SURVEY OF NATURAL FIBERS PROPERTIES AIMING THE PRODUCTION OF NANOCOMPOSITES

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ABSTRACT

The demand of the humankind to fulfill their needs due to increasing rates of the world population and the modern life style, means a substantial increment in the synthetic materials consumption per capita. The introduction of renewable resource materials into the fabrication of components for several industrial segments has been enhanced by the recent environmental pressures. Combining agro-fibers (lignocellulosics) with other resources provides a strategy for producing advanced composite materials.

A survey about the natural fibers properties and some composites applications are described in the present paper. The composites based on different matrices (BOPP, PP and HDPE) were produced using nanocellulose. The composites used were prepared based on natural fibers and pulp and paper primary sludge, osites. The composites were produced and evaluated by mechanical testing (tensile, flexural, impact and surface hardness), chemical and microscopic analysis (SEM, DSC, TGA and FTIR).

KEYWORDS:

Natural fibers; composites; nanocellulose; biocomposites; residues.

INTRODUCTION

There has been a growing interest in polymer composites with lignocellulosic fibres in the latest years for two reasons: the production of composite materials based on lignocellulosics is more economic than the production of thermoplastics, and also the lignocellulosic fibres are an attractive and cheaper alternative to the development of renewable and biodegradable materials. Thus, new materials are being developed for use in several industrial sectors: construction, packaging, automobile sector among others. The composites with natural fibres (based on renewable resources) are particularly interesting since they can replace traditional materials as wood, mineral and plastics in some applications (LEÃO, A. L. 2007)..

The promising performance of cellulose nanofibres and their abundance encourages the utilization of agricultural waste residue, which acts as the main source of cellulose. In nature, a large number of plants and animals synthesize extra-cellular high-performance skeletal biocomposites consisting of a matrix reinforced by fibrous biopolymers. Cellulose is a classical example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner

MATERIAL AND METHODS

Chemical analysis of the fibres

Chemical constituents of fibres were determined according to ASTM standards. α-cellulose (ASTM D 1103-55T), hemicellulose (ASTM D 1104-56), lignin (ASTM D1106-56), Moisture content (ASTM D 4442-92).

The cellulose, hemicelluloses, lignin and moisture content of the fibre in the untreated raw, steam exploded and acid hydrolysed stages of the fibers were determined.

Methods for the isolation of nano cellulose from raw fibres

Alkali treatment of the fibre

The optimum alkali treatment is both a very effective surface modification and a low cost surface treatment for coir fibres. Locally available coconut husk were cut it into pieces and subjected for treatment. Both fibres were soaked in 2% caustic soda and placed for six hours at a temperature of 25°C.

Steam explosion of the alkali treated fibre

A laboratory autoclave which can work with 137 Pa (20 lbs) pressure was used for steam treatment. Steam explosion technique was applied on the alkali treated fibre for one hour. Steam pre-treatment was performed by loading the lignocellulosic material directly into the steam gun and treating it with high pressure steam at temperatures within 200 to 250°C. The paper refers 'steam exploded fibre' which means the alkali treatment followed by steam exploded natural fibre.

Bleaching of the steam exploded fibre

Alkali treated and steam exploded samples are then subjected to bleaching. After the successive chemical treatments, the bleaching treatment with a chlorine dioxide ($NaClO_2$) solution (pH 2.3) for 1 h at 50°C was performed to remove the remaining lignin. In the bleaching step, the absence of elemental chlorine is accomplished by using $NaClO_2$.

Acid treatment followed by steam explosion

The bleached sample is then subjected to mild acid treatment. 5% oxalic acid was used for the acid hydrolysis followed by second step of steam explosion for one hour. A pressure of 137 Pa (20 lbs) was used, followed by sudden release of pressure. The fibres were then washed thoroughly by water and then subjected to mechanical stirring followed by sonication.

One of the main aspect that drives the use of the natural fibers is the chemical composition. This information is crucial to determine the need of some reactions of even the number of cycles to proceed the complete removal of the lignin In Table 1, can be observed the chemical composition of several natural fibers

