

Review

## A Review on Potentiality of Nano Filler/Natural Fiber Filled Polymer Hybrid Composites

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**Abstract:** The increasing demand for greener and biodegradable materials leading to the satisfaction of society requires a compelling towards the advancement of nano-materials science. The polymeric matrix materials with suitable and proper filler, better filler/matrix interaction together with advanced and new methods or approaches are able to develop polymeric composites which shows great prospective applications in constructions and buildings, automotive, aerospace and packaging industries. The biodegradability of the natural fibers is considered as the most important and interesting aspects of their utilization in polymeric materials. Nanocomposite shows considerable applications in different fields because of larger surface area, and greater aspect ratio, with fascinating properties. Being environmentally friendly, applications of nanocomposites offer new technology and business opportunities for several sectors, such as aerospace, automotive, electronics, and biotechnology industries. Hybrid bio-based composites that exploit the synergy between natural fibers in a nano-reinforced bio-based polymer can lead to improved properties along with maintaining environmental appeal. This review article intended to present information about diverse classes of natural fibers, nanofiller, cellulosic fiber based composite, nanocomposite, and natural fiber/nanofiller-based hybrid composite with specific concern to their applications. It will also provide summary of the emerging new

aspects of nanotechnology for development of hybrid composites for the sustainable and greener environment.

**Keywords:** nanofillers; natural fibers; polymers; nanocomposites; hybrid composites

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## 1. Introduction

Huge biomass, forestry and agriculture-based residues existing in nature are extensively utilized as a potential resource of materials for renewable energy in different sectors of industry. Many plants, crops and pods from agricultural sources are being regarded as an important source of viable natural fillers raw materials for polymer composite industries. Research, development, and progress of these bio-based materials might straightly support eco-system, leading to socio-economic development for cultivation, farming, and remote or rural areas in many of the developing and under developed countries as well. From a long time, natural or lignocellulosic fibers have been extensively being used in the development and preparation of composites. Owing to increase in the concept of ecological safety and utilization of renewable materials towards greener society, the application of natural fibers in the industries as bio-filler/reinforcement materials in composites are considerably improved [1]. Natural fibers have attracted the interest of researchers, material scientists, and industries, owing to their specific advantages as compared to conventional or synthetic fibers from the past [2]. The attractive and possible advantages, such as reduced tool wear, low cost, and low density per unit volume and acceptable specific strength, along with their sustainable renewable and degradable features are some of the important properties of the natural fibers, which make them suitable to use as filler in polymer composites. Large and wide varieties of natural fibers that are being applied as fillers or reinforcement are well recognized. Synthetic fibers, such as carbon fibers and glass fibers, create severe ecological, and health hazard problems for the workers employed in manufacturing of their corresponding composites as compared to composites derived from natural fibers [2].

Natural fiber shows comparatively poor fiber/matrix interactions, water resistance, and relatively lower durability. The weaker interfacial or adhesion bonds between highly hydrophilic natural fibers and hydrophobic, non-polar organophilic polymer matrix, leads to considerable decrease in the properties of the composites and, thus, significantly obstructs their industrial utilization and production. However, several approaches and schemes have been established to supplement this deficiency in compatibility, including the introduction of coupling agents and/or various surface modification techniques [3]. The surface of the natural fibers can be modified and this can be achieved by physical, mechanical, and/or chemical means. For any composite, the circumstances for substantial reinforcement and virtuous properties are the homogeneous distribution of the reinforcing component, orientation, good adhesion, and relatively high aspect ratio.

Nano-particles are presently considered as a high-potential filler materials for the improvement of mechanical and physical properties of polymer composites [4]. As the nano scale fillers are usually free of defects, hence, their applications in the field of polymer composite area setup, new trends of prospect to overwhelm the restrictions of traditional/conventional micrometer scale. High matrix-filler interfacial area results because of uniform and homogeneous dispersion of nanoparticles are

responsible for changing relaxation behavior, as well in ensuing the mechanical, molecular mobility, and thermal properties [5,6]. Generally, nano sized filler present in the minor zone whereas only few of the micro particles participate in the plastic zone deformation. This provides a way for the nanofillers to improve fracture and mechanical properties of the matrix having brittle property. Nanofillers, which possess greater aspect ratio (ratio of largest to smallest dimension) are of considerable interest, and, thus, show better reinforcement for the nanocomposites production [5]. Nanofillers are generally incorporated on a weight basis for the nanocomposite development [7]. The composite properties are greatly influenced by the specific surface area of nano fillers, which shows uninterrupted influence.

Nano fillers could be belongs to organic and inorganic in nature. The particles like silica ( $\text{SiO}_2$ ), titanium dioxide ( $\text{TiO}_2$ ), calcium carbonate ( $\text{CaCO}_3$ ), or polyhedral oligomeric silsesquioxane (POSS), *etc.*, are inorganic filler. However, the filler, such as coir nanofiller, carbon black and cellulosic nanofiller, and many others are derived organically and naturally represent organic nanfillers.

A perfect substitutes to traditional or conventional construction and buildings materials are the fiber reinforced polymer (FRP) composites due to a number of factors, including: higher strength and stiffness with reference to specific gravity; better resistance to corrosion, fire, acids, and natural hazardous environments; no conductivity and non-toxicity; longer service life and lower life-cycle costs; and higher fatigue strength and impact energy absorption capacity [8]. When natural FRPs are used to prepare construction or building modules, then, under developed or developing countries, with rural regions, will tend to forces the cultivation of required manufacturing crops and this would be empowering to address their own housing, poverty and financial issues without any outsider support [9]. From past few years virtually, everything became “nano”, even materials, which have been around for more than a hundred years, like carbon black, which have been extensively used as the reinforcement or fillers in rubbers. The general idea of nanocomposites is based on the concept of creating a very large interface between the nanosized-building blocks and the polymer matrix. Very often, the homogeneous distribution of the nanosized particles is problematic [7]. Nanocomposites, a high-performance material, exhibit unusual properties, combinations, and unique design possibilities [10]. Aggregation phenomena is a major subject in composites having spherical nanoparticles [7]. Traditional particulate-filled micro-composites are somewhat different from nanocomposites as their configuration/arrangement is often less complicated and the interactions results are more well defined. Natural fiber-reinforced composites and nanocomposites are more environmentally friendly, hence, more frequently applied to military applications, building and construction industries (partition boards, ceiling paneling), transportation (automobiles, railway coaches, aerospace packaging, consumer products), *etc.* [11].

Hybrid composite developed by various researchers, by combining natural fibers/natural fiber and natural fibers/synthetic fibers with epoxy, polyester, phenolic, poly vinyl ester, poly urethane resins, *etc.*, are well established [2,12]. The environmental awareness attracted researchers to develop new composites with addition of more than one reinforcement from natural resources, such as natural fiber/natural fiber or natural fiber/nanofiller from organic sources as an alternative to synthetic fibers [13]. Hybridization involving the combination of nanofiller and natural fiber in the matrix results reduction of water absorption properties and increased in mechanical properties [14]. Several research works depicts all these facts. The mechanical and thermal properties of rice husk flour/high density polyethylene composites get improved by addition of small amount of nanoclay [15]. Mechanical and tribological performance of the date palm fiber/epoxy composites get enhanced by addition of graphite

filler but high content of the graphite deteriorates the mechanical properties [16]. Natural fiber/nanofiller-based hybrid composites can be utilized in building and construction materials, transportation (automobiles, railway coaches, aerospace packaging, consumer products, *etc.*, and also could be possible to produce acoustic insulator and extremely thermally stable materials.

## 2. Lignocellulosic Fibers

### 2.1. Source, and Classification of Lignocellulosic Fibers

Lignocellulosic fibers are natural fibers. Natural fibers are the most copious and renewable bio-based materials source in nature [17]. Some of the important aspects of biofibers, such as their species and origin, are listed in Table 1. Natural fibers are primarily based on their origins, either coming from plants, animals, or minerals fibers. All plant fibers are composed of cellulose, while animal fibers consist of proteins (hair, silk, and wool) [18]. The natural fibers are classified according to their origin or botanical type [19]. Complete classification of the various natural fibers is shown in Figure 1 [2]. Lignocellulosic fibers have been being used as reinforcing or filling materials for the past 3000 years, in association with polymeric materials. Biofibers are used for composites because of their low cost, ease of separation, lower density, higher toughness, enhanced energy recovery, reduced dermal, respiratory irritation, and significant biodegradability [20]. The stiffness and strength are provided by the natural fibers to the composites, also they are easily recyclable, and moreover, bio fibers will not be fractured when processing over sharp curvatures, unlike brittle fibers, such as glass. In terms of strength per weight of the material biofibers also compete perfectly when compared with conventional or traditional fibers, such as mica and glass, that are generally used for composites [21]. Natural fibers carbon dioxide neutrality is particularly attractive. Natural-fiber-based packaging materials possess various benefits over synthetic packaging materials, such as stiffness *vs.* recyclability and weight ratio [22].

