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# Fiber-Matrix Relationship for Composites Preparation

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## Abstract

Fiber-matrix interaction at the interphase is one very important property that is of great concern to all polymer scientists involved in polymer composites. Many of the failures can be traced to the type of interfacial interaction existing in the composites. That is why highlighting the factors that dictate the type of and the extent of interactions at the interphases become very necessary. Natural fiber polymer composites have found application in many fields of human endeavors. To continue this growth being experienced, the factors that determine the formation of good interaction at the interphase must be understood, so that they can be manipulated for a better result.

**Keywords:** interfacial interaction, polymer composites, natural fibers, surface treatment, filler dispersity

## 1. Introduction

Composites have been defined as materials made by mixing more than two chemically and physically dissimilar components together, physically or chemically, to form one new material [1–3]. In a composite, there is the continuous component known as the matrix and there is the discrete or discontinuous component called the fillers. In the composite material, both the matrix and the fillers come together to act as one material. The filler is the load bearing component of the composites while matrix bind the fillers together, which is the reinforcing material [4, 5]. There are different types of composites. These include: ceramics matrix composites (CMC), polymer matrix composites (PMC) and metal matrix composites (MMC) [6–8]. PMC's are of great interest around the world today with notable advantages that include its light weight, high stiffness, high strength and the ease of fabrication [9–12]. Polymer composites have been reported to be in use for numerous years with a market share reported to have increased tremendously in the last decade [9]. This has been attributed to the introduction of environmentally friendly natural fibers from plant sources. The processing and application of polymer composites requires a good understanding of all the factors that governs the relationship between all components that makes up the composite [4, 13–15]. The structure-property's relationship of any polymer composite is of fundamental importance right from their design which includes material selection. Many research have tried to explain the

relationship through various experimental designs [16–18]. One important factor that was generally accepted to have pronounced impact on the processing and application properties is the interfacial interaction between the matrix and the fibers. This interfacial interaction can vary from mere physical interfacial to real chemical interaction [3, 11, 15, 19–22]. To properly understand which interaction has taken place, a good understanding of the materials involved is necessary. Therefore, this chapter seeks to give an insight explanation to the different types of matrixes and fibers available for polymer composite preparation and their possible interactions.

## **2. Fiber-matrix interaction in polymer composite**

Polymer composites is an heterogeneous components material and so their properties, will be governed by factors such as component properties, composition of the individual components, chemical and physical structures and interfacial interactions [17, 23, 24]. Although, all the factors are equally important, the first three can be controlled before processing while the interfacial interactions can only be determined after processing and the extent of interaction can only be predicted using the necessary characterization techniques. Particle/particle interactions in polymer composites induce aggregation while filler/matrix interactions lead to an interphase development which yields characteristics which are modifications of those of the individual component [25]. In order to achieve a good migration of stress from the matrix to the fibers, a strong interaction is necessary, such as coupling that creates covalent bonds between the polymer matrix and the fibers. Although, secondary forces like Van der Waal forces or hydrogen bond may occur amongst the components [26–28].

For polymer composites filled with natural fibers, there are conditions that are necessary for the natural fiber polymer composites (NFPCs) to be able to carry out the objective principle effectively. These include (i) the length of fibers used must be sufficiently long, (ii) the orientation of the fibers must be in sync with that of the load, and (iii) the interfacial adhesion must be sufficiently strong enough [29, 30]. Therefore, the type of interfacial adhesion determines the performances of the NFPCs (such as barrier properties, mechanical and thermal properties). Other types of interactions reported include electrostatic forces, inter diffusion and mechanical interlocking.

## **3. Polymer matrix**

In polymer composite preparation, the polymer matrix serves as the binding material (binder). It helps to hold the fillers in position and also helps to transmit stress within the material [31–33]. Therefore, if the interfacial interaction is poor, the transmission of an externally applied stress will be poorly done, leading to failures in the material. To ensure that there is a good stress transfer in polymer composites, the right polymer matrix is selected. Polymers are known for their unique properties which differ from one polymer to the other, even within the same group. Based on this, polymers are categorized on the basis of their chemical behavior (i.e. thermoplastic or thermosetting) or on the basis of their source (i.e. synthetic or natural). Thermoplastic are polymers that once processed and are harden to shape, can be reprocessed again and again as desired. Examples are polyethylene (PE), polypropylene (PP), poly(caprolactone) (PCL), poly(lactic acid) (PLA). Thermosetting are polymers that once processed at an elevated temperature and are set into shape, can harden and cannot be reprocessed again. Examples are

