Biocomposites reinforced with natural fibers: 2000–2010

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A B S T R A C T

Due to environment and sustainability issues, this century has witnessed remarkable achievements in green technology in the field of materials science through the development of biocomposites. The development of high-performance materials made from natural resources is increasing worldwide. The greatest challenge in working with natural fiber reinforced plastic composites is their large variation in properties and characteristics. A biocomposite’s properties are influenced by a number of variables, including the fiber type, environmental conditions (where the plant fibers are sourced), processing methods, and any modification of the fiber. It is also known that recently there has been a surge of interest in the industrial applications of composites containing biofibers reinforced with biopolymers. Biopolymers have seen a tremendous increase in use as a matrix for biofiber reinforced composites. A comprehensive review of literature (from 2000 to 2010) on the mostly readily utilized natural fibers and biopolymers is presented in this paper. The overall characteristics of reinforcing fibers used in biocomposites, including source, type, structure, composition, as well as mechanical properties, will be reviewed. Moreover, the modification methods; physical (corona and plasma treatment) and chemical (silane, alkaline, acetylation, maleated coupling, and enzyme treatment) will be discussed. The most popular matrices in biofiber reinforced composites based on petrochemical and renewable resources will also be addressed. The wide variety of biocomposite processing techniques as well as the factors (moisture content, fiber type and content, coupling agents and their influence on composites properties) affecting these processes will be discussed. Prior to the processing of biocomposites, semi-finished product manufacturing is also vital, which will be illustrated. Processing technologies for biofiber reinforced composites will be discussed based on thermoplastic matrices (compression molding, extrusion, injection molding, LFT-D-method, and thermoforming), and thermosets (resin transfer molding, sheet molding compound). Other implemented processes, i.e., thermoset compression molding and pultrusion and their influence on mechanical performance (tensile, flexural and impact properties) will also be evaluated. Finally, the review will conclude with recent developments and future trends of biocomposites as well as key issues that need to be addressed and resolved.

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1. Introduction

There is a growing trend to use biofibers as fillers and/or reinforcement in plastics composites. Their flexibility during processing, highly specific stiffness, and low cost (on a volumetric basis) make them attractive to manufacturers. This century has witnessed ever-increasing demands for the utilization of plastics as important raw materials, more than 80% of which are thermoplastics. Biofiber reinforced plastic composites are gaining more and more acceptance in structural applications.

Technological development connected with consumer demands and expectations continues to increase demands on global resources, leading to major issues of material availability and environmental sustainability. Over the last few decades biofiber composites have been undergoing a remarkable transformation. These materials have become more and more sufficient as new compositions and processes have been intensively researched, developed and consequently applied. The petroleum crisis made biocomposites significantly important and biocomposites have become engineering materials with a very wide range of properties. However, like all materials, they are constantly under competitive pressure from the global market, which in turn, necessitates continuous research. The times of simply mixing plastics with natural waste fillers and characterizing their main properties are gone.

The concept of using bio-based plastics as reinforced matrices for biocomposites is gaining more and more approval day by day. The developments in emerging bio-based plastics are spectacular from a technological point of view and mirror their rapid growth in the market place. The average annual growth rate globally was 38% from 2003 to 2007. In the same period, the annual growth rate was as high as 48% in Europe. The worldwide capacity of bio-based plastics is expected to increase from 0.36 million metric ton (2007) to 2.33 million metric ton by 2013 and to 3.45 million metric ton in 2020. The main product in terms of production volumes will be starch-based plastics, PLA and PHA [1].

The increasing number of publications during the recent years including reviews [2–9] and books [10–14] reflect the growing importance of these new biocomposites. Bledzki and Gassan have reviewed the reinforcement of the most readily used natural fibers in polymer composites up until 1999 in their review paper [15]. This paper aims to review more current reinforcement of natural fibers in polymer composites from 2000 to 2010. This paper will not address natural fibers from animals (e.g., silk or wool) or cotton or man-made cellulosic fibers. This review also excludes wood fiber or flour. Given the broad scope of this article, it will inevitably be incomplete, but will hopefully provide a sensible overview of the most popular natural fibers in polymeric composite materials in the last 11 years.

2. Reinforcing fibers

An increased awareness that non-renewable resources are becoming scarce and our inevitable dependence on renewable resources has arisen. This century could be called the cellulogenic century, because more and more renewable plant resources for products are being discovered. It has been generally stated that natural fibers are renewable and sustainable, but they are in fact, neither. The living plants are renewable and sustainable from which the natural fibers are taken, but not the fibers themselves.

2.1. Fiber source

The plants, which produce natural fibers, are classified as primary and secondary depending on their utilization. Primary plants are those grown for their fiber content while secondary plants are plants in which the fibers are produced as a by-product. Jute, hemp, kenaf, and sisal are examples of primary plants. Pineapple, oil palm and coir are examples of secondary plants. Table 1 shows the main fibers used commercially in composites, which are now produced throughout the world [16].

2.2. Fiber types

There are six basic types of natural fibers. They are classified as follows: bast fibers (jute, flax, hemp and kenaf), leaf fibers (abaca, sisal and pineapple), seed fibers (coir, cotton and kapok), core fibers (kenaf, hemp and jute), grass and reed fibers (wheat, corn and rice) and all other types (wood and roots).

2.2.1. Flax

Flax, Linum usitatissimum, belongs to the bast fibers. It is grown in temperate regions and is one of the oldest fiber crops in the world. The bast fiber flax is most frequently used in the higher value-added textile markets. Nowadays, it is widely used in the composites area.

The static and dynamic mechanical properties of non-woven based flax fiber reinforced PP composites were

<table>
<thead>
<tr>
<th>Fiber source</th>
<th>World production (10^3 ton)</th>
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<tbody>
<tr>
<td>Bamboo</td>
<td>30,000</td>
</tr>
<tr>
<td>Jute</td>
<td>2300</td>
</tr>
<tr>
<td>Kenaf</td>
<td>970</td>
</tr>
<tr>
<td>Flax</td>
<td>830</td>
</tr>
<tr>
<td>Sisal</td>
<td>378</td>
</tr>
<tr>
<td>Hemp</td>
<td>214</td>
</tr>
<tr>
<td>Coir</td>
<td>100</td>
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<tr>
<td>Ramie</td>
<td>100</td>
</tr>
<tr>
<td>Abaca</td>
<td>70</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>75,000</td>
</tr>
<tr>
<td>Grass</td>
<td>700</td>
</tr>
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studied considering the effect of zein coupling agent [17]. Zein is a protein, extracted from corn and used as solution. Composites containing zein coupling agent were found to possess improved mechanical properties. The storage modulus of composites was found to increase with zein coupling agent coating due to enhanced interfacial adhesion.

The tensile mechanical properties of flax fibers are estimated according to their diameter and their location in the stems [18]. The large scattering of these properties is ascribed to the variation of the fiber size along its longitudinal axis. The higher values of the mechanical properties of the fibers issued from the middle of the stems are associated with the chemical composition of their cell walls. The mechanical properties of unidirectional flax fiber/epoxy matrix composites are studied as a function of their fiber content. The properties of the composites are lower than those expected from single fiber characteristics.

Various investigations of flax fiber/polypropylene composites have been completed. These studies focus on many different variables, including: comparison between NMT (natural fiber thermoplastic mat) and GMT (glass fiber thermoplastic mat) [19], the influence of fiber/matrix modification and glass fiber hybridization [20], the effect of fiber treatment on thermal and crystallization properties [21], the influence of surface treatment on interface by glycerol triacetate, thermoplastic starch, γ-methacryl oxypropyl trimethoxy-silane and boiled flax yarn [22], comparison of matrices (PP and PLA) on the composite properties [23], the effects of material and processing parameters [24], and the influence of processing methods [25]. Buttler [26] presented the feasibility of using flax fiber composites in the coachwork and bus industry.

The effect of bio-technical fiber modification [27], fracture behavior and toughness [28], the influence of alkaline fiber treatment on unidirectional composites [29], the effect of processing parameters [30] on the consecutive decortication stages of flax fibers (retting, scutching, and hackling) on the flax fiber reinforced epoxy composites have also been evaluated.

Flax fiber composites reinforced with polyester resin have been evaluated for thermal degradation and fire resistance [31], chemical treatments on surface properties and adhesion [32], and the effect of chemical treatments on water absorption and mechanical properties [33]. Three resins from soybean oil (methacrylated soybean oil, methacrylic anhydride modified soybean oil, and acetic anhydride modified soybean oil) were used also as matrices for flax fiber reinforced biocomposites [34].

2.2.2. Hemp

Another notable bast fiber crop is hemp, which belongs to the Cannabis family. It is an annual plant that grows in temperate climates. Hemp is currently the subject of a European Union subsidy for non-food agriculture, and a considerable initiative in currently underway for their further development in Europe.

Composites of PP with hemp fibers, which were functionalized by means of melt grafting reactions with glycidyl methacrylate (GMA) and prepared by batch mixing, were examined [35]. The modification of fibers and the PP matrix, as well as the addition of various compatibilizers were carried out to improve the fiber–matrix interactions. Compared to the unmodified system, a modified composite showed improved fiber dispersion in the PP matrix and higher interfacial adhesion as a consequence of chemical bonding between the fiber and the polymer (PP/Hemp). The thermal stability and phase behavior of the composites was largely affected by the fiber and matrix modification. Changes in the spherulitic morphology and crystallization behavior of PP were observed in the composites due to the nucleating effect of the hemp fibers. Moreover, a marked increase in the PP isothermal crystallization rate (in the range 120–138 °C) was recorded with increasing content of modified hemp. All composites displayed a higher tensile modulus (about 2.9 GPa) and lower elongation at break as compared to plain PP: compatibilization with modified PP (10 phr) resulted in an increased stiffness of the composites as a result of improved fiber–matrix interfacial adhesion.

Pickering and co-workers [36–38] investigated the effects of chelator, white rot fungi, and enzyme treatments on the separation of hemp fibers from bundles, and the improvement of the interfacial bonding of the hemp fibers with the PP matrix. The obtained results showed that the interfacial shear strength of the treated fiber composites was higher than that for untreated fiber composites. This verifies that the hemp fiber interfacial bonding with PP was improved by the white rot fungi treatment. Composites consisting of hemp fibers treated with chelator concentrate had the highest tensile strength of 42 MPa, which equals an increase of 19% compared to composites with untreated hemp fiber.

Hemp fiber reinforced PP composites exhibited interesting recyclability [39]. The obtained results prove that the mechanical properties of hemp fiber/PP composites remain well preserved, despite the number of reprocessing cycles. The Newtonian viscosity decreases with cycles, indicating a decrease in molecular weight and chain scissions induced by reprocessing. The decrease of fiber length with reprocessing could be another reason for decrease of viscosity.

Epoxy resins, which were used as a matrix for hemp fiber reinforced composites, were studied regarding the effect of fiber architecture on the falling weight impact properties [40], properties and performances of composites for curved pipes [41], impact load performance of resin transfer molded composites [42], micro-mechanics of the composites [43], the influence of hybrid blends made of soybean oil and nanoclay [44], and the usefulness of unretted hemp as a source of fiber for biocomposites [45].

Kunanopparat et al. [46,47] studied the feasibility of wheat gluten as a matrix for hemp fiber reinforced composites regarding their thermal treatment and plasticization effect on the mechanical properties.

2.2.3. Jute

Jute is produced from plants of the genus Corchorus, which includes about 100 species. It is one of the cheapest natural fibers and is currently the bast fiber with the highest production volume. Bangladesh, India and China provide the best condition for the growth of jute.

Ray and co-workers [48–50] extensively investigated alkali treated jute fiber reinforced with vinyl ester resin.
In their studies, they regarded the dynamic, mechanical, thermal, and impact fatigue behavior compared to that of untreated jute fiber–vinyl ester composites. Longer alkali treatment removed the hemicelluloses and improved the crystallinity, enabling better fiber dispersion. The dynamic, mechanical, thermal and impact properties were superior owing to the alkali treatment, comprising treatment time, concentration and conditions.

Mohanty et al. [51] investigated effects and influence of surface modification on the mechanical and biodegradability of jute/Biopol and jute/PA (Poly Amide) composites. Enhancements in tensile strength of more than 50%, 30% in bending strength and 90% in impact strength were observed in the composites and are comparative to values achieved for pure Biopol sheets. Degradation studies showed that after 150 days of compost burial more than 50% weight loss of the jute/Biopol composites occurs.

The effects of hybridization [52] on the tensile properties of jute–cotton woven fabric reinforced polyester composites were investigated as functions of the fiber content, orientation and roving texture. It was observed that tensile properties along the direction of jute roving alignment (transverse to cotton roving alignment) increase steadily with fiber content up to 50% and then show a tendency to decrease. The tensile strength of composites with 50% fiber content parallel to the jute roving is about 220% higher than pure polyester resin.

Jute fiber reinforced PP composites were evaluated regarding the effect of matrix modification [53], the influence of gamma radiation [54], the effect of interfacial adhesion on creep and dynamic mechanical behavior [55], the influence of silane coupling agent [56,57], and the effect of natural rubber [58].

The properties of jute/plastic composites were studied, including the thermal stability, crystallinity, modification, trans-esterification, weathering, durability, fiber orientation on frictional and wear behavior, eco-design of automotive components, and alklylation [59–66].

Polyester resin was used as matrix for jute fiber reinforced composites and the relationship between water absorption and dielectric behavior [67], the elastic properties, notched strength and fracture criteria [68], impact damage characterization [69], weathering and thermal behavior [70], and effect of silane treatment [71] were examined.

2.2.4. Kenaf

Kenaf belongs to the genus Hibiscus and there are about 300 species. Kenaf is a new crop in the United States and shows good potential as a raw material for usage in composite products. Latest advances in decortication equipment which separates the core from the bast fiber combined with fiber shortages, have renewed the interest in kenaf as a fiber source.

Thermoforming has proven to enable the successful fabrication of kenaf fiber reinforced PP sheets into sheet form [72]. The optimal fabrication method found for these materials was at the compression molding process, which utilizes a layered sifting of a micro-fine PP powder and chopped kenaf fibers. The fiber content (30 and 40 wt%) provided adequate reinforcement to increase the strength of the PP matrix. The kenaf–PP composites compression molded in this study proved to have superior tensile and flexural strength when compared to other compression molded natural fiber composites such as other kenaf, sisal, and coir reinforced thermoplastics. With the aid of the elastic modulus data, it was also possible to compare the economic benefits of using kenaf composites instead of other natural fibers and E-glass. The manufactured kenaf-maleated PP composites have a higher modulus/cost and a higher specific modulus than sisal, coir, and even E-glass. Thus, they provide an option for replacing existing materials with a higher strength, lower cost alternative that is environmentally friendly.

Hybrid composites of wood flour/kenaf fiber and PP were prepared to investigate the hybrid effect on the composite properties [73]. The results indicated that while non-hybrid composites of kenaf fiber and wood flour exhibited the highest and lowest modulus values respectively, the moduli of hybrid composites were closely related to the fiber to particle ratio of the reinforcements. With the help of the hybrid mixtures equation it was possible to predict the elastic modulus of the composites better than when using the Halpin–Tsi equation.

Variations of the mechanical and thermal properties induced by the exposure of kenaf fiber reinforced composites with PP to electron beam radiation [74], the comparison of kenaf/PP composites with feather fiber/PP, recycled kraft pulp fiber/PP, and recycled news pulp fiber/PP composites [75] and, surface modified kenaf fibers with modified polyester resin as matrix [76], and influence of toughening by natural rubber on kenaf fibers with polyester resin as matrix [77] were also evaluated.

2.2.5. Sisal

Sisal is an agave (Agave sisalana) and commercially produced in Brazil and East Africa. Between 1998–2000 and 2010, the global demand for sisal fiber and its products is expected to decline by an annual rate of 2.3% as agricultural twine. The traditional market for fibers continues to be eroded by synthetic substitutes and by the adoption of harvesting technologies that utilizes less or no twine.