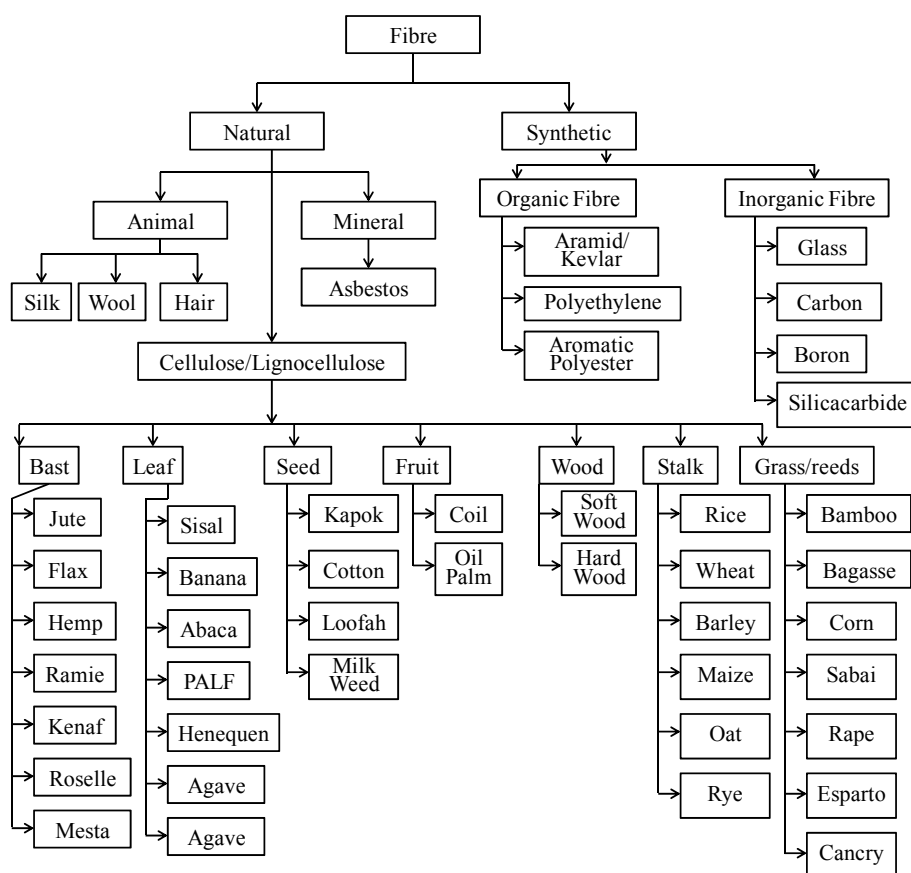
**Table 1.** List of important biofibers. Reprinted with permission from Elsevier, 2008 [18].

Fiber Source	Species	Origin
Abaca	<i>Musa textilis</i>	Leaf
Bagasse	–	Grass
Bamboo	(>1250 species)	Grass
Banana	<i>Musa indica</i>	Leaf
Broom root	<i>Muhlenbergiamacroua</i>	Root
Cantala	<i>Agave cantala</i>	Leaf
Caroa	<i>Neoglaziovia variegata</i>	Leaf
China jute	<i>Abutilon theophrasti</i>	Stem
Coir	<i>Cocosnucifera</i>	Fruit
Cotton	<i>Gossypium sp.</i>	Seed
Curaua	<i>Ananaserectifolius</i>	Leaf
Date Palm	<i>Phoenix Dactylifera</i>	Leaf
Flax	<i>Linumusitatissimum</i>	Stem
Hemp	<i>Cannabis sativa</i>	Stem
Kapok	<i>Ceibapentranda</i>	Fruit
Kenaf	<i>Hibiscus cannabinus</i>	Stem
Oil Palm	<i>Elaeisguineensis</i>	Fruit

Table 1. Cont.

Fiber Source	Species	Origin
Piassava	Attaleafunifera	Leaf
Pineapple	Ananuscomosus	Leaf
Sisal	Agave sisilana	Leaf
Straw (Cereal)	—	Stalk
Sun hemp	Crorolariajuncea	Stem
Cadillo/urena	Urenalobata	Stem
Wood	(>10,000 species)	Stem

**Figure 1.** Classification of natural and synthetic fibers. Reprinted with permission from Elsevier, 2011 [2].



## 2.2. Chemical Compositions and Properties of Natural Fibers

The chemical composition of natural fibers greatly depends on the type and nature of fiber. The overall properties of each fiber are influenced by the properties of each constituent [23]. The variation in chemical composition from plant to plant, and within different parts of the same plant are quite obvious [24]. The main and prime constituent of all cell walls are sugar based polymers (cellulose, hemicellulose) chiefly on dry basis [24]. The cell structure and chemical composition of natural fibers are quite complicated. Chemical composition of some important natural fibers are illustrated in Table 2 [25]. Natural fibers themselves regarded as the naturally occurring composites comprising mainly of helically wound cellulose micro fibrils, embedded in amorphous lignin matrix. Cellulose (α-cellulose), lignin, pectins, hemicellulose, and waxes are the major components of natural fibers. The component

hemicellulose present in the natural fibers is regarded to be a compatibilizer between lignin and cellulose [26].

**Table 2.** Chemical compositions of some important natural fibers. Reprinted with permission from Elsevier, 2008 [25].

Natural Fibers	$\alpha$ -Cellulose	Lignin	Pentosans
Sisal	47–62	8–9	21–24
Pine apple	69.5	4.4	17.8
Wheat grass	21.4	–	–
Bamboo	26–43	21–30	15–26
Rice	28–48	12–16	23–28
Ryegrass	33–50	16–19	27–30
Sugar grass	32–48	19–24	27–32
Wheat straw	29–51	16–21	26–32
Kenaf bast	44–57	15–19	22–23
Jute	45–63	21–26	18–21
Oat straw	31–48	16–19	27–38
Esparto grass	33–48	17–19	27–32
Hemp bast	57–77	9–13	14–17
Barley	31–45	14–15	24–29
Wood grass	40–45	26–34	7–14
Marsh grass	25–27	–	–
Sorghum	27–31	12–16	23–28
Corn stalk	32–34	5–34	20–41
Coconut coir	28–29	16–45	7–23
Rush grass	26–29	–	–
Peanut hulls	35–36	32–33	19–20
Flax seed	43–47	21–23	24–26
Okra	23–35	–	–
Ramie bast	87–91	0.5–0.7	5–8
Sabai	–	22–23	24–25
Cotton linter seed hull	90–95	0.7–1.6	1–3
Reed fiber	44–46	22–24	20
Silver maple (Hardwood)	42.0	21.0	19.0
Groundnut husk	–	30.6	11.1
Seed flax tow	34.0	23.0	25.0

Hemicellulose is responsible for thermal degradation, moisture absorption, and biodegradation of the fiber as it shows least resistance but lignin is thermally stable and is greatly accountable for the UV degradation [23]. Phenylpropane derivative constitutes the lignin and it is an amorphous natural polymeric material that regulates the transference of fluid in the plant [17]. Fiber width and length is an important parameter of information used for comparing diverse variety of natural fibers. Thus, the fiber strength can also be an important factor in selecting a specific natural fiber for specific applications. The morphology and the anatomy of the aquatic plant fibers are quite different from those of terrestrial plant fibers [19]. The necessary strength and stiffness to the fibers are provided by the

hydrogen bonds and other linkages. Fiber variability, crystallinity, strength, dimensions, defects, and structure are the important factors governing the properties of different natural fibers [23]. Table 3 shows the average diameter of frequently used natural fibers. All fibers are tinny in diameter or width except for bagasse, oil palm, and coconut [27]. The major drawback of natural fibers is their tendency of high water absorption and this make them inequitable with nonpolar polymer matrices [28]. Most of the resins are usually hydrophobic in nature and absorb little humidity. Table 3 shows the equilibrium moisture content of different natural fibers at 65% relative humidity (RH) and 21 °C [25]. The void content and non-crystalline parts of the fibers are determined by the humidity of the fibers. The strength or mechanical properties of the natural fibers are affected by the hydrophilic nature of the fibers. The characteristic properties of natural fibers are affected by many factors, such as climatic conditions, maturity, harvesting and collection time, retting degree, decortications, disintegration (mechanical, steam explosion treatment), fiber modification, textile, and technical processes [29]. Being natural in origin, the lignocellulosic fiber has several different stages of production, moreover, within each stage there are many factors that determined the quality of fiber, as shown in Table 4 [9].

Mechanical and physical properties of natural fibers provides important information that are required to know prior of its use to attain maximum level. Several efforts have been made to substitute the natural fiber composites in place of glass mostly both in non-structural and structural applications. Thus far, a large number of automotive parts and their components, which were formerly prepared with glass fiber composites, are recently being manufactured using environmentally friendly natural fibers and composites [30,31]. The mechanical properties of natural fibers are, relatively, much lower than those of glass fibers. Table 5 shows the mechanical properties of natural fibers and glass fibers. Researchers in many cases reported the comparison of mechanical and physical properties of natural fibers with E-glass [32]. Elongation to break is higher in the case of natural fibers than glass or carbon fibers, which promotes the composite performance.

**Table 3.** Average diameter and equivalent moisture content (EMC) of natural fibers [2,17,25].

Fibers	Diameters (μm)	EMC (%)
Oil palm Fronds	19.7	–
Oil palm EFB	19.1–25.0	–
Banana	12–30	15
Sisal	7–200	11
Pineapple Leaf	20–80	13
Ramie	18–80	9
Coconut husks	100–450	10
Bagasse	10–34	–
Jute	5–200	12
Hemp	10–500	9
Flax	5–600	7
Aloe	–	12
Wood	–	12
Abaca	–	9.5
Cotton	10–45	8
Kapok	–	10

**Table 4.** Factors effecting fiber quality at various stages of natural fiber production. Reprinted with permission from Elsevier, 2012 [9].

Stage	Factors Effecting Fiber Quality
<b>Plant Growth</b>	Species of plant
	Crop cultivation
	Crop location
	Fiber location in plant
	Local climate
<b>Harvesting stage</b>	Fiber ripeness, which effects:
	Cell wall thickness
	Coarseness of fibers
	Adherence between fibers and surrounding Structure
<b>Fiber extraction stage</b>	Decortication process
	Type of retting method
<b>Supply stage</b>	Transportation conditions
	Storage conditions
	Age of fiber

**Table 5.** Properties of natural fibers in relation to those of E-glass. Reprinted with permission from 010 Publishers, 2005 [32].

Properties	Fiber							
	E-glass	Hemp	Jute	Ramie	Coir	Sisal	Flax	Cotton
Density (g/cm <sup>3</sup> )	2.55	1.48	1.46	1.5	1.25	1.33	1.4	1.51
Tensile strength (MPa)	2,400	550–900	400–800	500	220	600–700	800–1,500	400
E-Modulus (GPa)	73	70	10–30	44	6	38	60–80	12
Specific (E/d)	29	47	7–21	29	5	29	26–46	8
Elongation at failure (%)	3	1.6	1.8	2	15–25	2–3	1.2–1.6	3–10
Moisture absorption (%)	–	8	12	12–17	10	11	7	8–25

### 3. Polymer/Matrix

The matrix may be metallic, ceramic or polymeric in origin. Polymers are of three types if classed with regard to degree of reticulation; thermoplastic polymers, thermosetting polymers, and rubbers. Thermoplastic polymers have little or no reticulation, are often solvent soluble, and melt easily. Rubbers are slightly cross linked, which prevents the chain from sliding when stretched and the last thermosetting polymers or thermosets are heavily cross linked, insoluble in solvents and also infusible [33]. In the composite industries most applicable and important thermosetting materials are phenolic resins (including phenol-formaldehyde); epoxy resins and unsaturated polyesters (UP); amino resins (e.g., melamine-formaldehyde and urea-formaldehyde). Unlike thermoplastic resins, cured thermosets will not melt and flow but soften when heated and, once formed, cannot be reshaped [19].