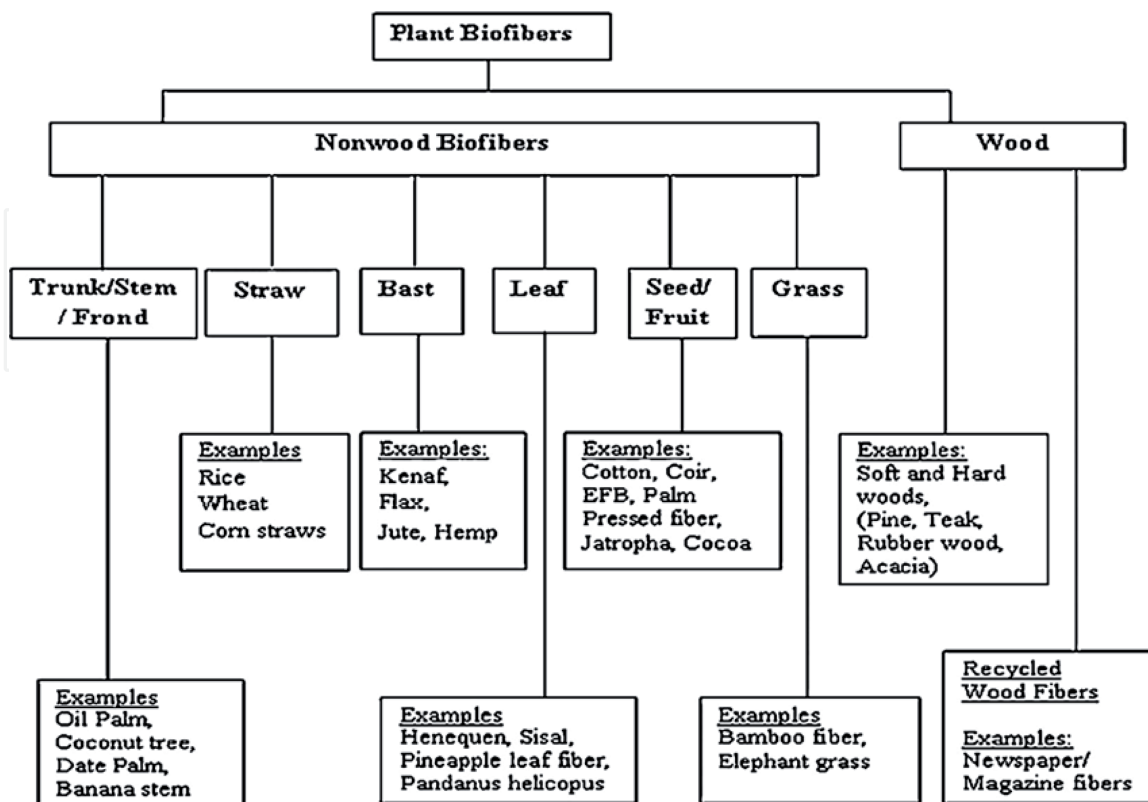
Biodegradable polymer matrices	
Natural	Synthetic
Polysaccharides—starch, cellulose, chitin	Poly(amides)
Proteins—collagen/gelatin, casein, albumin, fibrogen	Poly(anhydrides)
Polyesters—polyhydroxyalkanoates (PHAs)	Poly(amide-enamines)
Other polymers—lignin, lipids, shellac, natural rubber	Poly(vinyl alcohol)
	Poly(vinyl acetate)
	Polyesters—poly(glycolic acid), poly(lactic acid), poly(caprolactone), poly(orthoesters), poly(ethylene oxides), poly(phosphazines)

