

Biodegradable polymer composites based on brazilian lignocellulosic

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ABSTRACT

Use of eco friendly and energy saving biomaterials and processes have enabled to overcome the effects of growing urbanization and population along with increasing agro-industrial wastes. This has led to a new approach to the industrial design of products and processes along with the implementation of sustainable manufacturing strategies to “optimize the total material cycle from virgin material to finished material, to component, to product, to waste product and to ultimate disposal”. Developing countries such as Brazil possess abundantly available but underutilized biomaterial resources, which may possibly give excellent opportunities for scientists to discover methods for their better utilization. This talk presents attempts made so far on the developments of biodegradable composites based on biomaterials of Brazil, with details on their processing matrix-reinforcement combinations, morphology properties and market. Some results of the studies carried out by the author and his colleagues at UFPR-Curitiba are also included.

Keywords: Biopolymers, lignocellulosic fibers, processing of composites.

1 INTRODUCTION

Recent times have witnessed fierce discussions on the climate changes stressing the need for clean environment and utilization of renewable resources thus minimizing the dependence on dwindling natural resources such as wood and oil. These aspects have led to the development of new materials, a change from non-renewable, but difficult to degrade or non-degradable ones, particularly composite materials. Use of synthetic polymers in every segment of our life has increased the plastic waste in large quantities, which forms one of the major environmental problems the world is facing today. One strategy to overcome this is the use of biobased polymers, which are derived from renewable materials, leading to the development of ‘green or eco-composite materials’ that can be easily degraded or bio assimilated [1]. These materials are expected to be one of the important materials to realize and maintain a sustainable productive society [2].

Brazil having a unique position among the South American countries, occupies approximately 50% of this region, with an area of about 8.5 million km². Of this, about 58% are forests and woodlands [3]. Brazil has abundant availability of some of the renewable natural resources, which can be used as matrix and reinforcement materials. This has led to their development and use as biodegradable polymeric materials. They include starches (cassava, corn, potato, wheat, soya); cashew resin, natural rubber, PHB, PLA, banana, coir, curaua fibers, sugar cane bagasse and luffa cylindrica. Like all governments, Brazil has been taking necessary steps towards finding means and ways for the utilization of these resources through their funding agencies such as the Brazilian Farming Research Commission (EMBRAPA) and the National Council for Scientific and Technological Research (CNPq).

1.1 Market and Cost Aspects

It may be noted that the international market for biopolymers/bioplastics is still in its infancy. However, due to increasing prices of petrochemical feed stocks for plastics along with growing environmental considerations will only pave way for bright future for these materials including biodegradable composites. For example, a new market study by Helmut Kaiser Consultancy has reported that the availability of bioplastics during the last one decade has the potential to reduce the petroleum consumption for plastic by 15-20% by 2025 [4]. Non-biodegradable plant-based plastics will be the primary driver for the demand of bioplastics with the expected opening of plants by Dow Chemical and Braskem to produce polyethylene from bio-based ethanol in Brazil, in addition to others plan for the same [4]. The

demand for non-biodegradable plant-based plastics is expected to increase from mere 23,000 metric tons in 2008 to nearly 600,000 metric tons in 2013 [5]. Further, production of these bioplastics, which is presently concentrating in developed countries, is expected to change by 2013 considering that China's expected new capacity to 100,000 metric tons and Brazil becoming leading producer of bioplastics by 2018 due to its plan to start online bio-based polyethylene and polyvinyl chloride plants [5]. One of the reasons for this is developing countries such as Brazil, which have agriculture as the main industry, will enjoy both as late-comers and competitiveness in the area of biopolymers and their composites. It is reported [5] that the global demand for bioplastics (which include plastic resins that are biodegradable or derived from plant-based sources) by 2013, will rise to more than fourfold (890,000 metric tons) over the present demand, and by 2018 this is expected to reach nearly two million metric tons, with a market value of over \$5 billion.