### 4. Nanofillers

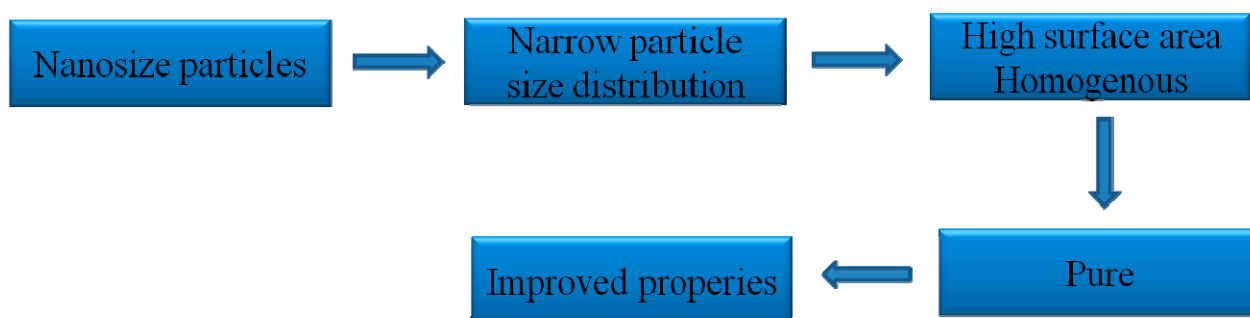
In order to define nanometer scale items ( $10^{-9}$  m) the term nano is used. A nanometer is, therefore, equivalent to the billionth of a meter, or 80,000 times thinner than a human hair. The nanometer range

covers sizes smaller than the wavelength range of visible light but bigger than several atoms [34]. Nanomaterials are categorized into three groups; nanotubes, nanoparticles, and nanolayers, depending on the number of measurements of the dispersed particles that are in the nanometer range [35,36]. Nano-particles regarded as the important potential filler materials for the enhancement of physical and mechanical properties of polymer matrix [4]. The unique nanometric size, capable of producing huge and vast specific surface areas, even more than  $1000 \text{ m}^2/\text{g}$ , along with their other distinctive properties currently shows exhaustive research activities in the fields of engineering and natural sciences [37]. Nanofillers possess tendency to improve or adjust the altered or variable properties of the materials into which they are incorporated, such as fire-retardant properties, optical or electrical properties, mechanical and thermal properties, significantly, sometimes in synergy with conventional or traditional fillers. Nanofillers are incorporated in polymer matrices at rates from 1% to 10% (in mass) [38]. The diverse nanofillers that are used in nano composites are nanoclays, nano-oxides, carbon nanotubes, and organic nanofillers. However, according to the nanofillers the nanocomposites can be distributed, as classified in ISO/TS 27687 [39] and presented in Table 6. In the composite the incorporation of nanoparticles leads to changes in the following way, as shown in Figure 2.

**Table 6.** Classification of nanofillers with reference [39].

One-dimensional nanofiller	Dimension measurement (thickness)	Two-dimensional nanofiller	Dimension measurement (diameter)	Three-dimensional nanofiller	Dimension measurement (All dimension)
	Plates < 100 nm		Nano tubes < 100 nm		Nanometric < 100 nm
	Laminas < 100 nm		Nano fibers < 100nm		Silica beads
	Shells < 100nm		–		–

**Figure 2.** Changes due to incorporation of nanoparticles in composites.



## 5. Biocomposites

Composite materials are the most advanced and adaptable engineering materials. The perfect combination of a plastic polymeric matrix and reinforcing natural fibers produces composites, possessing the finest properties of each component. The term “natural fiber reinforced composite” usually refers to natural fibers in any sort of polymeric matrix (thermoplastic or thermoset; natural or synthetic). However, these composites found to be eco-friendly to a greater degree. These materials offer many of the same and equivalent advantages in terms of strength and toughness as conventional composites together with their own unique advantages including lower density [40], better matrix–fiber compatibility, and recyclability [41–43].

Performance of the natural fiber polymer composites influenced by several factors, such as fibers microfibrillar angle, defects, structure, physical properties, chemical composition, cell dimensions, mechanical properties and the interaction of a fiber with the polymer matrix. Thus, to understand the properties of natural fiber-reinforced composite materials, it is essential to recognize the mechanical, physical, and chemical composition/properties of natural fibers [3]. The most important matters in the development of natural fiber reinforced composites are (i) surface adhesion characteristics of the fibers, (ii) thermal stability of the fibers, and (iii) dispersion of the fibers in the case of thermoplastic composites [23]. The polarity characteristic of the natural fiber produces incompatibility difficulties with many polymers. Hydrophilic or polar characters of natural fibers produce composites with weak interface. Several chemical modifications or pretreatment of surface are being made to improve and enhance the adhesion or interfacial bonding between polymers and natural fibers [44,45]. Pretreatments of the natural fiber used to clean and unpolluted the fiber surface, to modify chemically the surface, decreases the rate of moisture absorption tendency, and to increase the external unevenness. The incorporation of natural fibers as filler or reinforcement produces significant changes in thermal stability of polymeric matrix. The manufacturing and the processing of these composites involves the collaboration of fibers and matrix at sufficiently high temperatures, hence, can lead to degradation of the bio-material, which results in unfavorable effects on the final properties [17]. Almost all production techniques can be used to manufacture the natural fiber-containing composites. Table 7 displays the list of manufacturing techniques used for composite preparation involving either thermoset or thermoplastic matrix.

**Table 7.** Techniques for the composite preparation with the polymer.

<b>Processing of natural fiber-thermosetting composites</b>	<b>Processing of natural fiber-thermoplastic composites</b>
Hand lay-up and spraying	Extrusion
Compression	Injection molding
Transfer	Thermoforming
Resin transfer molding	Compression method
Injection molding	Cold pressing
Compression injection	Heating
Pressure bag molding	Direct long fiber reinforced thermoplastics
Pultrusion	Filament Winding
Vacuum assisted resin transfer molding	Foam molding
Casting Injection molding	Rotational molding, calendaring
Polyurethane foam molding	Co-extrusion

A significant and effective method in formulating biocomposites of desired and superior properties include proficient chemical modification of fiber, efficient processing of fabrication techniques, and matrix modification by blending and functionalizing [18] (Figure 3).



polymeric matrix and reinforcing by a wide variety of clays, which exhibited improved and better properties. Reported work on nanocomposites are listed in Table 8 to make a review of technology of nano and micro-scale particle reinforcement regarding several polymeric fiber-reinforced systems including polyamide (PA), polyimide (PI), polyarylacetylene (PAA), poly(ether ether ketone) (PEEK), epoxy resin (ER), polyester, polyurethane (PU), and poly *p*-phenylenebenzobisoxazole(PBO). Researchers show the various processing techniques in nanocomposites and the characterization with their corresponding techniques [4,48–52]. Over conventional composites, nanocomposites display improvements in mechanical, electrical, thermal, and resistant (barrier) properties. Furthermore, the nano particles cause significant reduction in flammability and also preserve the transparency or clearness of the polymer matrix [24,53].

**Table 8.** List of reported work on nanocomposite type from different polymeric matrix with natural fiber/nanofiller.

Polymer Matrix	Natural Fiber/Nano Filler	References
Polyamide 11 (PA-11)	Nano clay	[54]
<i>ε</i> -Caprolactam	Organo clay	[55]
Polyamide (PA-6)	Montmorillonite (MMT)	[56]
Polyamide (PA-6)	Organically modified MMT (OMMT)	[57–59]
Polyamide (PA-6)	Fe <sub>2</sub> O <sub>3</sub> particles	[60]
Polyurethanes (PU)	Carbon nano tube	[61]
Polyaniline and sulfonated urethane	Carbon nano tube	[62]
Polypropylene (PP)	Nano clays	[63]
Polypropylene (PP)	Nano carbon fiber	[64]
Polypropylene (PP)	Nanoclays.	[65]
Poly(ethylene) (PE)	Carbon nanotube	[66]
Ultra-high MW poly(ethylene) (UHMWPE)	Carbon nanotube	[67]
Polystyrene (PS)	Carbon nanotube	[68]
Polystyrene (PS)	Carbon nanotube	[69]
Poly(ether ether ketone) (PEEK)	Nanoparticles of SiO <sub>2</sub>	[70]
Poly(ether ether ketone) (PEEK)	Carbon nanofibers CNFs	[71]
Poly(ether ether ketone) (PEEK)	organo-alkoxysilanes	[72]
Poly(ether ether ketone) (PEEK)	SiC nanoparticles.	[73,74]
Phenylethynyl-terminated imide (PI)	multi-walled carbon nanotube	[75]
Polyarylacetylene (PAA)	Carbon fiber	[76]
Polyarylacetylene (PAA)	carbon fiber/LiAlH <sub>4</sub>	[77]
Polyarylacetylene (PAA)	carbon fiber	[78]
Poly <i>p</i> -phenylenebenzobisoxazole (PBO)	SWNT (Single-walled nanotubes)	[79]
Epoxy resin (ER)	Coir-fiber nano filler	[80]

Bio-nanocomposites are regarded as an emerging and attractive groups of nanostructured materials that brings the expansion of the conception of biocomposites [81]. The two following ways used for defining the term bio-nanocomposites are (i) the nanocomposites materials developed from renewable and sustainable nanoparticles (e.g., cellulose whiskers and MFC) and petroleum-derived polymers like PP, PE, and epoxies, (ii) nanocomposites derived from biopolymers (e.g., PLA and PHA) and synthetic or inorganic nanofilers (e.g., carbon nanotubes and nanoclay), also come under bio-nanocomposites [82,83].

