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Polymer Reviews

ISSN: 1558-3724 (Print) 1558-3716 (Online) Journal homepage: http://www.tandfonline.com/loi/lmsc20

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To cite this article: Olgun Güven, Sergio N. Monteiro, Esperidiana A. B. Moura & Jaroslaw W. Drelich (2016): Re-Emerging Field of Lignocellulosic Fiber – Polymer Composites and Ionizing Radiation Technology in their Formulation, Polymer Reviews, DOI: 10.1080/15583724.2016.1176037

To link to this article: http://dx.doi.org/10.1080/15583724.2016.1176037

POLYMER REVIEWS
http://dx.doi.org/10.1080/15583724.2016.1176037

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Re-Emerging Field of Lignocellulosic Fiber – Polymer Composites and Ionizing Radiation Technology in their Formulation

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ABSTRACT
Natural cellulose-based fibers offer low cost, low density composite reinforcement with good strength and stiffness. Because of their annual renewability and biodegradability, natural fibers have materialized as environmentally-friendly alternatives to synthetic fibers in the last two decades. They are replacing synthetic materials in some traditional composites in industrial manufacturing sectors such as automotive, construction, furniture, and other consumer goods. In this work, the use of lignocellulosic fibers in green materials engineering, particularly their application as polymeric composite reinforcement and surface treatment via ionizing radiation are reviewed. Because these cellulose-based materials are intrinsically hydrophilic, they require surface modification to improve their affinity for hydrophobic polymeric matrices, which enhances the strength, durability, and service lifetime of the resulting lignocellulosic fiber-polymer composites. In spite of a long history of using chemical methods in the modification of material surfaces, including the surface of lignocellulosic fibers, recent research leans instead towards application of ionizing radiation. Ionizing radiation methods are considered superior to chemical methods, as they are viewed as clean, energy saving, and environmentally friendly. Recent applications of controlled ionizing radiation doses in the formulation of natural fiber –reinforced polymeric composites resulted in products with enhanced fiber-polymer interfacial bonding without affecting the inner structure of lignocellulosic fibers. These applications are critically reviewed in this contribution.

KEYWORDS
Composite; gamma radiation; ionizing radiation; lignocellulose; lignocellulosic fibers

1. Introduction

The incorporation of synthetic fibers with high aspect ratio and high stiffness into a polymeric matrix results in the creation a new composite material with tailored mechanical properties. Composites have rapidly emerged as favored lightweight materials beginning in the

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middle of the twentieth century. Cellulose-based fibers (also referred as plant, vegetal, and lignocellulosic fibers, or biofibers) offer low density, good strength, and high stiffness. Because of their annual renewability and biodegradability, they are currently being realized as environmentally friendly alternatives to synthetic fibers. However, the use of cellulose-based natural fibers as reinforcements in fact has deep roots in human history. Archeological artifacts suggest that cellulose-based natural fibers such as grass, hemp, banana, pineapple, sisal, coconut, palm, etc., have been used for millennia by humans all over the world to manufacture daily and ceremonial clothing, food storage vessels, to preserve foodstuffs, in hunting and defense tools, in early seafaring, and for construction purposes. The strength of natural fibers made them useful in lines, ropes, and nets for carrying and moving heavier objects, fishing, the construction of suspended footbridges, rigging for naval ships, and probably many others. A variety of ropes, textiles, nets, baskets, carpets, canvas, and paper produced from natural fibers are still in use today.

Research and innovation working towards so-called "green materials"—those with lower embodied energies and low-impact process chains—has thrived in recent decades. This also holds true in the plastics industry, where there has been a renewed interest in using natural fibers as composite reinforcement. Particularly in the last two decades, thousands of research works have been dedicated to natural fibers and their incorporation in polymeric composites, as has been summarized in several review papers.[1–17] The natural fiber-polymer composite materials are gaining traction in research laboratories as indicated by escalating the number of publications on this topic in the last two decades. According to ISI Knowledge only 24 papers with keyword "natural fiber" were published in 1990. This number surpassed 1,000 in 2010 and it is becoming an increasingly topical subject (Fig. 1). Among those papers, the contribution with keyword "natural fiber composite" increased from 12.5% (3 papers) in 1990 to 46% (686 papers) in 2014 (Fig. 1).

Natural fibers are gradually replacing synthetic materials in traditional composites found in the automotive, construction, furniture, and commodity industrial sectors.[18] Both natural

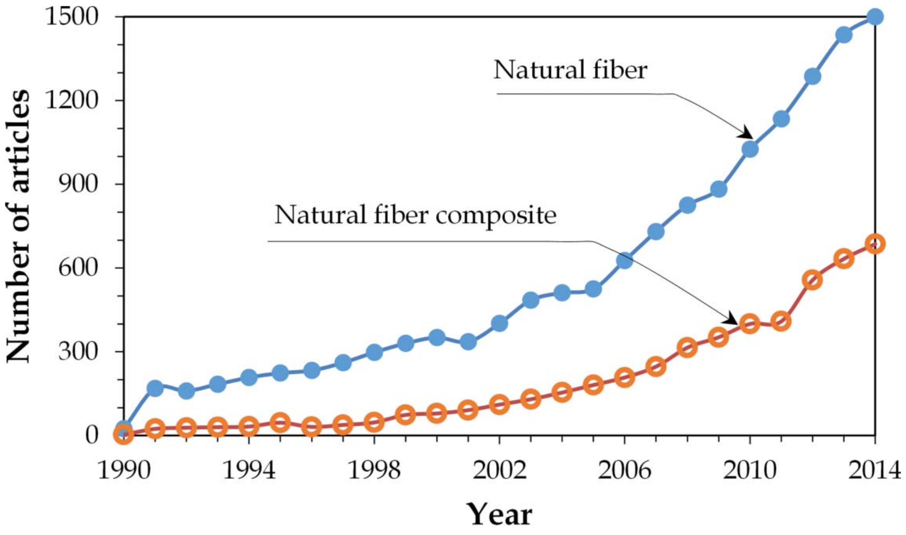

Figure 1. Number of papers with keywords "natural fiber" and "natural fiber composite" reported by ISI Knowledge between 1990 and 2014.

fiber-thermoset and fiber-thermoplastic composites have found applications in automotive interiors (i.e., door panels, dash boards, seat backs, headrests, trim, etc.) and in household interiors (i.e., ceiling tiles, door and window frames, decking material, railings for the parapet wall systems, furniture sections, etc.).[18–21] Increasing social demand for eco-friendly products and consumer goods is not the only driving force for natural fibers to make a successful comeback. An increasing body of data on the physical and mechanical properties of natural fibers, including structure-property relationships for natural fiber containing composites, has helped to justify replacement of synthetic fibers with natural alternatives in recent years.[11–17]

The primary aim of this contribution is to summarize the last 20+ years of research on the addition of lignocellulosic fibers to polymeric matrices, with a secondary goal of bringing awareness to this new class of "green" composite materials. We also dedicate a portion of this review to the cleaning and functionalization of lignocellulosic fiber surfaces using ionizing radiation, which is considered to be a largely waste-free, energy saving, and environmentally friendly technology that promises to improve the compatibility of natural fibers with polymers. We also briefly review the effects of radiation on curing of natural fiber matrix composites, radiation cross-linking, and grafting of materials. These treatments of lignocellulosic fiber reinforcements, if appropriately executed, result in composites of enhanced tensile strength, impact resistance, thermal stability, etc.[22–24] To put this topic in context, the properties of the lignocellulosic fibers are also discussed.

The paper is organized as follows: The review starts with a brief history of lignocellulosic fiber – polymer matrix composites and its current status, followed by discussion of the advantageous and disadvantageous properties of lignocellulosic fibers. Then the classification of lignocellulosic fibers and their properties are reviewed, along with the benefits derived from their use as polymer composite reinforcement. The structure, morphology, chemical composition, and mechanical properties of lignocellulosic fibers and their relation to reinforced composites are reviewed in Section 3. Section 4 summarizes fiber surface characteristics in terms of wettability, surface energy, and adhesive bonding. Ionizing radiation methods and their effects on fiber surface chemistry are summarized in Section 5. The paper concludes with a summary of the current state of the research in this area and future directions.

2. Lignocellulosic fiber reinforcements: Origins, appeal, and drawbacks

2.1 A brief history of lignocellulosic fiber composites

The concept of reinforcing other materials with vegetation dates back nearly to the dawn of man. Grass and straw were used as reinforcement in prehistoric clay bricks by some of the earliest civilizations (Table 1). As early as 1500 B.C.E., Egyptian and Mesopotamian settlers mixed mud with straw, which, after drying in sunlight to create bricks, were used in durable structures.[25] Similar, primitive mud-grass composites were also used in ancient pottery and as a marine sealant.[25] Wooden boats and barrels were typically waterproofed (caulked) by patching with natural fibers and then sealing with asphalt, tar, and bitumen or tree resin. The waterproofing of boats and barrels originated in biblical times, if not earlier.[26] In 1200 C.E., the Mongolian archers were armed with a powerful and accurate bow that gave the army of Genghis Khan a substantial military advantage. This bow was made of wood,

Table 1. The use of composite materials with plant reinforcement before 1990.