Magnesium hydroxide and zinc borate were incorporated into sisal/PP composites as flame retardants [78]. Adding flame retardants into sisal/PP composites reduced the burning rate and increased the thermal stability of the composites. No synergistic effect was observed when both magnesium hydroxide and zinc borate were incorporated into the sisal/PP composites. In addition, the sisal/PP composites exhibited insignificant differences in shear viscosity at high shear rates indicating that the types of flame retardants used in this study had no impact on the processability of the composites. The sisal/PP composites which flame retardants were added to, exhibited tensile and flexural properties comparable to those of the sisal/PP composites, which flame retardants had not been added to.

Sisal/PP composites were investigated regarding the environmental effects on the degradation behavior [79], the influence of coupling agents on the abrasive wear
properties [80], and the effect of ageing on the mechanical properties [81].

Zhang et al. [82] developed all plant fiber composites by converting wood flour into thermoplastics using an appropriate benzoylation treatment and compounding both discontinuous and continuous sisal fibers to produce composites from renewable resources. The degradation tests demonstrated that the prepared sisal/plasticized wood flour composites were fully biodegradable. To accelerate the decomposition process, both cellulose and lignin in the composites should be considered. The hydrophobicity and flame resistance of composites is important when regarding practical applications. Molecular modification and/or incorporation of inorganic additives are proper measures provided that the composites biodegradability remains unchanged.

Many other studies were carried out on sisal fiber reinforced polyester composites regarding their moisture-absorption properties [83], and fiber treatment with admicellar [84]. Sisal fiber reinforced phenolic resin composites were investigated with regard to the chemical modification of such with lignins [85], the modification using hydroxy terminated polybutadiene rubber [86], the effect of cure cycles [87], using glyoxal from natural resources [88], and the effect of alkali treatment [89]. Furthermore epoxy resin was used as a matrix for sisal fiber reinforced composites and examined regarding the influence of fiber orientation on the electrical properties [90], and the degree of reinforcement [91]. Investigations were also carried out using cement as a matrix for sisal fiber reinforced composites focusing on their cracking micro-mechanisms [92], and the effects of accelerated carbonation on cementitious roofing [93].

Towo et al. [94,95] prepared the treated sisal fiber composites with an epoxy and polyester resin matrix. Fatigue evaluation and dynamic thermal analysis tests were performed. Composites containing alkali treated fiber bundles proved to have better mechanical properties than those with untreated fiber bundles. Alkali treatment had the greatest effect on the polyester resin matrices. An improvement in the fatigue lives of composites was observed for the alkali treatment of sisal fiber bundles. Constant-life diagrams of epoxy matrix composites with untreated or alkali treated fiber bundles show the superiority of the alkali treated fiber composites regarding low cycle fatigue. Epoxy matrix composites have a longer fatigue life than polyester matrix composites. The effect of chemical treatment on the fatigue life is significantly positive for polyester matrix composites but has much less influence on the fatigue life of epoxy matrix composites.

Sisal fibers were also investigated with other matrices, such as rubber [96,97], phenol formaldehyde [98], cellulose acetate [99], bio polyurethane [100], and polyethylene [101] regarding their mechanical, morphological, chemical, and Cure characteristics.

2.2.6. Abaca

The abaca/banana fiber, which comes from the banana plant, is durable and resistant to seawater. Abaca, the strongest of the commercially available cellulose fibers, is indigenous to the Philippines and is currently produced there and in Ecuador. It was once the preferred cordage fiber for marine applications.

Bledzki et al. [102,103] examined the mechanical properties of abaca fiber reinforced PP composites regarding different fiber lengths (5, 25 and 40 mm) and different compounding processes (mixer-injection molding, mixer-compression molding and direct compression molding process). It was observed that, with increasing fiber length (5–40 mm), the tensile and flexural properties showed an increasing tendency though not a significant one. Among the three different compounding processes compared, the mixer-injection molding process displayed a better mechanical performance (tensile strength is around 90% higher) than the other processes.

When abaca fiber PP composites were compared with jute and flax fiber PP composites, abaca fiber composites had the best notched Charpy (Fig. 1) and falling weight impact properties. Abaca fiber composites also showed higher odor concentration (Fig. 2) compared to jute and flax fiber composites.

A dynamic mechanical analysis of, polarity parameters of banana fiber reinforced polyester composites were carried out by Thomas and co-workers [104,105] with special reference to the effects of fiber loading, frequency and temperature. The storage modulus was found to be highest for composites with 40% fiber loading, indicating
that the incorporation of abaca fiber in the polyester matrix induces reinforcing effects at higher temperatures. Increased dynamic modulus values and low damping values verified improved interactions between the fiber and the matrix.

Abaca fibers have been investigated with cement [106], polyurethane [107], aliphatic polyester resin [108], PP [109], urea formaldehyde [110], PE [111], polyester [112], and polyvinyl alcohol [113] as matrices, in order to evaluate the composites properties.

2.2.7. Pineapple leaf fiber

Pineapple (Ananas comosus) is a tropical plant native to Brazil. Pineapple leaf fiber is rich in cellulose, relatively inexpensive and abundantly available. Furthermore, it has the potential for polymer reinforcement. At present pineapple leaf fibers are a waste product of pineapple cultivation and therefore these relatively inexpensive pineapple fiber can be obtained for industrial purposes.

Pineapple leaf fiber was reinforced with polycarbonate to produce functional composites [114]. The silane treated modified pineapple leaf fibers composite exhibited the highest tensile and impact strengths. The thermogravimetric analysis showed that the thermal stability of the composites is lower than that of neat polycarbonate resin. In addition, the thermal stability decreased with increasing pineapple leaf fiber content.

The thermal conductivity and thermal diffusivity of pineapple leaf fiber reinforced phenol formaldehyde composites were studied using the Transient Plane Source (TPS) technique [115]. It is found that the effective thermal conductivity and effective thermal diffusivity of the composites decrease, as compared with pure phenol formaldehyde at the fraction of fiber loading increases.

The quality enhancement of pineapple leaf fiber has been attempted using different surface modifications like dewaxing, alkali treatment, cyanoethylation and grafting acrylonitrile onto dewaxed fibers [116]. The mechanical properties reach an optimum at fiber load of 30 wt% and among all modifications, 10% acrylonitrile grafted fiber reinforced polyester composite exhibited the maximum tensile strength (48.36 MPa). However, cyano-ethylated fiber composites exhibited better flexural and impact strengths, i.e., 41% and 27% more than the detergent washed composite respectively.

The influence of surface treatment and fiber content of pineapple leaf fiber was also investigated with PP [117] and natural rubber as matrix [118].

2.2.8. Ramie

Ramie belongs to the family Urticaceae (Boehmeria), which includes about 100 species. Ramie’s popularity as a textile fiber has been limited largely by regions of production and a chemical composition that has required more extensive pre-treatment than is required of the other commercially important bast fibers.

Ramie fiber reinforced PP composites were fabricated using a hybrid method of melt-blending and injection molding processes [119]. Different ramie fiber/PP composites were fabricated by varying the fiber length, fiber content and method of fiber pre-treatment. The results exhibited increases in fiber length and fiber content also show increased tensile strength, flexural strength and compression strength noticeably in turn. Yet, they also result in negative influences on the impact strength and elongation behavior of the composites.

Thermoplastic biodegradable composites consisting of ramie fibers and a PLA/PCL matrix were manufactured using the in situ polymerization method [120]. The effects of fiber length and content on the tensile and impact strengths of this natural-fiber-reinforced biodegradable composite were discussed, including the influence of a silane coupling agent for improved interfacial adhesion. The results showed that the tensile strength and impact strength were highest when a silane coupling agent was employed, the ramie fiber length was 5–6 mm and when the fiber content was 45 wt%.

Bulletproof panels were made from ramie fiber reinforced composites by hand lay-up process with epoxy as a matrix [121]. These prototype bulletproof panels were believed to be lighter in weight and more economical than conventional bulletproof panels. Conventional bulletproof panels are made from ceramic plates, kevlar/aramid composites, and steel-based material, which are popular in military standard antiballistic equipment today. The bullet testing results showed that the panels could resist the penetration of a high-impact projectile (level II) obtaining only minimal fractures. Level IV ballistic testing showed that all prototype panels could not resist the high-impact velocity of the projectile. Therefore, tests proved that ramie fibers have sufficient breaking strength and toughness for level II bullet testing.

Ramie fibers were also reinforced using polyester [122,123], epoxy–bioresin [124], soy protein [125,126], epoxy [127] and PP [128] for the matrix.

2.2.9. Coir

Coir husk fibers are located between the husk and the outer shell of the coconut. As a by-product of the production of other coconut products, coir production is largely determined by demand. Abundant quantities of coconut husk imply that, given the availability of labor and other inputs, coir producers can adjust relatively rapidly to market conditions and prices. It is estimated that approximately 10% of all husks are utilized for fiber extraction, satisfying a growing demand for fiber and coir products.

Characterization and utilization of coir fiber in coir/natural rubber composites [129], dynamic mechanical behavior of coir/natural rubber composites [130], durability of coir/cement composites [131], the effect acetylation on the coir/epoxy composites [132], the influence of treated coir fiber on the physico-mechanical properties of coir/PP composites [133,134], and the effect of fiber physical, chemical and surface properties on the thermal and mechanical properties of coir/PP composites were investigated and evaluated [135].

2.2.10. Bamboo

Bamboo (Bambusa Shreb.) is a perennial plant, which grows up to 40 m in height in monsoon climates. Generally, it is used in construction, carpentry, weaving and plaiting etc. Curtains made of bamboo fiber can absorb ultraviolet
radiation in various wavelengths, making it less harmful to human body.

The development of composites for ecological purposes (eco-composites) using bamboo fibers and their basic mechanical properties were evaluated [136]. The steam explosion technique was applied to extract bamboo fibers from raw bamboo trees. The experimental results showed that the bamboo fibers (bundles) had a sufficient specific strength, equivalent to that of conventional glass fibers. The tensile strength and modulus of PP based composites increased about 15 and 30% when using steam-exploded fibers. This increase was due to good impregnation and a reduction of the number of voids, in comparison to composites using fibers that were mechanically extracted.

The mechanical and thermal properties of bamboo fiber reinforced epoxy composites [137], the effects of fiber loading, coupling and bonding agents on the mechanical properties of bamboo fiber/natural rubber composites [138,139], the isothermal crystallization kinetics of modified bamboo cellulose/PCL composites [140], the influence of environmental aging on the mechanical properties of bamboo/glass fiber reinforced PP hybrid composites [141], and the effect of ceramic fillers on mechanical properties of bamboo fiber/epoxy composites [142] were evaluated.

2.2.11. Rice husk

Rice is only one of the large group of cereal grains that can be used to produce hull fibers. Nowadays wheat, corn, rye, oats and other cereal crops are used to produce fibers and investigating to reinforce in composites area.

Ismail et al. [143–147] studied the mechanical properties of rice husk filled polymer composites and their relation to fiber loading, coupling agent, processability, hygrothermal aging, and hybridization effect.

Other studies have focused on: flame retardant properties of rice husk/PE composites [148], the using of rice husk as filler for rice husk/PP composites [149], the thermogravimetric analysis of rice husk filled HDPE and PP composites [150], the enhancement of the processability of rice husk/HDPE composites [151], the effect of the percentage of rice husk content, hydroxyl groups and size on the flexural, tensile, and impact properties of rice husk/polyurethane composites [152], nonlinear viscoelastic creep characterization of HDPE-rice husk composites [153], the effect of the rice husk size and composition on the injection molding processability of rice husk/PE composites [154], photocatalytic performance of a carbon/TiO₂ composite with rice husk [155], the effect of different concentrations and sizes of particles of rice husk ash—in the mechanical properties of rice husk/PP composites [156], the effect of different coupling agent on rice husk/co-polymer PP composites [157], dimensional properties of rice husk/unsaturated polyester composites [158], and carbon/silica composites fabricated from rice husk by means of binder-less hot-pressing [159].

2.2.12. Oil palm

Oil palms (Elaeis) comprise two species of the Arecaceae or palm family. Nowadays, oil palm empty fruit bunch fibers possess potential as a reinforcement fiber for plastic. Thomas et al. [160,161] investigated the stress relaxation behavior of phenol formaldehyde resins reinforced with oil palm empty fruit bunch fibers and hybrid composites composed of oil palm fibers and glass fibers. The effects of fiber loading, fiber treatment, physical ageing and strain level on the stress relaxation behavior were examined and the rate of relaxation at different time intervals was calculated in order to explain gradual changes in relaxation mechanisms.

Abu Baker et al. [162,163] investigated the effect of oil palm empty fruit bunch and acrylic impact modifier on mechanical properties and influence of oil extraction of oil palm empty fruit bunch on the processability of PVC composites.

The effects of oil extraction, compounding techniques and fiber loading [164], and the effect of matrix modification [165] on the mechanical properties of oil palm empty fruit bunch filled PP composites were examined. In addition, a comparative study of oil palm empty fruit bunch fiber/PP composites and oil palm derived cellulose/PP composites [166] were studied. The influence of chemical modification on oil palm/phenol formaldehyde composites [167], a comparison of epoxy and polyester matrixes reinforced with oil palm fibers [168], dielectric relaxation properties of oil palm/polyester resin composites [169], the effect of palm tree fiber orientation on dynamic electrical properties of palm tree fiber-reinforced polyester composites [170] have also been investigated.

2.2.13. Bagasse

Bagasse is the fibrous residue which remains after sugarcane stalks are crushed to extract their juice. It is currently used as a renewable natural fiber for the manufacture of composites materials.

The compression and injection molding processes were performed in order to evaluate which is the better mixing method for fibers (sugarcane bagasse, bagasse cellulose and benzylated bagasse) and PP matrixes [171]. The injection molding process performed under vacuum proved to work best. Composites were obtained with a homogeneous distribution of fibers and without blisters. Although, the composites did not have good adhesion between the fiber and the matrix according to their mechanical properties.

The effect of botanical components of bagasse on the setting of bagasse/cement composites [172], design and optimization of PHB/bagasse fiber composites [173], tribological properties of bagasse/polyester composites [174], creep properties of bagasse fiber reinforced PVC and HDPE composites [175], bagasse/HDPE composites for radiation shielding [176], molecular mobility information of bagasse fiber and their distribution in bagasse/EVA composites [177], silane treated bagasse fiber reinforcement for cementitious composites [178], using polyurethane from castor oil [179], durability of bagasse/PP composites exposed to rainbow fungus [180], and ecodesign and life cycle assessment as strategy for automotive components from bagasse/PP composites [181] were examined.

2.3. Structure and chemical composition

Climatic conditions, age and the degradation process influence not only the structure of fibers, but also the chemical composition. The major chemical component of a living
Table 2
Chemical composition of some common natural fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Cellulose (wt%)</th>
<th>Hemicellulose (wt%)</th>
<th>Lignin (wt%)</th>
<th>Waxes (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>55.2</td>
<td>16.8</td>
<td>25.3</td>
<td>–</td>
</tr>
<tr>
<td>Bamboo</td>
<td>26–43</td>
<td>30</td>
<td>21–31</td>
<td>–</td>
</tr>
<tr>
<td>Flax</td>
<td>71</td>
<td>18.6–20.6</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Kenaf</td>
<td>72</td>
<td>20.3</td>
<td>9</td>
<td>–</td>
</tr>
<tr>
<td>Jute</td>
<td>61–71</td>
<td>14–20</td>
<td>12–13</td>
<td>0.5</td>
</tr>
<tr>
<td>Hemp</td>
<td>68</td>
<td>15</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>Ramie</td>
<td>68.6–76.2</td>
<td>13–16</td>
<td>0.6–0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Abaca</td>
<td>56–63</td>
<td>20–25</td>
<td>7–9</td>
<td>3</td>
</tr>
<tr>
<td>Sisal</td>
<td>65</td>
<td>12</td>
<td>9.9</td>
<td>2</td>
</tr>
<tr>
<td>Coir</td>
<td>32–43</td>
<td>0.15–0.25</td>
<td>40–45</td>
<td>–</td>
</tr>
<tr>
<td>Oil palm</td>
<td>65</td>
<td>–</td>
<td>29</td>
<td>–</td>
</tr>
<tr>
<td>Pineapple</td>
<td>81</td>
<td>–</td>
<td>12.7</td>
<td>–</td>
</tr>
<tr>
<td>Curaua</td>
<td>73.6</td>
<td>9.9</td>
<td>7.5</td>
<td>–</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>38–45</td>
<td>15–31</td>
<td>12–20</td>
<td>–</td>
</tr>
<tr>
<td>Rice husk</td>
<td>35–45</td>
<td>19–25</td>
<td>20</td>
<td>14–17</td>
</tr>
<tr>
<td>Rice straw</td>
<td>41–57</td>
<td>33</td>
<td>8–19</td>
<td>8–38</td>
</tr>
</tbody>
</table>

differences in the fiber structure due to the overall environment conditions during growth. Natural fibers can be processed in different ways to yield reinforcing elements with different mechanical properties. Mechanical properties of natural fibers can be influenced by many factors. Such as either fiber bundles or ultimate fiber is being tested. Table 3 [182,183] presents the important physico-mechanical properties of commonly used natural fibers.

