

Recent Developments in ‘Green’ Composites based on Plant Fibers- Preparation, Structure Property Studies

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Abstract

Recognizing the effects of dwindling natural feed stocks of energy and synthetic materials, their high costs along with the resulting effects by their use on the environment and emission of greenhouse gases into the environment, greater thrust has been placed on the use of eco friendly and energy saving biomaterials and processes. These efforts have led to a new approach to the development of new materials, products and processes along with the implementation of sustainable manufacturing strategies. Such strategies would help in optimizing the total material cycle from virgin material up to finished products. These also include utilization of wastes generated whereby ultimate disposal of wastes is achieved. Such efforts will have great impact on the world economy and improvement of quality of life. Considering the above and the abundantly available, but underutilized biomaterial resources, several attempts have been made all over the world giving excellent opportunities for scientists to discover methods for their better utilization. This paper discusses some of the recent research efforts made, including the author's involvement in these, to develop environmentally friendly and sustainable ‘green’ composites based on plant fibers with details on their processing matrix-reinforcement combinations, morphology and properties. These materials have found use in automotive, construction, packaging, medical and other sectors.

Keywords: Biodegradable; Biopolymers; Bio-reinforcements; Nanofibers; Mechanical properties; Morphology; Fractography

Introduction

The word ‘green’ affixed with materials refers to those materials which are ‘biodegradable’ and ‘renewable’ and thus addresses the twin issues of ‘sustainability’ and ‘environmental impact’. Such materials would naturally be attractive in view of their attributes of environmentally friendly and complete degradability. Greater attention has been given to these types of materials in recent times due to persistent discussions on the climate changes and regulatory demands underlining the need for clean environment and utilization of renewable resources. This is mainly due to the demerits of synthetic materials such as polymers, to chemical, physical and biological degradation posing serious concerns, when used in certain human related areas such as surgery, pharmacology, agriculture and the environment. Consequently, time resistant polymeric wastes are becoming highly unacceptable, necessitating search for alternate materials to the existing polymers, which should satisfy the conditions of biodegradability, biocompatibility and release of low-toxicity degradation products. Use of renewable resources such as plant based materials in particular helps in minimizing the dependence on dwindling natural resources such as wood and oil for many applications. The development of new bio-based materials has been a great motivating factor for materials scientists as seen from the increasing trend of publications in one decade (~2000 in 2003 to projected number of ~8000 in 2013 as per the data obtained using SciFinder on October 10th 2013) [1]. Besides, it has become an important provider of opportunities to improve the standard of living of people around the world [2]. Thus, new paradigm for the development of new materials has taken place from ‘non-renewable, but difficult to degrade or non-degradable ones to completely degradable and therefore easily disposed of or composted without harming the environment, at the end of their service life’. Figure 1 depicts time line for the evolution of materials from the traditional to the latest of bio based and nano types. It is pertinent to understand the classification of ‘bio-based materials’ as those which are not only organic in nature, but should also contain recently fixed new carbon present in biological sources [3].

Such bio based and biodegradable materials have become invaluable gifts to the mankind by the modern science and technology as they are

preferred in products having single use, short-life, and are disposable. Besides, they have controlled-life and hence used in applications such as packaging, consumer products [disposable plastics, agricultural films], marine disposable, etc. In view of the above attributes, they have become indispensable to the mankind at present time.

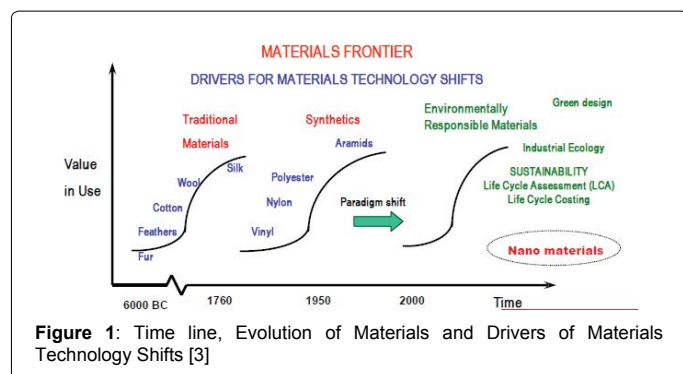
Search for and development of new materials with high performance at affordable costs has been a dynamic process to meet the demands of the time. Therefore there is time line for such developments particularly in the case of composites. Being macroscopic combination of two or more distinct materials with recognizable interface separating them, composite materials, exhibit synergetic effects in their properties. They pervade almost all application fields required by the society starting from human basic needs of habitat and living to food packaging, transportation, entertainment, etc. Having overcome the limitations of performance of monolithic materials, composite materials have gone through series of improvements, referred to as ‘five generations’ [2]. Simultaneously, there have been attempts to develop new polymers, called ‘green’ polymers from natural sources, which possess environmentally favorable properties such as renewability and degradability. These, along with the increased use of plant fibers as reinforcements, have led to the development of ‘biodegradable’ composites, which can be termed as ‘green’ composites provided they fulfill the criteria of ‘green materials’ defined earlier. This development stage of composites is termed as “fourth generation”. Thus, the challenge to obtain ‘green’ composite involves basically the challenge of obtaining ‘green’ polymers that are used as matrices in the production of composite materials. Biodegradability implies complete assimilation

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of the degraded products of materials such as polymers and their composites in natural environment through changes in the chemical structure, loss of mechanical and structural properties. Besides they may be a food source for the soil microorganisms to ensure safe and effective method of return of carbon into the ecosystem [3-5].

Of course, use of both the natural polymers and biodegradable composites has historical background as evident from the some of the available antiquities. For example, polymeric materials such as paper, silk, etc., have been used from historical times. The biodegradable composites also existed. These include (i) the strong Great Wall of China made of clay bricks during 121 B.C. to 221-206 B.C made of local materials initially using red willow reeds and twigs with gravel and later with clay, stone, willow branches, reeds; and (ii) sand adhesively bonded laminates of animal horns and tendons, wood or silk for making bows made in 1200 A.D. [2]. On the other hand, Research and Development (R&D) on biopolymers and biodegradable composites including 'green' composites has shown continuous progress. These are evident from the number of review articles as well as research papers on these two subjects, of which only selected few are cited here for the sake of brevity [2-58].

Considering the above and based on some of the selected published reports, this paper briefly reviews development of 'green' composites based on plant fibers, mostly discussing about the processing aspects and presenting their properties, which are explained on the basis of the observed structures (morphology and fractography).