Date	Product	Matrix	Plant Reinforcement
1500s B.C.	Mud bricks (Egypt and Mesopotamia)	Clay	Grass, straw
Biblical times	Wooden boat waterproofing (Roman Empire and beyond)	Asphalt/tar/bitumen Tree resin pitch	Natural fibers
1200 AD	Hunting bow (Mongolia)	Bone and animal glue	Wood
Mid-late 1800s	Waterproofing roofing	Bitumen	Jute and straw
1908	Sheets, tubes and pipes for electronics and electrical systems	Phenol-formaldehyde and melamine-formaldehyde	Cotton, cellulose/paper
1960s	Automotive car seats made of rubber	Rubber	Coconut fiber
1960s	Car interior	Polypropylene	Wood flour

bone, and animal glue wrapped with birch bark.[25] Waterproofing of building roofs started in the mid-to-late 1800s and was typically done with bitumen reinforced with either jute or straw.[26]

Experimental reinforcement of the first plastics came soon after their invention and commercialization. In 1908, paper and cotton were added to phenol-formaldehyde and melamine-formaldehyde plastics. These resulting composites were used to fabricate large quantities of sheets, tubes, and pipes. More recently, in the 1960s, coconut fiber reinforced natural rubber latex was used extensively by the automotive industry to manufacture car seats. Similarly, polypropylene was reinforced with wood flour and used in other car interior parts. However, glass fibers and other synthetic fibers have since displaced natural fiber reinforcements in the polymeric composite market in the second half of twenty century. Renewed interest in lignocellulosic fiber reinforcements emerged approximately 20–25 years ago and is driven, as indicated earlier, by a demand in the marketplace for environmentally friendly, renewable, and biodegradable materials and products.

Currently, cellulose-based fibers are replacing glass fibers in composites in automotive and construction industries as well as consumer goods.[18] Light natural fiber-based composites are attractive to practically all sectors of the automotive industry, as they offer weight savings relative to their counterparts made of glass fibers and ultimately improve the fuel economy, sound absorption, and vibration damping of vehicles in which they are used. For example, car linings featuring plastic composites reinforced with flax and hemp fibers are about 30% lighter than other versions that employ glass fibers.[27] This new lining has mechanical properties comparable to glass fiber based lining, offers control over humidity, is free of release of any unpleasant odors, absorbs sounds and vibrations, and provides thermal insulation.[27] Other parts of cars made with natural fibers include door frames, dash boards, seat backs and headrests, shelves, interior sound proofing layers, and others.[18,27] These examples from the automotive industry have driven similar developments in both the aviation and railway transportation sectors.[27] Many other examples of applications of natural fiber-polymeric matrix composites can be found in the book edited by Kalia et al.[28] and references therein, and will not be repeated here.

Whether the lignocellulosic fibers successfully compete with the glass and other synthetic fibers as reinforcement in structural composites depends on specifications and characteristics of the particular application. However, only green composites with enhanced fiber-matrix compatibility and adhesion, which have attractive mechanical and other properties, can seriously compete with existing synthetic fiber reinforced composites.[15] Indeed, the interfacial adhesion between lignocellulosic fibers and polymers remains a challenge as will be discussed later in this contribution. Before the roots and details of this problem are discussed a general overview of the attributes offered by lignocellulosic fibers and challenges that need to be dealt with are discussed.

2.2 Pros and cons of lignocellulosic fiber reinforcements

The worldwide availability and eco-friendly image of natural fibers, their increasingly attractive price relative to synthetic fibers, and a set of favorable physical properties have resulted in industry taking a favorable view towards lignocellulosic fiber reinforcements. The lignocellulosic fibers are also typically stiffer than synthetic fibers. Potential advantages and benefits in replacing synthetic fibers with natural ones are listed in Table 2 and include low cost, low density, good specific mechanical properties, less energy consumption and pollution emission during manufacturing, availability from renewable resources, biodegradable and bio-friendly nature, and less abrasion and concomitant damage to processing equipment.

There are also more environmental, social, and economic reasons behind the renaissance in natural fiber engineering observed in recent years. Since they come from cultivated and cropped vegetation and trees, any waste generated during agricultural activities and plant processing, being organic in nature, is typically organic in nature and either biodegradable or useful as biochemical and biofuel precursors. Also, the use of agricultural and forestry resources opens additional business development opportunities in countries that are short of fossil fuel resources. India, Malaysia, Indonesia, Philippines, Brazil, and some African countries have already established national priority projects for the utilization of agricultural resources and wastes generated by farms and food processing plants. Examples include utilization of coconut-related materials, wastes from rubber and palm oil industries, rice husks, etc. Natural fibers thus attract a lot of attention in developing countries as their mass production could generate badly needed employment in impoverished rural areas.[29,30] The development of natural fiber-based composite materials has been seen, therefore, as an important provider of opportunities to improve the standard of living for people around the world.

The picture drawn in this section would not be complete without discussing disadvantages of lignocellulosic fibers. There is the reason that glass, carbon, and aramid fibers and their fabrics are still the most common reinforcements used in formulation of polymeric

Table 2. Advantages and disadvantages of lignocellulosic fibers as reinforcements.

Attributes of Interest	Points of Concern
• Lowering the cost of product; • Lowering the density of composite; • Higher specific mechanical properties; • Reducing the energy consumption and pollution emission during manufacturing; • The use of material from renewable (endless) resources; • Biodegradable and bio-friendly nature of fibers; • Less abrasiveness to the processing equipment.	• Large scatter of physical properties; • Structure of plant fibers is highly inhomogeneous; • Fibers are short; • High level of moisture absorption; • Dimension instability as a negative effect of water absorption; • Susceptibility to microbial attack and rotting; • Restricted processing temperature due to low decomposition temperature of chemical components; • Insufficient adhesion and incompatibility with the matrix; and • Degradation and aging.

composites in spite of the low cost of natural fibers. Poor adhesion, reduced toughness, low thermal resistance, intrinsic hydrophilicity, and variable properties have prevented the use of plant fibers from competing with synthetic fibers at large scale for a few decades until recently.[31]

Lignocellulosic fibers such as flax, hemp, jute, and ramie are a promising renewable and sustainable substitute for glass fibers in composites due to their good intrinsic mechanical properties, low density, and low price. For example, it has been known for over a decade that composites reinforced with flax fibers showed stiffness comparable or even better than that of commercial composites reinforced with glass mat and thermoset sheet molding compound.[32–34] However, due to the composite-like structure of lignocellulosic fibers, the opposite of single filament synthetic fibers,[35] the strength of composites with flax fibers was low compared to the strength of composites reinforced with glass fibers.[33]

Natural fibers can take different forms that depend on the degree of fiber isolation, variable surface characteristics, and fiber processing and treatment conditions. By improving these aspects of natural fibers, the quality and mechanical behavior of natural fiber-polymer composites may be enhanced. These challenges lie ahead of researchers who have just begun a journey in the formulation of composites with natural fiber reinforcements. Overarching challenges to lignocellulosic fiber reinforced polymers are listed in Table 2 and include[36,37] large scatter of physical properties, inhomogeneity of fibers, short length of fibers, moisture absorption and dimensional instability associated with this absorption, susceptibility to microbial attack and rotting, degradation and aging, low decomposition temperature, and insufficient adhesion and incompatibility with the polymeric matrix. These disadvantages impose some limits on applications of lignocellulosic fibers as reinforcement, but also provide opportunities to researchers to find a way to either eliminate or minimize their effects. In this contribution, we concentrate on the modification of fibers through ionizing radiation, which leads to improvements in adhesion and compatibility of lignocellulosic fibers. To put this topic in proper context, the structure and properties of the plant fibers are discussed.

3. Plant fibers: Structure, composition, morphology, and mechanical properties

3.1 Classification of fibers

Natural fibers are either mined (minerals such as asbestos) or are supplied from renewable resources including wool (hair) from several animals, silk produced by insects, and lignocellulosic fibers separated from a variety of plants. Since this review is limited to renewable lignocellulosic fibers, the classification in Fig. 2 and Table 3 is limited to a few of the most common fibers from plants. Scanning electron micrographs of lignocellulosic fibers are shown in Fig. 3.

The plants from which fibers are separated are cropped and cultivated throughout the world, but mostly in tropical and subtropical climates and mostly in developing countries. Technologies widely used by the textile industry to extract fibers from the plants are not discussed in this review, although it should be recognized that both plant growth conditions and extraction processes affect mechanical and moisture retention properties of the fibers.[31,38–40] Plant fibers on the market are graded according to color, luster, cleanliness, strength, fineness, and uniformity.[41]

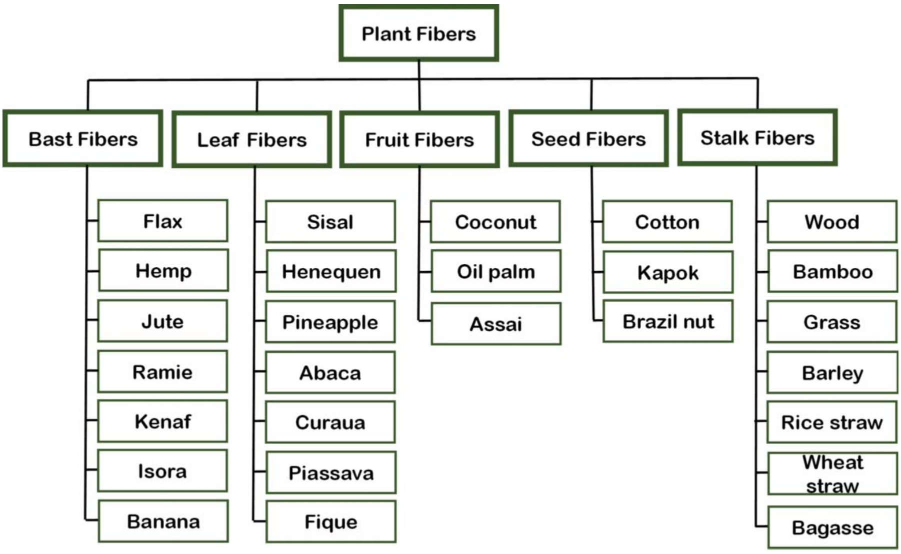

Figure 2. Classification of plant fibers.

Table 3. Source of some fiber plants (after Wayne's Word, An Online Textbook on Natural History. http://waynesword.palomar.edu/traug99.html).