**Table 1.**  
 Some common polymer matrices used for composite preparation [34].

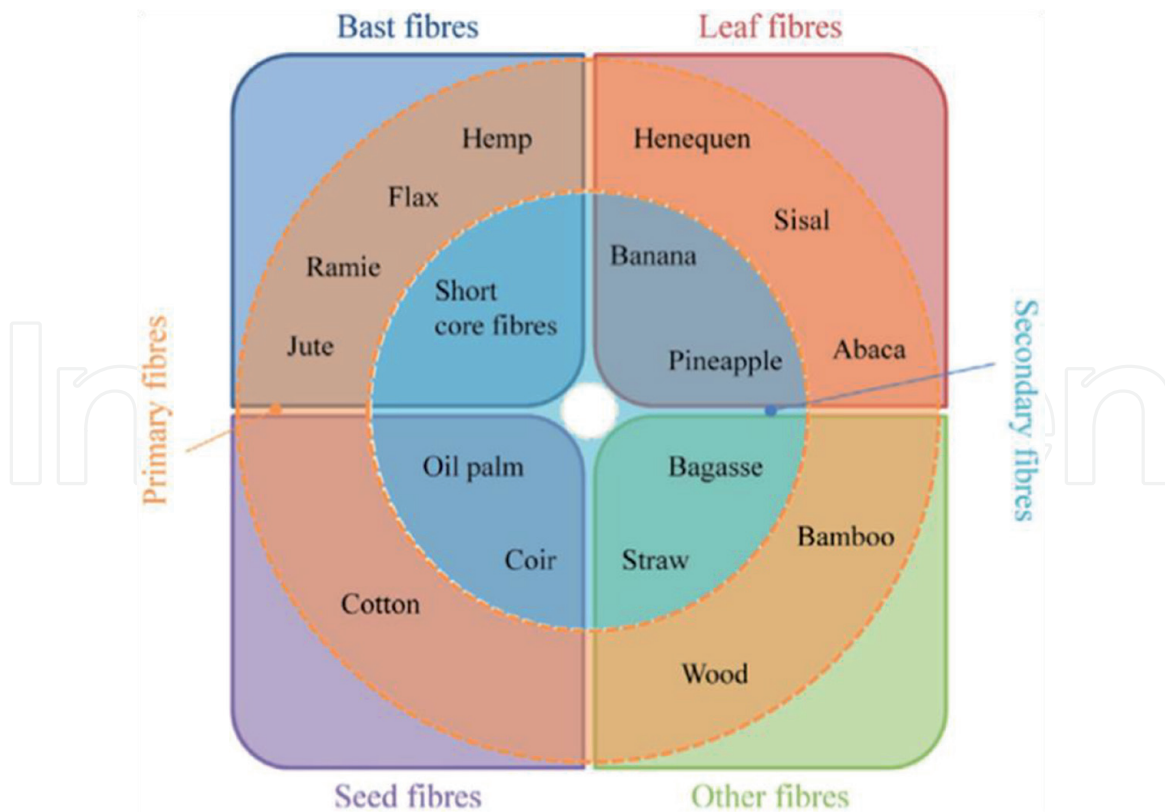
polyesters, epoxies. Also these polymers are either synthesized or are obtained from nature. **Table 1** shows a list of polymer matrices grouped into natural and synthetic. All these influence the choice of polymer matrix.

#### 4. Fibers

Fibers are one form of fillers that can be used to prepare polymer composites. Researchers have fibers in natural or synthetic forms [35–39]. Fibers such as aramid, carbon and glass are known as synthetic fibers. Due to increased environmental awareness, synthetic fibers are now being replaced with natural fibers which are more environmental friendly [5, 40–42]. Natural fibers have emerged as a viable alternative to their synthetic counterparts in polymer reinforcement, owing to the



**Figure 1.**  
 Representation diagram showing the classification of natural fibers based on the part of plants they are extracted from [43].



**Figure 2.** Schematic classification of natural fibers as primary and secondary fibers [50].

large scale research output [40]. Natural fibers are obtained from natural source such as minerals, animals or plants [34]. Fibers from plant sources consist of cellulose, while those obtained from animal sources consist of proteins (wool, silk and hair). Natural fibers offer large diversity in terms of sources. Plant fibers are generally categorized based on their location with the plant as illustrated in **Figure 1** [4].

Fibers from plant source have been widely used in preparing polymer composites [44–49]. This is because of the availability and the easy of processing them. Plant fibers can further be classified a primary fibers, or secondary fibers [40, 50]. Primary fibers are the fibers obtained from plants, which were specifically grown for their fiber recourses. However, in cases where the fibers are by-products of other primary use of the plant, the fibers are referred to as secondary fibers (**Figure 2**).

The mechanical properties and morphology of these fibers are influenced greatly by the value of the ratio of fiber diameter to the cell wall thickness which by extension is influenced by the extraction methods used [40, 51, 52]. These factors dictate the type of interaction that will occur between the plant fibers and the polymer matrix, whether thermoplastic or thermoset [53, 54]. Natural fibers are good materials for many applications as they provide reinforcement properties at very low cost with low density, good strength and stiffness [8]. Their advantages over synthetic fibers have been well documented and they are based generally on environmental sustainability which include health and safety concerns [55, 56].