The hydrophilic nature of fibers is a major problem for all cellulose-fibers if used as reinforcement in plastics. The moisture content of the fibers is dependent on the content of non-crystalline parts and the void content of the fibers. Overall, the hydrophilic nature of natural fibers influences the mechanical properties. Table 4 [185] shows the equilibrium moisture content of some natural fibers.

The moisture content at a given relative humidity can have a great effect on the biological performance of a composite made from natural fibers. For example, a composite made from abaca fibers would have much greater moisture content than would a composite made from flax fibers.

The physical properties of each natural fiber are critical, and include the fiber dimensions, defects, strength and structure. There are several physical properties that are important to know about for each natural fiber before that fiber can be used to reach its highest potential. Fiber dimensions, defects, strength, variability, crystallinity, and structure must be taken into consideration.

Table 3
Physico-mechanical properties of natural fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abaca</td>
<td>400</td>
<td>12</td>
<td>3–10</td>
<td>1.5</td>
</tr>
<tr>
<td>Bagasse</td>
<td>290</td>
<td>17</td>
<td>–</td>
<td>1.25</td>
</tr>
<tr>
<td>Bamboo</td>
<td>140–230</td>
<td>11–17</td>
<td>–</td>
<td>0.6–1.1</td>
</tr>
<tr>
<td>Flax</td>
<td>345–1035</td>
<td>27.6</td>
<td>2.7–3.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Hemp</td>
<td>690</td>
<td>70</td>
<td>1.6</td>
<td>1.48</td>
</tr>
<tr>
<td>Jute</td>
<td>393–773</td>
<td>26.5</td>
<td>1.5–1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Kenaf</td>
<td>930</td>
<td>53</td>
<td>1.6</td>
<td>–</td>
</tr>
<tr>
<td>Sisal</td>
<td>511–635</td>
<td>9.4–22</td>
<td>2.0–2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ramie</td>
<td>560</td>
<td>24.5</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Oil palm</td>
<td>248</td>
<td>3.2</td>
<td>25</td>
<td>0.7–1.55</td>
</tr>
<tr>
<td>Pineapple</td>
<td>400–627</td>
<td>1.44</td>
<td>14.5</td>
<td>0.8–1.6</td>
</tr>
<tr>
<td>Coir</td>
<td>175</td>
<td>4–6</td>
<td>30</td>
<td>1.2</td>
</tr>
<tr>
<td>Curaua</td>
<td>500–1150</td>
<td>11.8</td>
<td>3.7–4.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Knowledge about fiber length and width is important for comparing different kinds of natural fibers. A high aspect ratio (length/width) is very important in cellulose based fiber composites as it give an indication of possible strength properties. The fiber strength can be an important factor in selecting a specific natural fiber for a specific application. Changes in the physical properties can be due to differences in fiber morphology. Major differences in structure such as density, cell wall thickness, length and diameter result in differences in physical properties. It is also interesting to note that the morphology of the land plant fibers is very different to that of water plant fibers.

In between fiber qualities, the cellulose content and spiral angle is differed from fiber to fiber and also in a single fiber design. Natural fiber is a composite of the three polymers (cellulose, hemicelluloses and lignin), in which the unidirectional cellulose microfibrils constitute the reinforcing elements in the matrix blend of hemicellulose and lignin. The structure of such a fiber was built as multiply construction with layers P, S1, S2 and S3 of cellulose microfibrils at different angles to the fiber axis (Fig. 3) [186].

Depending on the single fiber cell layer, the different spiral angle of those layers will have a pronounced influence on the properties of the fiber. The elastic modulus dependency on the spiral angle of the fiber is determined (Fig. 4) assuming that the fibers (holocellulose fibers) were lignin-free with a cellulose content of 65 wt% (which is typical cellulose content for natural fibers [186]). The relative thickness of the different layers were chosen to be P = 8%, S1 = 8%, S2 = 76%, and S3 = 8%. It is seen that the elastic modulus decreases with increasing spiral angle.

Crystallinity values of natural fibers vary in different parts of the plant. The crystallinity tends to decrease as the plant matures, but the difference between bast and core fibers is inconclusive. The permeability of kenaf core is highest and is closely followed by cotton.

The effect of transcrystallinity on the interface in flax fiber (green flax, dew-retted flax, Duralin-treated flax and stearic acid-treated flax fiber)/isotactic PP composites has been investigated [187,188]. A significant strengthening of the interface was observed when transcrystallinity was present. Surface modification (stearation) of flax fiber also induced transcrystallinity. The interfacial shear strength increased from 12.75 MPa for the samples without transcrystallinity to 23.05 MPa for the transcrystallized samples according to the single fiber fragmentation test.

### Table 4

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Equilibrium moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sisal</td>
<td>11</td>
</tr>
<tr>
<td>Hemp</td>
<td>9.0</td>
</tr>
<tr>
<td>Jute</td>
<td>12</td>
</tr>
<tr>
<td>Flax</td>
<td>7</td>
</tr>
<tr>
<td>Abaca</td>
<td>15</td>
</tr>
<tr>
<td>Ramie</td>
<td>9</td>
</tr>
<tr>
<td>Pineapple</td>
<td>13</td>
</tr>
<tr>
<td>Coir</td>
<td>10</td>
</tr>
<tr>
<td>Bagasse</td>
<td>8.8</td>
</tr>
<tr>
<td>Bamboo</td>
<td>8.9</td>
</tr>
</tbody>
</table>

*Fig. 3. Illustration of a single fiber cell.*

*Fig. 4.* Correlation between spiral angle and elastic modulus of a natural fiber.
The chemical composition varies from plant to plant, and within different parts of the same plant. It also varies within plants from different geographical regions, ages, climate and soil conditions.

The chemical properties are influenced by the fiber growth time (days after planting), the botanical classification of the fiber and the stalk height. The chemical composition can also vary within the same part of a plant. Both the root and stalk core have a higher lignin content than that of the fibers.

2.5. Summary

There are thousands of different fibers in the world and in fact only few of these fibers have been studied. Most research has been carried out to study the potential use of natural fibers for technical applications and this review paper has only covered the most widely studied and used natural fibers in reinforced composites materials. Among the most popular natural fibers: flax, jute, hemp, sisal, ramie, and kenaf fibers were extensively researched and employed in different applications. But nowadays, abaca, pineapple leaf, coir, oil palm, bagasse, and rice husk fibers are gaining interest and importance in both research and applications due to their specific properties and availability.

It should be mentioned that there are also shortcomings; a lack of consistency of fiber qualities, high levels of variability in fiber properties related to the location and time of harvest, processing conditions, as well as their sensitivity to temperature, moisture and UV radiation. A multi-step manufacturing process is required in order to produce high quality natural fibers, which contributes to the cost of high-performance natural fibers as well as the improved mechanical properties of the composites.

3. Modification of natural fibers

The main disadvantages of natural fibers in reinforcement to composites are the poor compatibility between fiber and matrix and their relative high moisture absorption. Therefore, natural fiber modifications are considered in modifying the fiber surface properties to improve their adhesion with different matrices. An exemplary strength and stiffness could be achieved with a strong interface that is very brittle in nature with easy crack propagation through the matrix and fiber. The efficiency of stress transfer from the matrix to the fiber could be reduced with a weaker interface.

3.1. Physical method

Physical methods include stretching, calendaring, thermotreatment, and the production of hybrid yarns for the modification of natural fibers. Physical treatments change structural and surface properties of the fiber and thereby influence the mechanical bonding of polymers. Physical treatments do not extensively change the chemical composition of the fibers. Therefore the interface is generally enhanced via an increased mechanical bonding between the fiber and the matrix.

3.1.1. Corona treatment

Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the cellulose fibers. Corona discharge treatment on cellulose fiber and hydrophobic matrix was found to be effective for the improvement of the compatibilization between hydrophilic fibers and a hydrophobic matrix.

Tossa jute fibers [189] were corona discharge treated to improve the mechanical properties of natural fiber/epoxy composites. Corona-treated fibers exhibited significantly higher polar components of free surface energy with increasing treatment energy output. Owing to difficulties in effective treatment of three-dimensional objects with corona discharge, the increased polarity of treated yarns is relatively small. Furthermore a decrease in the yarn tenacity was observed with an increasing corona energy level.

The mechanical properties of corona treated hemp fiber/PP composites were characterized by tensile and compressive stress–strain measurements [190]. The treatment of compounds (fibers or matrix) leads to a significant increase in tensile strength. The modification of cellulotic reinforcements rather than PP matrix allows greater improvement of the composites properties with an enhancement of 30% of Young modulus. The observation of the fracture surfaces enables discussion about adhesion improvement.

Flax and Hemp fiber mats were corona treated and the optimum length of corona treatment to improve the composites’ (with a natural resin matrix) tensile modulus and strength was determined [191]. The composite tensile breaking strength reaches a maximum earlier, namely after only 5 min of corona treatment and declines rapidly afterwards. The fiber appearance confirmed that relatively short periods of corona treatment are more than sufficient to improve adhesion in the fibers. In addition, it was also proven that there is no further improvement achieved when longer corona treatments are applied, because the surface opening of the fiber does not improve further after 15 min of treatment. However, the degradation of the fibers proceeds further.

3.1.2. Plasma treatment

Plasma treatment is another physical treatment method and is, similar to corona treatment. The property of plasma is exploited by the method to induce changes on the surface of a material. A variety of surface modifications can be achieved depending on the type and nature of the gases used. Reactive free radicals and groups can be produced, the surface energy can be increased or decreased and surface cross-linking can be introduced.

Polyester composites reinforced with flax fibers, which were submitted to helium cold plasma treatment, were investigated by means of water permeation measurements and mechanical tests [192]. The analysis of the permeation and mechanical results showed that plasma treatment improves the fiber/matrix adhesion and enhances the mechanical property stiffness.

Martin et al. [193] prepared sisal–HDPE composites and showed that some improvements of the mechanical
properties of the composites are achieved due to the plasma treatments.

Jute fibers were subjected to oxygen plasma treatment as a function of the plasma power in order to enhance interfacial adhesion [194]. The interlaminar shear strength of plasma treated jute fiber/HDPE composites, which were exposed to plasma powers of 30W and 60W, increased by approximately 32 and 47%, respectively compared to untreated composites. In turn, the flexural strength of untreated composites increases by only 45%. It can be concluded that exposure to plasma powers of 60W for 15 min in the studied range is the most suitable parameter for oxygen plasma treatment of jute fibers and enables the achievement of the best interfacial adhesion with HDPE.

The influence of plasma treatment on the morphology, wettability, and fine structure of jute fibers and its impact on the interfacial adhesion of jute fibers/unsaturated polyester were investigated [195]. A scanning electron microscopic micrograph showed the rough surface morphology and degradation of fiber due to an etching mechanism caused by the plasma. Plasma treatment resulted in the development of hydrophobicity in fibers. However, among all treated fiber composites, the flexural strength of composites prepared with fibers treated for 10 min with plasma only showed an improved mechanical strength of approximately 14% in comparison to raw fiber composites.

Jute fibers were treated indifferent plasma reactors (radio frequency “RF” and low frequency “LF” plasma reactors) using O2 for different plasma powers to increase the interface adhesion between the jute fiber and polyester matrix. The interlaminar shear strength increased from 11.5 MPa for the untreated jute fiber/polyester composite to 19.8 and 26.3 MPa for LF and RF oxygen plasma treated jute fiber/polyester composites, respectively. The tensile and flexural strengths improved of jute fiber/polyester composites for both plasma systems. It is clear that oxygen plasma treatment of jute fibers by using RF plasma system showed greater improvement on the mechanical properties of jute/polyester composites compared to using LF plasma system [196].

Chemical modifications of natural fibers aimed at improving the adhesion within the polymer matrix using different chemicals were investigated.

3.2.1. Silane treatment

The surface energy of fibers is closely related to the hydrophilic nature of the fiber. Some investigations are concerned with methods to decrease hydrophilicity. Silane coupling agents may contribute hydrophilic properties to the interface, especially when amino-functional silanes, such as epoxies and urethanes silanes, are used as primers for reactive polymers. The primer may supply much more amine functionality than can possibly react with the resin in the interphase. Those amines, which could not react, are hydrophilic and therefore responsible for the poor water resistance of bonds. An effective way to use hydrophilic silanes is to blend them with hydrophobic silanes such as phenyltrimethoxysilane. Mixed siloxane primers also have an improved thermal stability, which is typical for aromatic silicones.

The surface of the kenaf fibers was modified using a silane coupling agent to promote adhesion with the PS matrix [197]. The fiber–matrix adhesion increased through a condensation reaction between alkoxy silane and hydroxyl groups of kenaf cellulose. Due to the fiber modification, kenaf/PS composites exhibited higher storage modulus and lower tan δ than those with untreated fiber indicating a greater interfacial interaction between the matrix resin and the fiber.

Silane treatment improved the storage modulus of abaca fiber reinforced polyester composites [198]. Chemical modifications with silane A174 (γ-methacryloyloxypropyl trimethoxy-silane) and also with NaOH resulted in maximum increase of the modulus. The hydrogen-bond donating acidity is found to be the lowest for fibers treated with silane A174, after pre-treatment with 0.5% NaOH. On the contrary, the highest value was noted for fibers treated with silane A151 (vinyl triethoxysilane). The overall polarity was found to be at a maximum for fibers treated with silane A151 (vinyl triethoxysilane).

The effects of different chemical treatments on the fiber–matrix compatibility in terms of the surface energy and the mechanical properties of composites were reported [199]. The composites were compounded with two kinds of flax fibers (natural flax and flax pulp) and a PP matrix. The applied treatments were vinyl trimethoxy silane (VTMO), maleic anhydride (MA) and maleic anhydride-polypropylene copolymer (MAPP). The three treatments reduced the polar component of the surface energy of the fiber. Composites containing MAPP-treated fibers possessed the highest mechanical properties, while the MA and VTMO-treated fibers obtained similar values to those of the untreated ones.

Ismail et al. [200,201] treated oil palm empty fruit bunch and coir fibers with silane coupling agents and found that with the addition of silane, the scorch time and cure time increased. Furthermore, the tensile strength, tensile modulus, tear strength, fatigue life and hardness of oil palm empty fruit bunch and coir fiber reinforced polyester and natural rubber composites were enhanced.

3.2. Chemical method

Cellulose fibers, which are strongly polarized, are inherently incompatible with hydrophobic polymers due to their hydrophilic nature. In many cases, it is possible to induce compatibility in two incompatible materials by introducing a third material that has properties intermediate between those of the other two. There are several coupling mechanisms in materials (e.g., weak boundary layers, deformable layers, restrained layers, wettability, chemical bonding, and acid–base effect).