Commercial Name	Scientific Name	Plant Family
	Stem (Bast) Fibers	
Flax	Linum usitatissimum	Linaceae (Flax)
Ramie	Boehmeria nivea	Uriticaceae (nettle)
Jute	Corchorus capsularis	Tiliaceae (Basswood)
Kenaf	Hibiscus cannabinus	Malvaceae (Mallow)
Sunn Hemp	Crotalaria juncea	Fabaceae (Legume)
Indian Hemp	Apocynum cannabinum	Apocynaceae (Dogbane)
	Cannabis sativa	Cannabaceae (Marijuana)
	Leaf Fibers	
Sisal	Agave sisalana	Agavaceae (Agave)
Henequen	Agave fourcroydes	Agavaceae (Agave)
Yucca	Yucca elata	Agavaceae (Agave)
Bowstring Hemp	Sansevieria trifaciata	Agavaceae (Agave)
	Sansevieria roxburghiana	
	Sansevieria hyacinthoides	
New Zealand Flax	Phormium tenax	Agavaceae (Agave)
Abaca	Musa textilis	Musaceae (Banana)
	Seed Fibers	
Cotton	Gossypium hirsutum	Malvaceae (Mallow)
	Gossypium arboretum	
	Gossypium herbaceum	
	Gossypium barbadense	
Coir	Cocos nucifera	Arecaceae (Palm)
	Fibers from Seed Pods	
Kapok	Ceiba pentandra	Bombacaceae (Bombax)
Floss silk	Chorisia speciosa	Bombacaceae (Bombax)

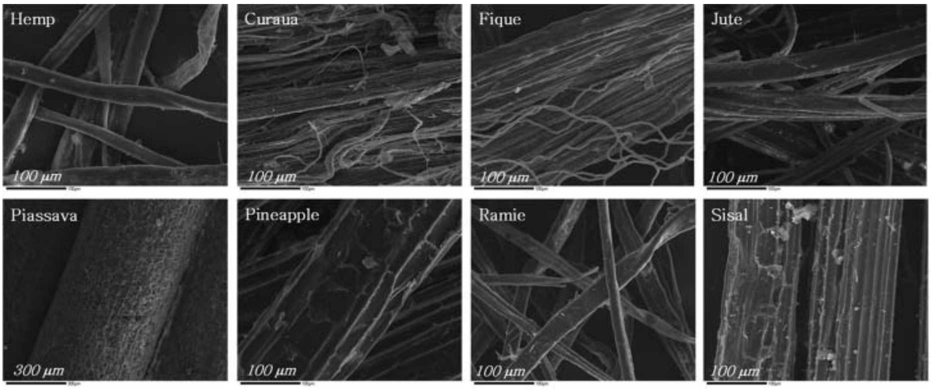

Figure 3. Examples of plant fibers.

According to Fig. 2 and Table 3, the fibers are classified per their location in the plant. Flax, hemp, jute, ramie, kenaf, isora, and banana fall under the category of bast fibers, which are extracted from the plant after harvesting by rotting the stems by submerging them in ponds or streams.[42,43] Leaves of sisal, agave, abaca, curaua, piassava, and fique are also sources of fibers. However, these are separated through crushing and scraping, followed by washing.[44,45] Since the fibers in bast and leaves are integral to the plant structure, they provide strength and support. Fibers may also be extracted from plant seeds[46] and fruit[47] (Fig. 2). Stalks of other plants including grass, bamboo, straws of wheat, rice, barley, bagasse, or even tree wood may also be used as a source of fibers. Different plant fibers, along with their origins and properties, are described in detail by Faruk et al.[15] and Thakur and Thakur.[48]

3.2 General structure and morphology of plant fibers

The structure of flax fiber is the most commonly discussed in the literature and in online resources. Figure 4 shows an intricate structure of a flax stem with fibers.

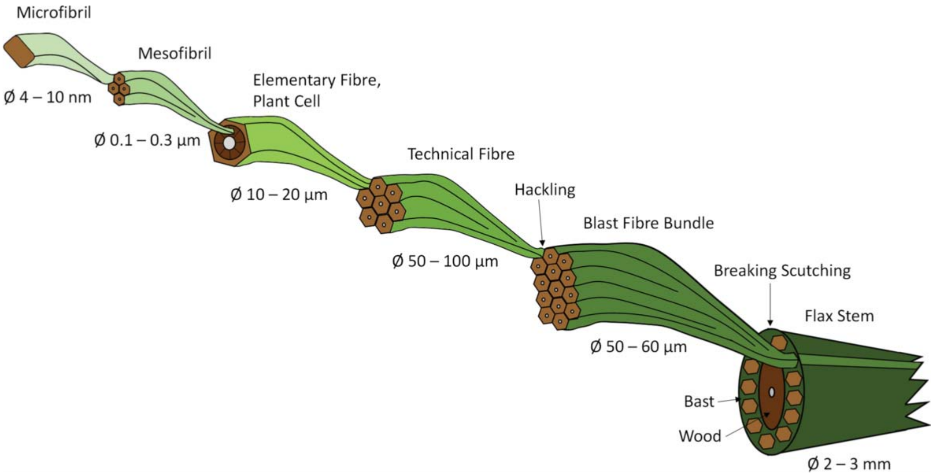

Figure 4. Structure of the flax stem, together with the images of flax plant and flax fiber.

Flax fibers used in composites can vary from fiber bundles to elementary fibers, or to even further opened-up shapes (Fig. 4). Mechanical properties can differ significantly between these different forms. Technical fibers (fiber bundles) up to a meter in length, consisting of 2–5 cm long and 10–20 μm diameter elementary fibers, are typically isolated from the flax plant through breaking and scotching processes, and are often used in the textile industry.[36,49] The technical fibers serve as reinforcements in thermoplastic and thermoset composites due to their acceptable price-performance ratio.[49] The individual polyhedron-cross section fibers are, unfortunately, weakly bonded together with pectin in these bundles, making the lateral strength of this reinforcement poor compared with their axial strength. However, the individual fibers are strong, with tensile strengths of up to about 1,500 MPa.[49]

3.3 Chemical make-up of plant fiber

Plant fibers are composed of cellulose and hemicellulose (sugar-based polymers), lignin (complex polymer of aromatic alcohols), pectin (complex set of polysaccharides), structural water, and wax or oil.[31,48,50] Since cellulose is the principal chemical component of plant fibers, with varying amount of hemicellulose and lignin, they are often referred to as lignocellulosic or cellulosic. Elementary fibers are built of oriented, highly crystalline cellulose fibrils, and amorphous hemicellulose. The crystalline cellulose fibrils form due to hydrogen bonding between macromolecules, and their orientation in the cell wall give the fiber its high tensile strength.[31,51] Lignin is covalently linked to hemicellulose and crosslinks polysaccharides, and it fills spaces in the cell wall between the cellulose, hemicellulose, and pectin components, thus providing strength to the cell wall. The chemical structure of a cellulose monomer, along with some segments of hemicellulose and lignin are shown in Fig. 5. The primary functional groups for all three structures include hydroxyl groups, which are vulnerable to chemical modification. This becomes important when considering routes to make the surface chemistry of fibers more compatible and adhesive to a polymeric matrix.

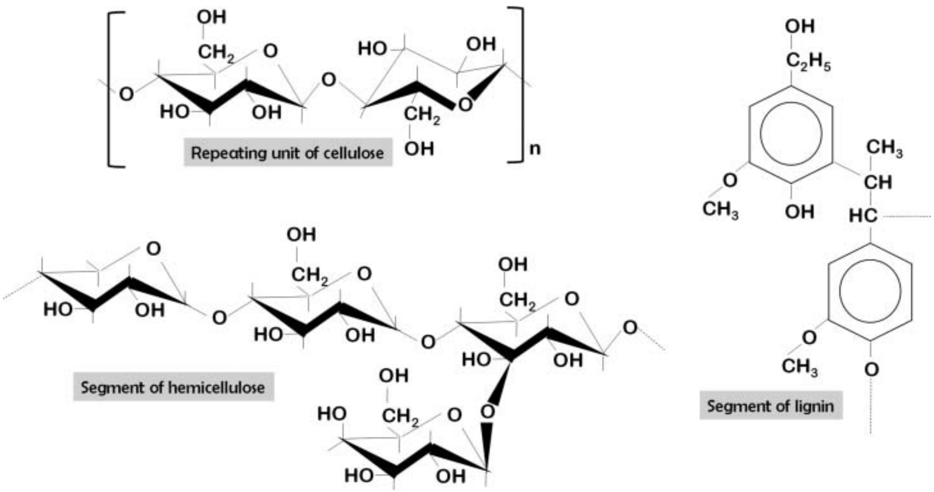

Figure 5. Chemical structure for cellulose monomer, a segment of hemicellulose and a segment of lignin.

3.4 Mechanical properties of lignocellulosic fibers

Characterization of lignocellulosic fibers takes into account the same physical properties as synthetic fibers. However, the physical parameters measured are typically spread over a broader range of values, reflecting variability in chemical composition, crystallinity, diameter, and cross-sectional shape, strength, and stiffness from fiber to fiber, and even from one section of the fiber to another.[36] The variability of fiber properties is also affected by the climate and weather conditions under which the plants were cultivated, harvesting conditions, as well as conditions of separation and processing of the fibers.[36] Inconsistency in the properties of lignocellulosic fibers requires the application of rigorous quality control so that uniformity in the resulting composite may be achieved. If variability in the fiber-to-fiber mechanical properties is controlled, then theories and models developed for traditional, synthetic fiber composites may also be applied to those containing natural fibers.