## 7. Hybrid Composites

The word “hybrid” is of Greek-Latin origin. Hybrid composites are the systems where one type of reinforcing or filler material is incorporated or added in a mixture of dissimilar or different matrices (blends) [84], or two or more reinforcing or filling materials are present in a single matrix [85,86] or, also, both approaches are combined. The integration of variety of fibers in a single matrix results in the development of hybrid biocomposites. Reinforcements have been incorporated either by: (i) intermingling of two types of short fibers thoroughly before incorporating them into the polymer in a mixer, or added alternately into the polymer with or without modification [87–89]. (ii) sandwiching of fibers or their mats or fabrics [20,89] or (iii) using non-woven or woven fabrics of both types of reinforcements, as in the case of glass fiber-LC fiber composite systems [20,89,90].

Hybrid biocomposites are usually designed and processed by the combination of a synthetic fiber and natural fiber (biofiber) in a matrix or with combination of two natural fiber/biofiber in a matrix [18]. The behavior of hybrid composites is a weighed sum of the individual components. The hybrid composite properties exclusively governed by the length of individual fibers, orientation, fiber to matrix bonding, content, extent of intermingling of fibers, and arrangement of both of the fibers. Rule of mixtures can be used to determine the properties of the hybrid system consisting of two components. Moreover, successful use of hybrid composites is determined by the mechanical, chemical, and physical stability of the fiber/matrix system. Several researchers developed hybrid composite by combining natural fibers with poly-urethane resins, phenolic, polyester, epoxy, poly vinyl ester, *etc.*, as polymeric matrices. Table 9 shows reported and exclusive work on cellulosic/synthetic and cellulosic/cellulosic fibers reinforced hybrid composites.

**Table 9.** Reported work on hybrid composites.

Natural Fiber	Polymer Matrix	References
Palmyra/glass	Rooflite resin	[91,92]
Bamboo/glass	Vinyl ester	[93]
Jute/glass	Polyester (isothalic)	[94,95]
Coir/glass	Phenolic resin	[96]
Banana/kenaf	Polyester	[97]
Natural fiber/glass	Epoxy vinyl ester	[98]
Jute/biomass	Bisphenol-C-formaldehyde	[99]
Sisal/kapok	Unsaturated Polyester	[100]
Oil palm EFB/jute	Epoxy resin	[101]
Kenaf/glass	Epoxy resin	[102]
Cellulose/glass	Epoxy resin	[103]
Jute/cotton	Novolac phenolic	[104]
Jute/glass	Polypropylene (PP)	[105]
Flax/glass	Polypropylene (PP)	[106]
Kenaf/glass	Natural rubber	[107]
Cotton/waste silk	Polycarbonate (PC)	[108]
Wood flour/glass	Poly vinyl chloride (PVC)	[109]

*Nano Filler/Natural Fiber Hybrid Composites*

Natural fiber-reinforced polymer composites have established a huge attraction and concern as innovative material in several applications. Although, natural fiber–plastic composites have been commercialized, but their potentiality for use in many industries has been limited. Therefore, most studies in this area focus on improving the physical-mechanical properties and impact resistance of the composites. One way to improve the mechanical properties of natural-fiber-based composites is to produce hybrid composites by combining several types of reinforcement/filler such as nanoclay with polymers. The nanoclay materials are commonly selected for their particular dimension and high aspect ratio in most of the research work [110] (Table 10).

**Table 10.** Reported work on fiber/nanofiller hybrid composites.

Matrix	Filler	Reference
Polyamide (PA-6)	carbon fiber/nanoclay	[111]
Polyamide (PA-6)	carbon fiber/glass fiber/nanoclay	[111]
Polyamide (PA-6)	chopped glass fibers/hectorite-type clays (nano size)	[112]
Polyamide (PA-6)	glass fiber/layered silicate	[113]
Polyamide 12 (PA-12)	Carbon nanotubes and nanofibers	[114]
Polyester	Nanoclay/glass fiber	[115]
Polyvinyl ester	Organoclay/glass fiber mats	[116]
High density polyethylene(HDPE)	nanoclay/rice husk	[15]
Ethylene–propylene copolymer	Nano clay/cellulose	[79]
Polyarylacetylene (PAA)	carbon fiber/LiAlH <sub>4</sub>	[77]

The hybridization of natural fiber with carbon [117], and mica [118] have produced encouraging results. The decrease in the water absorption and thickness swelling is observed by the hybridization of nanoclay with reed flour besides this it also upgraded the tensile properties of the whole system. Researchers also show the effect of coupling agent on mechanical and physical properties of reed flour/PP/nanoclay hybrid composite [119]. In other work, integration of nanoclay to the HDPE/rice husk system greatly enhanced their mechanical properties [15]. The study involving the hybrid effect of nanoparticles on the flexibility and stiffness on the hemp fiber/PP based hybrid composites was also found to be increased [120]

A substantial reduction in water absorption tendency and thickness enlargement by swelling get increased by nanoparticles loading also been reported in some cases. Researchers also studied the effect of compatibilization and incorporation of organoclay on mechanical and thermal properties of wood flour/HDPE composites systems, which emerges as an attention-grabbing work [121]. Researcher also found that hybridization of 5 wt% of nanoclay with micro-crystalline cellulose in the micro-crystalline cellulose reinforced ethylene–propylene (EP) copolymer shows remarkable changes in the Young’s modulus from 1.04 to 1.24 GPa [79]. In another study, effect of nanoclay dispersion on mechanical and physical properties of the wood–plastic–nanoclay hybrid composites, are also been reported [122]. The pronounced effect of compatibilization and organoclay incorporation on mechanical and thermal performance of the pine cone fiber hybrid polymer composite are also been studied by researchers [123]. Reduction in the stiffness/modulus of the systems, contrary to fiber, also notably

observed. In another study a good dispersion and interfacial interaction of clay and pine cone fiber within the polymer are perfectly revealed by scanning electron microscopy in the clay/pine cone fiber hybrid polymer nanocomposite. The incorporation of nanoclay to the formed HDPE/wheat straw flour polymer composite also improved the properties of polymer composite including an increase in modulus and strength, heat resistance, low gas permeability, fire resistance and physical properties, even at the small scale of nanoclay [110]. The effects of azodicarbonamide (AZD) as the exothermic chemical foaming agent (CFA) and nanoclay on the physical, morphological and mechanical properties of nanocomposites produced from wheat straw flour (WSF) and HPDE were also studied [124]. The tendency of water absorption and thickness swelling properties of HPDE/WSF composites increased by adding AZD and a reduction by adding the NC into the matrix was witnessed. Impact resistance also decreased by adding NC and the CFA. The mechanical properties of HPDE/WSF composite get improved by adding 2 phr of NC, all these results are supported by SEM micrographs.

## 8. Applications and Challenges

Nanotechnologies are estimated to impact and influence at least \$3 trillion in the worldwide economy by 2020. Furthermore, it has been expected that industries based on nanotechnology, considering nano particles, globally, might require at least six million workers to sustain them by the end of the decade [125]. Nanocomposites proposed perfections over conventional composites in mechanical, electrical, thermal, and resistance (barrier) properties [53]. A large variability of diversity in industrial applications for polymer nanocomposites includes automotive industry (interior-exterior panels, gas tanks and bumpers), construction industry (structural panels and building sections), aerospace (flame retardant panels and high performance components), electrical and electronics (printed circuit boards and variety of electrical components), in food packaging (containers and wrapping films) and in the cosmetics industry [49].

Construction is one of the most traditional and oldest industries, having been around for almost as long as mankind. Over time, significant technological changes have occurred, mainly in the way in which buildings are erected [126]. This is the most interesting application area, which relates to enhancing the functional properties of concrete, steel, wood, and glass, as the primary construction materials. Specifically, the embodiment of nanoparticles in the micro-matrices, or through coatings on the surface areas of these materials can improve their strength, stress tolerance, and durability [127]. Nanotechnology addresses environmental concerns in construction through many routes. The enabling nature of nanotechnology implies that it can provide traditional construction materials with completely new and eco-efficient functionalities [126].

Examples of nanotechnology-enabled applications in construction [127] are listed below:

- Long-lasting scratch-resistant floors using nano-structured materials;
- Super strong structural components using CNTs;
- Healthier indoor climates by nano-enabled filter technology;
- Antimicrobial steel surfaces using nano-scaled coatings;
- Improved industrial building maintenance using nano-enabled sensors;
- Lower energy consuming buildings using electrochromic “smart” windows;
- Self-cleaning low maintenance windows using new nano-scaled coatings.

Moreover in medical field polymer nano fibers extensively applied for the cure of burns or wounds of a humanoid skin, and also to designed haemostatic procedures and devices with certain special and exclusive features. Through, the aid of electric field, biodegradable polymers finest fibers, are able to directly sprayed/spun on to the damaged and injured area of skin to form a fibrous mat dressing (Figure 4), thus, assisting in healing wounds by boosting the development of normal skin growth and also help in eradication to reduce the formation of scar tissue.

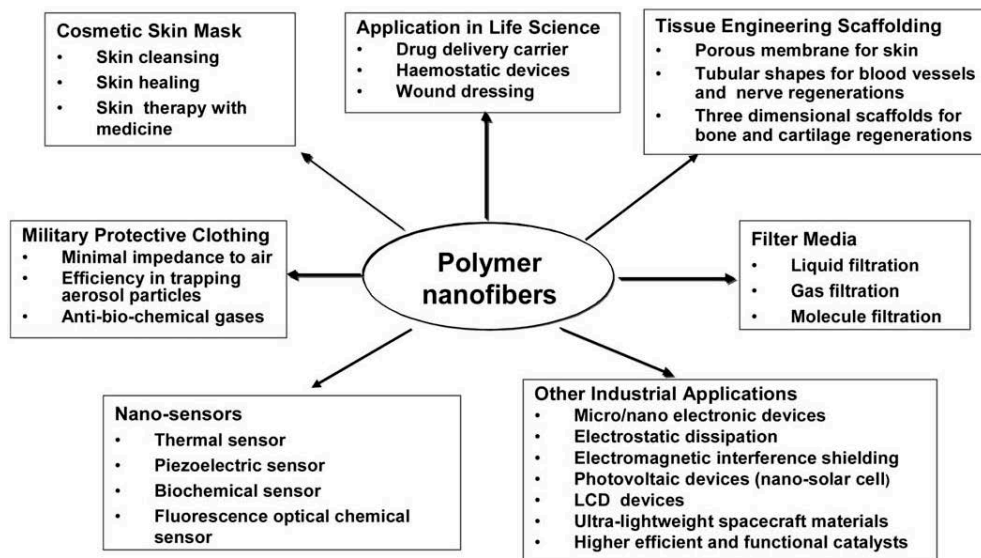
**Figure 4.** Showing the use of nanofibers for wound dressing. Reprinted with permission from Elsevier, 2003 [128].