The development of a definite theory for the mechanism of bonding using coupling agents in composites is a complex problem. The main chemical bonding theory alone is not sufficient. So the consideration of other concepts appears to be necessary. These include the morphology of the interphase, the acid–base reactions in the interface, surface energy and the wetting phenomena.
3.2.2. Alkaline treatment

Alkaline treatment or mercerization is one of the most used chemical method (removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall) for natural fibers when used to reinforce thermoplastics and thermosets. The important modification achieved with alkaline treatment is the disruption of the hydrogen bonding in the network structure, thereby increasing the surface roughness.

The effect of alkali treatment on the wettability and coherence of sisal–epoxy composites has been examined [202]. Treatment of sisal fiber in a 0.5 N solution of sodium hydroxide resulted in more rigid composites with lower porosity and higher density. The treatment improved the adhesion characteristics, due to improved work of adhesion because it increases the surface tension and surface roughness. The resulting composites showed improvements in the compressive strength and water resistance. It was also discovered that the removal of intracrystalline and intercrystalline lignin and other waxy surface substances by the alkali substantially increases the possibility for mechanical interlocking and chemical bonding.

The effects of alkali treatment of pineapple leaf fiber on the performance of the pineapple leaf fiber/PLA composites have been shown [203]. It was found that alkali-treated fiber reinforced composite offered superior mechanical properties compared to untreated fiber reinforced composites. This study also suggested that the appropriate modification of fiber surfaces significantly contributes to improving the interfacial properties of the biocomposites. Since improvement of the interfacial adhesion increases the impact performance, surface properties of fibers can be greatly modified in terms of different treatments as characterized by an increased surface energy, which improves wettability of the fiber when compounding with a PLA matrix. DMA showed that treated fiber composites have a higher storage modulus, which indicates greater interfacial bond strength and adhesion between the matrix resin and the fiber. The alkaliized fiber composites have high storage modulus values, which correspond with their high flexural modulus.

The effect of alkali on the tensile properties of ramie fiber was explored [204]. The load application technique was employed during alkali treatment, in order to improve the mechanical properties of the fiber. The ramie fiber was alkali-treated with a solution containing 15% NaOH and was subjected to applied loads of 0.049 and 0.098 N. The results showed that the tensile strength of the treated ramie fiber was by improved 4–18% more than for untreated ramie fibers. The treated fibers’ Young’s modulus decreased. It should be noted that fracture strains of the treated ramie fiber drastically increased to 0.045–0.072. That equals twice to three times higher than those of the untreated ramie fiber. It was considered that such property improvements upon alklyation were correlated with a change of the morphological and chemical structures in microfibrils of the fiber.

Jute fibers were subjected to alkali treatment with a solution containing 5% NaOH for 0, 2, 4, 6 and 8 h at 30°C [205]. The modulus of the jute fibers improved by 12%, 68% and 79% after 4, 6 and 8 h of treatment, respectively. The tenacity of the fibers improved by 46% after 6 and 8 h treatment and the percentage of breaking strain was reduced by 23% after 8 h treatment. For 35% of the composites with fiber treated for 4 h, the flexural strength improved by 20% from 199.1 to 238.9 MPa. The flexural modulus improved by 23% from 11.89 to 14.69 GPa and the laminar shear strength increased by 19% from 0.238 to 0.283 MPa.

Ramie fiber [206], green coconut fiber [207], sisal [208], jute [209] and coir [210] fibers were alkaliized and their properties evaluated.

The variation of mechanical and structural properties of hemp yarn upon alklyation in dissimilar conditions was investigated [211]. Alklyation with a rather high alkali concentration (22%) never led to a complete lattice conversion of cellulose I in cellulose II (Table 5). As expected, the highest degree of conversion (70%) was reached by a freely shrinking yarn. Further, the alklyation of hemp yarn under isometric conditions or with constant fiber load (100 p) at a NaOH concentration of 22% results in a crystalline lattice conversion of only 40–50%. However, this occurs only when combined with the highest strengths and moduli of the fiber bundles. It was also observed that only the tensile modulus of elasticity exceeds the value of the original unmodified material.

Table 5

<table>
<thead>
<tr>
<th>Mercerization temperature (°C)</th>
<th>Mercerization time (min)</th>
<th>Stress at the mercerization</th>
<th>Degree of conversion cell I in cell II (%)</th>
<th>Tensile strength (cN/tex)</th>
<th>Elongation at break (%)</th>
<th>Tension modulus (cN/tex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>Isometric</td>
<td>≈50</td>
<td>29.8</td>
<td>3.15</td>
<td>1148</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>Isometric</td>
<td>≈50</td>
<td>28.5</td>
<td>2.34</td>
<td>1617</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>Isometric</td>
<td>≈50</td>
<td>24.9</td>
<td>2.45</td>
<td>1214</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>Free shrinkage</td>
<td>≈70</td>
<td>17.6</td>
<td>6.86</td>
<td>357</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>Constant load (100 g)</td>
<td>≈40</td>
<td>29.2</td>
<td>2.60</td>
<td>1499</td>
</tr>
</tbody>
</table>

Note: Distance of clamped support = 500 mm, test speed = 250 mm/min.

Table 6

<table>
<thead>
<tr>
<th>Fiber treatment</th>
<th>Flexural strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>77</td>
</tr>
<tr>
<td>Mercerized</td>
<td>115</td>
</tr>
<tr>
<td>MAH–PP</td>
<td>127</td>
</tr>
<tr>
<td>Mercerized + MAH–PP</td>
<td>149</td>
</tr>
</tbody>
</table>

Note: Lengthwise, fiber content: 36 vol%.

* 25% NaOH at 20 °C, 20 min, isometric.

* 1% Licomont AR 504 in toluene, 10 min.
Table 6 [211] explicitly shows that, besides the significant effects of single alkylation and MAH--PP treatments, a combination of the isometric alkylation procedure (e.g., increasing fiber strength) and coupling agents results in the highest increase of the composite properties (90%) in comparison to a composite with untreated flax fibers for reinforcement.

3.2.3. Acetylation

Acetylation is another method of modifying the surface of natural fibers and making them more hydrophobic. It describes the introduction of an acetyl functional group into an organic compound. The main idea of acetylation is to coat the OH groups of fibers which are responsible for their hydrophilic character with molecules that have a more hydrophobic nature.

The influence of acetylation on the structure and properties of flax fibers were investigated. Modified flax fiber reinforced PP composites were also prepared [212]. The effect of acetylation on the degree of polymerization and crystallinity of flax fiber is illustrated in Fig. 5.

It was observed that the degree of polymerization slowly decreased while the degree of acetylation increased until 18%. Once reaching an acetyl content of 18% acetyl content, the degree of polymerization decreased rapidly due to vigorous degradation of cellulose. It was also notable that the degree of crystallinity increased a little bit regarding the degree of acetylation, because of the removal of lignin and extractibles. After that, the degree of crystallinity of the cellulose decreased with respect to the degree of acetylation owing to the decomposition of acetylated amorphous components on the cellulose surface.

The influences of the degree of acetylation of flax fibers on the moisture absorption properties are illustrated in Fig. 6 [212]. At 95% RH, the 3.6%, 12%, 18% and 34% degree of acetylated flax fibers showed about 14%, 18%, 27% and 42% lower moisture absorption properties than untreated flax fiber respectively. The moisture absorption properties decreased proportionally with the increase of acetyl content of fibers due to the reduction of hydrophilicity of the fibers.

Seena et al. investigated the effect of acetylation on abaca fiber reinforced phenol formaldehyde composites and reported that the tensile strength, tensile modulus and impact strength were found to improve compared to non-treated abaca fiber composites [213].

Tserki and co-workers [214] investigated the acetylation of flax, hemp and wood fibers. A removal of the non-crystalline constituents of the fibers, an alteration of the characteristics of the surface topography, a change of the fiber surface free energy and an improvement of the stress transfer efficiency in the interface took place.

The effects of acetylation on the biological degradation and shear strength of coir and oil palm fiber reinforced polyester composites were evaluated [215,216]. It was reported that acetylated natural fiber reinforced polyester composites exhibit higher bio-resistance and less tensile strength loss compared to composites with silane treated fiber in biological tests.

Zafeiropoulos and co-workers extensively investigated the influence of acetylation on the engineering and characterization of the interface in flax fiber/PP composites [217,218]. Furthermore, they also investigated the application of Weibull statistics [219] and Gaussian statistics [220] to the tensile strength of flax fibers.

3.2.4. Maleated coupling

Nowadays, maleated coupling is widely used to strengthen natural fiber reinforced composites. The fundamental difference with other chemical treatments is that maleic anhydride is not only used to modify fiber surface but also the polymeric matrix to achieve better interfacial bonding in between fiber and matrix and improved mechanical properties in composites. There are numerous published studies in which the effect of maleic anhydride grafting on the mechanical properties of natural fibers has been investigated and it is impossible to list all of them here. Hence, only a few representative studies are discussed here.

Mohanty et al. [221] used MAPP as a coupling agent for the surface modification of jute fibers. It was found that a fiber loading of 30% with a MAPP concentration of 0.5% in toluene and 5 min of impregnation time with 6 mm average fiber lengths resulted in the best possible outcomes. An increase in flexural strength of 72.3% was observed for the treated composites. In addition to the PP matrix, Mishra et al. [222] reported that maleic anhydride treatment reduced the water absorption to a great extent in abaca, hemp and sisal fiber-reinforced novolac composites. Mechanical properties like Young’s modulus,
flexural modulus, hardness and impact strength of plant fiber-reinforced composites increased after maleic anhydride treatment.

The effects of MAH–PP coupling agents on rice-husk flour reinforced PP composites were evaluated [223]. The tensile strengths of the composites decreased as the filler loading increased, but the tensile properties were significantly improved with the addition of the coupling agent. Both the notched and unnotched Izod impact strengths remained almost the same with the addition of coupling agents. A morphological study revealed the positive effect of a compatibilizing agent on interfacial bonding.

Abaca fiber reinforced composites based on HDPE/Nylon-6 blends were prepared [224]. Maleic anhydride grafted styrene/ethylene–butylene/styrene triblock polymers (SEBS-g-MA) and maleic anhydride grafted polyethylene (PE-g-MA) were used to enhance the impact performance and interfacial bonding between the abaca fibers and the resins. By employing SEBS-g-MA, better strengths and moduli were obtained for HDPE/Nylon-6 based composites than for corresponding HDPE based composites. It was found that the addition of SEBS-g-MA had a positive influence on the reinforcing effect of the Nylon-6 component in the composites. Thermal analysis results showed that fractionated crystallization of the Nylon-6 component in the composites was induced by the addition of both SEBS-g-MA and PE-g-MA. The thermal stability of both composite systems differed slightly, except for an additional decomposition peak, which is related to the minor Nylon-6 for the composites from the HDPE/Nylon-6 blends. In combination with SEBS-g-MA, the addition of Nylon-6 and the increased fiber loading level led to an increase in the water absorption value of the composites.

The influence of MAH–PP on the fiber–matrix adhesion in jute fiber-reinforced PP composites and on the material behavior under fatigue and impact loadings was investigated [225]. The fiber–matrix adhesion was improved by treating the fibers’ surface with the coupling agent MAH–PP. It was shown that a strong interface is connected with a higher dynamic modulus and reduction in stiffness degradation with increasing load cycles and applied maximum stresses. The specific damping capacity resulted in higher values for the composites with poor bonded fibers. Furthermore, the stronger fiber–matrix adhesion reduced the loss-energy for non-penetration impact tested composites about roughly 30%. Tests, which were performed at different temperatures, showed higher loss energies for cold and warm test conditions compared to those carried out at room temperature. The post-impact dynamic
modulus roughly 40% after 5 impact events and was 30% lower for composites with poor and good fiber–matrix adhesion, respectively.

The effectiveness of MAH as coupling agent has discussed also on thermal and crystallization properties of sial fiber/PP composites [226], tensile properties of hydro-gardenia fiber/PP composites [227], wetting behavior of flax fiber/PP composites [228], transcristallinity of jute fiber/PP composites [229], surface properties and water uptake behavior of flax, hemp fiber reinforced PP composites [230], effects of micro-sized cellulose based corn fibers as reinforcement agents in PP composites [231], and dynamic mechanical properties of flax and hemp fiber/PP composites [232].

3.2.5. Enzyme treatment

The use of enzyme technology is becoming increasingly substantial for the processing of natural fibers. Currently, the use of enzymes in the field of textile and natural fiber modification is also rapidly increasing. A major reason for embracing this technology is the fact that the application of enzymes is environmentally friendly. The reactions catalyzed are very specific and have a focused performance [233].

Bledzki et al. [233] investigated PP composites with enzyme treated abaca fibers. The surface morphologies of enzyme treated and untreated abaca fibers are shown in Fig. 7. In Fig. 7a, it was observed that the untreated fiber surface is rough, containing waxy and protruding parts. The surface morphology of treated fibers is observed in Fig. 7b and c. If the waxy material and cuticle in the treated surface are removed, the surface becomes smoother. Fibillation is also known to occur when the binding materials are removed from the surface of the treated fibers. Fiber surface damage was also observed for naturally digested fibers which occur in natural digestion systems.

The effects of enzyme treatment of abaca fiber on the tensile and flexural strength are shown in Fig. 8. The tensile strength of enzyme treated abaca composites was found to have increased 5–45% due to modification. Natural digestion system (NDS) modified abaca fiber composites showed little improvement in comparison to unmodified abaca fiber composites. The tensile strength of fungamix modified composites increased by 45% as compared to unmodified fiber composites. A conventional coupling agent (MA–PP) has a positive effect on the tensile strength. It was found to improve by 40%. Enzymatic treatment was also investigated with hemp fiber [234,235], and flax fibers [236].

3.3. Summary

Though natural fiber reinforced composites have developed significantly over the past few years because of their low cost, low relative density, and high specific strength, the interfacial adhesion between fiber and matrix is still an issue. Extensive research was carried out and reported in literature and reviewed in this paper, showing the importance of the interface and the influence of various types of surface modifications on the physical and mechanical properties of biocomposites. The observed trend lied with the chemical modification compared to physical modification. It has also been shown that maleated and silane treatment is becoming a choice method due to beneficial results. Additive suppliers improved the additives with higher amounts of anhydride functional groups than previous grades (used in 1980s and 1990s), which create more sites for chemical links, resulting in significant performance improvement at low additive contents. Using coupling agents reduces the water absorption of the composites but has not resulted in decreased long term performance. As described above that enzyme technology to modify the natural fiber surface, is increasing substantially due to environment friendly. In addition, enzyme technology could be cost effective, improved product quality compared to mostly use maleated and silane modification.

4. Matrices for biocomposites

The composites’ shape, surface appearance, environmental tolerance and overall durability are dominated by the matrix while the fibrous reinforcement carries most of the structural loads, thus providing macroscopic stiffness and strength. The polymer market is dominated by commodity plastics with 80% consuming materials based on non-renewable petroleum resources. Governments, companies and scientists are driven to find an alternative matrix to the conventional petroleum based matrix through public awareness of the environment, climate change and limited fossil fuel resources. Therefore biobased plastics, which consist of renewable resources, have experienced a renaissance in the past few decades. Fig. 9 shows that the matrices currently used in bio fiber composites depend on biobased or petroleum based plastics and also on their biodegradability.

4.1. Petrochemical based

The effects of the incorporation of natural fibers in petrochemical based thermoplastics and thermoset matrixes were extensively studied. Polypropylene (PP), polyethylene (PE), polystyrene (PS), and PVC (polyvinyl chloride) were used for the thermoplastic matrixes. Polyester, epoxy resin, phenol formaldehyde, and vinyl esters were used for the thermoset matrices and are reportedly the most widely used matrices for natural fiber reinforced polymer composites.
4.1. Thermoplastic

4.1.1. PE (polyethylene). Several mechanical properties (deformation, fracture, thermal diffusivity, thermal conductivity, and specific heat) of flax fiber/HDPE biocomposites were evaluated [237,238]. Strength and stiffness improvement combined with high toughness can be achieved by varying the fiber volume fraction and controlling the bonding between layers of the composite. The thermal conductivity, thermal diffusivity, and specific heat of the flax/HDPE composites decreased with increasing fiber content, but the thermal conductivity and thermal diffusivity did not change significantly at temperatures in the range (170–200 °C) studied. The specific heat of the biocomposites increased gradually with temperature.