Mechanical properties for lignocellulosic fibers were recently compiled by Celino et al.,[31] and they are shown in Table 4. A single-fiber tensile testing method is commonly used to measure the tensile strengths of individual fibers, in addition to their elongations to fracture, and elastic moduli.[37,53–56] The Weibull distribution is recommended to approximate the distribution of measured values.[37,54,55] Nonlinearity in the stress-strain response during hardening observed for many fibers relates to reorganization of the cellulose fibrils along the loading axis.[56] A plant fiber is a composite with unidirectional cellulose microfibrils that constitute the reinforcing elements in a matrix of hemicellulose and lignin.[15,48] The cellulose microfibrils spiral angle, which has a pronounced influence on the fiber properties, is stretched under applied tensile constraints. This causes nonlinear elastic behavior and contributes to significant changes in the stiffness and toughness of a fiber reinforced polymer composite.[13] In fact, the complex micro rupture process of a plant fiber, with a sequence of individual stretching, separation from the matrix, and breaking of microfibrils, provides both improved strength and higher absorbed mechanical energy for a macro-composite.

Looking into the properties of individual classes of lignocellulosic fibers in Table 4, flax, nettle, and ramie appear to be the most attractive. Compared to synthetic fibers, these three natural fibers compete with glass fibers vis-à-vis specific strength, especially for lignocellulosic fibers with a tightly controlled distribution of tensile strengths.

Table 4. Typical physical and mechanical properties of natural fibers (based on data compiled in Celino et al.[31])

				Tensile Strength	
Fibers	Density [g/cm^3]	Elastic modulus [GPa]	Elongation at break [%]	Strength [MPa]	Specific strength
Bamboo	0.6–1.1	11–17	NA	140–230	127–383
Coconut	1.15	4–6	15–40	131–175	114–152
Cotton	1.5–1.6	5.5–12.6	7–8	287–597	179–398
Flax	1.54	28–85	1–4	345–2000	224–1300
Hemp	1.47	17–70	1.6	368–800	250–544
Jute	1.44	10–30	1.5–1.8	393–773	273–537
Kenaf	1.2	14–53	1.6	240–930	200–775
Nettle	1.51	25–87	2.1–2.5	560–1600	370–1060
Ramie	1.5–1.56	27–128	1.2–3.8	400–1000	256–667
Sisal	1.45–1.5	9–22	2–7	350–700	233–483
E-glass	2.5	70	2.5	2000–3500	800–1400
Carbon	1.4	230–240	1.4–1.8	4000	2860

As mentioned above, significant differences between natural and synthetic fibers include dimensional and compositional non-uniformity. The effect of fiber diameter on the tensile strength was studied in detail for several lignocellulosic fibers[52,57] including bamboo, coir, curaua, jute, piassava, ramie, sisal, banana, and buriti. For all fibers examined, the tensile strength versus fiber diameter correlations conformed to the Weibull distribution function,[58] with correlation coefficients typically above 90% (Table 5). Table 5 summarizes the findings. Only in the case of coir and ramie fibers were the correlations less convincing, suggesting that these two types of fibers have a broader range of structural inhomogeneity than other lignocellulosic fibers tested. For all fibers tested, their strength increased with decreasing diameter. This clearly suggests that grading of natural fibers by diameter could ultimately improve the quality of such reinforcement, resulting in higher, more consistent composite strength values.

4. Surface characteristics and compatibility of fibers

Sufficient natural fiber-polymeric matrix adhesion is needed to ensure good mechanical performance of the composite. This is primarily due to the fact that the magnitude of the stress borne by the composite is related to the transfer stress from the matrix to the fibers. Indirect information on natural fiber-polymeric matrix adhesion may be gathered through analysis of the fibers' surface chemical and physical surface structure. Key surface properties include surface roughness, which provides the foundation for mechanical interlocking, and wettability and surface energy, which signal compatibility and surface functionality, and reveal opportunities for chemical bonding.

As discussed earlier, many lignocellulosic fibers have rough surfaces, and their specific characteristics depend on the fiber type and processing conditions (Fig. 3). Rough and uneven surfaces provide anchorage points for mechanical interlocking with the polymeric matrix. Rougher surfaces provide larger surface area for interacting with polymeric matrix. Typically, however, processing of lignocellulosic fibers to enhance their roughness is not considered to be a practical option, since roughening might deteriorate mechanical properties of the natural fibers.[59]

4.1 Wetting and surface energy

Compatibility of reinforcement with a polymeric matrix can be analyzed through wettability studies. Contact angle measurements for molten polymers on fibers are not convenient, as

Table 5. Relationship between tensile strength (σ_c) and diameter of the plant fiber (d).[52]

Plant Fiber	Diameters Examined [μm]	Equation on tensile strength [MPa]	Correlation coefficient [%]
Bamboo	200–700	$\sigma_c = 54/d + 49$	98
Banana	30–450	$\sigma_c = 24/d + 17$	98
Buriti	400–800	$\sigma_c = 96/d + 15$	99
Coir	50–750	$\sigma_c = 13/d_c + 68$	74
Curaua	50–275	$\sigma_c = 67/d_c - 196$	95
Jute	50–170	$\sigma_c = 19/d_c - 64$	99
Piassava	250–2300	$\sigma_c = 620/d_c + 349$	92
Ramie	25–193	$\sigma_c = 21/d_r + 389$	88
Sisal	50–350	$\sigma_c = 39/d_c + 209$	93

they require set-ups in which the temperature can be raised to above the melting point of the polymer; they are not typically used in practice. Instead, the wetting of natural fibers is analyzed by using water and organic solvents to determine either the critical surface tension of wetting or the surface free energy for the fiber. Determination of the Zisman's critical surface tension of wetting,[60] which can predict conditions under which liquids, including molten polymers, spread completely on the surface of the material under consideration, is not commonly executed on natural fibers however. For example, the critical surface tension of wetting was reported for cellulose and flax fibers to be 39–41 mN/m and 35–40 mN/m, respectively.[61] Any polymer with a surface tension close to or less than these values (which includes a majority of thermoplastics and thermosets) will easily spread on the surface of cellulose and flax fibers. The polymers would therefore have the ability to penetrate the fiber reinforcement architecture (i.e., fabric, aligned fibers, randomly oriented mat, etc.) without the use of vacuum (vacuum is sometimes used to accelerate the penetration of molten polymer into filler structure).

Surface free energy is a more useful quantity, as it can be used in thermodynamic relationships describing both wetting and adhesive properties of material. The surface free energy of fibers is commonly evaluated through contact angle, particle-substrate adhesion, or inverse chromatography measurements.[59] Table 6 summarizes surface free energy values reported in the literature for lignocellulosic fibers. In a few studies, both the total and dispersive components of surface free energy were determined. In inverse gas chromatography studies, the outcome is often limited to the dispersive component of the surface free energy. The dispersive component typically contributes 80–100% to the total surface free energy of organic solids. Based on existing evidence, this also appears to apply to cellulose-based materials.

Table 6. The literature values for the surface free energy and dispersive component of surface free energy of natural materials. The values reported were determined using either contact angles (CA), inverse gas chromatography (IGC) or atomic force microscopy (AFM) measurements.

'Natural Fiber/Material	Surface Free Energy [mJ/m^2]	Dispersive Component of Surface Free Energy [mJ/m^2]	Method and Ref.
Bamboo	45.5	42.3	CA[62]
	38.8	35.4	CA[63]
	NA	38.9	IGC[59]
Cotton linter	50.3	41.2	CA[62]
Cellulose pulp	53.5	34.5	CA[64]
Cellulose (crystalline)	60–66	NA	IGC[65]
Hemp	41	NA	AFM[66]
	NA	40.7	IGC[59]
	NA	46.7	IGC[67]
Cotton cellulose	NA	46–48	IGC[68]
Lyocell	NA	48.6	IGC[69]
	NA	39.0	IGC[59]
Corn husk	NA	37.8	*ibid*
Sisal	NA	38.3	*ibid*
	NA	37.5	IGC[67]
Flax	NA	43.1	IGC[59]
	NA	51.4	IGC[67]
Coir	38.4	31.5	CA[70]
	37.5	35.5	CA[71]
Kenaf	NA	42.8	IGC[67]
Agave	NA	42.0	*ibid*
Pineapple	NA	39.6	*ibid*

As shown in Table 6, a typical value for the surface free energy of lignocellulosic fibers is close to 40 mJ/m^2, although it can increase to as much as 60 mJ/m^2 for cellulose. Heng et al.[59] found that the changes in surface free energy are directly related to the content of crystalline cellulose in lignocellulosic fibers. They suggested that processing routes that increase the cellulose content of lignocellulosic fibers can lead to higher surface free energies.

Variation in surface free energies for the same fiber types measured in different laboratories (Table 6) is, again, an indication of fiber variability with respect to quality and physical structure of the fibers, with variations among external and internal roughness and porosity.[72] Liquids used in contact angle measurements will often cause lignocellulosic fibers to swell, which further complicates the interpretation of experimental contact angle data from which surface free energy is calculated.

As mentioned earlier, mechanical properties of fiber reinforced polymer composites are controlled by stress transfer efficiency at interfaces, among other factors.[15,24,73,74] Major drawbacks of natural fibers in composites include their poor compatibility with polymeric matrix and a relatively high potential for moisture sorption. The surface OH groups attract free water, which worsens the ability of the fiber to develop adhesive binding with polymer.[2,18] Due to the presence of large numbers of hydroxyl groups in the structure of cellulose, hemicelluloses, and lignin, all natural fibers are considered hydrophilic and they absorb moisture easily, up to 30 wt% at 95% relative humidity.[75] However, only hydroxyl groups in an amorphous state are accessible to surrounding and wetting liquids (including molten polymers), whereas the vast majority of OH groups in crystalline phases are involved in the formation of cellulose crystals through hydrogen bonding.[18] Studying the degree of crystallinity in lignocellulosic fibers is therefore an important part of their characterization, as well as in understanding their compatibility with other materials.