A comparison of costs of feed stocks for biopolymers in Brazil with that of USA reveals [6] the former is less about 50% than over that of the latter. For example, the production cost per ton of industrial cassava from cassava is US\$ 262 in Brazil while in USA it is US\$ 478; production cost per ton of sugars based on sugarcane used for producing biopolymers is US\$ 150-200 in Brazil compared to US\$ 450 for glucose from corn starch; production costs of PLA is one half and that of PHB is one third in Brazil compared to that in USA. This along with the freight and the import taxes at the destination country will have significant cost advantages for Brazil and USA produced biopolymers over those produced in Europe and Japan. Thus, Brazil has the advantage of not only producing low cost biopolymers, but also technical and commercial success in development of these positioning her to develop necessary technology particularly for PHB research and pilot-scale production of this material. However, the report [6] states the hindrance for the large scale production of these biopolymers in the country for possible exports due to the limited investment capital and lack of well developed government incentives.

Taking all these in to considerations and the importance of biodegradable materials in the present context, this paper presents availability of biodegradable polymers and reinforcements in Brazil and attempts made so far on the developments of biodegradable composites based on these. Some details on their processing, matrix-reinforcement combinations, morphology, properties, market and cost aspects along with some results of the studies carried out by the author and his colleagues at UFPR-Curitiba, Brazil are also presented.

2 BIODEGRADABLE MATRICES AND REINFORCEMENTS

Importance of biodegradable polymers/composites assumes significance due to the problem of the solid waste generated by plastic materials after their final use. Many definitions of biodegradable polymers/composites are proposed of which most acceptable one seems to be as follows: "*Those materials obtained from nature or by synthetic route, whose chemical bonds are cleaved at least in one step by enzymes from the biosphere, with appropriate pH and temperature conditions and total processing time for completion*" [3]. Such attempts have led to expansion of the utilization of plant based materials for sustainable manufacture of industrial products similar to the expansion of the utilization of lignocellulosic fibers for sustainability through networks formed by industry and academy forums such as Bio Fiber Net and International Biodegradable Polymers Association & Working Groups in Europe (IBAW) [3]. In Brazil, the Amazonian Phoenix project works towards the sustainable technologies based on the renewable plant materials with the aim of producing some production systems based on simple and low cost machinery and secondly, developing composites with advance production technology [7].

Biopolymers are classified broadly as natural or synthetic depending on their source of availability or method of their polymerization, viz., biological or synthetic [1]. Accordingly they may be biosynthetic (natural or produced from natural sources), semi-biosynthetic and chemo-synthetic. Important characteristics of these polymers for their utilization, including in the development of composites, are density (to predict the weight of the composite to be produced), characteristic temperatures, viz., glass transition temperature T_g and melt temperature T_m , (to know about the thermal stability of the resulting composites, which may also have some bearing on the mechanical properties) water absorption, degradation time and mechanical properties.

Biobased reinforcements such as lignocellulosic fibers, clays, etc are available in plenty in Brazil. Of these, extensive studies have been reported on lignocellulosic fibers including some recent systematic studies about their properties and morphologies along with their availability, present as well as future possible uses [3, 5, 8]. Figure 1 shows some of the main Brazilian fibers used in biodegradable polymer composites, while Table 1 lists their major chemical constituents and typical physical and mechanical properties. Similarly, developments of their composites with polymers including biopolymers matrices have also been reported [3, 8, 10-14].

3 PROCESSING OF BIODEGRADABLE COMPOSITES

Necessary factors for the production of biodegradable composites include proper mixing of lignocellulosic fibers (LC) fibers, selection of appropriate biopolymer matrix, suitable surface treatments if required, along with low-cost but high-speed fabrication techniques. In view of the similar chemical nature of both the fiber and matrix, though surface modification of LC fibers is not necessary to improve the bonding during the preparation of biodegradable composites, it is resorted mainly to achieve specific aspects such as providing greater adhesion and reduced moisture sensitivity in the case of biodegradable composites. Further, processing of LC-based biodegradable composites exhibits some attractions less abrasiveness for tooling unlike glass fiber composites and absence of airborne particles, reducing respiratory problems for workers. In addition, availability of reinforcements in suitable form will add to the advantages.