Figure 5 shows some of the future potential of nanocomposite or polymer nanofibers. The promising prospective of development and utilization of nanofibers or nanocomposite are thought to be interesting or appealing investments, and are able to grab more attention from governments, academia, and the growing industry around the globe [128]. The pulp and paper industry is a materials industry which provides an excellent platform for developing nano-material fiber composites for use in higher value printing, barrier packaging, and intelligent communications media [34].  $\text{TiO}_2$ , and the sucrose as the nano-additive can be added, revealing a much higher opacity for the synthetic sample [129].

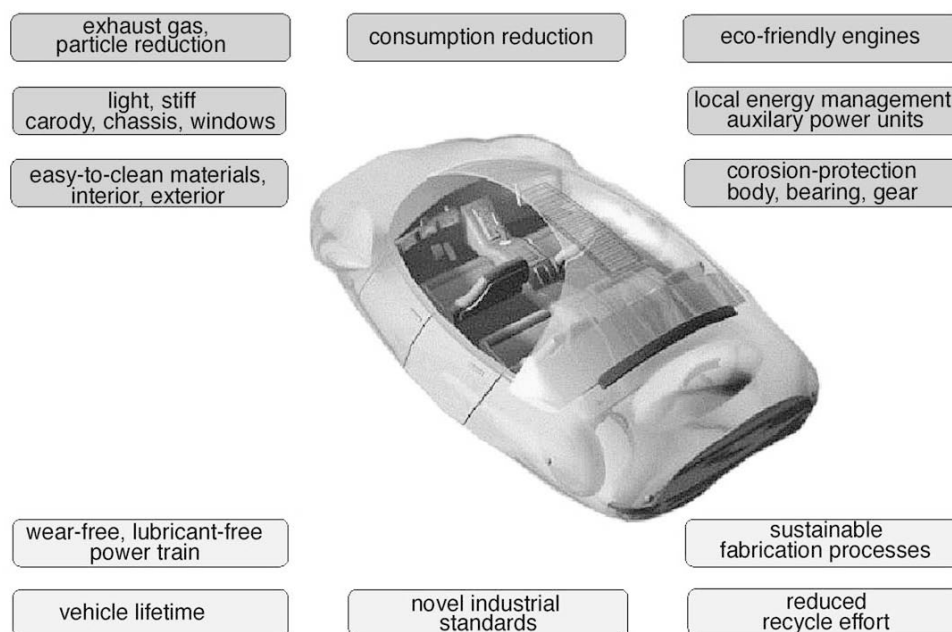
Nanocomposite materials are also being used in cosmetic dentistry, and are the primary dental filling materials as they can be conveniently applied and yield a high esthetic quality. Nanocomposite materials are used to fabricate core and post systems and dental brackets, and are applied in various restorations (inlays, on-lays, veneers, and crowns). Novel liquid crystalline epoxy nanocomposites, which exhibit reduced polymerization shrinkage and effectively bond to tooth structures, can be applied in esthetic dentistry, including core and post systems, direct and indirect restorations, and dental brackets [130]. Although in manufacturing equipment the applications of nanotechnology are not truly recognizable to many customers, but they offer remarkable profits in the fabrication process. In the cosmetics industry the prime requirements, including easy-to-clean surfaces, low abrasion details, non-sticky materials for machinery, and value-added energy efficiency products, are a few illustrations of benefits gained by consuming nanotechnology in various manufacturing techniques [131]. The origination of cosmetic goods and products using nano carriers basically aims at improving the effectiveness of the product, decreasing the amount of constituents used with accompanying decrease in toxicity or irritation. This also aims to obtain better stability, increasing the infusion of the active material thus enables producing a more graceful product [131].

**Figure 5.** Potential applications of polymer nanofibers. Reprinted with permission from Elsevier, 2003 [128].

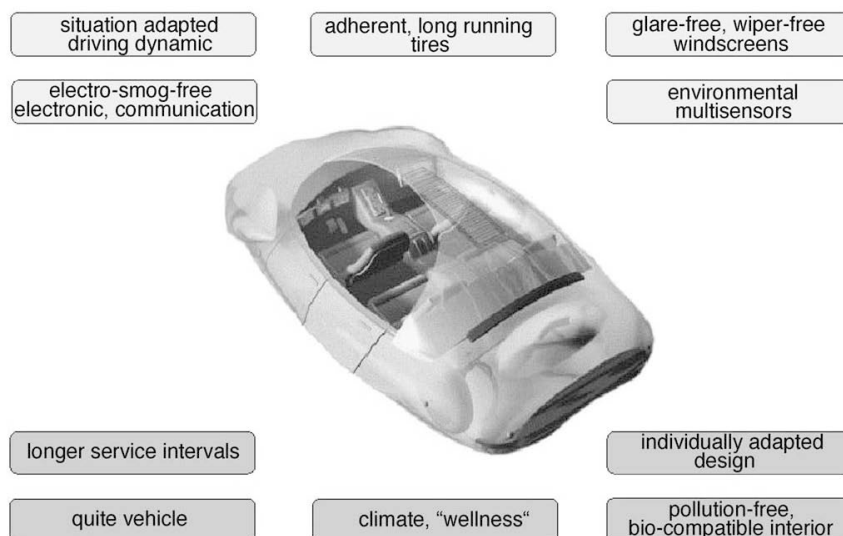


The application of nanotechnology in the automotive industry is diverse or manifold. They show diversity from energy conversion, light-weight construction, interior cooling, power train, surveillance control up to recycle potential, pollution sensing and reduction, driving dynamics and wear reduction *etc.* [132]. The concept of “nano in cars” conforms its assistances for quiet cars, CO<sub>2</sub>-free engines, up to a mood-depending choice of colour, self-healing body and windscreens, safe driving and a self-forming car body. Figures 6 and 7 show the potential areas of nanocomposite towards automotive applications. The automotive components in automotive industry includes nanoparticles such as dots, tubes, whisker, pores, layers, and fibers, either distributed or dispersed within a polymeric matrix material referred as “nanocomposites”.

**Figure 6.** Potential areas where nanotechnology can contribute to satisfy society demands in the automotive industry. Reprinted with permission from Elsevier, 2003 [132].

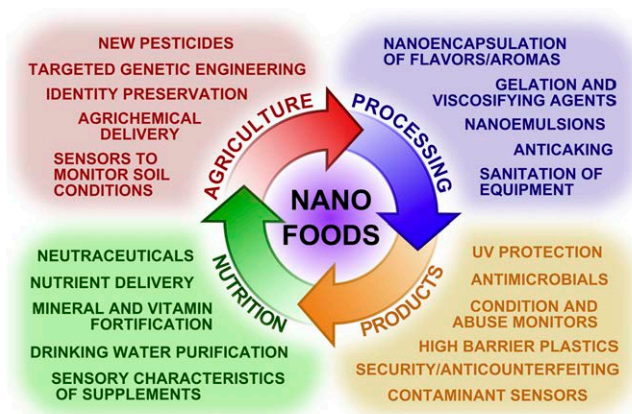


**Figure 7.** Customer-specific requirements to future automobiles where nanotechnology has an impact. Reprinted with permission from Elsevier, 2003 [132].



Nanotechnology might revolutionize the food processing and food safety industries by creating more effective antimicrobial agents, providing high-barrier packaging materials. A stronger series of sensors that are able to detect even trace contaminants, impurities, microbes or gasses in packaged foods, can be made by considering polymer/clay nanocomposites, as high barrier packaging materials. In another study silver nanoparticles as potential antimicrobial agents, nanomaterial, and nanosensor-based assays for revealing food-relevant analytes (small organic molecules, gasses and food-borne pathogens) also been reported [133]. The well-established and recognized prospective applications of nanotechnology in virtually every segment of the food industry (Figure 8) from agriculture (e.g., pesticide, fertilizer or vaccine delivery; animal and plant pathogen detection; and targeted genetic engineering) to food processing (e.g., encapsulation of flavor or odor enhancers; food textural or quality improvement; new gelation, or viscosifying agents) to food packaging (e.g., pathogen, gas or abuse sensors; anti-counterfeiting devices, UV-protection, and stronger, more impermeable polymer films) to nutrient supplements (e.g., nutraceuticals with higher stability and bioavailability) are well known [133].

**Figure 8.** Some potential applications of nanotechnology in all areas of food science, from agriculture to food processing to security to packaging to nutrition and nutraceuticals. Reprinted with permission from Elsevier, 2011 [133].



## 9. Conclusions

Polymer nanocomposites signify as the most encouraging and promising family of materials science from the last decades and consequently gained much attention due to their unique characteristics of enhancing the mechanical and barrier properties of construction, cosmetics, medical sciences, food packaging and many other composite-based industries. Nanocomposites obtained from polymeric matrix (thermoplastics or thermosets) reinforced with nano-sized fillers, such as nano-size particles, carbon nano-tubes or intercalated layers designated as a dynamic and active area of research. The synergistic reactions involving the matrix polymer and nanoparticle filler at the nanoscale level responsible for the enhanced properties; developed by the assimilation of slight quantity of nanofiller in polymer matrix. Hybrid filler filled composites tremendously delivers pronounced prospective in order to overwhelm many of the limitations such as the weak interfacial attractions between matrix polymer and the fiber, and characteristics moisture absorption properties of many natural fibers, thus hampering their applications in several industries. The nanoparticle reinforcement enhances the performance and properties, and, hence, shows great value for fiber-reinforced composite based industry. A great possibility has been shown by the incorporations of nanoparticle as the reinforcement of composites.