## 5. Preparation

With a careful selection of appropriate preparation, some level of desired interaction at the interface can be achieved. The processing of NFPCs has the ability to influence the final properties if carefully handled. Polymer composites can be

prepared using the existing methods and technologies. These include injection molding, compression molding, blow molding, electro spinning, batch mixing or continuous mixing methods (extrusion), solution casting [34]. Different researchers have employed different methods to achieve their goal or specific property improvement. An experiment to toughen polylactide/poly(butylenes succinate co-adipate) blends was reported [57]. This was achieved through melt blending (batch mixing) of the mixture in the presence of a reactive compatibilizer triphenyl phosphate. Polypropylene/carbon nanotube composites were prepared using a twin screw extrusion mixer [58]. Their intention was to characterize the rheological behaviors and develop a model for the flow inside the machine. To investigate the micro mechanical characteristics of jute fiber/polypropylene composites, Liu et al. prepared the PP reinforced jute fiber Mat using film—stacking methods [7]. This was done by placing two layers of pre-dried non-woven jute mats in a mixture with three layers of PP films. In trying to prepare a novel composite films of polypyrrole-nanotube/polyaniline, Zhang et al., used facile solvent-evaporation method [59]. Also, recycling of biodegradable polymers for composites preparation has been done using extrusion processing [60]. The earlier mentioned methods of processing of polymer composites can be grouped into three primary systems, namely: solution blending, in-situ polymerization and melt blending [61].

### **5.1 Solution blending or casting**

This involves the formation of the composites through dissolution of the polymer and fibers in a suitable solvent and subsequent drying of the solvent after the processing of the composites [62–64]. In solution casting, obtaining the right solvent that will dissolve the polymer and be removed with easy is a major task, although there are water-soluble polymers [65, 66]. Examples are polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), poly(ethylene oxide) (PEO) and poly(ethylene-co-vinyl acetate) (PEVA). Many others are dissolved using non-aqueous solvents such as chloroform, xylene, benzonitrile, tetrahydrofuran (THF), toluene, dimethylformamide (DMF) and acetone [67–69].

Solution casting helps to avoid thermo-mechanical degradation usually observed with the other methods of polymer processing which involve heating and vigorous mixing. It is used mostly for film formation. The amount of solvent used in this method makes solvent casting environmentally unsustainable. In addition, most of the organic solvents are hazardous to health and are temperature sensitive. Sur et al., in their work, prepared polysulfone nanocomposites using solution casting at elevated temperature [70]. To improve miscibility amongst the fibers and polymer matrix, the fibers were soaked using the solvent separately first before mixing with the dissolved polymer. In some cases, researchers coated the fibers with selected polymers to improve the fibers miscibility and interaction [71]. In general, solution casting is preferred for polymers with poor thermal stability and susceptible to thermo-mechanical degradation.

### **5.2 Melt blending**

For the past decade now, melt blending has become a method of choice in the processing or preparation of natural fiber composites. It involves the heating of the polymer matrix up to 10–30°C above its melting point and then introduced the fiber into the molten polymer with thoroughly mixing under shear [72]. Melt blending has gained much ground in terms of acceptability, because of the existent compatibility with existing processing technology (such as injection molding and

extrusion) [73–75]. These methods are environmentally friendly and do not involve the use of hazardous solvents. Many research works have reported the use of melt blending method [58, 76, 77]. One area of concern is the processing condition and the level of interaction between the fibers and the polymer matrix used. According to [61], to obtain good distribution of the fibers within the matrix, which is one of the conditions for improved mechanical and thermal properties, there should be a favorable enthalpy of interaction between the fibers and the polymer matrix. This results in good distribution of the fiber inside the matrix. In the absence of this favorable energy, the fibers will be poorly dispersed. The conditions for processing natural fiber composites will be discussed elaborately in subsequent sections.

### 5.3 In-situ polymerization

This technique involves the polymerization of a monomer in the presence of another polymer, mostly in small quantities [78]. In-situ polymerization has been described as one of the important methods for compatibilizing polymer blends [79]. It allows the formation of covalent bonding between constituents which can result into graft or block copolymers that ultimately results in the development of a stable interface [72]. In-situ polymerization is noted to yield specific properties with conventional melt blending methods. Furthermore, it allows the preparation of composites with high fiber weight fraction because the homogeneity of the resultant composites is much greater than that obtainable from melt blending and solution casting [80]. Most thermoset NFPCs are prepared using in-situ polymerization methods [17, 78, 81]. According to Bounor-Legaré et al. [82], subject to the nature and reactivity of the organic or inorganic precursors and the processing factors, different types of functionality can be fashioned.