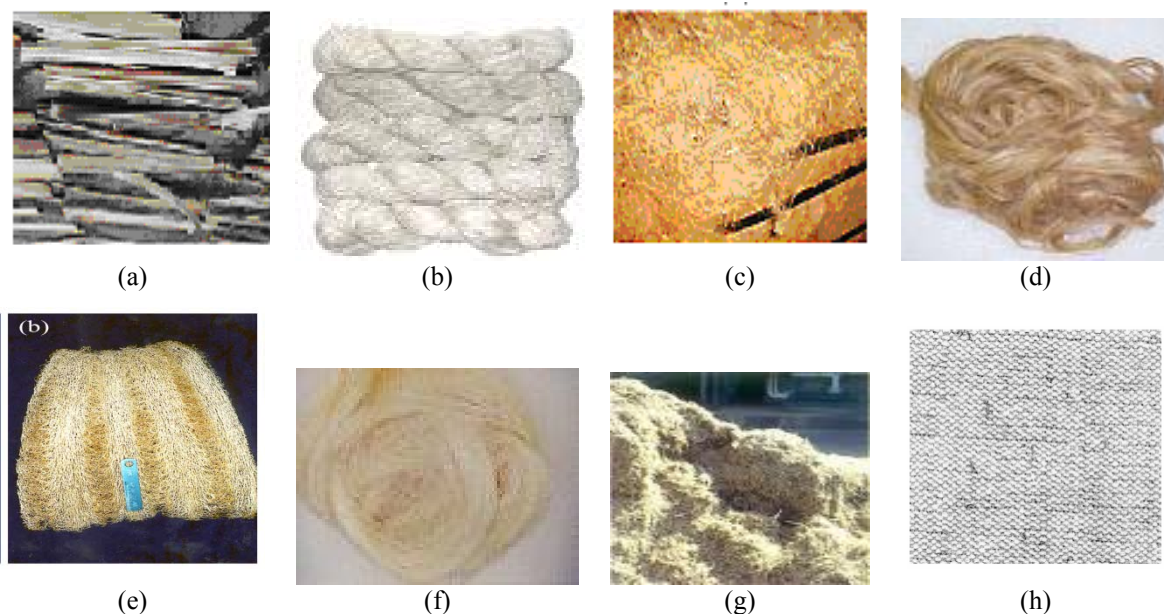


Figure 1: Some of Brazilian Fibers (a) Banana Sheath, (b) Banana Fiber, (c) Coir, (d) Curaua, (e) Sponge Gourd, (f) Sisal, (g) Sugarcane Bagasse, (h) Ramie-Cotton fabric.

Table 1: Physical/Chemical and Tensile Properties of some lignocellulosic fibers used for biocomposites. [Adopted from Ref. 3, 8, 10].

Fiber	Dimensions L(mm)/D(μ m)	α -Cellulose (%)	Lignin (%)	Young's Modulus (GPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)
Sugarcane Bagasse	10-300/10-34	32-44	19-24	17.9 ^a -27.1	222	1.1
Banana	300-900 /12-30	60-65	5-10	27-32	700-800	2.5-3.7
Jute	120/25-30	59-71	11.8- 12.9	10-30	400-800	1.5-1.8
Ramie	900-1200 / 20-80	80-85	0.5	44	500-870	1.2
Curauá Wet	35/7-10	70.7-73.6	7.5-11.1	30-80 ^b 10.5	1250-3000 ^b 439-495 (MOR) ^c	4.5-6 ^b 1.3
Curauá Dry				27.1 34-96 ^d	117 (MOR) ^c /495 87-310 ^d	1.3-3.2 4-4.9 ^d
Sisal	900/8-50	60-67	8-12	17-22	530-630	3.64-5.12
Coir	20-150/10-50	43.77	45	6	220	23.9-51.4
Luffa- cylíndrica	25-60 (Diameter)	62	11.2	-	-	-

a – Calculated; b - Diameter: 30-60m; Test length- 20mm and Strain rate-5mm/min;
c- MOR: Modulus of Rupture. d – Diameter range 26-64 μ m