TABLE 1 – Chemical composition of selected fibres

CHEMICAL COMPOSITION				
FIBER	**Cellulose**	**Hemi-cellulose**	**Lignin**	**REFERENCES**
	(wt. %)	**(wt. %)**	**(wt. %)**	
Phormium	45,1	30,1	11,2	(1)
Abaca	56 - 63	20 - 25	7 - 9	(2)
Sugarcane Bagasse	30,27	56,73	13	(3)
Caroá	35,5	17,9	30,1	(4)
Luffa	63	19,4	11,2	(5)
Bamboo	55	20	25	(6)
Curaua	70,4	10,8	11,1	(7)
Piaçava	29	11	45	(8)
Flax	60 - 81	14 - 18,6	2 - 3	(9)
Juta	51 - 72	12 - 20,4	5 - 13	(9)
Sisal	43 - 88	10 - 13	4 - 12	(9)
Kenaf	36	21	18	(9)
Ramie	68,6 - 76	13,1 - 15	0,6 - 1	(9)
Hemp	70 - 78	17,9 - 22	3,7 - 5	(9)
Cotton	82,7 - 92	2 - 5,7	0,5 - 1	(9)
Coir	43	0,3	45	(9)
Banana	60 - 65	6 - 19	5 - 10	(9)
Henequén	60 - 78	4 - 28	8 - 13	(9)
Bagasse	40	30	20	(9)
Pineapple	80 - 81	16 - 19	12	(9)
Wood	45 - 50	23	27	(9)

(1) DANIELS, V., 1999; (2) JOHN, M. J. e ANANDJIWALA, R. D., 2007; (3) JÚSTIZ-SMITH, N. G et al, 2008; (4) BLEDEZKI, A. K. e GASSAN, J., 1999; (5) JOHN, M. J. e ANANDJIWALA, R. D., 2007; (6) JASSEN, J. J. A., 1991; (7) SOUZA, S. F., 2010; (8) AQUINO, R. C. M. P, 2003; (9) LEÃO, A.L., 2011.

In Table 2, can be observed the main characteristics of selected natural fibers. In this aspect, the strength itself is important, but other properties are important as well as fineness index. As can be seen, the range of the data are high, meaning that the maybe the sampling, testing and reporting are not under the same conditions. Therefore, anyone working with natural fibres, have to generate its own data, mainly chemical and physical characterization.

The produced nanocellulose and its composites confirmed to be a very versatile material having the wide range of medical applications, including scaffolds for tissue engineering, cardiovascular implants and vascular grafts. These implants were produced from bioresorbable and/or biodegradable materials. Progressive degradation of the implant material may then be accompanied by the formation of the new tissues. The developed material can also be utilized for construction of non latex condoms, breathable wound dressing, surgical gloves, surgical gowns or drapes, medical bags, organ retrieval bags and medical disposables.

TABLE 2 – Physical properties of selected fibres

PHYSICAL PROPERTIES					
FIBERS	**Diameter**	**Elongation at break**	**Tensile strength**	**Young's Modulus**	**REFERENCES**
	(µm)	**(%)**	**MPa**	**GPa**	
Phormium (gage length = 20mm)	104.48 +/- 23.18	5.040 +/- 80	770,68 +/- 320,52	23,89 +/- 9,45	(1)
Abaca	*	2,9	756	31,1	(2)
Sugarcane Bagasse	*	1	222	27,1	(3)
Bambo	*	~2	140 - 230	11 - 17	(4)
Curaua	*	4,3	502	11,8	(5)
Caroa	*	*	71,3 - 182,2	3,5 - 7,4	(6)
Piaçava	*	6	143	5,6	(7)
Flax	40 - 620	2,7 - 3,2	343 - 1035	27 - 80	(8)
Juta	30 - 14	1,4 - 3,1	187 - 773	3 - 55	(8)
Sisal	100 - 300	2 - 2,9	507 - 855	9 - 28	(8)
Kenaf	40 - 90	3,7 - 6,9	295 - 930	22 - 53	(8)
Ramie	40 - 60	3,6 - 3,8	400 - 938	44 - 128	(8)
Hemp	16 - 50	1,3 - 4,7	580 - 1110	3 - 90	(8)
Cotton	16 - 21	2 - 10	287 - 597	5,5 - 12,6	(8)
Coir	100 - 450	15 - 47	106 - 270	3 - 6	(8)
Banana	50 - 280	3 - 10	529 - 914	7,7 - 32	(8)
Henequén	20 - 500	3 - 5	430 - 580	10,1 - 16,3	(8)
Bagasse	200 - 400	0,9	20 - 290	2,7 - 17	(8)
Pineapple	200 - 8800	0,8 - 3	170 - 1627	6,21 - 82	(8)

(1) DE ROSA et al., 2010; (2) SHIBATA et al, 2002; (3) JÚSTIZ-SMITH, N. G et al, 2008; (4) SREENIVASULU, S., REDDY, A. C., 2014; (5) LEÃO, A.L et al, 2009; (6) LOPES, F. F. M et al, 2011; (7) AGOPYAN e SAVASTANO JR., 1997; (8) LEÃO, A.L., 2011

Chemical analysis of the fibres

The crystallinity was found to vary depending on the conditions applied. The maximum crystallinity was obtained when acid hydrolysis was carried out on the bleached fibre. In natural cellulose fibres, the regions of intermediate order in the structure plays an important role in the determination of the degree of crystallinity.