## 6. Factors to consider before and during the processing of natural fiber polymer composites

The preparation of natural fiber polymer composites with good strength is dependent largely on some factors mainly connected to (i) the fiber properties, (ii) the polymer matrix and (iii) the fiber-matrix interface properties. The strength and stiffness of any polymer composite is a direct function of the reinforcing fiber properties [83]. On the other hand, the matrix helps to keep in position the fibers and also helps in the transfer of load from fibers to fibers [84]. This segment dwells on the factors that contribute to the fiber-matrix relationship.

### 6.1 Fiber types and surface treatment

Natural fibers used for NFPC are abundant and can be sourced from different kinds of plants and from any part of the plant. **Figure 2** shows the classification of NF as primary and secondary fibers.

Plant fibers contain primarily cellulose, hemicellulose and lignin [85, 86]. However, the component of interest is the cellulose. It is a linear polymer of D-glucose units that are linked by  $\beta$ -1,4-glycosidic bonds. They are hydrophilic with the hydroxyl groups in each unit available to form hydrogen bonds which could be inter or intra molecular. This property helps the cellulose chain to be more stiff and enhance its rigidity [87, 88]. Cellulose is a semi crystalline polymer. However, because cellulose is surrounded by cementitious materials such as lignin and hemicelluloses, the percentage content of cellulose in any plant fiber determines its usefulness [87]. **Table 2** gives a summary of % cellulose content in some selected plant fibers.

Fiber type	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Abaca	12	56–70.2	5.6–12
Bagasse	17	32–55.2	19.9–25.3
Banana	9.4–22	60–65	5–32
Bamboo	11–17	26–43	21–31
Coir	4–6	32–46	32.7–45
Cotton	5.5–12.6	82–96	0.5–1
Flax	27.6–70	60–81	2–3
Hemp	6–70	68–92	2.9–13
Jute	26.5	45–84	5–26
Kapok	4	13.16–64	5.54–22
Kenaf	6.26–53	37–72	9–21
Pineapple	1.44	80–85	4.6–12.7
Ramie	24.5	68–91	0.6–9.25
Sisal	9.4–22	43–78	4–12.0

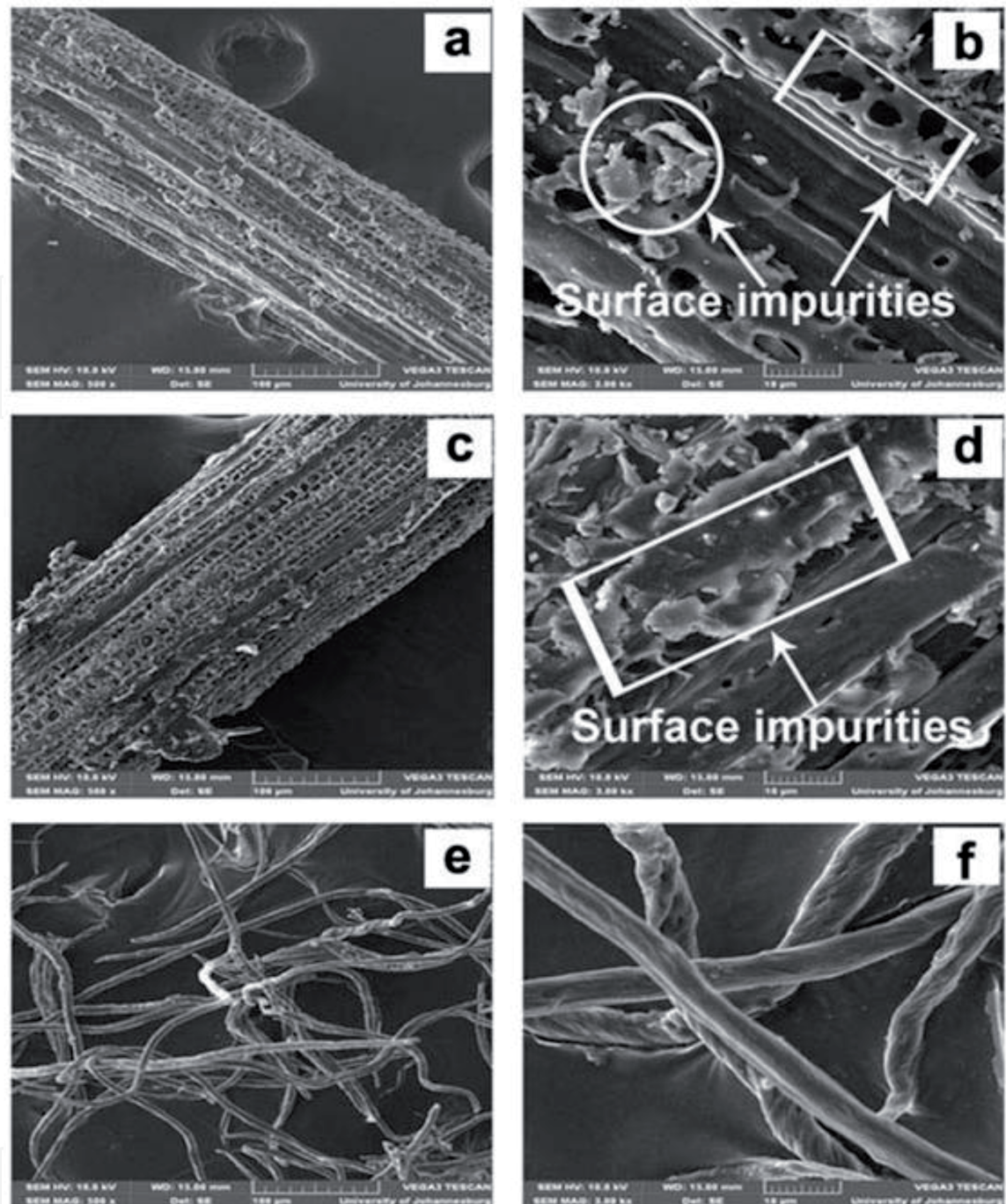
**Table 2.**  
 Percentage cellulose contents of some selected plants [18].