The nature of the fiber-matrix interface critically influences the overall properties of composite materials.[76] The control over the stress transfer between fiber and matrix, stress distribution, and mechanisms of damage propagation and accumulation rely on the fiber-matrix adhesion and the nature of the interphase. Even with high-strength fibers as reinforcement, low mechanical performance of the composite is expected if fiber-matrix adhesion is weak. Common structural polymers such as polyethylene, polypropylene, and polyester are hydrophobic and interact weakly with hydrophilic lignocellulosic fibers. The tendency of lignocellulosic fibers to swell and to hold bound water on their surfaces only worsens their compatibility with matrix polymers. In addition, the waxy substances in plant fibers can also influence their wettability and matrix-fiber adhesion characteristics.[15,24,73,74] Other factors including surface area, physical surface structure, and porosity of the fibers should also be taken into account as factors that control interfacial adhesion and ultimately affect the performance of composites.

4.2 Adhesive characteristics

Because of the complexity of fiber-matrix interactions and indirect correlations with wetting and surface free energy parameters, the most reliable testing on compatibility and adhesion is through direct pullout tests. In the past, the fiber-matrix bonding conditions were analyzed through the single fiber-matrix pull out tests for several lignocellulosic fibers embedded in polyester, epoxy matrix,[77–83] and other polymers.[71] Through the critical length pullout curves, both the critical length (ℓ_c) for effective matrix reinforcement with the lignocellulosic fibers and interfacial shear strength of lignocellulosic fibers in polymeric matrix were determined.[13,84] Table 7 summarizes the results.

As shown in Table 7, the values of the interfacial shear strength range from 2.3 to 7.3 MPa for untreated fibers. These values indicate a weak adhesion between lignocellulosic fibers and polyester and epoxy, common thermoset polymers, and thermoplastics such as polypropylene and poly(vinylidene fluoride). Substantial improvement to the matrix adhesion of lignocellulosic fibers is needed. For example, an interfacial shear strength greater than 50 MPa was reported for the carbon fiber/epoxy systems.[85] Improvements in fiber-matrix adhesion can be accomplished through means similar to synthetic fibers, such as by cleaning and applying chemical or biological treatments. For example, interfacial shear strengths exceeding 15 MPa were reported for natural fibers after surface chemical treatments were used.[86,87]

In the following section, a short discussion is presented on methods used to modify lignocellulosic fiber surfaces with the purpose of improving its adhesion to a polymer matrix. Physical and chemical methods that have already been extensively reviewed are only briefly highlighted in order to contrast them with ionizing radiation.

4.3 Surface modification alternatives

Several different technologies for natural fiber surface treatment were developed in the past two decades to improve compatibility with polymer matrix and reduce water sorption.[88–102] Both physical and chemical methods have been proposed for surface modification. As indicated by Bledzki et al.,[88] some physical modifications might include stretching, calendaring, thermal treatments, electric discharge (corona, cold plasma), and production of hybrid yarns. These conventional physical treatments do not change the chemical composition but modify the structural and surface properties of natural fibers and thereby influence their mechanical adhesion with a polymer matrix. Chemical modifications, including alkaline mercerization, esterification, methylation, silylation, acetylation, and maleate coupling agents, as well as treatments with potassium permanganate, sodium chlorite, and isocyanate stearic acid have been the subject of both specific and review papers.[2,15,48,86–96] Some very recent review papers on chemical modifications[15,48,96] exempt the present review from going into further detail.

Unfortunately, chemical treatments often involve toxic and/or hazardous chemicals, the handling and disposing of which increases both the cost and complexity of new technologies,

Table 7. Critical length (ℓ_c) and corresponding interfacial shear strength (IFSS) of lignocellulosic fibers in different polymers (ND – not disclosed).

Plant fiber/polymeric matrix	ℓ_c [mm]	IFSS [MPa]	Ref.
Piassava/polyester	15.3	2.4 ± 0.5	[84]
Curaua/polyester	10.2	3.4 ± 1.2	
Coir/polyester	5.4	3.8 ± 1.1	
Ramie/polyester	1.6	6.2 ± 2.3	
Sisal/polyester	8.1	7.3 ± 2.0	
Curaua/epoxy	3.0	6.5 ± 6.7	[84]
Coir/epoxy	5.6	3.4 ± 1.0	
Coir/polypropylene	ND	2.4 ± 0.9	[71]
Coir/polyvinylidene fluoride	ND	3.3 ± 2.1	
Coir/maleic anhydride-grafted polypropylene	ND	5.6 ± 2.7	

not always leading to desirable results.[92,93] In addition, Kalia et al.[92] concluded in their review that most chemical treatments decrease the fiber strength. As a result, chemical treatments might not be attractive options for future improvement of natural fiber/polymer matrix composites. In contrast, both ionizing radiation and biological methods appear friendlier from an environmental perspective. They generate a hazardous waste at a minimum level, if any. A review of biological methods use in the treatment of natural fibers is beyond the scope of this review. The reader may find relevant information on this topic in selected works[97–99] and references therein.

Radiation methods used in the treatment of natural fibers and formulation of polymeric composites have become popular in recent years. Radiation of natural fibers using UV light,[103–118] electron beam,[73,119–133] and gamma rays[100,102,134–140] has been increasingly utilized for surface modification and adhesion property enhancement. Such pretreatment removes the surface impurities and changes the surface characteristics of the fibers leading to enhanced compatibility of fibers with the polymeric matrix.

Radiation-assisted grafting, which generates surface functionality on the fibers tailored to encourage chemical bonding and crosslinking at the polymer interface, may utilize UV light,[105,108,111,115–117,141] electron beam,[122] gamma rays,[102,139,140,142,143] and even microwave radiation.[144] Nonionizing UV light and microwave radiation, owing to their comparatively lower energies, are not as effective as ionizing radiation. In principle, the modifications introduced by nonionizing are accentuated by ionizing radiation, but remain fundamentally the same. Therefore, discussion on modification using UV light and microwaves will not be extended.

In the next section, the applications of ionizing radiation methods in the treatment of natural fibers and the formulation of polymeric composites that include gamma rays and electron beam radiation are reviewed. Ionizing radiation processing is a dry, clean, and cold method with advantages including energy savings, high-speed processing, uniformity of the treatment, and environmental friendliness.[22,145–147]

5. Ionizing irradiation of natural fibers for composite preparation

Irradiation of synthetic or natural polymers with ionizing radiation such as gamma rays, X-rays, accelerated electrons, and ion beams leads to the formation of very reactive intermediates in the forms of excited states, ions, and free radicals.[148] These intermediates participate almost instantaneously in several reaction pathways that result in the rearrangement and/or formation of new bonds and structures. The ultimate effect of these reactions can sometimes be the formation of oxidized products if irradiation is carried out in air; grafted polymers when either during or after irradiation the irradiated polymer is brought into contact with a vinyl monomer; scission of the main chain, generally termed as "degradation" or crosslinking with the concomitant formation of covalent bonds among polymer chains. The degree of these transformations depends on the structure of the base polymer and conditions of treatment before, during, and after irradiation. Precise control of these factors allows well-controlled modification of polymer properties by radiation processing.[149]

The use of ionizing radiation in initiating chemical processes has many advantages over other conventional methods. In radiation processing of polymers, no catalysts or additives are required to initiate the reaction. Absorption of radiation energy by the polymer generally initiates a free radical reaction. With chemical initiation, free radicals are produced by the decomposition of initiators into small fragments, which subsequently attack the base polymer leading to the formation of free radicals on polymer backbones. The efficiency of these two processes has been compared. It is estimated that roughly the same number of initiating radicals are produced per unit time with a radiation dose rate of 1 rad/s as are produced with a chemical initiator, such as benzoyl peroxide, at a concentration of 0.1 M is used (Dr. Keizo Makuuchi – private communication). The concentration and purity of chemical initiators are additional limiting factors. In the case of radiation processing, however, the dose rate can be easily varied, which makes reaction control easier. Chemical initiation has often been associated with problems arising from local overheating of the initiator. Again, radiation processing is exempt from this consideration as it is temperature independent. Its temperature-independent nature and ease of initiation results in its consideration as a "zero activation energy process."[150]

As discussed in Section 4, the hydrophilic nature of cellulosic fibers often results in poor compatibility with hydrophobic polymer matrices. Surface modification of natural fibers and/or polymers may greatly enhance the interfacial strength between fiber and matrix. A variety of chemical treatment methods, physical treatments, and irradiation with the aforementioned gamma rays and accelerated electrons have been used to make the fiber surface compatible with the polymer matrix. Although electron beam irradiation of synthetic fibers is already in use commercially, the same cannot be said for natural polymers in general and natural fibers in particular. Examination of ionizing radiation effects is the major focus in the following paragraphs.