Traditionally the mechanism of moisture absorption is defined by diffusion theory; but the relationship between the microscopic structure-infinite 3D-network and the moisture absorption could not be explained. Wang et al. [239] introduced the percolation theory and a percolation model was developed to estimate the critical accessible fiber ratio; the moisture absorption and electrical conduction behavior of composites. At high fiber loading when fibers are highly connected, the diffusion process is the dominant mechanism; while at low fiber loading close to and below the percolation threshold, the formation of a continuous network is key. Hence, percolation is the dominant mechanism. The model can be used to estimate the threshold value which can in turn be used to explain moisture absorption and electrical conduction behavior. Fig. 10 shows the increment of electrical conductivity with the increasing moisture content of the composite with 65% rice hull fiber loading. The composite started showing conductivity after it absorbed approximately 50% of maximum moisture. After this, conductivity increased quickly with further moisture absorption. The pattern of the increment of electrical conductivity suggests a diffusion process of moisture absorption.

![Fig. 9. Current and emerging plastics and their biodegradability.](image)
The hygrothermal weathering properties of rice hull reinforced HDPE composites were studied by Wang et al. [240]. The samples (50% rice hull and 50% HDPE) absorbed 4.5% moisture after 2000 h of exposure to a relative humidity (RH) of 93% at 40 °C. The walls of the samples swelled significantly (7.1%) in thickness and ultimately developed about 5 mm of longitudinal bowing (Fig. 11) based on 61 cm long boards. Both expansion and bowing were partially recovered after another 2000 h exposure to 20% RH at 40 °C.

Deformation results in increased moisture contents. Temperature also played a significant role by causing direct thermal expansion or contraction and by affecting the rate and the amount of moisture adsorption.

Sisal fiber reinforced PE [241] and HDPE [242,243] composites were examined regarding their interfacial properties, isothermal crystallization behavior and mechanical properties. Sisal fiber treatment with stearic acid increased the interfacial shear strength by 23% compared to untreated fibers in sisal/PE composites. Permanganate (KMnO₄) and dicumyl peroxide (DCP) roughen the fiber surface and introduced mechanical interlocking with the HDPE. Sisal fiber reinforced HDPE shows a stable de-bonding process with Permanganate and DCP treatment. Silane treated sisal fiber reinforced HDPE exhibits an unstable debonding process. A high crystallization rate and short crystallization half time were observed for sisal/HDPE composites compared to neat HDPE. This demonstrates the strong nucleating abilities of sisal fibers. With increasing fiber content, the crystallization activation energy of the composites decreased.

Similar investigations (PE as matrix) were carried out using soya powder [244], curaua [245], rape straw [246,247], hemp [248], rice straw [249], bagasse [250] rice hull fibers [251] and LDPE as matrices with wheat straw [252], abaca, bagasse and rice straw fibers [253].

4.1.1.2. PP (polypropylene). The thermo-mechanical behavior of hemp fibers was studied with focus on manufacturing high performance natural fiber reinforced PP composites. Hemp fibers subjected to quasi-static tensile experiments and temperature-controlled harmonic tests revealed a complex behavior, involving several mechanisms [254]. The hemp fiber behavior was affected by temperature and acted not only as an activation factor, but also as a degradation factor with respect to the visco-elastic properties of the fibers. It was discovered that PP–hemp fiber composites with relatively high performance can be achieved with some specific mechanical properties.

The effect of sisal fiber degradation and aging on the PP/sisal fiber composites was investigated. The fiber mat production method allowed the fibers to avoid much of the processing degradation, which is often encountered during conventional shear mixing processes [255]. The best possible mechanical properties for the sisal fiber/PP composites were achieved when the fiber length was greater than 10 mm and the fiber mass fraction was in the range of 15–35%. The aged sisal fiber showed lower tenacity, breaking strength and elongation with in comparison to fresh sisal fibers. On the contrary, in sisal/PP composites, aged sisal fiber composites exhibited better mechanical properties than fresh sisal fiber/PP composites [256].

Rana et al. [257] observed an increase in impact strength in jute fiber/PP composites as a result of fiber loading. It was also found that both the impact and tensile properties showed increasing trends with the addition of compatibilizers. However, the opposite was true for the flexural properties. Improvements of physico-mechanical properties achieved by post-treatment [258], and the interfacial and durability evaluation [259,260] of jute fiber/PP composites were studied.

The environmental performance of hemp fiber reinforced PP composites based on natural fiber mat thermoplastic (NMT) was evaluated by quantifying carbon storage potential and CO₂ emissions. The results were compared with commercially available glass fiber composites [261].

![Fig. 10. The moisture absorption and electrical conductivity for HDPE–rice hull composite with 65% fiber content.](image)

Adopted from [239]. Copyright 2006. By permission from Elsevier Ltd.

![Fig. 11. Partial recovery of bowing (a) before recovery: 5.00 mm of bowing (b) after recovery: 3.00 mm of bowing.](image)

Adopted from [240]. Copyright 2005. By permission from Elsevier Ltd.
Fig. 12. CO$_2$ emissions per ton composite and reduction in emissions by substituting glass fiber with hemp fibers. Adopted from [261]. Copyright 2003. By permission from Elsevier Ltd.

Fig. 14. TGA curves of wheat straw fibers prepared by different processes. Adopted from [262]. Copyright 2006. By permission from Elsevier Ltd.

The SEM photomicrographs (Fig. 13). The surface of the chemically processed fibers was more uniform and homogeneous while the fibers processed mechanically exhibit more surface irregularities. Mechanically processed fibers still contained the cellular residues such as lignin and hemicellulose, which cement the fibers together.

The influence of chemical and mechanical processes on the TGA of the wheat straw fibers is shown in Fig. 14. The onset of degradation of wheat straw fibers prepared by mechanical and chemical processes were 217°C and 242°C respectively indicating the suitability of these fibers for processing with thermoplastics, especially polyolefins. The higher onset of degradation temperature indicates the improved thermal stability of the fibers prepared by chemical processing.

Similar to PE, PP is also widely used as a matrix in combination with different natural fibers: such as hemp [263,264], flax [265–267], kenaf [268,269], oil palm [270].
date palm [271], coir [272,273], bamboo [274,275], abaca [276,277], rice hull [278–280], jute [281,282], and wheat straw [283].

4.1.2.1. **PS (polystyrene) and PVC (polyvinyl chloride).** Only limited studies were reported regarding the usage of PS and PVC as matrices for natural fibers. The thermal and dynamic mechanical behavior [284], as well as the rheological [285] and mechanical properties [286] of PS composites reinforced with sisal fibers were studied. The PS composites reinforced with agave fiber were also studied regarding their fiber surface modification [287]. The impact properties of PVC composites reinforced with bamboo fibers [288], the interfacial modification of bagasse fiber [289] and the thermal degradation of abaca fiber [290] reinforced PVC composites were also evaluated.

4.1.2. **Thermosets**

4.1.2.1. **Polyester.** The possibility of using date palm fibers as reinforcement in polyester composites was investigated [291]. Flexural properties and impact strength of date palm fiber/polyester composites were found to be influenced by fiber content and fiber treatment method. Soda treated fibers exhibited higher mechanical properties compared to untreated fiber/polyester composites. The fiber fraction and fiber length for this system were optimized for 9 wt% and 2 cm, respectively. Water absorption was lightly affected by surface modification of the fibers and was relatively low.

The hybrid effect on the mechanical properties of abaca and sisal fiber reinforced polyester composites was evaluated [292]. A positive hybrid effect was observed for the flexural properties. The tensile strength was found to be increased when the volume fraction of banana was increased. A negative effect was observed for the impact properties. Recent works regarding sisal and jute fiber [293], sisal [294], abaca [295], abaca and sisal [296], flax [297], jute fibers [298], sisal, abaca and bamboo fiber [299] reinforced polyester composites have been developed.

4.1.2.2. **Epoxy.** The excellent properties of epoxy (good adhesion, mechanical properties, low moisture content, little shrinkage, and processing ease) make it one of the best matrix materials for composites. The effect of fiber treatment on the mechanical properties of unidirectional sisal/epoxy composites was reported [300]. Ganen et al. [301] evaluated the mechanical and thermal properties of sisal/epoxy composites as a function of fiber modification. Kenaf [302], hemp and flax [303], oil palm [304], sisal [305,306], flax [307], sisal and hemp [308], flax, hemp and kenaf [309], lantana camara fiber [310] and sugar palm fiber [311] were reinforced with an epoxy matrix. Their mechanical properties, processing methods, water absorption, and fracture toughness were evaluated.

4.1.2.3. **Phenolic.** Phenolic resins show superior fire resistance to other thermosetting resins. Sreekala et al. [312–316] extensively investigated oil palm fiber reinforcement in phenolic resins. The fiber surface modification [312], a comparison of mechanical properties to glass fiber/phenolic resin composites [313], the dynamic mechanical properties regarding the fiber content and hybrid fiber ratio [314], the water absorption [315] and stress–relaxation behavior [316] of oil palm/phenolic resin composites were evaluated. Bamboo [317], jute [318,319], date palm fiber [320], and grewia optiva fiber [321] were also investigated with phenol formaldehyde resin as a matrix.

4.2. **Bio-based**

Public concern about the environment, climate change and limited fossil fuel resources are important driving forces, which motivate researchers to find alternatives to crude oil. Bio-based plastics may offer important contributions by reducing the dependence on fossil fuels and, in turn, the related environmental impacts. Biopolymers have experienced a renaissance in the recent years. Many new polymers were developed from renewable resources, such as starch, which is a naturally occurring polymer that was re-discovered as a plastic material. Others are poly lactic acid (PLA) that can be produced via lactic acid from fermentable sugar and polyhydroxyalkanoate (PHAs), which can be produced from vegetable oils next to other bio-based feed stocks.

4.2.1. **PLA (polylactic acid)**

Kenaf fiber reinforced PLA composites were studied extensively. Investigations have been undertaken concerning chemical modifications such as alkylation [322] and silane treatments [323], the biodegradability [324] and the mechanical and dynamic mechanical properties [325]. The alkali treated fiber reinforced composites, followed by silane-treated fiber reinforced composite possessed significantly improved mechanical properties. The heat deflection temperature (HDT) of the kenaf reinforced PLA composites was significantly higher than that of neat PLA resin. The biodegradability of kenaf/PLA composites corresponds to the weight of the composites, which decreased approximately 38% after four weeks of decomposition. Young's modulus (6.3 GPa) and the tensile strength (62 MPa) of the kenaf/PLA composites (fiber content = 70 vol%) were comparable to those of traditional composites. In addition, the storage modulus of the composite remained unchanged until the melting point of PLA was reached.

The interfacial characterization of flax fiber/PLA composites was performed on a micro-scale using the microbond testing method [326]. The interfacial mechanisms of flax/PLA biocomposite were exposed to varying thermal treatments (i.e., different cooling rates and annealing to release thermal stress). The treatments resulted in different micro-structures and residual stress states inside the material. Cooling kinetics is shown to modify the interfacial properties and when the cooling rate is slow, the interfacial properties improve. In addition, a high degree of crystallinity was measured, including transcrysallinity around the flax fiber. The higher crystalline morphology of the PLA results in an improvement of the tensile and shear properties and higher residual compressive stress.

Bledzki et al. [327] investigated PLA biocomposites with abaca and man-made cellulose fibers and compared these
to PP composites. The composites were processed using combined molding technology: first a two-step extrusion coating process was carried out and consecutively an injection molding was completed. With man-made cellulose of 30 wt%, the tensile strength and modulus increased by factors of 1.45 and 1.75 times in comparison to neat PLA. Reinforcing with abaca fibers (30 wt%) enhanced both the E-modulus and the tensile strength by factors of 2.40 and 1.20, respectively (Fig. 15).

The fibers’ length distribution in pellets after compounding and in samples after injection molding is depicted in Fig. 16. The measurement was evaluated using approximately 500 fibers. A significant decrease in the fiber length after compounding on the single-screw extruder can be observed, from the cut length of 15 mm to about 1–2 mm. Moreover, the injection molded samples show merely an insignificant drop in length, when put side by side to pellets. This indicates to massive fiber length reduction during extrusion processes. Processing on the single-screw extruder already affected the length significantly. Compounding on twin-screw extruders, which is often carried out during composite processing, can exceedingly increase the fiber length even more. The minimal fiber length achieved during compounding is not being affected during the injection molding process; however, the occurrence of the fiber length seems to be more uniform. As a result, most of the fibers, which remain longer than 2 mm after compounding, are shortened less than 2 mm during injection molding.

PLA as a matrix for biocomposites reinforced with biofiber was extensively investigated for jute fiber [328–331], flax fiber [332,333], kenaf [334,335], coir [336], bamboo [337] and cellulose fibers [338,339]. Special attention was paid to the influence of chemical treatments, processing techniques, coupling agents, micro-fibrillated fiber bundles, and reinforcement using man-made cellulose fibers.

The mechanical properties of PLA reinforced with flax fibers [340], the influence of the additives on the interfacial strength [341], as well as the effects of recycling [342] and sea water aging [343] on the mechanical properties was investigated. It was found that the composite strength is about 50% better compared to similar PP/flax fiber composites, which are used in many automotive panels today. The different additives significantly influenced the interfacial strength of the PLA/flax fiber composites while extraction with acetone had no effect compared to the untreated fibers. The use of TDP (4,40-thiodiphenol) imparted the most significant increase in interfacial shear strength whilst HB (Hyper Branched Polyester) had an opposing effect. The repeated injection molding cycles were influenced by many parameters; i.e., the reinforcement geometry, the molecular weight of PLA and, the thermal and rheological behavior. The tensile stiffness of PLA is hardly affected by seawater at temperatures approximately of 40 °C, but the composite does loses stiffness and strength. The interfacial adhesion weakens more due to wet aging. Cracks also appear in the PLA and flax fibers after longer periods of time.

Huda et al. [344,345] examined the effect of reinforcing recycled newspaper, the addition of silane and talc on the thermal and mechanical properties of PLA/recycled newspaper fiber composites. The results indicated that the addition of fibers increased the thermal stability of the composites compared to neat PLA. The heat deflection temperature of the PLA/recycled newspaper fiber composites was found to be comparable to that of the glass fiber-reinforced PLA composites. The silane treated talc reinforced PLA/recycled newspaper fiber hybrid composites flexural and impact strength was found to be significantly higher than that of those made without silane treated composites. The silane treated hybrid composites showed improved properties such as a flexural strength of 132 MPa and a flexural modulus of 15.3 GPa, while the untreated composites exhibited flexural strength and modulus values of only 77 MPa and 6.7 GPa, respectively.

PLA and PHBV were compounded with man-made cellulose; jute and abaca fibers and their mechanical performance were studied and compared to PP based composites [346]. It is clearly seen in Table 7 that the tested biopolymer based composites clearly show better or comparable mechanical characteristic values than the ‘common’ natural fiber reinforced PP composites.

4.2.2. PHB (polylhydroxybutyrate)

The biopolymer polylhydroxybutyrate (PHB) was also reinforced with flax fiber. Barkoula et al. [347] investigated the effects of fiber and copolymer HV (hydroxyvalerate) contents, the biodegradability, and the influence of manufacturing methods (compression molding of non-woven mats and injection molding of short fiber composites) and processing conditions (cooling temperature and annealing) on the mechanical properties of the composites. It can be concluded that the addition of flax fibers, along
with controlled processing conditions, is a convenient technique to toughen the PHB matrix. The injection molded composites exhibited lower impact strength than other manufactured composites. The tensile strength dropped significantly in the initial stage of degradation and was more gradual in later stages of biodegradation.