Table 3 describes the chemical composition and moisture content of the coir fibres at different processing stages. Chemical constituents of fibres were determined according to ASTM standards. The raw coir fibre is mainly composed of cellulose (~40%), lignin (~40%) and other components. Upon alkali treatment, the lignin starts to dissolve out and increases the relative percentage of crystalline cellulose components. It is clearly demonstrated in the data presented in the Table 3. The fine structure of cellulose materials is composed of crystalline and amorphous regions.

TABLE3 - Constituents of the coir fibres in different stages of nanocellulose production

Fibre Stage	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Moisture Content (%)
Raw coir fibre	39.3 (±4)	49.2 (±5)	2 (±0.5)	9.8 (±1)
Alkali treated fibre	50.5 (±3)	38.8 (±4)	<1	10.3(±1)
Steam expl. fibre	57.4 (±3)	30.9 (±3)	-	8.8 (±1)
Bleached fibre	88.3 (±3)	0.3 (±0.1)	-	8.5 (±1)
Acid hydro. fibre	93.7 (±2)	-	-	8.1 (±0.5)

The amorphous regions easily absorb chemicals such as dyes and resins, whereas the compactness of the crystalline regions makes it difficult for chemical penetration. The mercerization of the coir fibers may result in the removal of the surface impurities, the swelling of the crystalline region, and alkalisation of the peripheral hydroxyl groups. The common trend from the observation is the gradual decrease of amorphous components like lignin and hemicellulose from raw fibre to bleached fire.

The lignin will react with $NaClO_2$ and an oxidative fragmentation of lignin takes place and some part of lignin will dissolve out as lignin chloride. The percentage increase of the pure cellulose component (39.3 to 93.7%) and decrease of the lignin components (49.2 to 0.3%) with each processing steps are the main observation.

Moisture content shows an increase from raw to alkali treated fibre followed by a gradual decrease. During alkali treatment, the swelling of the fibre takes place, which promote the absorption of moisture by capillary action. The alkali treatment of the fibre will lead to the swelling which facilitate the breakdown during acid hydrolysis.

During every processing step there is an increase in the percentage of crystalline cellulose content. Since most hydroxyl groups in the final stage are bonded by intra and inter molecular hydrogen bonding, moisture absorption decrease.

As discussed in chemical analysis, the main components in the coir fibre are cellulose, hemicellulose and lignin. These three components are mainly composed of alkanes, esters, aromatics, ketones and alcohols, with different oxygen-containing functional groups.

Acid hydrolysis of cellulose leads to hydrolytic cleavage of glycosidic bond between two anhydroglucose units. Thus the amorphous portion gets dissolved by acid hydrolysis, leaving behind the crystalline regions. Acid hydrolysis followed by mechanical treatment (sonication) results in disintegration of the cellulose structure into nanocrystalline form. From the calculations for the yield of the product formed, it was found that 234 gm of dry nanocellulose is obtained from 1 kg of dry raw coir fibre.

CONCLUSION

The objective of this work was to study the potential application of natural fibre and thereby enhance its effective utilization of these natural resources. The natural fibres can be an important soure of high performance composites for many different applications, including light weight composites, biomaterials, textiles, etc…

Morphological and dynamic light scattering analyses of the fibres at different processing stages revealed that the gradual removal of the cementing materials and isolation of cellulose nano fibres occurs in the final step of the process as an aqueous suspension. FT-IR and XRD analysis revealed that the pre-treatments led to the removal of lignin and gradual increase in the crystallinity of the fibre at each processing stages. The presence of lignin-cellulose complex in the raw coir fibre plays a major role in its structural and thermal properties. The thermal stability of the extracted nanocellulose has a lower value than the nanocellulose present in the raw coir fibre because of the presence of this strong lignin-cellulose complex in raw fibre. Homogenous cellulose nanofibrils with a diameter of 5-50 nm are obtained from coir fibre by this process. Since the pure cellulose has a variety of properties, its nano form can find applications in various industrial and biomedical fields by exploring the nanotechnological possibilities.

The produced nanocellulose and its composites confirmed to be a very versatile material having the wide range of medical applications, including scaffolds for tissue engineering, cardiovascular implants and vascular grafts. These implants were produced from bioresorbable and/or biodegradable materials. Progressive degradation of the implant material may then be accompanied by the formation of the new tissues. The developed material can also be utilized for construction of non latex condoms, breathable wound dressing, surgical gloves, surgical gowns or drapes, medical bags, organ retrieval bags and medical disposables.

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