The effect of ionizing radiation on cellulose is predominantly degradation by scissioning of α-glucoside linkages. The absorption of radiation also causes a reduction in the crystallinity of cellulose. Although these two effects of ionizing radiation on cellulose cause deterioration in some properties, cellulose also becomes more amenable to further processing and chemical modification. In a recent publication, Driscoll et al.[126] reported that the molecular weight of cellulose was reduced from 82,000 to 5,000 at an absorbed dose of 100 kGy. A reduction in crystallinity, however, requires a much higher dose of about 1,000 kGy to bring crystallinity down to 45% from an initial value of 87%. The available surface area, an indication of how well cellulose would react with chemical agents, was increased from 274 m^2/g for the control sample (0 kGy) to 318 m^2/g at a dose of 1000 kGy.[126] The radiation-induced changes in the structure of cellulose presumably make it more amenable to further chemical treatments. The high doses mentioned above are applied to cellulosics when they are used as raw materials for the production of biofuel.[151] In order to maintain the mechanical properties of pristine natural fibers for composite preparation, the absorbed dose of radiation should be kept at the minimum. Gamma irradiation in doses not exceeding 15 kGy does not appear to cause significant deterioration in the mechanical properties of lignocellulosics fibers.[136]

The main advantage of irradiating cellulosic fibers at low doses is to make use of resulting radicals as sites for initiating the grafting of polymers. Grafting is one of the most promising techniques for imparting desired properties to a polymer backbone, synthetic or natural.[152] Considering the radiation susceptibility of cellulosic fibers, the aim should be to perform grafting at low doses. Properly performed, it is a simple, powerful method to incorporate desired functional groups onto natural cellulosic fibers.[153] Grafting of a polymer onto a substrate can be achieved in different ways. The monomer to be grafted and the substrate can be simultaneously irradiated in an inert atmosphere in a process called "mutual irradiation." The main disadvantage of this technique is the homopolymer formation together with the grafted polymer, which requires solvent extraction to remove any ungrafted material from the surface of the substrate. "Preirradiation" has therefore been the preferred technique to date. In preirradiation, the substrate is first irradiated (either under vacuum or in air) and brought into contact with the monomer afterwards. Cellulose being a semicrystalline natural polymer, it is well-suited to vacuum preirradiation due to the long life of the free radicals trapped in the crystalline domains. Irradiation in air, on the other hand, leads to the formation of peroxy radicals that are also a long lived species. These peroxy radicals can also be used to initiate grafting at moderate temperatures in the presence of the monomer.[154]

In contrast to low doses, irradiation with relatively high doses usually results in the degradation of natural fibers. When lignocellulosic fibers are subjected to high irradiation doses of electrons, radicals are primary produced in the cellulose chain following carbon-carbon, carbon-oxygen, carbon-hydrogen, or oxygen-hydrogen bond cleavage. This occurs by means of hydrogen and hydroxyl abstraction as well as ring opening and chain scission.[123] If chain scission is predominant, then mechanical degradation becomes pronounced. The extent of microstructural degradation of a natural fiber will mainly depend on the electron radiation absorbed dose and the delivered dose rate. At high electron dose rates in air, oxygen cannot diffuse into the fiber at a rate comparable to radical formation during irradiation, and internal oxidation is thus reduced.[123] Degradation of the fiber will instead occur by destruction of its constituents, especially the microfibrils, as well as damage to the microstructure through the generation of microvoids that may coalesce into larger cavities.

The effects of electron beam irradiation on the strength and microstructure of buriti fiber (*Mauritia flexuosa*) were reported by Barbosa et al.[131] Figure 6 shows the variation of the tensile strength of buriti fibers (average diameter of 0.47 mm) as a function of irradiated dose using a 1.5 MeV electron beam accelerator at a dose rate of 22.4 kGy/s. In this figure a tendency for improvement in strength of the 50 kGy irradiated fibers (272 MPa) as compared to the non-irradiated control (250 MPa) was observed. A

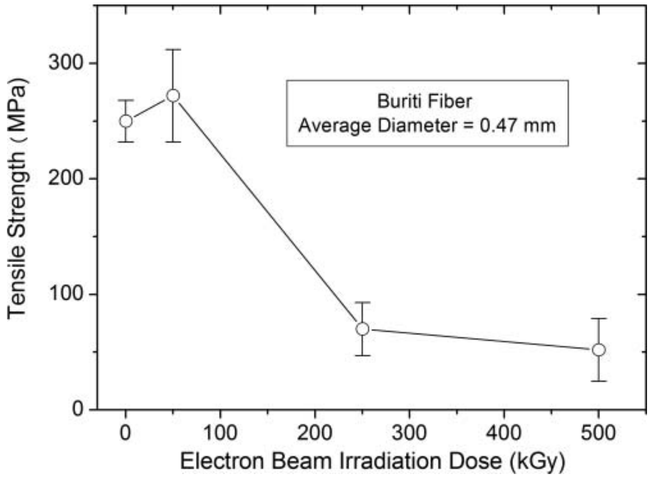

Figure 6. Variation of tensile strength of buriti fibers with electron beam radiation dose.[131] © Revista Materia. Reproduced by permission of Revista Materia. Permission to reuse must be obtained from the rightsholder.

possible reason for this would be crosslinking formation. By contrast, a significant decrease in strength (70 MPa) occurred as the dose increased to 250 kGy. No further change occurs up to a dose of 500 kGy within the indicated precision (± one standard deviation).

Figure 7 illustrates scanning electron micrographs of tensile ruptured buriti fibers subjected to electron beam radiation doses of (a) 50 and (b) 250 kGy. One should observe that the rupture at a lower dose, Fig. 7(a), shows marked participation of microfibrils. In an undamaged lignocellulosic fiber, the sequential rupture of microfibrils is able to support increasing applied forces to a relatively higher fracture strength level.[13] The participation of individual microfibrils is no longer observed in Fig. 7(b) after a dose of 250 kGy. The buriti fibers subjected this higher dose became brittle and present evidence of damage associated with radiation-induced cavities. These degradation effects impair the mechanical behavior of the fibers, as observed in Fig. 6.

5.1 Natural fiber-polypropylene composites

It is predicted that in the near future polymer and polymer composites would comprise ~15–20% of a car by weight. Of all the thermoplastic matrices available, polypropylene (PP) benefits the most when reinforced with natural fibers in making composites for industrial applications. For natural fiber-PP composites, polypropylene-maleic anhydride copolymers, often termed "maleated PP," have been effectively used as adhesion promoters to improve physical and chemical properties of the composites. As it will be seen in the following discussion, however, in the preparation of natural fiber based composites, irradiation of either the natural fiber or the polymeric matrix or a combination of the two enhances the interaction of otherwise incompatible constituents of composites.

PP is favored for nonstructural automotive components due to its low density, excellent processability, mechanical properties, excellent electrical properties, good dimensional stability, and impact resistance.[20] Recent developments in natural fiber reinforced polypropylene composites were discussed in a review article by Malkapuram et al.[155] In another review by Sobczak et al.[156] natural fiber composites based on PP were explored from their general mechanical property profiles. The authors also

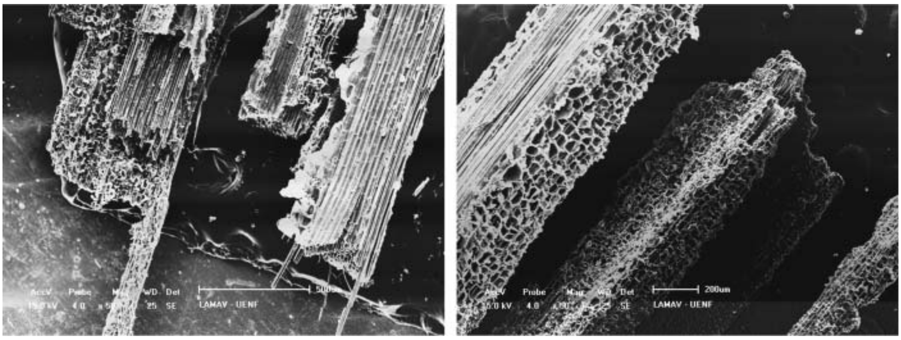

Figure 7. SEM micrographs of tensile ruptured buriti fibers subjected to electron beam irradiation doses: (a) 50 and (b) 250 kGy (SEM magnification of 50x).[131] © Revista Materia. Reproduced by permission of Revista Materia. Permission to reuse must be obtained from the rightsholder.

critically evaluated the potential of market penetration of these composites in comparison with PP reinforced with mineral particles, glass, and carbon fiber.

Czvikovszky[157,158] has been one of the pioneers in using radiation for the preparation of wood fiber polymer composites. After obtaining promising results by using preirradiated wood fiber and polypropylene to prepare fiber reinforced composites,[157] mutual electron beam (E-beam) irradiation was applied to wood fiber/PP blends to form chemical bonds between the components. Wood fibers were chemically bonded to the PP matrix through the formation of grafted side chains and crosslinking bridges. These were built using multifunctional, radiation-curable, double bond-containing reactive additives, which randomly initiated at radical centers created by the incident E-beam. E-beam irradiation of wood fiber and PP resulted in the formation of a composite which had not only a high modulus of elasticity, but also significantly higher flexural and tensile strengths. Moreover, thermal tolerances were improved relative to conventional wood fiber-PP blends and PP itself.[159]

Khan et al.[160] used jute fibers to prepare PP composites by compression molding. The polymer matrix (in the form of PP sheets) and sandwich composites were irradiated by gamma rays up to a dose of 10 kGy. Mechanical properties such as tensile strength, bending strength, tensile modulus, bending modulus, and impact strength of the irradiated composites and PP sheets were found to be higher than that of untreated composites. The enhancement in mechanical properties was attributed by Khan et al.[160] to the formation of crosslinks between the fiber and the polymer matrix. Also, the water resistance properties were improved for irradiated composites.