To increase this percentage of cellulose in the fibers, the material is subjected to different kinds of modification including alkaline treatment. Alkaline modification helps to remove the hemicelluloses, lignin and all other water soluble contents of the fibers, and by extension, increase the cellulose content [60, 89]. Some researchers have been able to extract nanocellulose crystals with improvement in the modification processes [90]. This includes the bleaching of the alkaline treated fibers and then subjecting them to acid hydrolysis, giving rise to better quality cellulose at the nanoscale [91–94]. The treatment given to the fibers confirm on them increased rigidity with cleaner surfaces which exposes more of the hydroxyl groups to any further chemical modification [95–97]. **Figure 3** shows SEM images of raw fibers and those treated at different condition. It can be seen that those treated with alkaline and then acid hydrolysis give a pulp like morphology.

These nanoscale cellulose fibers have been reported to lead to improved interfacial interaction [91–94, 96–98]. Although, fibers possess hydrophilic properties in nature and polymers are hydrophobic, to improve the interfacial interaction, further chemical modification of the fiber surface may be carried out. As earlier mentioned alkaline treated cellulose, especially the nanocellulose, have high concentration of hydroxyl groups on the surfaces that allow for their sites to chemically alter the natural fibers (NF). Different methods and strategies have been employed to achieve this by researchers as shown in the schematic diagram by [41, 73] given in **Figure 4**. Such chemical modification should be mild in order to prevent any deterioration of the other use properties.