The interfacial improvement of PHB/flax composites was also evaluated. The addition of TDP at various concentrations (up to 10% v/v) brought advantageous changes in the dynamic flexural properties and thermal stability (favorable shift of degradation temperatures to higher values). With increases of the TDP content, improvements were observed in the fiber–matrix bonding and a change in the matrix from brittle to ductile [348]. Zini et al. [349] illustrated that composites prepared by compression molding using long fiber mats showed better mechanical properties compared to composites obtained by batch mixing fibers with molten polymer. Chemically modified (by acetylation or by short-chain-PEG grafting) fibers exhibit better adhesion and the best results were obtained with acetylated fibers.

Several lines of transgenic flax were produced by overexpressing the PHB synthesis genes [350]. It was revealed that the cellulose in fibers from the transgenic plants was more highly structured than in fibers from the control plants and PHB was strongly bound to the cellulose of the fibers by covalent ester and hydrogen bonds. The PHB/flax composite with fibers from transgenic plants was significantly stronger and stiffer than the composites with fibers from the control plants.

Polyhydroxybutyrate-co-valerate (PHBV) bioplastic was reinforced with hemp [351], coir [352], and bamboo

![Graph](image)

**Fig. 16**. The fiber length of abaca/PLA composites after different processes. Adopted from [327]. Copyright 2009. By permission from Elsevier Ltd.

### Table 7
Mechanical properties of PLA, PHBV and PP based natural fiber reinforced composites.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fiber</th>
<th>Tensile E-modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile elongation-at-break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>–</td>
<td>3.4 ± 0.23</td>
<td>63.5 ± 0.4</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Man-made cellulose</td>
<td>5.8 ± 0.15</td>
<td>92.0 ± 4.7</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Abaca</td>
<td>8.0 ± 0.34</td>
<td>74.0 ± 0.7</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Jute</td>
<td>9.6 ± 0.36</td>
<td>81.9 ± 2.9</td>
<td>1.8 ± 0.0</td>
</tr>
<tr>
<td>PHBV/ecoﬂex</td>
<td>–</td>
<td>2.14 ± 0.07</td>
<td>27.3 ± 0.3</td>
<td>7.0 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>Man-made cellulose</td>
<td>4.4 ± 0.34</td>
<td>41.7 ± 3.8</td>
<td>2.3 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>Abaca</td>
<td>4.4 ± 0.06</td>
<td>28.0 ± 1.3</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Jute</td>
<td>7.0 ± 0.26</td>
<td>35.2 ± 1.3</td>
<td>0.8 ± 0.0</td>
</tr>
<tr>
<td>PP</td>
<td>–</td>
<td>1.5 ± 0.03</td>
<td>29.2 ± 0.4</td>
<td>&gt;50</td>
</tr>
<tr>
<td></td>
<td>Man-made cellulose</td>
<td>3.7 ± 0.11</td>
<td>71.6 ± 2.7</td>
<td>3.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Abaca</td>
<td>4.9 ± 0.11</td>
<td>42.0 ± 0.5</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Jute</td>
<td>5.8 ± 0.47</td>
<td>47.9 ± 2.7</td>
<td>1.4 ± 0.1</td>
</tr>
</tbody>
</table>
fibers. The mechanical, thermo-mechanical and morphological properties were evaluated.

4.2.3. Starch

Alvarez et al. [354–356] developed composites by mixing biodegradable starch matrixes with sisal fibers. The thermal, melt rheological and creep properties were investigated extensively. It was reported that the shear rate is the most influential processing condition regarding the material structure. The intercalation effectiveness of the matrix in the fibers is directly linked to the rheological behavior. The addition of sisal fibers to the polymeric matrix promotes a significant improvement of the composite creep resistance and thermal properties.

Investigations were carried out using starch as the matrix of composites with kenaf, bagasse [357], curaua [358], coir [359], bamboo [360], sisal [361], hemp [362,363], abaca and bagasse [364] fibers, wheat straw fibers [365], and kenaf fibers [366].

4.2.4. Others

A soy based biodegradable resin matrix was applied to cellulose from papers [367], flax [368], sisal [369] and pineapple leaf [370] fiber reinforced composites. Biodegradable resins have been tested, including cashew nut shells [371,372] with hemp and kenaf fibers, polybutylene succinate (PBS) with jute fibers [373,374] bamboo fibers [375], and hemp fibers [376], and polycaprolactone (PCL) with flax fibers [377] and bamboo fibers [378].

4.3. Summary

The petroleum derived thermoplastics PP and PE are the two most commonly employed thermoplastics in natural fiber reinforced composites. Day by day, there is great interest in developing biocomposites with a thermoplastic rather than thermostet matrix, mainly due to their recyclability. Also the choice of a thermoplastic matrix fits well within the eco-theme of biocomposites, but there are some important limitations on the recyclability and mechanical performance of thermoplastics. Generally, the mechanical properties of thermostets exhibit higher than the thermoplastic (lower modulus and strength). In addition, a dramatic loss in properties is observed above the glass transition temperature, which leads to decrease in other thermally sensitive properties such as creep resistance. On the contrary, thermoplastics show greater fracture toughness than thermostets and thus are more useful in resisting impact loads. Another remarkable change was the introduction of biopolymers in recent years with the aim of decreasing reliance on petroleum-based thermoplastics. The availability and outstanding mechanical properties of biopolymer PLA has led to this matrix system being one of the most thoroughly investigated in the biocomposites research area.

5. Processing techniques

Generally, natural fiber reinforced plastic composites are manufactured by using traditional manufacturing techniques (designed for conventional fiber reinforced polymer composites and thermoplastics). The processing techniques include compounding, mixing, extrusion, injection molding, compression molding, and resin transfer molding (RTM) and above mentioned techniques have been well developed and accumulated experience has proved their successability for producing composites with controllable quality. Innovative technologies and process solutions should be intensively researched to get the high strength engineering composites which is related to their new applications area.

5.1. Factors influencing processing

5.1.1. Moisture

The moisture content at a given relative humidity can have a great effect on the biological performance of a composite made from natural fibers and therefore fiber drying before processing is a significant step. A composite made from pennywort fibers would have much greater moisture content (57%) at 90% RH humidity than would a composite made from bamboo fibers (15%). The pennywort product would be much more prone to decay as compared to the bamboo product. Moisture content of natural fibers with time under different conditions (relative humidity) and for different fiber treatments were analyzed [379]. It was evident that the moisture content as well as the rate at which it accumulates is directly related to the ambient relative humidity. Fiber treatment can reduce both the moisture content level and the rate of absorption very significantly. It should be noted that bio based polymers can be more sensitive to moisture than natural fibers.

Panthapulakkal and Sain investigated the effect of compatibilizer on the water absorption behavior of HDPE composites with different fillers (wheat straw, cornstalk, and corncob). This is shown in Fig. 17 [380]. Presence of compatibilizer had no effect on the water absorption of
cornocob filled composites. Wheat straw and cornstalk filled composites showed a decrease in the water uptake with the incorporation of compatibilizers. This indicates that, the flaws and gaps at the interface of the filler and HDPE are the main factors for moisture diffusion in the composites without compatibilizer. As observed in mechanical properties, the observed reduction in water uptake is higher in wheat straw filled composites compared to cornstalk filled composites. After 40 days of water absorption, percentage reduction in the water uptake of composites is 19%, 12% and 0% respectively for wheat straw, corn stalk and cornocob filled composites.

It is already seen that the enhanced water content can dramatically affect mechanical properties (such as, compression, flexural and tensile) of the composites [381]. Nowadays new extruder screw design (higher L/D ratio) allows better degassing and, consequently, lower moisture content. In addition, the machine’s barrel must be redesigned.

5.1.2. Fiber type and content

The natural fiber type and content is generally essential for furthering the sustainability of the composite. In addition, natural fibers length (short or long), aspect ratio (length/diameter), chemical compositions (such as rice husk contains higher silicates than flax or jute fiber) have an great influence on the processing and therefore processing parameters and accessories should be developed. The compounding process significantly influences the shortening, fibrillation, as well as the thermal deterioration of the fibers in early stages; the final properties of the product are already determined at the beginning of the production process [382]. Fig. 18 shows the different compounding processes for injection molding of natural reinforced thermoplastics [383].

5.1.3. Influence on composites properties

As described above, the natural fiber type has strongly influence on the performance of the composite. There are
numerous types of natural fibers, which differ regarding their chemical structure [384–386]. The influence of the type of natural fiber on some mechanical parameters of PLA biocomposites is presented in Fig. 19 [387].

In general, increasing fiber content in the composites increases the composite’s stiffness significantly. Additionally, its strength is increased through the addition of natural fibers [388,389]. Higher fiber content improves the impact strength. Unfortunately, increased fiber content increases the composite’s odor (Fig. 20) as well as the water uptake [387]. Moreover, the composite’s ductility can be affected. The fiber length and its geometry also play a decisive role in composites. Usually, most mechanical properties of a fiber can be enhanced by increasing the aspect ratio [390].

In addition, the use of one appropriate additive (coupling agents, lubricants, light stabilizers, colorants, flame retardants, foaming agents, odor reduction agents, and biocides) in very small quantities (0.5–5%) can significantly improve most of physical, chemical or mechanical properties of natural fiber composite material [391].

5.2. Semi-finished product manufacturing

Mat production is one of the initial steps in semi-finished product manufacturing. Fiber mats (fiber fleece) from natural fibers could be manufactured by carding method, aerodynamic fleece making, the fiber spreading process, and wet fleece production. The other step is the production of slivers and fiber yarns. The fiber preparation (opening, mixing, and carding) is similar to fleece production. Granule production is the other important step in the manufacture of semi-finished products. Natural fiber granules can be produced via pelleting, compounding, pultrusion and the pull-drill process regarding the homogeneity of the granules and the desired fiber lengths.

5.3. Processing technologies for natural fiber reinforced thermoplastics

5.3.1. Compression molding

The pressure method is very popular in the manufacture of natural fiber composites because of its high reproducibility and low cycle time. The two methods in use are compression and flow compression molding. The processes differ concerning the kind of semi-finished product used and its cutting. In the compression molding process, flat semi-finished products or hybrid fleeces are usually used that are either larger than the form or are cut exactly to the size of the desired part.

Whole and split wheat straws with lengths up to 10 cm were used with PP to make lightweight composites by means of the compression molding process [392]. The effects of the wheat straw concentration, length, and split configuration (half, quarter, and mechanically split) on the flexural and tensile properties of the composites were investigated. Compared with whole wheat straws–PP composites, mechanically split wheat straw–PP composites have a flexural strength that is higher by 69%. They also have a 39% higher modulus of elasticity, 18% higher impact resistance properties, 69% higher tensile strength and a 26% higher Young’s modulus. Compared with jute–PP composites, mechanically split wheat straw–PP composites have a 114% higher flexural strength, 38% higher modulus of elasticity. In addition, they also have a 10% higher tensile strength, 140% higher Young’s modulus, a 50% lower impact resistance and better sound absorption properties.

The compression molding process was tested for jute fiber with PP [393], an ethylene propylene co-polymer [394] and, bagasse fibers with PET composites [395]. Also the abrasive wear behavior, interfacial adhesion, and degradability were evaluated.

5.3.2. Extrusion

The extrusion process is used by the plastics industry for the production of granules and also in the continuous production of semi-finished products or components. Single screw as well as twin-screw extruders that run either co- or counter-rotating may be used for this process. Single screw extruders are used when the mixing effect does not have to be very high. Owing to the excellent mixing effect of the twin-screw extruder the natural fiber materials can be homogeneously distributed and wetted in the thermoplastic melt.

HDPE composites with bagasse [396] and curaua [397] fibers reinforced HDPE composites were obtained by extrusion process. The effects of coupling agents on the mechanical and thermal properties of those composites were investigated and evaluated. Curaua fibers were also reinforced with PA-6 by using a co-rotating twin-screw extruder [398]. The fiber contents of 20 wt%, 30 wt% and 40 wt% and fiber lengths of 0.1 or 10 mm were studied. Fibers were treated with N2 plasma or washed with NaOH solution, to improve their adhesion to PA-6. The tensile and flexural properties of this composite are better than unfilled, but are still lower than those of glass fiber reinforced polyamide-6.

5.3.3. Injection molding

It is possible to produce complex geometric components with functional elements fast and also in great numbers by injection molding. It offers a number of advantages (economics of scale, minimal warping and shrinkage, high function integration, use of recycled materials) as compared to compression molding [399] and hardly any finishing needed.
Table 8

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Wet sample</td>
</tr>
<tr>
<td>PP</td>
<td>30.1 ± 0.1</td>
<td>29.9 ± 0.5</td>
</tr>
<tr>
<td>A</td>
<td>52.5 ± 0.5</td>
<td>34 ± 0.6</td>
</tr>
<tr>
<td>B</td>
<td>53.7 ± 1.6</td>
<td>34.8 ± 1.6</td>
</tr>
<tr>
<td>C</td>
<td>57.9 ± 0.7</td>
<td>34.9 ± 0.9</td>
</tr>
<tr>
<td>D</td>
<td>59.5 ± 0.9</td>
<td>35.5 ± 0.5</td>
</tr>
</tbody>
</table>

Pickering and his co-workers [400–403] extensively investigated hemp fiber reinforced PP composites used in the injection molding process. Their investigations included fiber treatments and modifications, model predictions of micro-mechanics and strengths, the optimization of hemp fiber quality, and the influence of bag retting and, white rot fungal treatments.

The effect of surface treatment on the injection molded pineapple leaf fiber reinforced polycarbonate composites was evaluated [404]. The modified pineapple leaf fibers composite produces enhanced mechanical properties. The results from the thermogravimetric analysis showed that the thermal stability of the composites is lower than that of neat polycarbonate resin and that the thermal stability decreased with increasing pineapple leaf fiber content. Injection molded jute [405] and sisal [406] fiber reinforced PP composites were also investigated regarding their thermal, hydrothermal and, dynamic mechanical behavior. The introduction of the pre-impregnation technique was also examined.

Panthapulakkal and Sain investigated the influence of water absorption on the tensile properties of injection molded short hemp fiber/glass fiber-reinforced polypropylene hybrid composites [407]. Tensile tests were performed on wet samples after the saturation level (3624 h) is reached (Table 8). A significant reduction in strength and stiffness is observed for all composites because of the changes to the fibers, mainly natural fibers, and the interface between the matrix and fiber, as the effect of water absorption on PP matrix is only secondary. Swelling of natural fiber as a result of prolonged exposure to water, leads to at reduction in the stiffness of the fibers. The loss in strength and modulus values of the hemp fiber composites are believed to be the inability of the swelled natural fiber to carry the stress transferred from the matrix through the disrupted interface as a result of water absorption. Despite the reduction in the equilibrium moisture content in hybrid composites, glass fibers did not alter the degradation of the hemp fiber composites.

Injection molded flax, hemp, core hemp, bleached kraft pulp (BKP) and wood flour reinforced PP composites were prepared and the effect of MAPP on the mechanical properties was investigated [408]. Table 9 clearly indicated that the BKP–PP composites have the highest tensile and flexural strength and unnotched impact strength. Flax and hemp-filled PP composites have similar strength properties. In comparison, wood flour-filled PP composites have the lowest mechanical strength. Such a trend can be attributed to the actual fiber length in the composites. It has been observed that after compounding, the fiber length of flax and hemp decrease significantly, whereas that of BKP fibers dose not change much. This is possibly due to the fact that the flax and hemp bundles are prone to being torn down to very small size by the high-shear force from the melted PP. To preserve the fiber length, less severe treatment is necessary but at the cost of poor dispersion of fibers in the resin matrix. The poor strength of wood flour reinforced composites is due to the low aspect ratio of wood flour particles, which is far below the critical fiber length required for reinforcement.