Table 2 shows some matrix-reinforcement-processing combinations used in Brazil, which are almost similar to those used elsewhere. It may be noted that methods, such as hot pressing / compression molding and extrusion followed by injection molding used for other polymer composites are most commonly used here also since these methods produce composites with adequate properties for some applications.

However, greater attention should be given to some important aspects, such as preservation of mechanical properties of the LC fibers involved by minimizing the attrition and mixing degradation, attaining a high degree of fiber dispersion and ensuring good wettability, whereby incorporation of a higher volume fraction of fibers with control of fiber orientation can be achieved.

Table 2: Matrix-Reinforcement-Processing and Characteristics of biodegradable Composites [Adopted from Ref. 3].

Matrix system	Reinforcement	Processing	Characteristics
Corn Starch 35%, Corn gluten 35%, Glycerol 20%, water 10% Thermoplastic starch	10%wt coir, jute or sisal Eucalyptus pulp 16% (w/w)	Mixing followed by Hot pressing 130 °C Hot pressing 170 °C	increase of 100% in tensile strength and more than 50% in modulus respect to starch matrix
Corn starch-Glycerol (30-50wt%)-	1-15wt% cellulose fibers	Intensive batch mixer at 100-150 °C	Characterization by HP size exclusion chromatography; glycerol content reduces starch degradation while increased fiber content increased degradation. Lower polydispersity index for matrix than that of native starch due to shear induced fragmentation of selective breakage of large amylopectin molecules
Commercial starch-cellulose acetate	pine wood flour (20-50w/w)-	Extrusion followed by injection molding	Mechanical properties dependent on fiber orientation with transverse properties being slightly higher than those in radial direction.
Natural rubber	cotton fiber. Surface modified with polyaniline	Hot pressing	Storage modulus (E') four times higher than the matrix. Tg matrix=-67°C, tg composite – 49°C.

4 PROPERTIES OF BIODEGRADABLE COMPOSITES

Studies carried out on biodegradable composites in Brazil have reported a number of physical, mechanical and thermal properties of various systems. Table 2 lists some of these. It may be seen that properties depend on the matrix, reinforcement and processing method used. Some details are given below:

4.1 Starch based Composites

Among the biodegradable composites, these composites are extensively studied. One study reports on the starch-30% glycerine-16% eucalyptus urograss pulp fiber ($l/d = 60$, $l = 1\text{mm}$) composite laminate. These exhibited 156% and 120 % increase in YM and TS, respectively, over the matrix, while % elongation and water absorption decreased by 33% and 40% respectively [3]. Good adhesion, as revealed by the fractographs of these composites was reported to be the reason for these properties. On the other hand, the thermal behavior of these biocomposites showed an increase of glass transition temperature and two transition peaks in the DSC curve. A dramatic reduction in water sorption of the composite at two humidity values (43 and 100%) was observed due to absorption of glycerin by the fiber, making the matrix less hydrophilic.

Other study has reported [3] the effect of processing parameters particularly in corn starch-glycerol (30-50wt%)-1-15wt% cellulose fiber composites processed by an intensive batch mixer at 100-150°C on the properties. It was observed that the glycerol content reduced the starch degradation, while increasing fiber content, increased degradation.