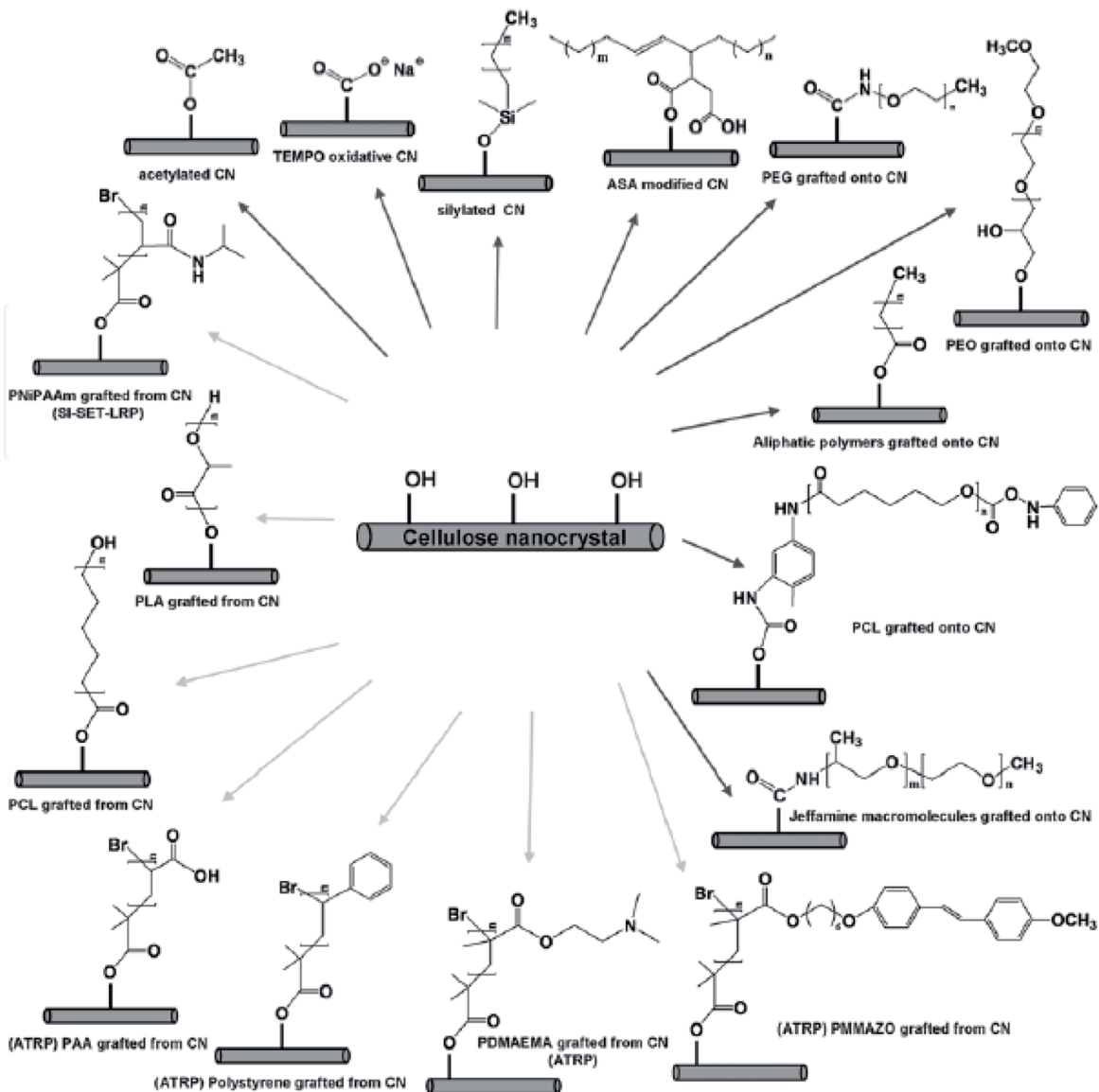
Furthermore, the physical properties, morphology and even the nano structure of the cellulose polymers depend greatly on the origin of the natural plant fibers and the processes and procedures of extraction. The extraction of nanocellulose from sisal, pineapple leaf and coir has been carried out [73, 99]. The results showed rod-like structures that are more separated with long, flexible and entangled morphology, especially from the banana rachis. This confirmed that the morphology and other physical properties of cellulose crystals is a function of the source of fiber. Furthermore, Le Bras et al. concluded in their work that the degree of crystallinity of the nanocellulose and its crystal structure depends on the method





**Figure 3.** SEM micrographs of untreated, alkaline treated and acid hydrolyzed treated fibers [73].

of extraction [100]. This was after the mechanical properties of the extracted nanocellulose were compared to each other and to those of their sources. Apart from this, the modified fibers have more uniform morphological structures. Also, there are reports that the thermal degradation property of natural fibers depends greatly on the level of modification given to the fibers (via acid hydrolysis, bleaching and alkaline treatment) and the source of the fibers [35]. This is because the nanocellulose obtained from such processes is more crystalline and rigid with uniform morphology. The factors that contribute to the variation in the lignocellulosic biomass include age of the plant, weather, plant type, soil nutrient, initial processes [87]. More recently, researchers have reported to have modified cellulose to allow for the introduction of functionalities to the polymer chains [41, 73]. The raw fiber can be pretreated using periodate oxidation and carboxymethylation techniques to introduce carboxyl and aldehyde functionalities which in turn could



**Figure 4.**  
 Typical chemistry modification for cellulosic fibers [41, 73].

form covalent bonds with other functional groups such as amine. Fibers pretreated with bacterial method were modified with xyloglucan. This improved the wettability and cell adhesion for biomedical applications [101]. Chemical modification of cellulose fiber surfaces can lead to increased viscosity thereby reducing the shear thinning effect expected during processing. Therefore, fiber type, its modification and functionality can greatly improve fiber-matrix interfacial interaction, leading to improved performance properties.