Future research on natural fiber/nano filler based hybrid composites not only driven by its automotive and construction applications but it required to explore further research on hybrid for aircraft components, rural areas and biomedical applications. However, more study and research remains to be achieved in order to recognized the possible ways of nano-reinforcement leading to major changes in material properties and their subsequent potential future applications in several composite based industries. There is need for more analysis of the different properties of natural fiber/nano filler based hybrid composites by modern equipment in the most of the areas covered in this review. The crucial success of outcomes of this research for future developments and wider acceptance of natural fiber/nano filler based hybrid composites in different applications depends on reliable scientific reports which confirm both the benefits and protective nature of nano materials. Apart from the benefits and safety aspects of nanotechnology-based products, public opinion, and attitudes towards nanotechnology are extremely important for the development of this emerging area.

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## Author Contributions

All authors have equally contributed.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Satyanarayana, K.G.; Arizaga, G.G.C.; Wypych, F. Biodegradable composites based on lignocellulosic fibers—An overview. *Prog. Polym. Sci.* **2009**, *34*, 982–1021.
2. Jawaid, M.; Abdul Khalil, H.P.S. Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review. *Carbohydr. Polym.* **2011**, *86*, 1–18.
3. Kalia, S.; Kaith, B.; Kaur, I. Pretreatments of natural fibers and their application as reinforcing material in polymer composites—A review. *Polym. Eng. Sci.* **2009**, *49*, 1253–1272.
4. Njuguna, J.; Pielichowski, K.; Desai, S. Nanofiller-reinforced polymer nanocomposites. *Polym. Adv. Technol.* **2008**, *19*, 947–959.
5. De Azeredo, H.M.C. Nanocomposites for food packaging applications. *Food Res. Int.* **2009**, *42*, 1240–1253.
6. Schadler, L.S.; Brinson, L.C.; Sawyer, W.G. Polymer nanocomposites: A small part of the story. *JOM* **2007**, *59*, 53–60.
7. Hari, J.; Pukanzsky, B. Nanocomposites: Preparation, structure, properties. In *Applied Plastics Engine Handbook: Processing Materials*; Kutz, M., Ed.; Elsevier Inc.: Waltham, MA, USA, 2011; pp. 109–142.
8. Liang, R.; Hota, G. Fiber reinforced polymer composites for civil infrastructures. In Proceedings of the International Conference on FRP Composites for Infrastructure Applications, San Francisco, CA, USA, 4–6 November 2009.
9. Dittenber, D.B.; GangaRao, H.V.S. Critical review of recent publications on use of natural composites in infrastructure. *Compos. A Appl. Sci. Manuf.* **2012**, *43*, 1419–1429.
10. Henrique, P.; Camargo, C.; Satyanarayana, K.G.; Wypych, F. Nanocomposites: Synthesis, structure, properties and new application opportunities. *Mater. Res.* **2009**, *12*, 1–39.
11. Kozłowski, R.; Władyska-przybylak, M. Review flammability and fire resistance of composites reinforced by natural fibers. *Polym. Adv. Technol.* **2008**, *19*, 446–453.
12. Sathishkumar, T.; Naveen, J.; Satheeshkumar, S. Hybrid fiber reinforced polymer composites—A review. *J. Reinf. Plast. Compos.* **2014**, *33*, 454–471.
13. Sathishkumar, T.P.; Navaneethakrishnan, P.; Shankar, S.; Al, E. Characterization of new cellulose sansevieria ehrenbergii fibers for polymer composites. *Compos. Interfaces* **2013**, *20*, 575–593.
14. Borba, P.M.; Tedesco, A.; Lenz, D.M. Effect of reinforcement nanoparticles addition on mechanical properties of SBS/Curauá fiber composites. *Mater. Res.* **2014**, *17*, 412–419.
15. Kord, B. Nanofiller reinforcement effects on the thermal, dynamic mechanical, and morphological behavior of HDPE/rice husk flour composites. *BioResources* **2011**, *6*, 1351–1358.
16. Shalwan, A.; Yousif, B.F. Influence of date palm fibre and graphite filler on mechanical and wear characteristics of epoxy composites. *Mater. Des.* **2014**, *59*, 264–273.
17. Majeed, K.; Jawaid, M.; Hassan, A.; Abu Bakar, A.; Abdul Khalil, H.P.S.; Salema, A.A.; Inuwa, I. Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Mater. Des.* **2013**, *46*, 391–410.
18. John, M.; Thomas, S. Biofibres and biocomposites. *Carbohydr. Polym.* **2008**, *71*, 343–364.
19. Pickering, K. *Properties and Performance of Natural-Fibre Composites*; Woodhead Publishing: Cambridge, UK, 2008.

20. Mohanty, A.K.; Misra, M.; Drzal, L.T. Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *J. Polym. Environ.* **2002**, *10*, 19–26.
21. Eichhorn, S.; Baillie, C. Review: Current international research into cellulosic fibres and composites. *J. Mater.* **2001**, *6*, 2107–2131.
22. Hirvikorpi, T.; Vähä-Nissi, M.; Nikkola, J.; Harlin, A.; Karppinen, M. Thin Al<sub>2</sub>O<sub>3</sub> barrier coatings onto temperature-sensitive packaging materials by atomic layer deposition. *Surf. Coat. Technol.* **2011**, *205*, 5088–5092.
23. Saheb, D.N.; Jog, J.P. Natural fiber polymer composites: A review. *Adv. Polym. Technol.* **1999**, *18*, 351–363.
24. Faruk, O.; Bledzki, A.K.; Fink, H.-P.; Sain, M. Biocomposites reinforced with natural fibers: 2000–2010. *Prog. Polym. Sci.* **2012**, *37*, 1552–1596.
25. Rowell, R.M. Natural fibres: Types and properties. In *Properties and Performance of Natural-Fibre Composites*; Pickering, K., Ed.; Woodhead Publishing: Cambridge, UK, 2008; pp. 3–66.
26. Hansen, C.M.; Björkman, A. The ultrastructure of wood from a solubility parameter point of view. *Holzforschung* **1998**, *52*, 335–344.
27. Hassan, A.; Salema, A.A.; Ani, F.N.; Bakar, A.A. A review on oil palm empty fruit bunch fiber-reinforced polymer composite materials. *Polym. Compos.* **2010**, *31*, 2079–2101.
28. Mohanty, A.K.; Misra, M.; Drzal, L.T. Surface modifications of natural fibers and performance of the resulting biocomposites: An overview. *Compos. Interfaces* **2001**, *8*, 313–343.
29. Van De Velde, K.; Kiekens, P. Thermoplastic pultrusion of natural fibre reinforced composites. *Compos. Struct.* **2001**, *54*, 355–360.
30. Dahlke, B.; Larbig, H.; Scherzer, H.D.; Poltrock, R. Natural fiber reinforced foams based on renewable resources for automotive interior applications. *J. Cell. Plast.* **1998**, *34*, 361–379.
31. Leao, A.; Rowell, R.; Tavares, N. Applications of natural fibres in automotive industry in Brazil-thermoforming process. In Proceedings of the 4th International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt, 4–9 January 1997; pp. 755–760.
32. Beukers, A. *Lightness: The Inevitable Renaissance of Minimum Energy Structures*, 4th ed.; Beukers, A., Hinte, E., Eds.; 010 Publishers: Rotterdam, The Netherlands, 2005; p. 72.
33. Peng, W.; Riedl, B. Thermosetting resins. *J. Chem. Educ.* **1995**, *72*, 587–592.
34. Kamel, S. Nanotechnology and its applications in lignocellulosic composites, a mini review. *eXPRESS Polym. Lett.* **2007**, *1*, 546–575.
35. Alexandre, M.; Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater. Sci. Eng. R Rep.* **2000**, *28*, 1–63.
36. Kumar, A.P.; Depan, D.; Singh Tomer, N.; Singh, R.P. Nanoscale particles for polymer degradation and stabilization—Trends and future perspectives. *Prog. Polym. Sci.* **2009**, *34*, 479–515.
37. Njuguna, J.; And, K.P.; Alcock, J.R. Epoxy-Based fibre reinforced nanocomposites. *Adv. Eng. Mater.* **2007**, *9*, 835–847.
38. Marquis, D.M.; Guillaume, É.; Chivas-Joly, C. Properties of nanofillers in polymer. In *Nanocomposites and Polymers with Analytical Methods*; Cuppoletti, J., Ed.; Intech Publishing: Rijeka, Croatia, 2011; pp. 261–284.