Processing

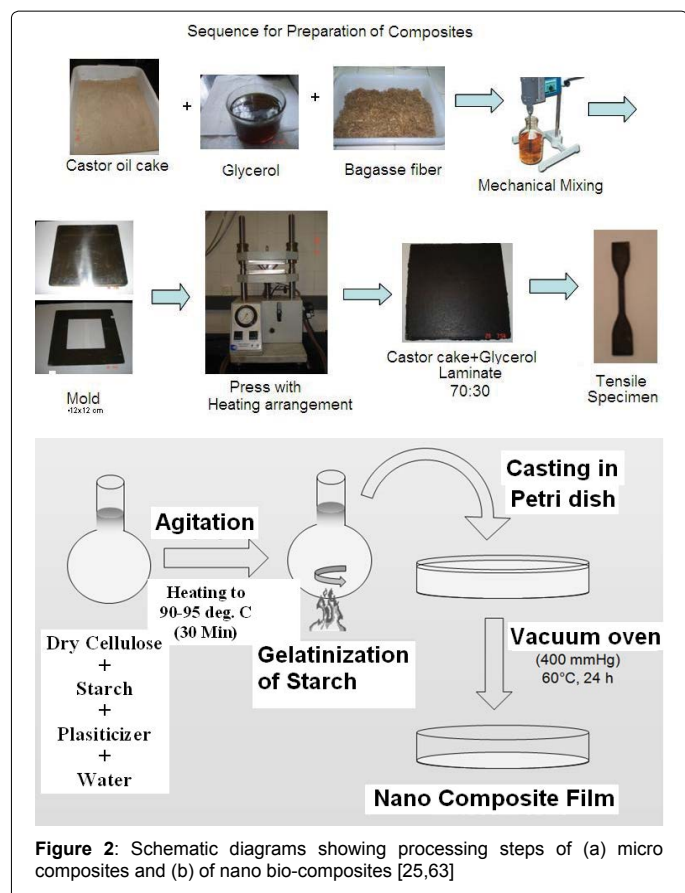
This step is the primary requisite for the development of any material including 'green' composites. In the latter case, based on the system to be studied or produced for desired application, the initial step is the selection of a proper bio-polymer as matrix and proper reinforcements (plant fibers-micro or nano). This is followed by the selection of suitable surface treatments to the reinforcements, if required, and then mix the reinforcements with the biopolymer before subjecting the mixture to some fabrication process. The latter should preferably be of low cost, but of high-speed. Further, when the products are produced, the processing is termed as 'manufacturing'. This (manufacturing) has undergone many developments from historical times to the present times with latest one being 'Nano manufacturing'. It should be noted that the processing techniques of any composite, micro or nano, are dictated by the intrinsic properties (solubility, dispersibility, degradation, etc.) of both constituents-matrix and the reinforcements. However, in the case of nano composites, 'nano-manufacturing', one of the 'recent' developments in the manufacturing processes, refers to 'reliable, and cost-effective methods for both the production of nano scaled materials (powders, fibers, whiskers, rods

or fluids) and manufacturing of parts such as structures, devices, and systems' [<http://en.wikipedia.org/wiki/Manufacturing>; <http://www.nano.gov/nanotech-101/what/manufacturing>]. It should be noted that nano scale materials [one billionth or 10^{-9} of a meter] have been used for over a millennium. For this one of the two approaches can be used. They are 'bottom up' process starting from nano scaled materials or 'top down' process involving in smallest steps for high precision. It should be noted that the former leads to creation of products by building them up from atomic-and molecular-scale components, thus resulting in more time-consuming. On the other hand, the latter approach reduces large pieces of materials all the way down to the nano scale thus requiring larger amounts of materials leading to waste, if excess material is discarded and thus rendering this approach to be expensive. In the case of nanobiocomposites, the processing methods being used include solution intercalation, *in situ* intercalative polymerization, melt intercalation, solution casting, mixing of cellulose whiskers with surfactants followed by freeze-drying and then dispersing the mixture in some organic solvent followed by the preparation of gel and then extrusion [6,59].

Further, it may be noted that some of the attractions in the processing of these types 'green' composites include: (i) availability of reinforcements in suitable form, (ii) low mold shrinkage, (iii) reduced molding cycle time up to 30%, (iv) less abrasiveness for tooling unlike in synthetic fiber reinforced composites, (v) natural appearance, etc. Of course, selection of processing or fabrication method depends on the selected matrix-reinforcement systems chosen. More details on these can be seen in some of the references mentioned earlier [2,4,5]. Some of the systems studied in recent times include: starch (cassava, castor oil cake, corn, pea, sorghum), Polyhydroxy alkanates (PHA), Poly-3 hydroxyl butyrate (PHB), Poly lactic acid (PLA), L-Poly lactide acid (PLLA), with plant based reinforcements, both micro and nano sizes (coir, bamboo and its cellulosic crystals, banana, cellulose or its fibers obtained from the bark of cotton stalks cellulose and cellulose fibers from milkweed stem, disposable chopsticks, flax, kenaf, luffa cylindrica, sugar cane bagasse, wheat bran, bleached wood pulp, etc.). Even, the plant oil based matrices such as soya oil and mango puree-based edible films have also been used in the preparation of nano-bio-composites [19,26]. This is because of the limited commercial use of some of the edible films of fruits and vegetables due to their poor mechanical and gas barrier properties when compared to synthetic polymers [28]. These poor properties (including thermal properties) of such films have been overcome by the addition of some fillers such as nano fibers of cellulose or nano particles, which could improve all the properties along with the possibility of providing cost-price efficiency [60]. Besides, better reinforcing effects are provided by the nano sized reinforcements due to their high specific surface area resulted from their high aspect ratio [61,62].

It may also be noted that although there are some bio-polymers from synthetic sources, composites based on these cannot be included under 'green' composites, since these polymers are not renewable and therefore do not conform wholly to the concept of renewability and degradability.

More details are already reported in some of the reviews mentioned earlier on the processing aspects of biodegradable and 'green' composites [2,4,5,9,11,50]. Only mention of two methods is made here. The first one is for the micro composites, which is schematically shown in Figure 2a [25] and the other for nano bio-composites, shown in Figure 2b [63].



Morphology and Properties

It is well known that morphology (microstructure) and properties of any composite material and its product produced depend on the properties of matrix, dimension and amount of reinforcement and the processing conditions (method, applied pressure, temperature, etc). Further, properties of composites are also dictated by the properties and amount of compatibilizers or plasticizers, when they are used. Large number of articles including reviews and Chapters in text books has been published over the years concerning biodegradable polymers (various types of starches-cassava, corn, castor oil cake, pie, potato, rice, wheat, etc., polypoly-Lactic Acid (PLA), polyhydroxy alkanates (PHA), polyhydroxy butyrate (PHB), etc, and other natural polymers) covering many aspects of biodegradation and biodegradable polymers such as their availability, synthesis, structure properties, mechanism of degradation and applications. Most of these have been excellently covered in some recent reviews [4,5,11,27,40,44]. Therefore, a brief discussion of some systems on some specific properties and morphologies of some systems is presented here avoiding repetition. Accordingly, Table 1a lists some of the starch based matrix-reinforcement systems (both micro and nano) their processing methods and properties, while Table 1b and 1c list similar information for poly families [Poly-hydroxy alkanates (PHA), Poly-3 hydroxyl butyrate (PHB), Poly lactic acid (PLA), L-poly lactide acid (PLLA)] and other types of matrices respectively.