Recent study on corn base system reported [3] an increase in the Young's modulus of 35% each of corn starch (28% amylose) and corn gluten, 20% glycerol and with individual fibers of coir, jute and sisal at 10 w% of total weight of starch and corn gluten over the matrix (161 MPa) for the untreated coir, jute and sisal fibers, respectively. Mercerization treatment of the fibers further improved in these values over their

untreated counterparts. Similarly, improvement in ultimate tensile strength (UTS) values also by 76, 86 and 90%, respectively, for these composites over the matrix for the three fibers respectively. Further, mercerization treatment of fibers improved these properties for coir and jute respectively, while they decreased in the case of sisal. However, all composites of untreated fibers showed significant decreases in elongation in relation to that for the matrix, while marginal increases over these values for mercerized jute and sisal fibers and about 35% for a coir fiber composite were observed. All these results were explained by SEM studies relating them to the adhesion between the fibers and matrix.

Other systems reported, include untreated/alkali treated curaua fiber-corn starch [3] and coir, sisal and jute fibers independently incorporated in starch-gluten or starch-ethylene vinyl alcohol (EVOH)/glycerol matrices [11, 12]. In the former case of curaua fibers, both tensile strength and failure strain increased and almost two times for the alkali treatment over the untreated fiber while significant increase of tensile strength of both composites over the matrix (10.6 MPa). However, failure strain of matrix (0.0650) was higher than that of both the composites. Young's modulus of both the composite remained almost constant while the value was significantly higher than that of the matrix. Also, untreated and 5% alkali treated fiber composite showed higher specific strength compared to that of alkali resistant glass fiber composite suggesting superior performance of lighter composites.

In the case of coir-starch-EVOH-glycerol composites, increase in tensile strength and reduction in ductility of the matrix was observed with increasing fiber content, while no significant changes in crystalline structure [11]. Large pull outs in the composites indicated poor adhesion between the fiber and the matrix. Biodegradability of composites was better than that of the matrix.

On the other hand, composites of 5-30 % of fibers in starch-gluten-glycerol matrix processed in torque rheometer and then molded by hot compressing showed decreased [12] water absorption at equilibrium, improved thermal stability of the matrix, increased Young's and storage moduli and tensile strength and decreased $\tan \delta$ with increasing fiber content. These results have been explained as due to good interfacial adhesion observed in their morphology. Biodegradability also improved with the addition of fibers except slow down of this in the case of increasing coir fiber content in the composite.

4.2 Poly(hydroxyalkanoates) based Composites

This system is the second highest researched system due to the excellent dispersability of fibers achieved in PHBs compared with synthetic polymers [3]. In addition, tensile properties of alkanolate-based composites depend on the type of poly(alkanoate)-based resins (PHB, PHBV, etc.), nature of (type and form) fiber and its content as well as the plasticizer used. These are illustrated as follows: Composites of 20 wt% bagasse fibers incorporated in biodegradable aliphatic polyester exhibited higher tensile strength flexural modulus and impact strength [3] without treatment to the fibers. With alkali treatments to the fibers, these properties further improved; with 65% fiber content, further improvement was also observed. On the other hand, constant density (1200 kgm^{-3}) between the matrix and its composite, but an increase in YM and Shore D hardness, a decrease in TS and % elongation, with increasing wood flour content from 10 wt% to 40 wt% [3] were observed in PHB/wood flour biocomposite. However, no changes in these properties were observed with the surface modification of the wood flour by either NaOH or corona (electric discharge, which changes surface energy of fibers). In another instance, PHB/starch blend incorporated individually with 30% each of wood flour, rice husk and sugarcane bagasse showed increase of tensile strength and elongation [3]. On the other hand, the Young's modulus of these increased in a slightly different order. In addition, crystallinity was found to decrease in similar order without any variation of the melting temperature for any combination. Above results suggested that the natural fibers can certainly improve only stiffness, while bagasse fibers imparted increase in the impact strength. Another reported results of effects of different types of matrix and fibers on the tensile properties indicated high tensile strength in PHB containing recycled cellulose fibers, while low values for these properties in wood flour and its pulp containing PHB [3].