39. *Nanotechnologies—Terminology and Definitions for Nano-Objects—Nanoparticle, Nanofibre and Nanoplate*; ISO/TS 27687; International Organization for Standardization (ISO): Geneva, Switzerland, 2008.
40. Alcock, B.; Cabrera, N.O.; Barkoula, N.-M.; Loos, J.; Peijs, T. The mechanical properties of unidirectional all-polypropylene composites. *Compos. A Appl. Sci. Manuf.* **2006**, *37*, 716–726.
41. Abraham, T.N.; George, K.E. Studies on recyclable nylon-reinforced PP composites: Effect of fiber diameter. *J. Thermoplast. Compos. Mater.* **2009**, *22*, 5–20.
42. Khondker, O.; Fukui, T.; Inoda, M.; Nakai, A.; Hamada, H. Fabrication and mechanical properties of aramid/nylon plain knitted composites. *Compos. Part A Appl. Sci. Manuf.* **2004**, *35*, 1195–1205.
43. Matabola, K.P.; Vries, A.R.; Moolman, F.S.; Luyt, A.S. Single polymer composites: A review. *J. Mater. Sci.* **2009**, *44*, 6213–6222.
44. Azwa, Z.N.; Yousif, B.F.; Manalo, A.C.; Karunasena, W. A review on the degradability of polymeric composites based on natural fibres. *Mater. Des.* **2013**, *47*, 424–442.
45. Shalwan, A.; Yousif, B.F. Investigation on interfacial adhesion of date palm/epoxy using fragmentation technique. *Mater. Des.* **2014**, *53*, 928–937.
46. Ajayan, P.M.; Schadler, L.S.; Braun, P.V. *Nanocomposite Science and Technology*; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2003; p. 239.
47. Biswas, M.; Ray, S.S. Recent progress in synthesis and evaluation of polymer-montmorillonite nanocomposites. *Adv. Polym. Sci.* **2001**, *155*, 167–221.
48. Denault, J.; Labrecque, B. *Technology Group on Polymer Nanocomposites*; Boucherville: Québec, QC, Canada, 2004.
49. Wypych, F.; Satyanarayana, K.G. Functionalization of single layers and nanofibers: A new strategy to produce polymer nanocomposites with optimized properties. *J. Colloid Interface Sci.* **2005**, *285*, 532–543.
50. Ray, S.S.; Okamoto, M. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog. Polym. Sci.* **2003**, *28*, 1539–1641.
51. Ellis, T.S.; D’Angelo, J.S. Thermal and mechanical properties of a polypropylene nanocomposite. *J. Appl. Polym. Sci.* **2003**, *90*, 1639–1647.
52. Greene, M.E.; Kinser, C.R.; Kramer, D.E.; Pingree, L.S.C.; Hersam, M.C. Application of scanning probe microscopy to the characterization and fabrication of hybrid nanomaterials. *Microsc. Res. Tech.* **2004**, *64*, 415–434.
53. Gacitua, W.; Ballerini, A.; Zhang, J. Polymer nanocomposites: Synthetic and natural fillers a review. *Maderas Cienc. Y Tecnol.* **2005**, *7*, 159–178.
54. Liu, T.; Lim, K.P.; Tjiu, W.C.; Pramoda, K.P.; Chen, Z.K. Preparation and characterization of nylon 11/organoclay nanocomposites. *Polymer* **2003**, *44*, 3529–3535.
55. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. Swelling behavior of montmorillonite cation exchanged for  $\alpha$ -amino acids by  $\epsilon$ -caprolactam. *J. Mater. Res.* **1993**, *8*, 1174–1178.
56. Lincoln, D.M.; Vaia, R.A.; Wang, Z.; Hsiao, B.S. Secondary structure and elevated temperature crystallite morphology of nylon-6/layered silicate nanocomposites. *Polymer* **2001**, *42*, 1621–1631.

57. Fong, H.; Liu, W.; Wang, C.S.; Vaia, R.A. Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. *Polymer* **2001**, *43*, 775–780.
58. Fornes, T.D.; Paul, D.R. Crystallization behavior of nylon 6 nanocomposites. *Polymer* **2003**, *44*, 3945–3961.
59. Li, L.; Bellan, L.M.; Craighead, H.G.; Frey, M.W. Formation and properties of nylon-6 and nylon-6/montmorillonite composite nanofibers. *Polymer* **2006**, *47*, 6208–6217.
60. Liang, Y.; Xia, X.; Luo, Y.; Jia, Z. Synthesis and performances of Fe<sub>2</sub>O<sub>3</sub>/PA-6 nanocomposite fiber. *Mater. Lett.* **2007**, *61*, 3269–3272.
61. Chen, W.; Tao, X.; Liu, Y. Carbon nanotube-reinforced polyurethane composite fibers. *Compos. Sci. Technol.* **2006**, *66*, 3029–3034.
62. Poulin, P.; Vigolo, B.; Launois, P. Films and fibers of oriented single wall nanotubes. *Carbon* **2002**, *40*, 1741–1749.
63. Roy, S.; Vengadassalam, K.; Hussain, F.; Lu, H. Compressive strength enhancement of pultruded thermoplastic composites using nanoclay reinforce. In Proceedings of the 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics & Materials Conference, Long Beach, CA, USA, 19–22 April 2004; pp. 2245–2259.
64. Kumar, S.; Dang, T.D.; Arnold, F.E.; Bhattacharyya, A.R.; Min, B.G.; Zhang, X.; Vaia, R.A.; Park, C.; Adams, W.W.; Hauge, R.H.; *et al.* Synthesis, structure, and properties of PBO/SWNT composites. *Macromolecules* **2002**, *35*, 9039–9043.
65. Zhang, X.; Huang, Y.; Wang, T.; Liu, L. Influence of fibre surface oxidation-reduction followed by silsesquioxane coating treatment on interfacial mechanical properties of carbon fibre/polyarylacetylene composites. *Compos. A Appl. Sci. Manuf.* **2007**, *38*, 936–944.
66. Ruan, S.L.; Gao, P.; Yang, X.G.; Yu, T.X. Toughening high performance ultrahigh molecular weight polyethylene using multiwalled carbon nanotubes. *Polymer* **2003**, *44*, 5643–5654.
67. Ruan, S.; Gao, P.; Yu, T.X. Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled carbon nanotubes. *Polymer* **2006**, *47*, 1604–1611.
68. Ji, Y.; Li, B.; Ge, S.; Sokolov, J.C.; Rafailovich, M.H. Structure and nanomechanical characterization of electrospun PS/clay nanocomposite fibers. *Langmuir* **2006**, *22*, 1321–1328.
69. Qian, D.; Dickey, E.C.; Andrews, R.; Rantell, T. Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. *Appl. Phys. Lett.* **2000**, *76*, 2868–2870.
70. Jen, M.H.R.; Tseng, Y.C.; Wu, C.H. Manufacturing and mechanical response of nanocomposite laminates. *Compos. Sci. Technol.* **2005**, *65*, 775–779.
71. Sandler, J.; Werner, P.; Shaffer, M.S.P.; Demchuk, V.; Altstädt, V.; Windle, A.H. Carbon-nanofibre-reinforced poly(ether ether ketone) composites. *Compos. A Appl. Sci. Manuf.* **2002**, *33*, 1033–1039.
72. Schmidt, H. Multifunctional inorganic-organic composite sol-gel coatings for glass surfaces. *J. Non-Cryst. Solids* **1994**, *178*, 302–312.
73. Lin, J. *In situ Syntheses and Phase Behavior Investigations of Inorganic Materials in Organic Polymer Solid Matrices*; The Pennsylvania State University: Nittany Valley Central County, PA, USA, 1992.
74. Wang, Q.H.; Xue, Q.J.; Liu, W.M.; Chen, J.M. The friction and wear characteristics of nanometer SiC and polytetrafluoroethylene filled polyetheretherketone. *Wear* **2000**, *243*, 140–146.

75. Ogasawara, T.; Ishida, Y.; Ishikawa, T.; Yokota, R. Characterization of multi-walled carbon nanotube/phenylethynyl terminated polyimide composites. *Compos. A Appl. Sci. Manuf.* **2004**, *35*, 67–74.
76. Fu, H.J.; Huang, Y.D.; Liu, L. Influence of fibre surface oxidation treatment on mechanical interfacial properties of carbon fibre/polyarylacetylene composites. *Mater. Sci. Technol.* **2004**, *20*, 1655–1660.
77. Lin, Z.; Ye, W.; Du, K.; Zeng, H. Homogenization of functional groups on surface of carbon fiber and its surface energy. *J. Huaqiao Univ. Sci.* **2001**, *22*, 261–263.
78. Zhang, S.; Hull, T.R.; Horrocks, A.R.; Smart, G.; Kandola, B.K.; Ebdon, J.; Joseph, P.; Hunt, B. Thermal degradation analysis and XRD characterisation of fibre-forming synthetic polypropylene containing nanoclay. *Polym. Degrad. Stab.* **2007**, *92*, 727–732.
79. Singh, A.P.; Pal, K.R. Novel hybrid of clay, cellulose, and thermoplastics. I. Preparation and characterization of composites of ethylene–propylene copolymer. *J. Appl. Polym. Sci.* **2007**, *104*, 2672–2682.
80. Sen, A.K.; Kumar, S. Coir-fiber-based fire retardant nano filler for epoxy composites. *J. Therm. Anal. Calorim.* **2010**, *101*, 265–271.
81. Mohanty, A.K.; Misra, M.; Drzal, L.T. *Natural Fibers, Biopolymers, and Biocomposites*; CRC Pr I Llc: Boca Raton, FL, USA, 2005; p. 852.
82. Oksman, K.; Mathew, A.P.; Bondeson, D.; Kvien, I. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. *Compos. Sci. Technol.* **2006**, *66*, 2776–2784.
83. Darder, M.; Aranda, P.; Ruiz-Hitzky, E. Bionanocomposites: A new concept of ecological, bioinspired, and functional hybrid materials. *Adv. Mater.* **2007**, *19*, 1309–1319.
84. Thwe, M.M.; Liao, K. Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Compos. Sci. Technol.* **2003**, *63*, 375–387.
85. Fu, S.Y.; Xu, G.; Mai, Y.W. On the elastic modulus of hybrid particle/short-fiber/polymer composites. *Compos. B Eng.* **2002**, *33*, 291–299.
86. Karger-Kocsis, J. Reinforced polymer blends. In *Polymer Blends*; Paul, D.R., Bucknall, C.B., Eds.; John Wiley & Sons: New York, NY, USA, 2000; p. 395.
87. Sreekala, M.S.; Kumaran, M.G.; Geethakumariam, M.L.; Thomas, S. Environmental effects in oil palm fiber reinforced phenol formaldehyde composites: Studies on thermal, biological, moisture and high energy radiation effects. *Adv. Compos. Mater.* **2004**, *13*, 171–197.
88. Mishra, S.; Mohanty, A.; Drzal, L.; Misra, M.; Parija, S.; Nayak, S.; Tripathy, S. Studies on mechanical performance of biofibre/glass reinforced polyester hybrid composites. *Compos. Sci. Technol.* **2003**, *63*, 1377–1385.
89. Satyanarayana, K.G.; Sukumaran, K.; Kulkarni, A.G.; Pillai, S.G.K.; Rohatgi, P.K. Fabrication and properties of natural fibre-reinforced polyester composites. *Composites* **1986**, *17*, 329–333.
90. Jacob, M.; Thomas, S.; Varughese, K.T. Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. *Compos. Sci. Technol.* **2004**, *64*, 955–965.
91. Velmurugan, R.; Manikandan, V. Mechanical properties of glass/palmyra fiber waste sandwich composites. *Indian J. Eng. Mater. Sci.* **2005**, *12*, 563–570.