Among various bio polymers, starch is the most abundantly and readily available inexpensive natural polymer. It has its high strength and rigidity due to its cellulose origin making its structure linear and having the hydrogen bonding [2,64]. Properties of 'green' composites

depend on the type of starch (source) selected as matrix, the amount of reinforcement (type and aspect ratio) incorporated into it, and the plasticizer used (type and amount) besides the processing technique and the relative humidity of the room of preparation and testing of composites. This is evident from Figure 3, which shows the plots of ratios of tensile strength of 'green' composites of different starch matrices (corn, maize, potato, and wheat) and different types (Micro wincette fiber, ramie cellulose nanocrystallites, Cellunier F and wood) and amounts of fibers [65]. It can be seen from the figure that tensile strength of composites increase with increasing amount of fibers incorporated in to each matrix except for maize, where it initially increases, but later it decreases.

Unlike other starch materials, castor oil cake is an interesting raw material, since it contains not only the starch (13-24%), but also some fibrous material (~13) [24,66]. and therefore, it has become a potential agro-waste to prepare 'green' composites. Since this raw material is available in many countries of the world, it can be used either fully or as substitute for other starches using a plasticizer with or without additional reinforcements to prepare 'green' composites [22,25,46]. Of course, there are other natural polymeric materials that are used, which include plant oils such as soybean oil and plant oil based polyurethane as well as mango puree-based edible films [2,4,5].

From Table 1a, it can also be seen that amongst various starches based composites, cassava starch based composites exhibit better mechanical properties. Observed properties have been explained on the basis of fractographs obtained after mechanical testing of the composites. They present bonding between the matrix and reinforcements, nature of interface and also inter and intra molecular bonding. All these can be understood from Figure 4a-4d and Figures 5a-5f, which are the fractographs of various starch based matrices and their 'green' composites respectively. It may be noticed that fracture surface of most of the starches is very smooth (Figures 4a-4d), while this changes by the incorporation of fibers (Figures 5 a-5f). Further, it can also be seen from Figure 5, that there is good dispersion of the fibers (micro or nano) indicating a good interaction between the matrix and the reinforcements. In some cases, the reinforcements are coated [mostly fully covered] (Figure 5f), which enable better interface between the constituents resulting in good mechanical properties.

On the other hand, other 'green' type of polymeric materials range from annually renewable feedstocks such as lignocellulosic materials to those that ultimately degrade to benign by-products after their useful lifetime. Polylactides (PLA), the most versatile material among biodegradable polymeric materials belonging to the poly family, is one of a subset of thermoplastic polymers belonging to both types of feedstocks mentioned above. Its ease of availability from renewable agricultural sources along with inherent and comparable properties such as biodegradability, biocompatibility, high mechanical strength and Young's modulus comparable with those of polyethylene and polystyrene, has made this polymer a very attractive matrix for the development of 'green' composites. The properties mentioned above are due to the presence of asymmetric carbon atoms, which generate structural particularities leading the lactic acid-derived polymers as special compared to other polymers [4]. It is interesting to note incorporation of fibers in to some of these 'poly families' enhance their properties. For example,

Tantatherdtam et al. have reported increased Young's modulus and flexural modulus of polybutylene succinate (PBS)-cassava root fiber composites with increasing amount of the fiber, suggesting that the composites became more rigid and stiff with increasing fiber loading

Matrix system	Reinforcement	Processing	Characteristics	Ref
Starch + glycerol	Bamboo cellulosic crystals(BCC)	Film Casting	Increase in elongation at break with decreasing BCC content; High relaxation peak with significant quantity of BCC incorporation; Higher reinforcing efficiency for plasticized starch at the optimal 8% loading level plastic than at any other loading level; TS: 12.8 MPa & YM: 210.3 MPa; Increase in storage modulus with increasing BCC content; increase in $\tan \delta$ with temperature suggesting composites becoming more viscous with the increase in temperature; Reduction in water absorption.	[31]
Starch acetates	Cellulose fibers (10-30%)	Twin screw extruder/150-170°C/170-230 rpm	Loss of crystallinity of the matrix; Functional groups and chemical bonds retained; Significant changes in M.P.	[7]
Cassava starch+ glycerol	Oat or sugar cane fibers (5 and 10 g /100 g starch)	Single screw extruder	No significant effect of the expansion index, density and Water Absorption Index (WAI), Water Solubility Index (WSI) and color (to dark) changed.	[28]
Cassava starch + glycerol+ Potassium Sorbate	Wheat bran (1.5 mg, 13.5 mg and 27.1 mg/g of matrix)	Casting	No change in density of the materials, Increased storage modulus and hardening with constant, but high deformation to rupture (beyond 70%). Decrease in loss tangent, moisture content with increase in bran contentà improvement in water vapor barrier properties. (Decrease water vapor permeability).	[22]
Cassava Starch+ glycerol (Commercial & Recovered)	Banana/Sugar cane bagasse	Thermo-molding	Not much variation in crystallinity index, but good thermal stability in composites with both types of glycerol; dependence of tensile properties on the processing methods; Increase in YM (by 186%, 294% and 201%), YS (129%, 141% and 133%) and decrease in % elongation (about 5-7 fold) and almost constant UTS over the matrix with increasing banana fiber content (20%, 25% and 35%, respectively); higher tensile properties in starch-25 wt.% bagasse composite than those of starch-30 wt.% banana composites. Improvements of YM, UTS, YS and % elongation values in starch-crude glycerine-25% bagasse fiber composites were about 59%, 41% 67% and 11%, respectively.	[32]
Cassava Starch+ glycerol	Coir fibers (5-30 wt. %)	Thermo-molding	Increase in strength properties with a higher amount of coir fiber incorporation as well as with the thermal treatment; TS: 3.24 MPa, YM: 59.81 MPa and maximum load: 112.68 N for Treated matrix; TS: 1.56 MPa, YM: 14.56 MPa and maximum load: 50.7768 N for the untreated matrix; TS:~373.5 MPa and YM:~176MPa for treated matrix composites; Decrease in water uptake, moisture absorption and linear swelling of TPS matrix with increasing coir fiber content; increased relative crystallinity from 39% to 62%; enhanced thermal stability; increasing storage modulus (from 2027 MPa to 3215 MPa, higher glass transition temperature and lower damping.	[35,54]
Plasticized Maize starch	Nanofibers from wheat straw	High shear mixer	Linear increase in both dynamic (YM, YS and TS) and static (storage modulus) with increasing nano fiber content in the composite with an overall improvement of ~ 195% over the TPS matrix; Highest YM of ~ 220 MPa and highest, YS (6.5MPa) at 15% fiber content, significant decrease in storage modulus with temperature for both TPS & its nanocomposites; Decreased sensitivity to moisture.	[29]
Castor bean oil cake + crude glycerin	Banana/Sugar cane bagasse fibers	Thermo-molding	TS of 25% banana and 20% bagasse fiber composites higher than those of corn starch composites	[25]
Castor bean oil cake + glycerol (15-20%)	Fibers in Castor bean oil cake	Thermo-molding	TS: 4.62-5.5 MPa; YM: 192.27-214.78MPa; Water Absorption: 16. -17.6%; Swelling thickness: ~14-15%	[46]
Castor bean oil cake + glycerol	Nano cellulose of raft wood	Thermo-molding	FS: 13.11MPa and FM: 1633MPa for 10 NC fiber composite compared to 12.27MPa and 1253.60 MPa for Matrix	[46]
Castor bean oil cake + crude glycerin	Sugarcane Bagasse (5-35%)	Thermo-molding	Highest YM: 64.26 MPa and highest TS: 0.80 MPa for 15 wt. % fiber containing composite, prepared with lowest load (4tons), and at highest temperature (130°C); Increasing temperature and/or pressureà reduction of water absorption; No significant effect of diameter (0.25- 0.85mm) or length (10-20mm) of sugarcane bagasse fibers; TS showed decreasing trend in both cases; increasing thermal stability compared to that of the plasticized polymer matrix with same applied load and processing temperature (4 ton/110°C) ability in both the 15% and 5% fiber content.	[24]