4.3 Other Matrices/Properties.

Studies have also been reported on composites of starch-cellulose acetate incorporated with pine wood flour (20-50w/w) [3] prepared by extrusion followed by injection molding. While it was difficult to process these composites, use of 15% glycerol improved the processing without affecting the properties, due to destruction of hydrogen bonds by glycerin, leading to decreased viscosity. Former composites showed decreasing viscosity with shear rate. The mechanical properties of these composites were reported to be dependent on fiber orientation. Observed increases in these properties were up to 50 wt%, where after they decreased, while the toughness almost remained constant when the flour content increased from 0 to 50 wt%. SEM of fractured composites showed coating of flours by matrix, suggesting good fiber-matrix adhesion.

4.4 Biodegradable Nano and Hybrid Composites

Very little is reported on the development of biodegradable hybrid and nanocomposites based on Brazilian raw materials. This aspect needs more attention in view of the advantages these new generations of composites offer for a variety of applications including strategic sectors. It should be noted that tremendous enhancement of properties can be obtained with nanocomposites even at low volume fraction (1-5%) of nanosized reinforcements, unlike large amounts in macro-composites, and the tremendous interest from industry and research in this type of composites. Some examples of such composites studied [3] in Brazil include starch and PLA with cotton microfibrils/wood pulp fibers and nitril rubber-rice husk ash. However, possibility exists to improve the properties of biodegradable nanocomposites further, which may open up the possibility for these composites to be used even in structural applications.

5 UFPR STUDIES

The following systems have been investigated by the author's Group in UFPR: (i) corn starch-glycerol-banana fiber/sugarcane bagasse; (cassava starch-glycerol-coir/sisal fiber); castor oil cake(mamona)-glycerol-corn and cassava starch-banana/sugarcane bagasse / Sponge guard-Luffa cylindrica and Balsa or Raft wood fibers; PHB-sugarcane bagasse. While systematic studies on the characterization of some of the fibers and their composites are reported [3, 8, 10, 13, 14] including two patents, which have also been filed, others are being published.

Using two different processing methods starch/banana and starch/bagasse fiber composites could be prepared by compression molding using both commercial glycerol and crude glycerin as plasticizers. Structural changes in both fiber composites, but without much variation in their crystallinity index (20–21%) were in their XRD studies. Preliminary results on these composites with commercial and recovered glycerol (byproduct of biodiesel) and different amounts of banana (20-35 wt. %) and 25wt. % bagasse fibers have shown [14] following trends:

The properties of the fibers rather than the properties of the matrix dictated the morphology of these composites. Starch coating on bagasse fibers indicated good bonding between these fibers and the matrix compared with the free surface of banana fibers.

Marginal improvements in tensile strength properties of these composites compared to those of the matrix were observed with their dependence on the processing methods with automatic control of temperature and applied pressure for composites; tensile properties of composites showed improved properties for the same amount of fiber content irrespective of type of glycerol used. Crude glycerin produced more homogeneous composites, which led to better properties than those produced with commercial glycerol, which offered possible use to the main co-product of the biodiesel industry, without any requirement for its chemical treatment and upgrading. Studies on cassava starch with coir and sisal fibers are continuing.

On the other hand, preliminary results of castor oil seed based composites indicated (Guimarães *et al.* to be published) that the crude glycerin and castor bean oil cake, both co products of the biofuel industry, could be used to prepare biodegradable composites with three types of plant based fibers (banana/sugarcane bagasse/luffa cylindrica) without any additive, which may increase the cost of the final product. Also, castor bean oil cake could partially replace starch or vice versa to produce biodegradable composites, which might have a great impact due to their large quantities usage, which otherwise could pose environmental hazards. Further, among the three lignocellulosic fibers used in this study, sugarcane bagasse fibers seemed to be the most favored followed by banana fibers and then Luffa cylindrica fibers based on the properties exhibited by their composites. Another interesting observation was that crude glycerin gave comparable properties when used in composites suggesting the use of this material to replace expensive commercial grade glycerol. These results are being published elsewhere.

