnation than the commercial product (for %V_f = 20.2%).

Table 2: Measured permeability and mold filling time (at 0.31 m) for the homogeneous and hybrid porous media - %V_f = 20.2%.

Porous media	K (m^2)	K normalized	Filling time (s)	Filling time reduction
GLASS	1.33×10^{-9}	---	350	---
PP CORE	1.94×10^{-9}	1.46 (over K_{GLASS})	211	40% (over t_{GLASS})
SISAL	3.97×10^{-9}	2.98 (over K_{GLASS})	106	70% (over t_{GLASS})
GGPGG	2.03×10^{-9}	---	250	---
GGSGG	2.99×10^{-9}	1.47 (over K_{GGPGG})	182	27% (over t_{GGPGG})

Next, hybrid reinforcements were built to mimic commercially available RTM light reinforcements. In these reinforcements, there are glass fiber mats at the top and bottom faces, with a highly permeable layer in the mid-plane, e.g. non-woven PP. The home-made built hybrid reinforcement called GGPGG is, in fact, quite similar to a reinforcement widely-used by the local composite automotive sector, which has 1200 g/m^2 of glass fiber mats per 250 g/m^2 of PP core. The permeability of the GGPGG reinforcement (Table 2) was measured as 2.03×10^{-9} m^2, whereas for the reinforcement GGSGG, where a PP layer was replaced by a sisal mat with the same volume fraction, the permeability increased to 2.99×10^{-9} m^2, with a corresponding decrease in filling time of 27%.

The better performance of sisal compared with non-woven PP in the conducted tests indicates that sisal allows the development of wider channels or pathways for the fluid flow, with less tortuosity. The higher tortuosity of the former may be a consequence of the larger diameter of sisal (average diameter = 195 μm) in comparison with the PP fiber (average diameter = 56 μm) and also because sisal is highly heterogeneous in diameter [15] which hinders compaction of the layer and therefore increases permeability.

There is another important characteristic that must be taken into consideration when comparing sisal and non-woven PP – the final mechanical properties. The reinforcement is primarily used to improve mechanical properties, whereas the infiltration medium is used to promote impregnation of the glass fibrous layers usually having a detrimental effect on strength, for instance. The mechanical properties of the hybrid composites are shown in Table 3. The strength and modulus results of the GGSGG composite were slightly higher than those of the GGPGG composite, except flexural modulus and short-beam strength. Poor bonding of the untreated sisal to the matrix and a higher void content may be responsible for decreasing the latter.

In all, for the same fiber volume content, the permeability of the sisal mats was much higher than that of the PP non-woven core, often used as an infiltration medium. Hybrid reinforcements with a sisal mid-plane layer yielded higher permeability than hybrid reinforcements with a PP layer because the thick and heterogeneous vegetable fibers provided an easier pathway for fluid flow that lead to through-the-thickness flow, speeding up the overall impregnation of the fibrous reinforcement. In addition, most mechanical properties of the hybrid glass/sisal were similar to those of the hybrid glass/PP, and the substitution of PP for sisal carries the extra benefit of promoting the use of a vegetable fiber instead of a synthetic polymer. Therefore, the sisal mat proved a viable alternative in engineering applications as a substitute for commercial flow media in dry environments, leading the group to deposit a patent on it [16].

Table 3: Mechanical properties of the hybrid composites [14].

		Polyester/GGPGG	**Polyester/GGSGG**
Tensile	Strength (MPa)	58.9 ± 9,3	62.6 ± 3.6
	Modulus (MPa)	1113 ± 73	1327 ± 199
	Strain at rupture (%)	4.7 ± 0.4	4.2 ± 0.5
Flexural	Strength (MPa)	172.6 ± 17.8	181.1 ± 17.7
	Modulus (MPa)	8746 ± 575	8613 ± 719
	Strain at rupture (%)	2.5 ± 0.3	2.6 ± 0.2
Impact	Strength (kJ/m^2)	59.9 ± 12.6	68.6 ± 10.7
Short-beam	Strength (MPa)	19.2 ± 4.4	14.5 ± 4.7

4 CASE STUDY 3 - REINFORCEMENT FOR COMPOSITES

Natural fiber composites (NFCs) are environmentally superior to glass fiber composites in most cases because [17]: (i) natural fiber production causes lower environmental impact compared to glass fiber production; (ii) NFCs have higher fiber content for equivalent performance, reducing more polluting base polymer content; (iii) the light-weight NFCs improve fuel efficiency and reduce emissions during use, especially in auto applications, and (iv) end of life incineration of natural fibers results in recovered energy and carbon credits.

John [18] mentioned that the application of these composites has extended to almost all fields nowadays, but the major industrial sectors worldwide are transportation (especially automotive), building (e.g. ceiling paneling, partition boards), insulation [3], packaging [7], furniture [19] and consumer goods. These composites offer specific properties comparable to those of conventional fiber composites and are being produced with either thermoset, mainly polyester, or thermoplastic matrices.

However, in the development of these composites, drawbacks like fiber heterogeneity, incompatibility between fiber and polymer matrix, poor fiber resistance to moisture and durability often reduce the potentiality of natural fibers [20]. Even their flammability may become an issue, like in building industry and transportation applications [21].

For the optimization of the interfacial bond, fiber pretreatments can separate natural fiber bundles into individual filaments, clean and chemically modify the fiber surface, prevent moisture absorption and increase surface roughness [22]. Physical methods in natural fiber processing include steam explosion, thermo-mechanical processes, plasma, dielectric barrier techniques and corona [23]. Chemical methods are numerous and include dewaxing, alkali treatment, alkali with sodium borohydrate [24], isocyanate treatment, peroxide treatment, vinyl grafting, bleaching, acetylation, benzoylation, acrylation, stearation, permanganate and the use of coupling agents (e.g. graft copolymerization, silane, maleated compounds) [18, 25].

Although the treatments improve adhesion [26], there is some controversy in the literature about the effect of the treatment on the mechanical properties of the fiber itself. Indeed, for instance Li [27] reports an increase in strength, Amico [15] a decrease in strength, and Zafeiropoulos [28] no significant change. Even when a more pronounced gain is noticed after chemical treatment, the improvement is often within the scatter of the results. It also appears that the overall gain for the composite regarding fiber treatment may be similarly achieved with a simple fiber washing/drying procedure, with the extra benefits of being much cheaper than some of these treatments and more environmentally friendly [29].

On this context, many authors are focusing on hybridization as a way of undoubtfully reaching noteworthy mechanical properties. According to Reddy [30], hybridization has the potential of making natural fabric composites more suitable for technical applications such as automotive interior parts. Recent literature on that may be found for the hybridization of sisal/glass [31-35], Bambu/glass [36], hemp/glass [37], palm fiber/glass [38], jute/glass [39, 40], curaua/glass [41], kapok/glass [30], kapok/sisal [30] and roselle/sisal [42], among others.

The reinforcements in a hybrid composite may be combined in various ways, such as fibre-by-fibre mixtures ("intimate" hybrids), tow-by-tow mixtures ("discrete" or "zebra" hybrids), layer-by-layer mixtures, skin-core-skin structures (i.e. sandwich structures), internal ribs and external ribs [43]. Some very interesting results may be found in the cited references.

5 CONCLUSIONS

In this invited article, distinct functionalities of vegetable fibers were discussed. The presented case studies were related to oil sorption, infiltration (flow) medium and reinforcement for composites, especially hybrid composites. A variety of positive characteristics of vegetable fibers along with stricter demands of legislative authorities are expected to promote their wider use, including more demanding and rewarding applications such as those presented here.

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