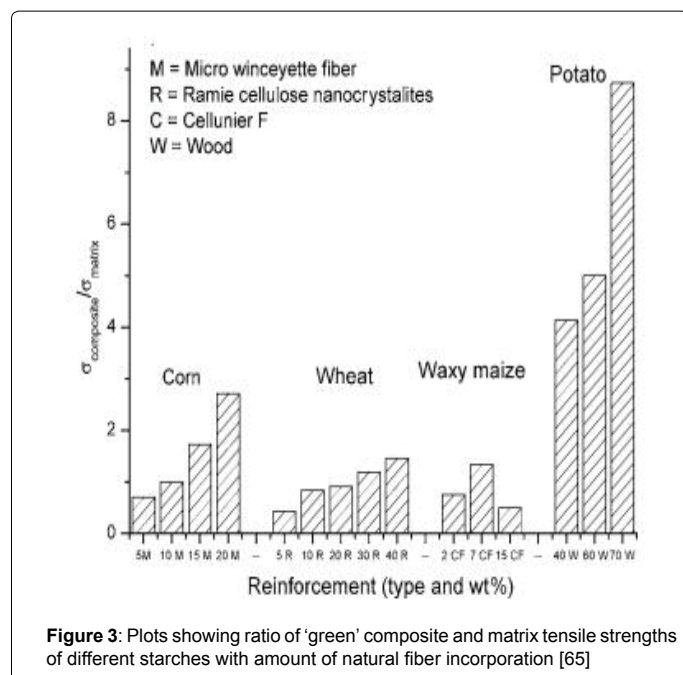
TS: Tensile Strength; YM: Young's Modulus; FS: Flexural Strength; FN: Flexural Modulus; IS: Impact Strength; SS: Shear Strength; Tg: Glass transition temperature.

Table 1(a): Starch Matrices-Reinforcement-Processing and Characteristics of 'Green' Composites

Matrix system	Reinforcement	Processing	Characteristics	Ref
Poly Lactic Acid (PLA)	Recycled disposable chopsticks fibers	Melt-mixing	Increase in Tg of PLA; Early start of degradation process compared to that of PLA matrix; higher char yield; Markedly increased TS with the fiber content reaching the max. 115 MPa for 40% fiber content.	[15]
Poly Lactic Acid (PLA) + Polyethylene glycol (PEG)	Cellulose fibrils of Bleached wood pulp	Solvent Casting	TS of PLA + Nano fibrils 30 MPa with 2.5% elongation, lower than that of pure PLA; 28.2% increase in TS and 25% in Elongation for PLA + PEG + nano fibrils compared with pure PLA, by 56.7% and 60% compared with the PLA+ Nano fibrils of cellulose; Improved intermolecular interaction shown by FTIR study due to the existence of intermolecular hydrogen bonding among PLA, PEG, and cellulose nano fibrils.	[30]
Poly(lactic acid (PLA), L-poly(lactide acid (PLLA), poly 3-hydroxybutyrate (PHB), poly-caprolactone and starch thermoplastic, poly butylene succinate (PBS) and poly butylene adipate-co-terephthalate (PBAT)	Flax fibers	Film Stacking	Higher TS and YM of PLLA and PLA flax composites than those of similar PP/flax fiber composites. Comparable specific TS and YM of flax fiber/PLLA composite with those of glass fiber- polyester composites. YM of PLLA-30% Flax: 9519 MPa compared to 3321 MPa for the matrix; Strain to failure: 1.5% from 2.4%; Critical strain energy: 705-1336 Gc Jm-2 [Initiation & Propagation] compared to 298-282 Gc Jm-2 of glass-polyester-Balsa sandwich composite.	[12]
L-poly(lactide acid (PLLA)	Flax fiber mats (28.5%) Sand witch of Flax mat and Balsa mat	Vacuum Bag Moulding	Increase in FS and SS with increasing temp. (180-200oC) and increase with time (45-60 min) of manufacture; YM: 8882 MPa, TS: 65.2MPa and % Elong ¹ 1.3, Stiffness: 23.9×10 ⁻⁶ Nm-2; TS: 70.5±7.2MPa.	[41,42]
PLA	Kenaf fibers		Unidirectional composites materials; TS, FS and YM of the composites increased linearly up to 50% with the highest TS of 223 MPa, FS: 254 MPa for 70% fiber content.	[17]
Poly (Lactic Acid) (PLA), Poly (Butylene Succinate) (PBS)	Bamboo fiber (BF)	Compression Moulding	Improved Tensile properties, water resistance, and interfacial adhesion of both PLA/BF and PBS/BF composites with the addition of lysine-based diisocyanate (LDI); Increased crystallization temperature and decreased enthalpy, heat of fusion in both composites with increasing LDI content; No significant change in melting temperature; Lower thermal degradation temperature of both composites than those of pure polymer matrix with LDI containing composites showing higher degradation temperature than those without LDI; Faster decomposition by enzymes, but delayed biodegradation of both composites due to the addition of LDI.	[8]
Poly(Lactic Acid) (PLA)	Cotton, hemp, kenaf and man-made cellulose fibres (Lyocell) (40%) and mixtures of these	Compression Moulding	Very high TS and YM in kenaf and hemp/PLA composites; Good IS in cotton/PLA composites; high TS, YM and IS in Lyocell/PLA composites suggesting all these composites could be applied in various fields, each meeting different requirements.	[23]
Mango puree-based edible films	Cellulose nano fibers (CNF) (0- 36 g/100 g)	Homogenize the Mixture at 6500 rpm for 30min Film Casting Dry for 16 h at 22°C and 42% RH	TS: from 4.06- 8.09 MPa; YM: 19.85- 322.05 MPa; % Elong: 44.07-31.54, although without much change in it up to CNF concentrations up to 10 g/100 g. Water vapor permeability: 2.66-1.67 g. mm/kPa.h.m2 à improved water vapor barrier; low, but significant effect on Tg [-10.63 to -6.04oC].	[21]