Another study conducted (ASSMANN, V. Masters Dissertation (In Portuguese), Federal University of Parana - Brazil, 2009) with factorial planning revealed that the operating temperature for plastification of castor oil seed cake should be below 130°C with appropriate time to avoid any fissures in the thermoplastic produced which should increase the flexibility of the sugarcane bagasse composites. Zirconium powder was used to get good homogenization of the composite produced whereby better mechanical properties could be achieved with low scatter in the values. No significant change in the structure was observed in the composite as seen by X-ray diffraction studies. Morphology studies indicated that granular structure of the matrix was destroyed during the thermo processing whereby homogenous phase was resulted. Also, up to 15% fiber content, the morphology showed good dispersion, while above 30% fiber, poor dispersion was observed.

Also, higher Young's modulus and higher tensile strength values along with good coating of castor oil cake seed starch were observed for fiber diameter of 250µm.

Studies on castor oil seed-sponge guard-Luffa cylindrica and Balsa or Raft wood fibers are being continued.

PHB and PHB containing different amounts of sugarcane bagasse fibers with and without steam explosion (SE) fibers showed [13] that more or less similar stress-strain curves for both the matrix and its composites, with differing slopes and strain at failure. This suggested a change in the behavior of PHB with the incorporation of sugarcane bagasse fibers due to the debonding with the matrix, leading to the beginning of the fracture of the composite as observed in fractographs. Comparable values of Young's modulus Y_M , tensile strength T_S , yield strength Y_S and % strain at break obtained from these curves with those reported for wood flour-PHB composites, but higher than that reported for biodegradable aliphatic polyester-bagasse fiber. Further, steam exploded fiber containing composites (5 and 30 wt. % fibers) showed a significant increase in the maximum stress, while the modulus remained almost constant for the composites, while its value increased compared to that of PHB matrix. The randomly distributed raw bagasse fiber leads to higher values. Also, identical values for crystallinity were obtained from both DSC and X-ray diffraction techniques. Surface defects on the fibers, lack of bonding between the untreated bagasse fibers and PHB, presence of some air bubbles leading to defects in the samples and lowering of PHB crystallinity under pressure were some of the causes for the observed strength properties of composites.

DMA studies of PHB composites containing different amounts of sugarcane bagasse fibers with and without steam explosion treatment, showed very close $\tan \delta$ values of the composites to those of the fibers at temperatures ca. 50°C, indicating load transfer from matrix to fiber. An abrupt decrease in the loss modulus E'' supplemented this result.

6 APPLICATIONS / PRODUCTS

Despite the fact that the environmentally friendly composites, provide designers new alternatives to meet challenging requirements, very few biodegradable composites have been developed and marketed even on the world scenario leave Brazil alone. This is contrary, to many biopolymer products, which are developed and marketed. Some of the possible application sectors include: aquatic and terrestrial environments, municipal solid waste management and compostable packaging, while those for automobiles include for parcel shelves, door panels, etc. It is reported that the hurricane resistant housing, structures and a variety of products developed using soy oil with lignocellulosic fibers could be the forerunner for diverse range of applications for these types of materials. In view of this along with the continued technical innovations, identification of new applications, persistent political and environmental pressures, and investments mostly by governments, markets for the biodegradable composites will grow in the future. Hence it is the right time for the Brazilian composite researchers to go steady fast in their efforts in the study of these composites.

7 CONCLUDING REMARKS

From the foregoing it becomes evident that Brazil has abundant resources of renewable lignocellulosic materials to develop biodegradable composites. Such attempts could open up new avenue, which becomes a new source of income for small producers meeting the social aspects of a country such as Brazil's "National Program for Production and Use of Bio-diesel" and similar program found in other countries. Though the country has good number of academic and research institutions carrying out research on these materials, still there is a long way to go to compete with others elsewhere both in terms of R&D as well as product development. A collaborative and possibly complimentary effort on the part of Brazilian researchers with appropriate funding by appropriate agencies will certainly take the outputs to match with the efforts elsewhere and benefit the nation in the long run.

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