Mohanty et al.[161] prepared natural fiber reinforced PP composites with 40 wt% fibers to investigate the effect of coupling agents in promoting adhesion between the fibers and PP matrix. Two types of natural fiber, bast fiber (kenaf, hemp, and flax) and leaf fiber (sisal) were investigated. The authors found that bast fiber-based composites exhibited a superior flexural strength and modulus of elasticity relative to their leaf fiber-based counterparts. On the contrary, leaf fiber-based composites show higher impact properties than bast fiber-based composites. These results imply that natural fiber composites with balanced mechanical properties can be designed through optimized blending of bast and leaf fibers.[161]

The effects of electron radiation on natural fiber reinforced polypropylene have been analyzed with single fiber fragmentation testing in the work of Huber et al.[128] Single-fiber or -fiber bundle specimens of hemp, flax, ramie, and cotton were embedded in a polypropylene sheet and irradiated with 10 MeV electrons to achieve total doses of 5, 15, and 33 kGy. The radiation led to improved adhesion between PP and the test fibers and fiber bundles, and caused a strain-to-failure reduction of the polypropylene. The critical fragmentation length and the interfacial shear strength (IFSS) of the composite specimens showed an increase of up to 50% in the IFSS compared to specimens with applied coupling agents. Due to the high strain-to-failure reduction of the PP at intensities of 15 and 33 kGy the different fibers could only be compared at 5 kGy. The ramie fiber specimens could be analyzed at both 5 and 15 kGy intensities, and showed a higher IFSS value at the higher intensity. A possible explanation for this improvement is the formation of radicals within the cellulose chains of the natural fibers. Polypropylene molecules may have also participated in crosslinking at the higher radiation dosage, resulting in better adhesion between the composite components.[128]

Kenaf fiber is regarded as one of the most promising natural fibers, as it has the potential to replace silica fibers.[162,163] This makes kenaf a natural choice for reinforcement in PP-based composites. The kenaf/PP composites that were compression molded in the work of

Zampaloni et al.[164] proved to have superior tensile and flexural strength when compared to those with sisal and coir. Elastic moduli gleaned from mechanical testing were used to compare the relative economic benefits of kenaf reinforced composites over other natural fibers and E-glass. They showed that the kenaf/maleated polypropylene composites manufactured in their study had a higher modulus-to-cost ratio and a higher specific modulus than comparable composites with sisal, coir, and even E-glass. This result proved that there are ample opportunities for replacing existing materials with lower-cost, environmentally friendly alternative.[164]

Rowell et al.[165] blended PP with several types of natural fibers up to 60 wt% and then injection molded the premixed material. A compatibilizer or a coupling agent was used to improve the interaction and adhesion between the non-polar matrix and the polar lignocellulosic fibers. The specific tensile and flexural moduli of a 50 wt% (39 vol%) of kenaf-PP composites compare favorably with 40 wt% of glass fiber (19 vol%)-PP injection molded composites. Furthermore, preliminary results suggest that natural fiber-PP composites can be regrounded and recycled.

Kenaf fiber/PP biocomposites were fabricated by compression molding using chopped kenaf fibers irradiated with electron beam with doses of 100, 200, 500 kGy and/or chemically treated with 2, 5, 10 wt% NaOH aqueous solutions.[121] The thermal stability, viscoelastic modulus, and interfacial properties of both processed and unmodified kenaf/PP biocomposites were investigated by thermogravimetric, dynamic mechanical and fractographic analyses. The modification of kenaf fiber surfaces at 200 kGy EBI and treatment with 5 wt% NaOH was most effective for improving the performance of kenaf/PP biocomposites. The reinforcing effects of kenaf fibers resulted in a higher storage modulus than the PP matrix itself, with an observed increase of ~150%. The results showed that irradiation of natural fibers with an electron beam can contribute to the improvement in the performances of kenaf/PP biocomposites.

In the work of Cho et al.[120] chopped henequen fibers were incorporated into a PP matrix. Prior to composite fabrication, bundles of raw henequen fibers were treated at various E-beam doses from 10 kGy to 500 kGy. The effect of E-beam radiation dosage on the interfacial, mechanical, and thermal properties of randomly oriented henequen/PP composites with fiber content of 40 vol% was investigated. This study focused particularly on the interfacial shear strength, flexural, and tensile properties, as well as dynamic mechanical analysis, thermal stability, and fracture behavior. The results indicated that henequen fiber surfaces can be successfully modified with an appropriate radiation dose administered via electron beam. Doses as small as 10 kGy resulted in improvement of not only interfacial properties, but also flexural behavior, tensile properties, dynamic mechanical responses, and the thermal stability of the henequen/PP composites.

The development of thermoplastic-natural fiber composites is constrained by two primary limitations: the upper temperature at which the fiber can be processed and the significant difference between the surface energy of cellulosics and the polymer matrix. The generally accepted upper limit before fiber degradation occurs is on the order of 150°C for relatively long processing periods. The result of prolonged high temperature exposure may be discoloration, the release of volatile compounds, poor interfacial adhesion, or the embrittlement of cellulosic components.[20] Therefore, it is necessary to obtain a rapid reaction rate at relatively low temperatures during both surface treatment and polymer processing to prevent degradation. At this point, the unique advantage of using ionizing radiation for surface modification of natural fibers becomes evident, since it is a room temperature process. In the case of temperature-sensitive substrates, irradiation can even be carried out below ambient temperature.

A further consideration for the widespread industrial adoption of polymer-natural fiber composites is their behavior at elevated temperatures. As a consequence of characteristically poor bonding between untreated natural fibers and polymer matrices, deformation of these composites under their own weight after being formed at relatively high temperatures (150–200°C) appears as a major shortcoming of these systems. Heat-induced deformation in service is also of concern, such as in automotive interiors that are left in the sun for extended periods. Kim et al.[166] irradiated PP/natural fiber (50/50) composites with 0.5 MeV electrons to a dose of 0–20 kGy. An amount of 3 wt% of maleated PP was used to improve compatibility between the fibers and the PP matrix. The authors observed that deformation of the composites was reduced after thermal cycling.

E-beam irradiation changes the surface characteristics of natural fibers. Both morphology and topography of henequen fiber irradiated with E-beam were studied with SEM and AFM by Han and Choi.[167] It was shown that E-beam irradiation of 10 kGy and 30 kGy was effective in removing pectin, wax, and the primary layer, and also created many nanopores ranging in size from 40 nm to 100 nm. Total surface area and pores increased with low doses ($\leq$ 30 kGy). Stronger E-beam irradiation ($>$10 kGy to 100 kGy) produced patterns on the fiber surfaces due to the removal of the primary layer and exposure of secondary wall layers. Degradation of secondary wall layer was observed at E-beam doses exceeding 50 kGy.

The same group investigated the effects of E-beam irradiation on the surface characteristics of henequen fibers and the interfacial properties of biocomposites fabricated with poly (butylene succinate) resin and henequen fibers.[119] The relationship between the surface characteristics of henequen fibers and the absorbed radiation dose was studied by examining changes in fiber morphology, by X-ray photoelectron spectroscopy (XPS), and through storage modulus measurement of a single henequen fiber. The interfacial behavior of biocomposites was also explored through a single fiber microbonding test and fracture surface observations. The results showed that the IFSS of biocomposites greatly depends on the E-beam treatment level applied to the henequen fiber surface. This study also suggests that appropriate modification of natural fiber surfaces at an optimum E-beam dose significantly improves the interfacial properties of biocomposites. The authors suggested that the use of an E-beam-induced dose of 10 kGy on henequen fiber surfaces may be useful for contributing not only to improving interfacial adhesion in the henequen/polybutadiene styrene (PBS) biocomposite system, but also to shorten the E-beam irradiation process and conserve energy.

5.2 Radiation-induced grafting for modification of fiber surface

Surface modification of natural or synthetic polymers by graft copolymerization has resulted in new materials with unique properties. The surface properties of the grafted polymer may stand in contrast to the properties of the original polymer. Thus, most industrial polymers which are hydrophobic in nature can be rendered hydrophilic through the introduction of proper functional groups to the surface. Similarly, mostly hydrophilic natural fibers can be grafted with hydrophobic polymers to make them more hydrophobic.[168] The interaction of ionizing radiation with the backbone of a polymer produces uniform, carbon-centered radicals that can initiate graft polymerization of vinyl monomers in specimens up to a few millimeters thick. Since the grafting of monomers on the substrate takes place by free radical polymerization, this technique is applicable to vinyl or vinylidene monomers with different functionalities and substituents.[152] Graft polymerization does not only change and modify the surface properties of the substrates, but also improves mechanical and thermal properties. Because radiation-induced grafting can be applied easily to natural polymers, fibers, and thermoplastics, it is just a matter of deciding which of these constituents should be modified to improve the overall integrity of the composite. In the following discussion, some examples of radiation-induced grafting of natural fibers will be given. Special emphasis is placed on the use of glycidyl methacrylate as the grafting monomer due to the advantages that come from using the epoxy group present in its monomer. By opening the epoxy ring, it is possible to insert new chemical functionalities to the graft chains, which facilitate further bonding to the cellulose structure.[169,170]

In solvent-mediated graft copolymerization, a solvent is added to the grafting mixture in order to enhance the swelling of the backbone polymer and facilitate monomer diffusion. This method has the advantage of reducing both monomer consumption and homopolymer formation. Hence, it has been frequently used in performing reactions in all types of radiation-induced grafting methods.[152] Use of a water/ethanol mixture in the grafting medium has the additional benefit of generating highly reactive OH radicals in the course of irradiation which then participate in the abstraction of hydrogen from the cellulose backbone. Some of the radiation energy is thereby absorbed by the solvent system, thereby reducing the amount of radiation absorbed by the cellulose and protecting it from degradation.[171] This implies that grafting should be performed at low doses. Although the employing of water in grafting reactions is highly preferred, most of the monomers of interest are not miscible with water. In such a case, grafting should be performed in the emulsion state. In the emulsion-mediated grafting technique, a monomer (e.g., glycidylmethacrylate) is grafted onto a backbone polymer after being diluted with water (as a dispersion medium) and emulsified with a small amount of surfactant. This method provides significant advantages in the form of irradiation dose reduction and monomer consumption and, thus, it is economically viable.[172]

Mohamed et al.[173] grafted a reactive monomer, 4-chloro methylstyrene (CMS) onto kenaf fibers by preirradiation in the emulsion state using Tween 20 as the surfactant. The CMS emulsions had a micelle size of ~350 nm, and grafting was performed at a dose of 150 kGy. It was found that the degree of grafting (Dg) was strongly dependent on the CMS monomer concentration and exposure time. Grafting percentage of about 100% could be easily achieved at 5.0% CMS concentration in less than one hour.[173]