TS: Tensile Strength; YM: Young's Modulus; FS: Flexural Strength; FN: Flexural Modulus; IS: Impact Strength; SS: Shear Strength; Tg: Glass transition temperature;

Table 1(b): Poly Matrices-Reinforcement-Processing and Characteristics of 'Green' Composites

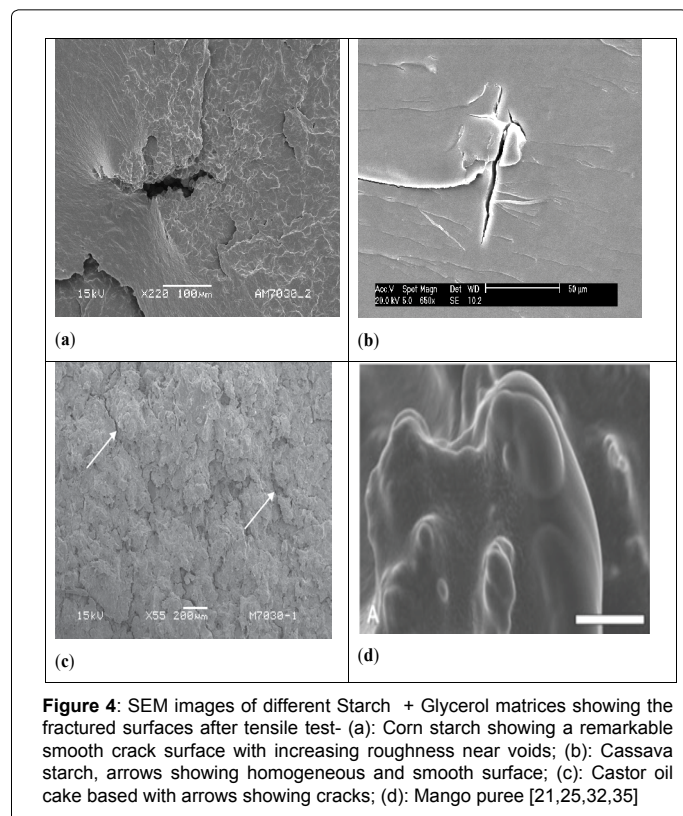


of compatibilizer such as PEG [30] or surface treatment of fibers by coupling agents such as silane treatment on disposable chopsticks [15] have been attempted. This is similar to the use of maleic anhydride compatibilizer with polypropylene (PP) in the preparation of PP-based composites or use of coupling agents such as silane on lignocellulosic fibers [2]. In these composites, improvement in mechanical properties compared to those of both the matrix and matrix + nano fibrils, has been observed (Table 1b). This improvement is attributed to good distribution of nano fibrils. There are some recent reviews on PLA based green composites [23,44]. One of them gives a comparison of various mechanical properties (TS, YM, IS) of PLA based composites reinforced with different bio fibers such as coir, cotton, flax, hemp, etc, processed by two different processing techniques [23], while the other is much more exhaustive involving more number of fibers and processing techniques [41]. Besides, a comparison of calculated and experimental values of various mechanical properties is also made in the former, while the latter review presents most of the processing methods used in the development of these green composites. In the first review, based on SEM studies, the results of mechanical properties have been discussed in terms of nature of bonding between various reinforcements and the matrix as well as the processing technique used. Possible use of these composites for different technical applications, each suiting specific requirements such as in automotive sector is also discussed based on the results of various mechanical properties.

Similar to the starch based composites, incorporation of bio based fibers (micro or nano) into 'Poly family' polymers, such as PLA affect the morphology of its surface. This is evident from Figure 6, which shows the fracture surfaces of PLA (Matrix), PLA+ Cellulose Nano fibrils and PLA+PEG+ Cellulose Nano fibrils as observed under the scanning electron microscope [30]. While the fracture surface of PLA matrix seems to be a smooth fragile fracture (Figure 6a), surface of its nanocomposite without compatibilizer shows uneven fracture surface having some irregular protusions and holes (Figure 6b) and the one with compatibilizer shows more uneven, more holes and thread-like structures (Figure 6c). Also, similar to starch base composites, PEG in this composite covers the surface of nano fibrils. More uneven surface caused by the adhesive force at the interface is attributed to the observed highest strength properties of this composite.

Careful reading of these tables also suggests proper selection of matrix-reinforcement system (both micro and nano fibers) with appropriate processing would result in optimal properties for any intended application in various areas such as building and construction, transportation, food science, nutrition and packaging, biomedical engineering, medical field, etc. It is also pertinent to note a great revolution in materials science has been observed since the emergence of composite materials (both micro and nano types) in recent times underlining the importance particularly of 'green'/ biodegradable polymer matrix in the development and use of composite materials in all areas of interest to mankind. Some examples of these applications are mentioned in the next Section.