Bledzki et al. [409] investigated the different separation processes (mechanical, refiner and enzymatic separation) with injection molded hemp and partially with flax and wheat straw reinforced PP composites. It was found that thermomechanical processed hemp fiber–PP composites possessed better mechanical properties compared to other process and composites.

5.3.4. Long fiber thermoplastic-direct (LFT-D) method

Different methods [410] to directly process natural fibers with the LFT-D-process are shown (Fig. 21). Express method, which is the basic thought of the combined extrusion and press method to combine the natural fiber mats with the polymer melt directly in the pressing tool. A film of molten polymer is placed into the pressing tool with the help of an adjustable extruder and a natural fiber fleece is added to the molten mass and the layers are pressed together. Another possibility to process natural fibers with

Table 9

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>BKP (MPa)</th>
<th>Flax (MPa)</th>
<th>Milled hemp (MPa)</th>
<th>Core hemp (MPa)</th>
<th>Wood hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>50</td>
<td>42</td>
<td>42</td>
<td>29</td>
<td>35</td>
</tr>
<tr>
<td>Modulus</td>
<td>3.0</td>
<td>3.2</td>
<td>3.0</td>
<td>2.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Flexural</td>
<td>78</td>
<td>67</td>
<td>70</td>
<td>52</td>
<td>59</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>3.3</td>
<td>3.4</td>
<td>3.5</td>
<td>2.6</td>
<td>3.0</td>
</tr>
<tr>
<td>Notched Izod (J/m)</td>
<td>40</td>
<td>44</td>
<td>42</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>U-notched Izod (J/m)</td>
<td>205</td>
<td>150</td>
<td>145</td>
<td>100</td>
<td>105</td>
</tr>
</tbody>
</table>
the LFT-D-method is to directly feed off fiber yarns or slivers into either a twin screw extruder or directly into an injection molding machine. Research has shown that it is possible to retain the long fiber structure through an optimal configuration of the screws; however, the handling of slivers is rather problematic in an industrial application (extrusion with high throughput).

5.4. Processing technologies for natural fiber reinforced thermosets

5.4.1. Resin transfer molding

Resin transfer molding (RTM) is a method for the production of component parts made of fiber-plastic composites. During the RTM procedure, dry semi-finished fiber parts are streamed and consequently soaked with reaction resin by a pressure gradient within a closed vessel. The following methods can be distinguished with regard to the admission by the pressure gradient: high pressure injection, twin wall injection, vacuum injection, and differential pressure injection.

Hemp fiber-unsaturated polyester composites were manufactured using a resin transfer molding (RTM) process [411]. RTM composites with various fiber contents, up to 20.6% by volume, were manufactured. The wetting of the fibers was very good. The resin injection time was observed to increase dramatically at high fiber contents due to the low permeability of the mat. Keeping a constant mold temperature is the key to obtain fast and homogeneous curing of the part. The cure of the resin in the mold was simulated. The results given by the modified model are presented in Fig. 22. The predicted temperatures were in very good agreement with the experimental data. The model predicted the degree of cure and the rate of cure of the resin with time as well.

The hemp fiber composites manufactured with RTM process were found to have a very homogeneous structure with no noticeable defects [412]. The tensile, flexural and impact properties of these materials was found to increase linearly with increasing fiber content (Table 10). It was observed that the optimum properties were not reached in this study and that fiber content higher than 35 vol% should yield better mechanical properties. When compared to a glass fiber composite however these natural fiber composites had much lower performances.

Hemp fiber reinforced polyester [413] and phenolic resin [414] composites were prepared using RTM process and their cure simulation, interfacial adhesion, and flow visualization were evaluated.

The effects of fiber surface modification [415] were evaluated. A comparison of the RTM process to the compression molding process [416] of sisal fiber reinforced polyester composites was made. Composites containing flax and hemp fiber with bio-resin [417], flax and jute fiber with epoxy and polyester resin [418], and jute fiber with polyester resin [419] were also prepared using the RTM process.

5.4.2. Sheet molding compound

The sheet molding compound (SMC) material made of natural fibers and a special resin based on vegetable oil and carbohydrates represents an effective alternative to the established systems within the technically specialized sector. Procedural modifications are not necessary in comparison to conventional SMC production of component

Table 10

<table>
<thead>
<tr>
<th></th>
<th>20 vol% glass fibers</th>
<th>20 vol% hemp fibers</th>
<th>35 vol% hemp fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>85.0</td>
<td>32.9</td>
<td>60.2</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>1.719</td>
<td>1.421</td>
<td>1.736</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>175.9</td>
<td>54.0</td>
<td>112.9</td>
</tr>
<tr>
<td>Flexural modulus (CPa)</td>
<td>7.74</td>
<td>5.02</td>
<td>6.38</td>
</tr>
<tr>
<td>Impact strength (kJ/m²)</td>
<td>60.8</td>
<td>4.8</td>
<td>14.2</td>
</tr>
</tbody>
</table>
parts [420]. The middle bumper part for a city bus was manufactured with standard tools. The risk potential for the fabricator is lower, both during production and treatment of the prepregs which are made of natural fibers and vegetable oil. Emissions do not occur; hence, there is no need for breathing protection [421]. Flax fiber reinforced SMC material was developed and the processing parameters regarding the physico-mechanical properties were optimized [422].

5.5. Other processes

5.5.1. Thermosets compression molding

The thermoset compression process uses mats made of natural fibers. As shown in Fig. 23, the mats are just sprayed, not moistened, with resin and compressed into their final contour in a hot tool; due to the air-permeability the parts can be covered easily in a vacuum covering process [423].

The dynamic and static mechanical properties of short abaca/sisal hybrid fiber reinforced polyester composite achieved using the thermoset compression molding process were determined [424]. Dynamic properties, such as the storage modulus, damping behavior and static mechanical properties (i.e., tensile, flexural and impact properties) were investigated as a function of the total fiber volume fraction and the relative volume fraction of the two fibers. The storage modulus was found to increase with fiber volume fraction above the glass transition temperature ($T_g$) of the matrix. A maximum value was obtained at a volume fraction of 0.40. The tensile modulus and flexural strength were found to be the highest at a volume fraction of 0.40, which indicates effective stress transfer between the fiber and the matrix. Sisal/polyester composites displayed the best damping behavior and highest impact strengths compared to abaca/polyester and hybrid composites. However, maximum stress transfer between the fiber and the matrix was obtained in composites with a volume ratio of banana and sisal equal to 3:1. The tensile strength and flexural modulus reached their maximum at this volume ratio, while the impact strength reached its minimum.

The thermal conductivity, diffusivity and specific heat of thermoset compression molded polyester/natural fiber (abaca/sisal) composites were investigated for several fiber surface treatments as functions of the filler concentration [425]. The thermo-physical behavior of hybrid pineapple leaf fiber (PALF) and glass fiber reinforced polyester composites were also evaluated regarding the constant total fiber loading equal to 0.40 volume fraction by varying the ratio of PALF and glass. The results show that the chemical treatment of the fibers reduces the composite thermal contact resistance. Hybridization of natural fibers with glass allows a significantly better heat transport ability of the composite. The thermal conductivity, which is measured in the direction transverse to the plane of composite plate, could be well represented by a series prediction model.

5.5.2. Pultrusion

Fibers are pulled from a creel through a resin bath and then on through a heated die. The impregnation of the fiber controls of the resin content and curing of the materials into their final shape is completed using the die. Although pultrusion is a continuous process, which produces a profile of constant cross-sections, a variant known as pulforming allows for some variation to be introduced into the cross-sections.

Flax fiber reinforced PP composites were developed by means of the thermoplastic pultrusion process and their physico-mechanical properties were evaluated [426]. The water absorption behavior of pultruded jute fiber reinforced unsaturated polyester composites was found to follow so-called pseudo-Fickian behavior [427]. The flexural and compression properties were found to decrease with the increase in water uptake in percentage. These flexural and compression behaviors were attributed to the plasticization of the matrix-fiber interface and the swelling of the jute fibers.

Pultruded kenaf fiber [428], jute fiber [429] and hybrid jute/glass and kenaf/glass fiber [430] composites were investigated and their flexural behavior using acoustic emission, dynamic properties and degradation of compressive properties were evaluated.

5.5.3. Summary

In recent years the processing and production technologies for biocomposites have also advanced. To date, injection molding, extrusion, compression molding, sheet molding and resin transfer molding are the major manufacturing processes for natural fiber reinforced plastic composites. But new downstream and auxiliary equipment has been designed. Such as: unique heating and single or dual venting systems for in-line drying, high-intensity
spray–cooling tanks, a variety of new configurations of feeding (gravimetric or vertical c rammer) systems, combinations of extrusion-injection molding or extrusion-compression molding as well as screw, die, and mold design. Although the majority of biocomposites produced today by the processes mentioned above, the manufacturers are improving the feasibility of using other processes like pultrusion and so on.

6. Performance of biocomposites

It is important to be knowledgeable of certain mechanical properties of each natural fiber in order to be able to exploit the highest potential of it. Among these properties are the tensile, flexural, impacts, dynamic mechanical and creep properties. In general, natural fibers are suitable for reinforcing plastics, due to their relatively high strength, stiffness and low density.

6.1. Tensile properties

The tensile properties are among the most widely tested properties of natural fiber reinforced composites. The fiber strength can be an important factor regarding the selection of a specific natural fiber for a specific application. A tensile test reflects the average property through the thickness, whereas a flexural test is strongly influenced by the properties of the specimen closest to the top and bottom surfaces. The stresses in a tensile test are uniform throughout the specimen cross-section, whereas the stresses in flexure vary from zero in the middle to maximum in the top and bottom surfaces.

The comparison of the tensile properties of the HDPE/hemp fiber composites showed that the silane treatment and the matrix–resin pre-impregnation of the fiber produced a significant increase in tensile strength, while the tensile modulus remained relatively unaffected [431,432]. The longitudinal tensile strength increased from 71.8 MPa to 79.3 MPa for the silane treated fibers, which equals an increase of approximately 10%. The increase in the transverse tensile strength from 2.75 MPa for the untreated fibers to 3.95 MPa for the treated fibers is higher, representing an increase of 43%. It is evident that the behavior is fiber dominated, as the longitudinal fiber direction, is 1900% higher compared to transverse direction. Fiber surface modification has little impact. However, the improvement in the fiber–matrix interactions plays a more important role for the matrix and/or interphase dominated behavior.

Rice husk reinforced PP composites with filler loadings of 10 wt%, 20 wt%, 30 wt% and 40 wt% were designed [433]. Six test temperatures (−30, 0, 20, 50, 80 and 110 °C) and five levels of crosshead speed (2, 10, 100, 500 and 1500 mm/min) were designed during tensile testing. The tensile strengths of the composites decreased slightly as the filler loading increased. The tensile modulus improved with increasing filler loading. As the crosshead speed increased, the composite became more brittle. At lower test temperatures (−30 and 0 °C), the composites exhibited strong and brittle properties similar to glass fiber, but the tensile strength and modulus decreased due to the glass transition of the matrix polymer PP as the test temperature was increased from 0 to 20 °C.

A study on the effect of alkaline treatment on tensile properties of sugar palm fiber reinforced epoxy composites was investigated [434]. The treatment was carried out using different concentrations of sodium hydroxide (NaOH) solutions and varying soaking periods. It was observed that as the alkali concentration and the length of soaking periods increased, the tensile strength decreased. However, the tensile modulus results are much higher than those of untreated fiber composite specimens, thus proving the effectiveness of the treatment.

Composites consisting of aliphatic polyester (Bionolle) with flax fibers were prepared via batch mixing [435]. The effects of processing conditions on the fiber length distribution and the dependence of the composite tensile properties on the fiber content were investigated. The tensile modulus changes with the amount of fiber content according to the modified rule-of-mixture equation. The tensile strength of Bionolle/flax composites tends to decrease with fiber loading, showing that there is no adhesion between the matrix and the fibers. Flax fibers with chemically modified surfaces were also tested as reinforcing agents. An increase in tensile strength of 30% was observed when flax fibers (25 vol%) were substituted with fibers containing acetate groups. No significant strength changes were observed in composites containing fibers with valerate groups or polyethylene glycol chains grafted at the surface.

The following investigations were completed with thermoplastic matrices; the effect of moisture absorption of sisal fiber/PP composites [436], the influence of surface treatment (NaOH solution) of coir fiber/PP composites [437], the surface esterification of bagasse/LDPE composites [438], the surface modification of olive husk/PP composites [439], the performance of hybrid jute/betel nut fiber reinforced PP [440], and the effects of surface treatments of luffa fiber/PP composites [441]. It was observed that the tensile properties were influenced by all the mentioned factors.

The tensile properties of natural fiber reinforced thermosets were investigated regarding the siloxane treatment of jute fiber/polyester and epoxy composites [442], the temperature and loading rate effects of kenaf fiber/epoxy composites [443], the effects of a differing geometry of abaca fiber/epoxy composites [444], the influence of moisture absorption of bamboo/vinylester composites [445], the effect of oil palm fibers volume fraction of oil palm/polyester composites [446], and the influence of the fiber orientation and the volume fraction of alfa fiber/polyester composites [447].

The effects of hybridization and the chemical modification of oil palm/sisal fiber reinforced natural rubber composites [448,449], the effects of high temperature on ramie fiber/biodegradable resin composites [450], effect of biodegradable matrix type (PLA, PHBV, PBS) on regenerated cellulose fiber/biopolymer composites [451], the influence of bio based coupling agent on bamboo fiber/PLA and PBS composites [452], preparation of sandwich composite panels for building applications from jute/polyester [453], and the structural and mechanical characterization of sugar
beet pulp/PLA composites [454] on the tensile properties were evaluated. Rao et al. [455] investigated the tensile properties of bamboo, date palm, abaca, oil palm, sisal, coir and vakka fibers regarding their fiber cross sections, atmospheric moisture content and density.

6.2. Flexural properties

The flexural stiffness is a criterion of measuring deformability. The flexural stiffness of a structure is a function based upon two essential properties: the first is the elastic modulus (stress per unit strain) of the material that composes it; and the second is the moment of inertia, a function of the cross-sectional geometry.

Zampaloni et al. [456] focused on the fabrication of kenaf fiber reinforced PP sheets that could be thermo-formed for a wide variety of applications with properties that are comparable to existing synthetic composites. The optimal fabrication method determined for these materials was determined to be a compression molding process which utilized a layered sifting of a microfine PP powder and chopped kenaf fibers. When comparing the flexural strengths of the kenaf fiber/PP composite materials, 40% kenaf/PP composites performed significantly better than the 30% kenaf/PP composites. The flexural strength of 40% kenaf/PP was equivalent to the flax/PP, larger than the hemp/PP and almost doubles that of the coir/PP and sisal/PP composites. The flexural strength of 30% kenaf/PP composites showed results equivalent to those of the 40% hemp/PP composites, while also outperforming the coir/PP and sisal/PP composites.

Composites of PP and HDPE reinforced with 20 wt% curaua fibers were prepared and the effect of screw rotation speed was evaluated by measuring the flexural properties of the composites [457]. The yield stress in flexural tests for the composites with PP and HDPE matrices, decreased with the increase in screw rotation speed. For HDPE a higher rate of decrease was shown. However, the flexural modulus was not affected by the screw rotation speed. The elongation at break exhibited different behavior; this effect strengthened HDPE at screw rotations above 300 rpm, and slightly increased for PP composites above 350 rpm.

The effect of acetylation [458] on the flexural properties of bagasse/PP composites (properties decreased due to acetylation), and the effect of different maleated coupling agents (flexural properties increased above 60% with optimum loading of coupling agent) on jute and flax fiber reinforced PP composites [459] have been evaluated.

Composites were fabricated using abaca fiber with varying fiber lengths and fiber loading [460]. The analysis of the flexural properties revealed the optimum length of abaca fibers required for abaca fiber/phenol formaldehyde resin composites. The flexural strength and modulus values increased with fiber length for composites with short fibers. Furthermore, the maximum flexural strength and modulus values were obtained for 40 mm fibers. Due to fiber loading up to 45%, the flexural modulus increased to about 25%. The flexural strength also showed good enhancement, because of increasing fiber loading.