In a similar work with delignified kenaf fibers, Sharif et al.[174] showed that a higher amount of glicydyl methacrylate (GMA) grafting can be achieved with lower doses. The lignin in kenaf was removed by treatment with sodium chlorite solution, reducing the total content from 14.3 wt% down to 3.3 wt%. At an absorbed dose of 50kGy, a reaction time of 3h, temperature of 40°C, and monomer concentration of 3 wt%, it was possible to achieve a Dg of about 150%.[174]

Fibers from the water hyacinth plant (*Eichhornia crassipes*) were functionalized by Madrid et al.[175] using radiation-induced graft polymerization of GMA through γ-rays from a ^{60}Co source. Simultaneous grafting was employed here, where the water hyacinth fibers were irradiated in a nitrogen atmosphere in the presence of GMA dissolved in a water/methanol solvent. The effects of different grafting parameters to the grafting yield were evaluated. The optimal values of solvent, absorbed dose, dose rate, and monomer concentration were found to be 1:3 (volume/volume) water–methanol solvent, 10 kGy, 8kGy per hour dose rate, and 5 vol% GMA, respectively. Using the optimum conditions, a Dg of approximately 58% was achieved. The grafted water hyacinth fibers were characterized using spectroscopic, thermal, and microscopic methods.[175]

Khan et al.[176] carried out graft copolymerization of methyl methacrylate (MMA) onto a jute fiber substrate using gamma radiation (^{60}Co) using both the preirradiation and "simultaneous irradiation and grafting" methods in an aqueous emulsion system. The variation in graft weight with radiation dose, intensity of radiation, and irradiation environment was investigated. In the case of the preirradiation method, irradiation in air produced up to 30% graft weight, compared to only 20% obtained when the irradiation was conducted in nitrogen environment. In preirradiation, the graft copolymerization reaction was initiated by reactive species having different life times, some of which were very long. In the simultaneous irradiation and grafting method, the graft weight passed through a maximum value ($>$15%), which was limited due to excessive homopolymerization at higher radiation doses. A comparative study on the mechanical properties of samples grafted by both preirradiation and simultaneous irradiation and grafting methods was carried out. The results showed that the grafting method has a significant influence on the mechanical properties of grafted jute.[176]

As can be seen from the examples listed above, the versatile nature of glycidyl methacrylate in grafting processes has made it the monomer of choice for a number of surface modification studies. Grafting under conventional free radical polymerization conditions, however, leads to the formation of graft chains of uncontrolled molecular weight and wide molecular weight distributions. This major drawback of free radical polymerization has been overcome in recent years by the introduction of so-called "controlled free radical polymerization" which has found extensive application in both polymerization and graft polymerization reactions.[177] By using a chain transfer agent, free radical polymerization and/or graft polymerization can be performed through a method called "reversible-addition-fragmentation chain transfer," or RAFT. This method allows tight control over the molecular weight of the grafted chains, resulting in very narrow molecular weight distributions. This has recently been used to graft glycidyl methacrylate on a cellulose surface.[178] The graft chains formed on the cellulose surface resemble polymeric brushes, with nearly uniform chain lengths across the entire surface. The implications of preparing graft surfaces with such high topological control remain to be seen, especially in the area of lignocellulosic fiber reinforced composites.[178]

5.3 Destructive effects of radiation

From an industrial application point of view, crosslinking of polymeric chains initiated by ionizing radiation has been considered as the driving force for radiation-based processing of polymers that leads to polymer enhanced mechanical properties and thermal stability. Chain scissioning of lignocellulosics is the ultimate effect of radiation if no specific precautions are taken. Molecular degradation associated with chain scissioning reduces the molecular weight of lignocellulosics and therefore, deteriorates their physical properties. Ershov reported the radiation-induced random degradation of cellulose at absorbed doses of 30–80 kGy which increased with temperature.[179] The presence of moisture has been shown to have a slight inhibiting effect on the degradation of cellulose. Such an effect has been observed in radiation-induced degradation of marine-based poysaccharaides as well.[180]

The effect of radiation in terms of absorbed dose can be estimated by knowing the relevant radiation-chemical yields of particular events. The radiation chemical yield of cellulose degradation has been found to be 6.0 +/− 1.0.[181] At the initial stage of gamma irradiation, the dependence of formation of carbonyl and carboxyl groups in cellulose is linear with yields of 6.5+/−0.2 and 1.8+/−0.2, respectively.[181] In radiation chemistry, radiation-chemical yield (G-value) is expressed as the number of molecules (events) taking part in the reaction per 100eV of the absorbed energy which corresponds to $\sim 0.1\ \mu\text{mol/J}$. Knowing the value of the absorbed dose, one can make a quantitative estimate of relevant radiochemical events by using these G-values.

The apparently negative effect of radiation on lignocellulosics has been turned into advantages in some cases. The radiation-induced chain scissioning of cellulose found an economically and environmentally beneficial application in the production of viscose rayon.[182] It has been shown that radiation treatment of pulp can replace the operationally and environmentally costly and hazardous aging step in the conventional viscose process.[183] Another potential application of radiation-degraded lignocellulosics is to make it more accessible to cellulolytic enzymes for easy bioconversion.[184] The irradiation of wheat straw by γ- radiation was found to cause significant breakdown of structure and increase the rate of enzymatic hydrolysis. The glucose yield of irradiated straw increased by increasing dose reaching a maximum value of 13.4% at 500 kGy.[185] The simple process of controlled degradation of lignocellulosics at room temperature by ionizing radiation has been considered to be one of the methods of choice for the pretreatment of these raw materials for further easy processing to produce value-added products.[186]

6. Cellulose nanofibers and bionanocomposites

The application of nano-sized cellulose crystals, particles, and fibers to reinforce polymers is a relatively new, but promising, research area. Numerous recent works on cellulosic nano-sized filler reinforced composites,[187–200] as well as review papers,[15,93,201] have emphasized the promise of this new class of materials. Indeed, as stated by Faruk et al.,[15] nanocrystalline cellulose may possess only one-tenth the strength of carbon nanotubes, but it costs 50–2000 times less to produce. The challenges associated with introducing nano-sized cellulose fillers into polymeric composites are no different from the problems associated with the use of larger scale lignocellulosic fibers, namely the lack of compatibility with hydrophobic polymers. Various chemical modification methods have been explored to enhance the possibility of combining nano-sized cellulose filler with hydrophobic polymers. Grafting appropriate monomers onto the filler surfaces and further functionalization of grafted polymers to control their wetting properties provides a good route for inducing compatibility. In this respect glycidyl methacrylate is one of the most versatile monomers since the epoxy group on the repeating unit can be easily functionalized to introduce a variety of ligands.[201] A recent review investigated the surface modification of nano-fibrillated cellulose for use in the preparation of bionanocomposites.[202] The improvement of nano-sized cellulosic fibers and related bionanocomposites by radiation has yet to be investigated. It appears to be a promising field ripe for investigation.

7. Summary and future recommendations

The development of commercially viable "green composites" using lignocellulosic fibers for polymeric matrix reinforcement has been on the rise for the last two decades. Lignocellulosic fibers are annually renewable and biodegradable, and therefore they have materialized as environmentally-friendly alternatives to synthetic fibers in general, and glass fibers in particular. Potential advantages and benefits in replacing synthetic fibers with vegetal fibers include low cost, low density, good specific mechanical properties, less energy consumption and pollution emission during manufacturing, and less abrasion and damage to the processing equipment. However, the formulation of lignocellulosic fiber reinforced polymeric composites still faces many challenges, such as large fiber-to-fiber scatter of physical properties, inhomogeneity of fibers, and the relatively short length of extracted fibers. A tendency towards moisture absorption also hampers their adoption, as swelling results in dimensional instability, susceptibility to microbial attack, rotting, and degradation. Processing of composites containing these fibers is made complicated by their low decomposition temperatures and insufficient adhesion and incompatibility with the polymeric matrix. These challenges impose limits on the application of lignocellulosic fibers as reinforcement, but also provide opportunities for researchers to find a way to either minimize or eliminate these negative effects.

Research into the development of lignocellulosic fiber reinforcements has heavily concentrated on the modification of the fiber surfaces. In particular, functionalization to enhance the compatibility of hydrophilic lignocellulosic fibers with hydrophobic polymers has been of interest. Ionizing radiation methods have recently emerged as clean, energy-saving, and environmentally-friendly alternatives to traditional chemical methods, which typically use coupling agents to modify the fiber surfaces. As has already been demonstrated by several research groups, using ionizing radiation methods is an efficient route to improve natural fiber-polymer matrix adhesion. This can be achieved through the removal of impurities and organic layers from the fiber surface, development of functionality, and the formation of reactive radicals on the fiber surface, and grafting organic functionalities to the surfaces of fibers. Radiation-induced graft copolymer synthesis is now considered the preferred technique to improve the properties of cellulose-based composites because it allows a considerable degree of control over the graft copolymer chain and its affinity for the polymeric matrix. Widespread commercial adoption of lignocellulosic fiber-polymer composites will be dictated by advances made in the coming years with respect to manufacturing uniform, high-quality lignocellulosic fibers, and the development of cost-effective ionizing radiation technologies for the formulation of green composites.

Acknowledgments

The authors appreciate editing corrections and comments received from Patrick K. Bowen in the final stage of manuscript preparation.

Funding

The authors acknowledge the Brazilian agencies: CNPq, CAPES, and FAPERJ for their financial support. JWD would also like to extend his grateful thanks to FAPERJ for the Visitor Researcher Grant that funded his visit in Brazil.

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