Recognizing the importance of weight gains, sandwich composites including bio-based ones have also been studied for their structure and properties keeping in mind weight critical applications designed for stiffness in sectors such as aerospace, transport including ships and boats [41,42,67-72]. It is well known that a sandwich-structured composite is one of the special classes of composite materials, which gives high stiffness to weight and strength to weight ratio. This is fabricated by attaching two thin but stiff skins [Eg: Natural fibers such as Basalt fiber or Recycled paper] to a lightweight, but thick core [Eg:



[18]. On the other hand, tensile, flexural and impact strength values of the PBS composites decreased with different amounts of fibers with the former (tensile and flexural strengths) decreasing with increasing fiber loads, whereas the latter (impact strength) showed a relatively small change with the fiber loading. Further, to overcome the interface problem due to poor compatibility of some hydrophobic natural polymers such as PLA and hydrophilic cellulose nanofibers, addition

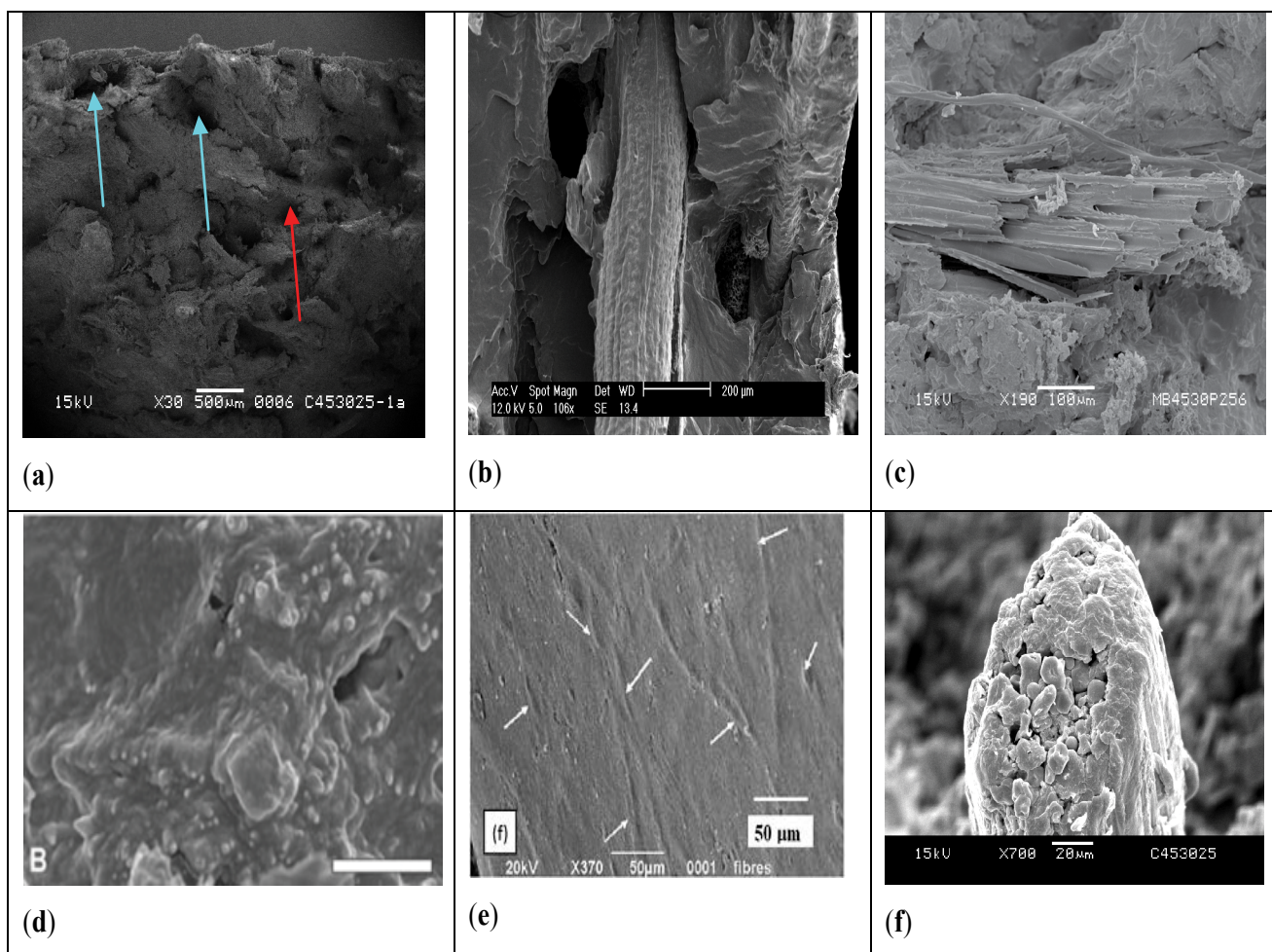


Figure 5: Fractographs of Starch+ Glycerin based 'green' Composites-(a): 45% Corn Starch + 25% Bagasse fiber composite shows high rough fracture surface with lot of small size fibers pull-outs (blue arrow) and micro cavities and pulled out fibers (red arrow); (b): Cassava Starch + coir fiber showing the interface with better fiber-matrix adhesion in the composite; (c): Castor bean oil cake + 25% banana fiber showing fractured fiber embedded in the matrix; (d): Mango puree + 36% (w/w) CNF (B). [Scale bar = 1 μ m]; (e): Maize starch + 10% cellulose nano fibrils of wheat straw showing fiber bundles embedded in the matrix (shown by arrows) without any fiber pull-out or debonding and (f): Coating of starch on the bagasse fiber surface in the composite [21,25,29,32,35]

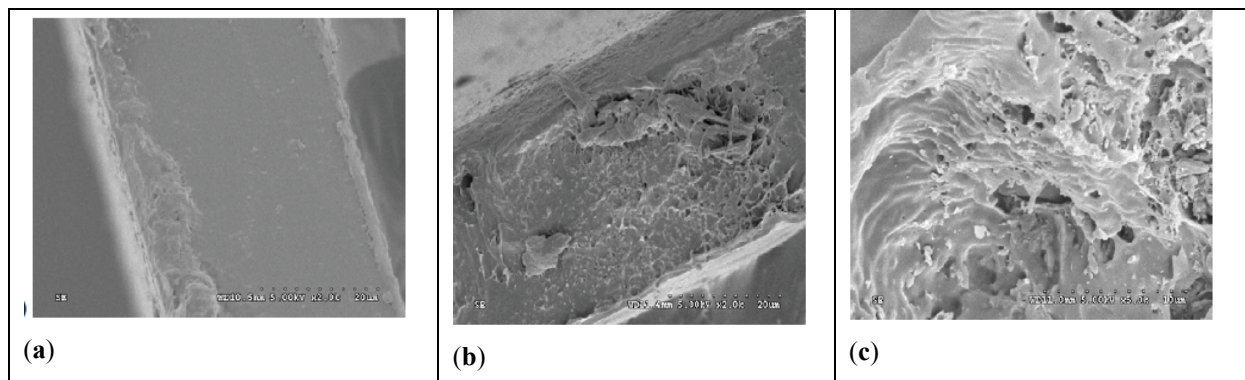


Figure 6: SEM Photographs of fracture surfaces of PLA (Matrix), PLA+ Cellulose Nano fibrils and PLA+PEG+ Cellulose Nano fibrils [30]

synthetic or natural fiber such as glass/carbon, cork, wood, etc]. Also, normally, many sandwich structures use synthetic polymer foams or honeycombs, or other synthetic material. Instead of synthetic core, bio based core materials such as cork or wood can also be used, which are entirely renewable resources and may be partly recyclable as well as easily composted. One example of 'green' sandwich composites studied is a composite facing with wood-based cores in view of the attraction of the completely bio-sourced materials such as waste management and their compostability at the end of their service life, in addition to them being partially recyclable [41]. In the case of sandwich composites, the interface properties and changes in the global sandwich response are reported to be affected by the the processing temperature [41,42]. This is illustrated in Table 1b, which is corroborated by the fractographs shown in Figure 7a-7c.