The flexural properties of coir fiber/polyester composites were evaluated [461]. Composites were prepared using two molding pressures and with amounts of coir fiber up to 80 wt%. When the fiber amount equaled up to 50 wt%, rigid composites were obtained. Higher fiber amounts resulted in composite performances similar to that of flexible agglomerates. The results obtained for the flexural strength made it possible to compare the technical performance of the composites with that of other conventional materials.

The flexural properties of thermoset resins, such as carboxyl reinforced with hemp, ramie, jute and flax fibers [462], epoxy resin with coir fibers [463], and hemp, kenaf, flax and henequen fibers [464], polyester resin reinforced bagasse fibers [465], coir and oil palm fibers [466], hemp and kenaf fibers [467], were also investigated.

Biocomposites were fabricated from chopped hemp fiber and cellulose ester biodegradable plastic via two different processes; powder impregnation by compression molding and an extrusion process followed by an injection molding process [468]. Fabricated through process extrusion followed by injection molding process of hemp (30 wt%) fiber reinforced cellulose acetate biocomposite exhibited flexural strength of 78 MPa and modulus of elasticity of 5.6 GPa as contrast to 55 MPa and 3.7 GPa for the corresponding hemp fiber/PP based composite. The corresponding biocomposites showed superior flexural strength and modulus values during the extrusion and ensuing injection molding processes, as compared to biocomposites powder impregnated through compression molding process.

Biodegradable composites were prepared with the melt blending technique using PCL and oil palm empty fruit bunch fiber [469]. Since oil palm fiber is not compatible with PCL, a binder (polyvinyl pyrrolidone), was used to improve the interaction between PCL and the fibers. The composites produced were irradiated with the aid of an electron beam to improve the mechanical properties. The flexural strength and modulus of the composites were improved by an additional 1% by weight of poly (vinyl pyrrolidone) and irradiated with a 10 kGy electron beam.

6.3. Impact properties

Impact strength is the ability of a material to resist fracture under stress applied at high speed. Biofiber reinforced plastic composites have properties that can compete with the properties of glass fiber thermoplastic composites, especially concerning specific properties. However, one property, namely the impact strength is often listed among the major disadvantages of biofiber reinforced composites. In recent years, the development of new fiber manufacturing techniques and improved composite processing methods along with enhancement of fiber/matrix adhesion has improved the current situation somewhat.

Jute fiber was treated with o-hydroxybenzenediazonium salt (o-HBDS) in alkaline media [470]. Treated and untreated jute fiber reinforced PP composites were prepared with different weight fractions (20, 25, 30, and 35%) of jute fiber. The increase of Charpy impact strength was
found to be exceptionally high (in some cases ~200%) as compared to those of literature values.

Composite panels consisting of virgin and recycled HDPE and four types of rice straw components including rice husk, rice straw leaf, rice straw stem, and whole rice straw were made via melt compounding and compression molding [471]. Composite panels with rice husk exhibited better impact strength than composites panels made of other straw fibers. Minor differences concerning the impact properties existed among leaf, stem, and whole straw fibers. The recycled HDPE resin and its composites possessed a significantly better impact strength compared to the virgin HDPE systems. This was attributed to the additives used during initial processing.

Recycled HDPE composites were reinforced with bagasse fibers and the influence of coupling agent types/concentrations on the composite impact properties were studied [472]. The addition of maleated polyethylene (MAPE), carboxylated polyethylene (CAPE), and titanium-derived mixture (TDM) improved the compatibility between the bagasse fiber and recycled HDPE. The impact properties of the resultant composites were comparable with those of virgin HDPE composites. The better impact strength of the composites was achieved, when a MAPE coupling agent was used. The impact strength increased with increasing MAPE content.

Oil palm empty fruit bunch fiber reinforced composite was studied. The effects of fiber loading and impact modifiers, namely chlorinated polyethylene (CPE) and acrylic, on the impact properties of oil palm fiber filled-PVC composites were of particular interest [473]. The results from the impact test showed that the unfilled PVC samples of both impact modifiers change from brittle to ductile with increasing impact modifier concentration. The incorporation of fibers into unmodified PVC and modified PVC resulted in the reduction of the impact strength. As the fiber content increased from 10 to 40 phr, the impact strength reduced about 40% and 30% for acrylic-modified PVC and CPE-modified PVC, respectively. The impact strength reduction was only marginal for unmodified PVC composites. The impact modifier enhanced the impact strength of fiber reinforced PVC composites. However, the effectiveness decreased with increased fiber loadings. The impact strength of CPE-modified PVC was higher than acrylic-modified PVC at fiber contents of 20 phr and higher.

The impact properties regarding the influence of the fiber microstructure of sisal, abaca, jute and flax fiber reinforced PP composites [474], the processing methods for flax fiber/PP composites [475], and the effect of impact modifiers (natural rubber and ethylene propylene diene monomer) on grass fiber/PP composites [476] were investigated.

Hemp fiber reinforced unsaturated polyester composites were subjected to low velocity impact tests in order to study the effects of non-woven hemp fiber reinforcement on their impact properties [477,478]. The composite specimen containing 0, 0.06, 0.10, 0.15, 0.21 and 0.26 fiber volume fractions ($V_f$) were prepared and their impact responses were compared with samples containing an equivalent fiber volume fraction of chopped strand mat E-glass fiber reinforcement. A significant improvement in

the load bearing capability and impact energy absorption was found after the introduction hemp fiber as reinforcement. The results indicated a clear correlation between fiber volume fractions, stiffness of the composite laminate, impact load and total absorbed energy. Unreinforced unsaturated polyester control specimens exhibited brittle fracture behavior with a lower peak load, lower impact energy and less time until failure occurred than hemp reinforced unsaturated polyester composites. The impact test results showed that the total energy absorbed by 0.21 fiber volume fraction (four layers) of hemp reinforced specimens is comparable to the energy absorbed by the equivalent fiber volume fraction of chopped strand mat E-glass fiber reinforced unsaturated polyester composite specimens.

The effects of the bi-dimensional orientation of leaf stalk fibers from peach palms (peach palm powder and weave) on the impact strength behavior of polyester/fiber reinforced composites were studied [479]. The Izod impact data obtained for the composites with only woven material was considerably superior to that of composites containing only powder, suggesting that the reinforcement in the form of powder is inefficient, independent of the size range of the particles used.

The impact strength of the bamboo fiber/PLA composites decreased after addition of bamboo fiber [480]. The impact strength of treated fiber reinforced composites improved after the addition of treated fibers. Good fiber/matrix adhesion provides an effective resistance to crack propagation during impact tests. The impact strength increased significantly (33%) for silane treated bamboo fiber/PLA composites compared to untreated bamboo fiber/PLA composites with 30 wt% fiber content.

The toughness of the short fiber reinforced composites can be influenced by a number of factors, such as the intrinsic properties of the matrix, the fiber volume fraction, and interfacial bond strength. Therefore, strong interactions between the hydroxyl groups of biofibers and the coupling agents are needed to overcome the incompatibility problem. In doing so, the impact, tensile and flexural strengths of biofiber reinforced composites can be increased.

### 6.4. Summary

Tensile, flexural and impact properties are the most commonly investigated mechanical properties of natural fiber reinforced plastic composites. Impact strength is one of the undesirable weak points of these materials in terms of mechanical performance. Besides these tensile, flexural and impact properties, the long-term performance (creep behavior), dynamic mechanical behavior, compressive properties are also investigated for natural fiber composites. To improve performance to the desired level, still much work is to be done considering fiber processing, non-linear behavior, fiber–matrix adhesion, fiber dispersion, composite manufacturing with optimized processing parameters.

### 7. Development and future trends of biocomposites

The advanced natural fiber reinforced polymer composite contributes to enhancing the development of
biocomposites in regards of performance and sustainability. Biocomposites have created substantial commercial markets for value-added products especially in automotive sector. However, in order to be able to expand into other markets, such as commercial construction and consumer goods, composites need to achieve high-quality performance, serviceability, durability, and reliability standards.

In recent years, the major advancement lies within the establishment of nanotechnology (i.e., reinforcing as well as producing nanocrystalline cellulose from natural fibers). Natural fibers consist of approximately 30–40% cellulose and about half of that is crystalline cellulose. The nanocrystalline cellulose may be only one-tenth as strong as carbon nanotubes but it costs 50–1000 times less to produce.

Wood pulp has often been used as the starting material for research on nano cellulose production. In the literature there are reports of cellulose nano/microfibril extraction from diverse non-wood sources including hemp fibers [481,482], sugar beet pulp [483,484], potato pulp [485], swede root [486], bamboo [487–491], sisal [492,493], algae [494], stems of cacti [495,496], banana rachis [497], flax fibers [498,499], plantain [500], water hyacinth [501], bamboo [502], coir [503], pea hull [504], pineapple leaf [505], and wheat straw [506].

Alemdar and Sain investigated the reinforcing potential of composites comprising a starch-based thermoplastic polymer and cellulose nanofibers obtained from agro-residues [507]. Cellulose nanofibers were isolated from wheat straw by a chemi-mechanical technique and determined to have diameters in the range of 10–80 nm and lengths of several thousand nanometers. Fig. 24 shows the structure of the wheat straw fibers after the chemical treatment. These images visually suggest the partial removal of hemicelluloses, lignin and pectin after the chemical treatment, which are the cementing materials around the fiber-bundles. It is clear from the image that the average diameter of the fibers is about 10–15 μm, which is lower than the average size of the fiber bundles, 25–125 μm before chemical treatment. TEM image (Fig. 24b) for the nanofibers obtained after the chemi-mechanical treatment. The mechanical treatment of the fibers resulted in defibrillation of nanofibers from the cell walls and the TEM image of the nanofibers shows the separation of these nanofibers from the micro-sized fibers.

Alemdar and Sain [508] extracted MFC from wheat straw and soy hulls via mechanical treatment involving cryocrushing followed by disintegration and fibrillation. These authors found that almost 60% of the nanofibers had a diameter within a range of 30–40 nm and lengths of several thousand nanometers. Cryocrushing is an alternative method for producing nanofibers in which fibers are frozen using liquid nitrogen and high shear forces are then applied. When high impact forces are applied to the frozen fibers, ice crystals exert pressure on the cell walls, causing them to rupture and thereby liberating microfibrils. The cryocrushed fibers may then be dispersed uniformly into water suspension using a disintegrator before high-pressure fibrillation.

A blend containing 10% cellulose nanofibers obtained from various sources, such as flax bast fibers, hemp fibers, Kraft pulp or rutabaga and 90% polyvinyl alcohol was used for making nanofiber reinforced composite material by a solution casting procedure [509]. Both tensile strength and Young’s modulus were improved compared to neat PVOH film, with a pronounced four- to five-fold increase in Young’s modulus observed.

Similarly, Wang and Sain [510,511] reported that soybean stock-based nanofiber-reinforced PVOH films (up to 10% nanofiber content) demonstrated a two-fold increase in tensile strength when compared with films without filler. With a higher loading of MFC, the relative enhancement of mechanical properties was even more remarkable. They also applied solid phase melt-mixing followed by compression molding to produce MFC-reinforced composites. In their study nanofiber was directly incorporated (up to 5 wt%) into PE and PP matrix using a Brabender mixer and an ethylene-acrylic oligomer emulsion was used as a dispersant. This work demonstrated that coating MFC fibers with the dispersant improved the cellulose dispersion in these polymers. As a consequence, the mechanical properties of PP and PE nanocomposites were slightly improved when compared to pure matrices; however, this enhancement was not considered significant.

Sain and Bhatnagar [512] invented a method to obtain MFC from renewable feedstocks such as natural fibers and root crops via cryocrushing of the pre-treated pulp with liquid nitrogen. The pulp was hydrolyzed at a moderate temperature of 50–90 °C and then both acidic and alkali extractions were performed.

Taniguchi [513] utilized natural cellulose fibers derived from different sources (such as cotton, hemp, wood pulp, seaweed, cereals, sea squirts, bacteria, etc.) for the production of MFC by fibrillating raw materials between rotating twin disks while adding shear stress in the vertical direction of fiber long axes. Joseph et al. [514–516] investigated the effect of microfibrillation of oil palm fiber on the dynamic mechanical properties of oil palm fiber reinforced rubber composites.

As technology improves for biocomposites reinforced with natural fibers to provide enhanced material and product characteristics, the products will become more diverse and enter markets that as of yet are unexplored. Today natural fiber reinforced biocomposites are found extensively in automotive sectors [517–521].

By the time, biocomposite materials and associated design methods are sufficiently mature to allow their widespread use, issues related to construction materials. The development of methods, systems and standards could see biocomposite materials at a distinct advantage over traditional materials. There is a significant research effort underway to develop biocomposite materials and explore their use as construction materials, especially for load bearing applications.

Burguen et al. manufactured cellular beams and plates as load bearing structural components from hemp, jute and flax fibers with unsaturated polyester resin [522–525] for housing panel applications. The material and structural performance was experimentally assessed and compared with results from short-fiber composites micro-mechanics models and sandwich analyses. It was demonstrated that cellular biocomposite components
can be used for load-bearing components by improving their structural efficiency through cellular material arrangements. Furthermore, it was verified that they could compete with components made from conventional materials. This research should continue in conjunction with development of conventional composite materials in order to provide a solution in the future to allow wider use of the bio composite materials by civil engineering applications.

In the future, these biocomposites will see increased use in structural applications. Various other applications depend on their further improvements. But there are still a number of problems that have to be solved before biocomposites become fully competitive with synthetic fiber composites. Biocomposites are sustainable and could be fully recyclable, but could be more expensive if fully bio-based and biodegradable and they are extremely sensitive to moisture and temperature. If a proper matrix is used, biocomposites could be 100% biodegradable, but their biodegradation can difficult to control. Biocomposites exhibit good specific properties, but there is high variability in their properties. Biocomposites showed non-linear mechanical behavior, poor long-term performance and low impact strength. Many of these weaknesses can and will be overcome with the development of more advanced processing of natural fibers and their composites. However fully environmental superiority of biocomposites compared to synthetic fiber composites is still questionable because of their relatively excessive processing requirements, which in turn consume more energy. Therefore, careful life-cycle assessment of biocomposites is essential in order to retain the main advantage in the process of developing high performance biocomposites. New markets will develop when these biocomposite products are more durable, dimensionally stable, moisture proof, and fire resistant.

Nanotechnology shows numerous opportunities for improving biocomposite products by providing nanotechnology-based coatings to increase water uptake, reduce biodegradation and volatile organic compounds and even flame resistance. The use of nanocrystalline cellulose is being explored for a variety of uses since it is stronger than steel and stiffer than aluminum. Nanocrystalline cellulose reinforced composites could soon provide advanced performance, durability, value, service-life, and utility while at the same time being a fully sustainable technology.

8. Conclusions

Biocomposites reinforced with natural fibers and/or biopolymers have developed significantly over the past years because of their significant processing advantages, biodegradability, low cost, low relative density, high specific strength and renewable nature. These composites are predestined to find more and more application in the near future, especially in Europe, where pressure from both legislation and the public is rising. Interfacial adhesion between natural fibers and matrix will remain the key issue in terms of overall performance, since it dictates the final properties of the composites. Many studies are examined, reviewed and highlighted in this review paper regarding the importance of the interface, the influence of various types of surface modifications, different types of matrices used for the composites, as well as fabrication methods, and the performance of composites.

Further research is required to overcome obstacles such as moisture absorption, inadequate toughness, and reduced long-term stability for outdoor applications. In particular, different weathering conditions, such as temperature, humidity, and UV radiation all affect the service life of the product. The major detrimental effect of hygrothermal and UV exposure are property deterioration, discoloring and deformation.

Significant research is currently underway around the world to address and overcome the obstacles mentioned above. This effort to develop biocomposite materials with improved performance for global applications is an ongoing process.

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