92. Velmurugan, R.; Manikandan, V. Mechanical properties of palmyra/glass fiber hybrid composites. *Compos. A Appl. Sci. Manuf.* **2007**, *38*, 2216–2226.
93. Mandal, S.; Alam, S.; Varma, I.K.; Maiti, S.N. Studies on bamboo/glass fiber reinforced USP and VE resin. *J. Reinf. Plast. Compos.* **2010**, *29*, 43–51.
94. Ahmed, K.S.; Vijayarangan, S.; Kumar, A. Low velocity impact damage characterization of woven jute glass fabric reinforced isothalic polyester hybrid composites. *J. Reinf. Plast. Compos.* **2007**, *26*, 959–976.
95. Ahmed, K.S.; Vijayarangan, S. Tensile, flexural and interlaminar shear properties of woven jute and jute-glass fabric reinforced polyester composites. *J. Mater. Process. Technol.* **2008**, *207*, 330–335.
96. Kumar, N.M.; Reddy, G.V.; Naidu, S.V.; Rani, T.S.; Subha, M.C.S. Mechanical properties of coir/glass fiber phenolic resin based composites. *J. Reinf. Plast. Compos.* **2009**, *28*, 2605–2613.
97. Thiruchitrambalam, M.; Alavudeen, A.; Athijayamani, A.; Venkateshwaran, N.; Perumal, A.E. Improving mechanical properties of banana/kenaf polyester hybrid composites using sodium laulryl sulfate treatment. *Mater. Phys. Mech.* **2009**, *8*, 165–173.
98. Cicala, G.; Cristaldi, G.; Recca, G.; Ziegmann, G.; El-Sabbagh, A.; Dickert, M. Properties and performances of various hybrid glass/natural fibre composites for curved pipes. *Mater. Des.* **2009**, *30*, 2538–2542.
99. Mehta, N.M.; Parsania, P.H. Fabrication and evaluation of some mechanical and electrical properties of jute-biomass based hybrid composites. *J. Appl. Polym. Sci.* **2006**, *100*, 1754–1758.
100. Venkata Reddy, G.; Shobha Rani, T.; Chowdoji Rao, K.; Venkata Naidu, S. Flexural, compressive, and interlaminar shear strength properties of kapok/glass composites. *J. Reinf. Plast. Compos.* **2009**, *28*, 1665–1677.
101. Jawaid, M.; Abdul Khalil, H.P.S.; Abu Bakar, A. Mechanical performance of oil palm empty fruit bunches/jute fibres reinforced epoxy hybrid composites. *Mater. Sci. Eng. A* **2010**, *527*, 7944–7949.
102. Davoodi, M.M.; Sapuan, S.M.; Ahmad, D.; Ali, A.; Khalina, A.; Jonoobi, M. Mechanical properties of hybrid kenaf/glass reinforced epoxy composite for passenger car bumper beam. *Mater. Des.* **2010**, *31*, 4927–4932.
103. Kong, K.; Hejda, M.; Young, R.J.; Eichhorn, S.J. Deformation micromechanics of a model cellulose/glass fibre hybrid composite. *Compos. Sci. Technol.* **2009**, *69*, 2218–2224.
104. De Medeiros, E.S.; Agnelli, J.A.M.; Joseph, K.; De Carvalho, L.H.; Mattoso, L.H.C. Mechanical properties of phenolic composites reinforced with Jute/cotton hybrid fabrics. *Polym. Compos.* **2005**, *26*, 1–11.
105. Esfandiari, A. Mechanical properties of PP/Jute and glass fiberscomposites: The statistical investigation. *J. Appl. Sci.* **2007**, *7*, 3943–3950.
106. Arbelaiz, A.; Fernandez, B.; Cantero, G.; Llano-Ponte, R.; Valea, A.; Mondragon, I. Mechanical properties of flax fibre/polypropylene composites. Influence of fibre/matrix modification and glass fibre hybridization. *Compos. A Appl. Sci. Manuf.* **2005**, *36*, 1637–1644.
107. Wan Busu, W.N.; Anuar, H.; Ahmad, S.H.; Rasid, R.; Jamal, N.A. The mechanical and physical properties of thermoplastic natural rubber hybrid composites reinforced with hibiscus cannabinus, L and short glass fiber. *Polym. Plast. Technol. Eng.* **2010**, *49*, 1315–1322.

108. Taşdemir, M.; Koçak, D.; Usta, İ.; Akalin, M.; Merdan, N. Properties of recycled polycarbonate/waste silk and cotton fiber polymer composites. *Int. J. Polym. Mater.* **2008**, *57*, 797–805.
109. Jiang, H.; Kamdem, D.P. Mechanical properties of poly(vinyl chloride)/wood flour/glass fiber hybrid composites. *J. Vinyl* **2003**, *9*, 138–145.
110. Babaei, I.; Madanipour, M.; Farsi, M.; Farajpoor, A. Physical and mechanical properties of foamed HDPE/wheat straw flour/nanoclay hybrid composite. *Compos. B Eng.* **2014**, *56*, 163–170.
111. Wu, S.-H.; Wang, F.Y.; Ma, C.C.M.; Chang, W.C. Mechanical, thermal and morphological properties of glass fiber and carbon fiber reinforced polyamide-6 and polyamide-6/clay nanocomposites. *Mater. Lett.* **2001**, *49*, 327–333.
112. Akkapeddi, M.K. Glass fiber reinforced polyamide-6 nanocomposites. *Polym. Compos.* **2000**, *21*, 576–585.
113. Vlasveld, D.P.N.; Parlevliet, P.P.; Bersee, H.E.N.; Picken, S.J. Fibre-matrix adhesion in glass-fibre reinforced polyamide-6 silicate nanocomposites. *Compos. A Appl. Sci. Manuf.* **2005**, *36*, 1–11.
114. Sandler, J.K.W.; Pegel, S.; Cadek, M.; Gojny, F.; van Es, M.; Lohmar, J.; Blau, W.J.; Schulte, K.; Windle, A.H.; Shaffer, M.S.P. A comparative study of melt spun polyamide-12 fibres reinforced with carbon nanotubes and nanofibres. *Polymer* **2004**, *45*, 2001–2015.
115. Jawahar, P.; Balasubramanian, M. Influence of nanosize clay platelets on the mechanical properties of glass fiber reinforced polyester composites. *J. Nanosci. Nanotechnol.* **2006**, *6*, 3973–3976.
116. Chandradass, J.; Kumar, M.R.; Velmurugan, R. Effect of nanoclay addition on vibration properties of glass fibre reinforced vinyl ester composites. *Mater. Lett.* **2007**, *61*, 4385–4388.
117. Rattanasom, N.; Saowapark, T.; Deeprasertkul, C. Reinforcement of natural rubber with silica/carbon black hybrid filler. *Polym. Test.* **2007**, *26*, 369–377.
118. Maldas, D.; Kokta, B.V. Performance of hybrid reinforcements in PVC composites. II: Use of surface-modified mica and different cellulosic materials as reinforcements. *J. Vinyl Technol.* **1993**, *15*, 38–44.
119. Najafil, A.; Kord, B.; Abdi, A.; Ranaee, S. The impact of the nature of nanoclay on physical and mechanical properties of polypropylene/reed flour nanocomposites. *J. Thermoplast. Compos.* **2012**, *25*, 717–727.
120. Kord, B. Effect of nanoparticles loading on properties of polymeric composite based on Hemp Fiber/Polypropylene. *J. Thermoplast. Compos. Mater.* **2012**, *25*, 793–806.
121. Zhong, Y.; Poloso, T.; Hetzer, M.; de Kee, D. Enhancement of wood/polyethylene composites via compatibilization and incorporation of organoclay particles. *Polym. Eng. Sci.* **2007**, *47*, 797–803.
122. Kord, B.; Kiakojoouri, S. Effect of nanoclay dispersion on physical and mechanical properties of wood flour/polypropylene/glass fibre hybrid composites. *BioResources* **2011**, *6*, 1741–1751.
123. Arrakhiz, F.Z.; Benmoussa, K.; Bouhfid, R.; Qaiss, A. Pine cone fiber/clay hybrid composite: Mechanical and thermal properties. *Mater. Des.* **2013**, *50*, 376–381.
124. Liany, Y.; Tabei, A.; Farsi, M.; Madanipour, M. Effect of nanoclay and magnesium hydroxide on some properties of HDPE/wheat straw composites. *Fibers Polym.* **2013**, *14*, 304–310.
125. Roco, M.C.; Mirkin, C.A.; Hersam, M.C. Nanotechnology research directions for societal needs in 2020: Summary of international study. *J. Nanopart. Res.* **2011**, *13*, 897–919.

126. Chaturvedi, S.; Dave, P.N. Design process for nanomaterials. *J. Mater. Sci.* **2013**, *48*, 3605–3622.
127. Bartos, P.; Hughes, J.; Trtik, P.; Zhu, W. *Freedonia Group*; Freedonia Group: Cleveland, OH, USA, 2009; p. 174.
128. Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Compos. Sci. Technol.* **2003**, *63*, 2223–2253.
129. Marques, P.A.A.P.; Trindade, T.; Neto, C.P. Titanium dioxide/cellulose nanocomposites prepared by a controlled hydrolysis method. *Compos. Sci. Technol.* **2006**, *66*, 1038–1044.
130. Tai, Y.-Y.; Hsu, S.-H.; Chen, R.-S.; Su, W.-F.; Chen, M.-H. Liquid crystalline epoxy nanocomposite material for dental application. *J. Formos. Med. Assoc.* **2014**, doi:10.1016/j.jfma.2014.01.018.
131. Mihranyan, A.; Ferraz, N.; Strømme, M. Current status and future prospects of nanotechnology in cosmetics. *Prog. Mater. Sci.* **2012**, *57*, 875–910.
132. Presting, H.; Konig, U. Future nanotechnology developments for automotive applications. *Mater. Sci. Eng. C* **2003**, *23*, 737–741.
133. Duncan, T.V. Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *J. Colloid Interface Sci.* **2011**, *363*, 1–24.

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