This figure shows the failure mode of long beam bio-sandwich specimens of PLLA-Flax-Balsa green composite manufactured at temperatures of 180, 190 and 200°C. It can be seen that the failure modes are similar when panels are manufactured at 180 and 190°C (Figure 7a), along with delamination in the lower facing (Figure 7b), and shear cracking of core and transverse crushing of the upper face of the balsa cells (Figure 7d). Separation of the upper facing can also be seen. On the other hand, failure is caused by debonding between skins and core (Figure 7a) is seen for the bio-sandwich manufactured at 200°C. The authors have observed some polymer remaining on the balsa (Figure 7c). Degradation of such composites and causes for the this have also been discussed [42].

For more details on structure and properties of 'green' or biodegradable polymers and their composites based on renewable resources, authors are suggested to read some of the references [2,4,5,11,16,22,26,36,37,44] mentioned in this paper.

Applications

Recognizing (i) the attributes of 'green' composites, (ii) continued research and (iii) growing interest in the development of these composites, attempts have been made to prepare some products with micro composites for different sectors [2]. These include building and housing sectors including hurricane resistant housing, infrastructure, automotive sector (Eg. Door panels, instrument panels, armrests, etc), textile (geotextiles and nonwoven textiles), entertainment accessories (archery bows, golf clubs and boat hulls), etc. Other uses of green composites include new low dielectric constant material suited to electronics applications based on hollow keratin fibers and chemically modified soybean oil [73]. Some of the proposed possible fields of application of the green composite systems include: transport (spare tire covers and circuit boards based on kenaf fiber-reinforced PLA matrix composites) [74], automotive and electronic industry (PLA/cordenka composite) [75] and different fields of human activity (furniture, suitcases, grinding discs, safety helmets using a variety of natural and man-made cellulose fiber-reinforced PLA composites) [23].

It is reported [2] that continued technical innovations, identification of new applications, persistent political and environmental pressures along with investments in new methods for fiber harvesting and processing of bio-fibers, phenomenal growth in market can be expected for the 'green' composites in the coming years.

On the other hand, nano bio (green) composites seemed to have overtaken their micro composites in the development, production and usage aspects. Some of the products developed or planned for development include automotive parts (mirror housings, door handles and panels, trunk liners, roofs, upholstery, engine covers) durable load bearing parts and building blocks in cars based on

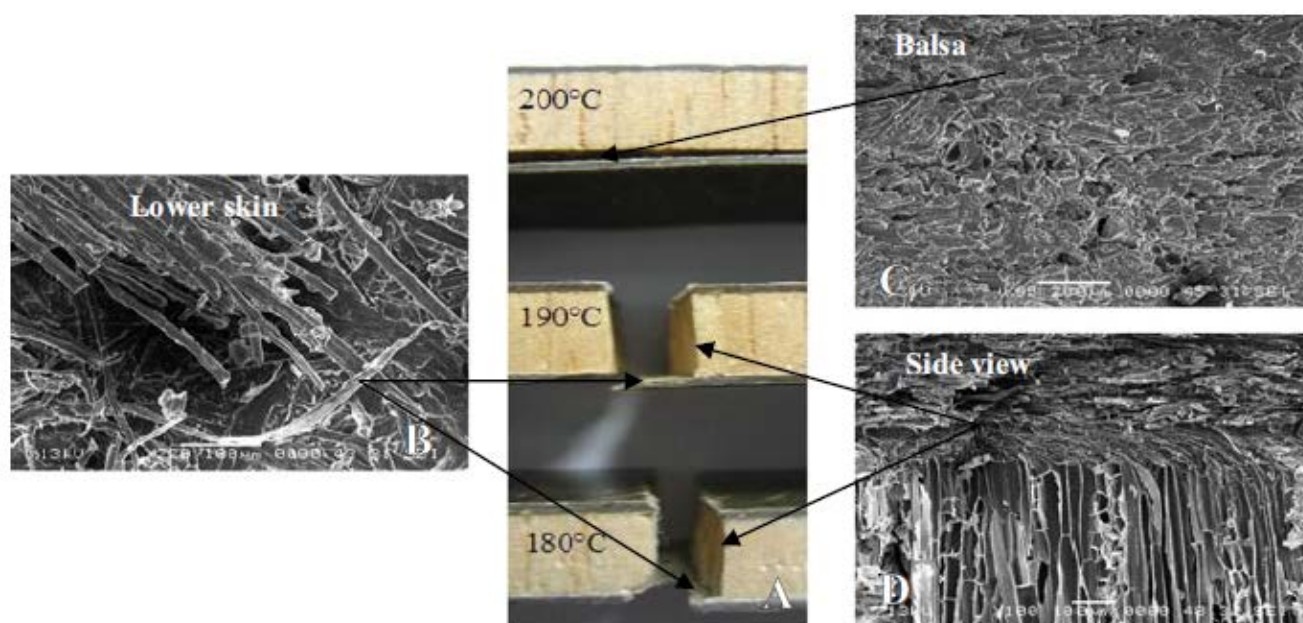


Figure 7: Failure mode of long beam bio-sandwich specimens for different manufacturing temperatures- (A): Overall view of damage versus temperature; (B): Lower skin of bio-sandwich formed at 180 and 190°C; (C): Top of balsa in bio-sandwich formed at 200°C and (D): Edge of bio-sandwich formed at 180 and 190°C [41]

Matrix system	Reinforcement	Processing	Characteristics	Ref
Mango puree-based edible films	Cellulose nano fibers (CNF) (0- 36 g/100 g)	Homogenize the Mixture at 6500 rpm for 30 min Film Castingà Dry for 16 h at 22°C and 42% RH	TS: from 4.06-8.09 MPa; YM: 19.85-322.05 MPa; % Elong: 44.07-31.54, although without much change in it up to CNF concentrations up to 10 g/100 g. Water vapor permeability: 2.66-1.67 g. mm/kPa.h.m2 à improved water vapor barrier; low, but significant effect on Tg [-10.63 to -6.04oC].	[21]
Soy Protein	Micro/nano-sized bamboo fibrils	Film making/Hot pressing	High strength and stiffness composites and nanocomposites. Proportional increase in FM with the amount of 1,1,1-tris(p-hydroxyphenyl)ethane triglycidyl ether (THPE-GE) as well as with increasing amount of fiber contents lower than 10 wt.%, but decrease thereafter; YM increased with both increasing amount of THPE-GE, but it increased with the fiber content 13.5 wt.%, (Max), where after it decreased.	[20]
Epoxidized Soya bean oil	Flax fiber and organo-clay reinforcement		No significant effect of the expansion index, density and Water Absorption Index (WAI), Water Solubility Index (WSI) and color (to dark) changed.	[14]

TS: Tensile Strength; YM: Young's Modulus; FS: Flexural Strength; FN: Flexural Modulus; IS: Impact Strength; SS: Shear Strength; Tg: Glass transition temperature

Table 1(c): Other Matrices-Reinforcement-Processing and Characteristics of 'Green' Composites [2]

cellulose nano fibers [Personal discussions with Prof. Mohini Saini, University of Toronto, Canada], impellers and blades for vacuum cleaners, power tool housings and covers for portable electronic equipment (Eg. Mobile phones [76,77]. Some of the others that are also being planned include: electronic devices [78] (E.g.: capacitors, smart paper as sensors, communication devices, and paper-based displays made from wood lignocellulose microfibers and anionic poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), paper batteries for Micro-Electro-Mechanical Systems (MEMS)) [79], food and pharmaceutical packaging materials including paperboards for fruit juice and dairy based on cellulosic nano fibers (in view of their outstanding performance as oxygen and water barriers in the polymer matrices) [4,80], ID tags printed on cellulosic paper possess impressive computer power and RF capability, and inexpensive ID tags printed on cellulosic paper (for applications to track commercial products remotely, detect counterfeit drugs and protect product integrity) [77]. Similarly, due to the biocompatibility of PLA+.PEG+nano fibers covering the surface of nano fibrils, potential use of this PLA based nano composites is reported to be in tissue engineering implant (in clinical applications) [30]. In general, in view of their light weight, the 'green' nano composites would have applications in strategic sectors such as aerospace defence sectors.

Concluding Remarks

'Green' materials in general and composites in particular, covering both the biodegradable micro and nano composites, have been known since long time. This is evident from the strong Great Wall of China during 121 B.C. to the consumer products such as lightweight nanotechnology-enabled automobile bumpers (which resist denting and scratching), golf balls (that fly straighter), tennis rackets (that are stiffer), wrinkle and stain-resistant clothing, deep-penetrating therapeutic cosmetics and improved displays for televisions, cell phones, and digital cameras, etc., during 1999 and early 2000's. Importance of such materials is underlined due to the decreasing non-renewable sources and their increasing costs, growing concern and regulatory demands for clean environment along with the thrust on increasing use of renewable resources. In addition, their unique characteristics such as biocompatibility, biodegradability and even exhibiting functional properties have driven scientists, engineers and technologists in academic and industrial research environments to transform the field of sustainable and green polymers and materials. Number of bio resources have been identified and used as matrix and reinforcements (both micro and nano size); preparation/manufacturing processes including nanomanufacturing to develop 'green' composites (both

micro and nano type) have been developed; structure properties of thus developed materials are reported and many products produced, being used and future applications have been projected for these materials. However, considering some of the limitations of these new materials mainly in respect of ductility, processability and dimensional stability, there is need to overcome these for future development on improved properties and multi-functionality of produced 'green' composites in view of their safe disposal through decomposing into CO₂, humus, etc., which may again produce lignocellulosic materials by photosynthesis. Recognizing the above facts, the following should be considered, some of which may be future perspectives:

a. Focus on use of modeling and simulation as well as Artificial Neural Network (ANN) to correlate various processing parameters (dimensions and amount of reinforcements, duration and temperature for processing without affecting the inherent properties of constituent materials) and properties obtained with a view to reduce the number of experiments to arrive at proper composite systems with suitable processing parameters to produce products for various intended applications.

b. Since the properties of nano bio-fibers depend on the source from which they are produced, probably, research on spinning of different nano bio-fibers either individually or hybridizing with others should be attempted.

c. One of the future processing possibilities of 'green' composites could be biomimetic processing approaches in view of their great potential in the development of new high-performance materials with low environmental impact [81], it being environmentally friendly and energy-efficient [82]. It is well known that biomimetics is a field of science that looks into biological structures and processes for their use as models for the development of artificial systems such as composites including metal and ceramic matrices as well as polymeric matrix based 'green' and nano composites and even textiles. In the case of development of diverse nanocomposites consisting of different combinations of nano materials (fibers or particles or platelets or tubes), and polymer matrices at various volume fractions, the self-assembly process, a simple approach belonging to biomimetic process of making nanocomposites, can be adapted. In fact, there have been many published reviews and papers since nintees dealing with various aspects of processing of such materials based on biomimetic engineering [81-88]. Some classical examples of natural high-performance composites abalone shells, bone and enamel with matrix proteins [89,90], high stiffness cactus spines, with their and the tunics of sea peaches composed of cellulose, proteins and mucopolysaccharides [91]. Even wood and

other plant based fibers can also be considered as natural, but a complex and highly sophisticated composites, since cellulose microfibrils in these materials are embedded in lignin matrix (self-assembly process). These can provide some insight along with inspiration regarding the design and fabrication of light weight composite materials including 'green' composites with unique properties [81]. This new approach to making biomimetic nanocomposites is also demonstrated by the exfoliation of graphite into a matrix of genetically engineered proteins having two well-defined binding blocks (diblock proteins) and native nano-fibrillated cellulose [87] and also in the case of textiles [84,85]. It is reported that new insights for the development of high performing materials such as fibrous composite materials including 'green' ones and technical textiles is provided by systematic bio-mimetic approach whereby biological structures, processes, and functionality could be comprehended thus providing a brilliant opportunity for transferring ideas inspired by biological models whereby production processes comparable to those used by nature could be used for the development of such materials [84].

d. Following the success of research on spinning of different nano bio-fibers either individually or hybridizing with others, incorporation of these into suitable bio-polymer may produce nano bio-composites as possible superior structural components (lighter than their micro counterparts) or for use in different areas such as biomedical, electrical and optical as a component for various functional devices.

e. When focus will be on 'green' materials with nano sizes, social implications of this technology dealing with both nano sized materials and their bio-composites should be properly attended to.

It is hoped with all the above new dimensions for green materials comprising of biopolymers and their composites would emerge in future considering them as a cost-effective alternative to wood and petro-based plastic products. However, larger acceptance of these new generation of materials by the society is still expected, while the demand for agricultural products will increase, which may pave way for environmental friendly and sustainable future.

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