NFPCs have exhibited significant potential for application in diverse sectors such as food packaging [102], fire retardant paperboard for semi structural applications [103], flexible printed electronics applications [104], etc. Nevertheless, there are numerous challenges to solve particularly associated with the development of proper large scale processing systems. The processing step of these materials is crucial because it is related to their final performance. Further studies are needed to prepare cellulose-based nanocomposites on industrial scale,

## 6.2 Dispersity of fibers

Natural fibers have the tendency to agglomerate in the polymer matrix as a result of formation of hydroxyl group's hydrogen bonding. This hydrogen bond formation

leads to poor dispersion of the fibers within the matrix and by extension poor matrix-fiber interaction [73, 105]. The dispersity of the polar fiber which is hydrophilic in nature is worsened by the nonpolar hydrophobic nature of the polymer matrix. This factor has limited the extent of applicability of natural fiber polymer composites. In order to expand the areas of application, the fibers would need to be consistently and uniformly distributed within the matrix. To enhance the dispersity of these fibers in their polymer matrices, the modification and functionalization discussed earlier will become very important. The OH groups could be replaced by more hydrophobic organic moieties to help increase the affinity amongst the polymer matrix and the modified fibers. This will reduce the possibilities of hydrogen bonding and increase the dispersity in the matrix. The functionalization of the fibers may depend on the end use application. Yang et al., improved celluloses' suspension in aqueous media by acrylamide grafting on the surface by redox initiation grafting of extracted nanocellulose [106]. This led to improved self-assembly of the lyotropic state. Also, phosphorylation techniques with negatively charged phosphoric acid as phosphoryl donor were used to modify the cellulose surfaces at the nanoscale level by [107]. Furthermore, with the right conditions, the hydroxyl groups were oxidized to dialdehyde using  $\text{NaIO}_4$  [108]. Bae et al., used bimolecular nucleophilic substitution to replace the hydroxyl groups with long hydrophobic alkyl chains, in order to impart hydrophobicity to the cellulose polymer chain [109]. Also polycaprolactone diol (PCL) long chains were suggested for the surface modification of cellulose using what they referred to as click chemistry and esterification reactions [110]. Although it was reported that greater grafting yields were detected with the click chemistry when compared to the esterification method. The pretreatment given to the fibers also affects the extent to which the fiber surface can be modified.

### **6.3 Processing condition**

During the processing of NFPCs, the processing temperature, mixing speed and residence time are all important for any melt blending process while for in-situ polymerization; the temperature and curing time are of importance [58, 78, 79]. For NFPCs to be prepared via melt blending, the temperature must not be too high to avoid the degradation of the natural fibers. Since natural fibers are thermally stable below  $200^\circ\text{C}$ , above this temperature, the integrity of the fibers cannot be guaranteed. Therefore, polymers with higher melting temperature may not be used in the preparation of NFPCs or alternative processing methods are applied. One factor to bear in mind is that the polymer must be molten enough to wet the fibers. This means that the Gibb's free energy of interaction tend towards negative. As the fibers are added, the viscosity increases. This increase is dependent on weight percentage of fibers added [13]. However, if the shear rates are increased it could minimize the effect of the increased viscosity [75, 77, 111–113]. Good fiber-matrix interaction can only be achieved if the polymer can wet the fiber surfaces properly. The resident time for processing the NFPC is also very important, one cannot use the same processing time as used for the neat polymer or blends, for NFPC, if other parameters are to remain the same. As mentioned earlier, the addition of fibers leads to change in viscosity; therefore NFPC will require more time to achieve good wettability. However, the option of increasing the shear rate or mixing speed might compensate for the change in viscosity. Therefore it may be possible to use the same resident time during processing. It must be mentioned that every option has its advantages and disadvantages. For example, longer time and increased mixing speed may lead to thermomechanical degradation [75].

## 6.4 Addition of other materials

In the preparation of composites, additives are added to help improve specific properties. For example, nanoparticles are added to enhance the mechanical and thermal properties through better crystallinity growth and stabilization of phase morphology [114, 115].

### 6.4.1 Compatibilizers

Compatibilizers are added to increase interfacial interactions amongst polymer-polymer in blends and polymer-fibers in composites [10, 41, 116]. The use of compatibilizers to improve interfacial interaction is widely reported [117]. In a series of works by Kamaker and other co-researchers [118–120], it was reported that Jute/PP composites' mechanical properties were improved drastically, when 3 wt% maleic anhydride grafted polypropylene (MAHgPP) was used to treat the Jute/PP composites as coupling agents. The tensile strength increased from 29.82 to 59.13 MPa, a 98% increase. Also, the bending strength was reported to increase from 49.97 to 87.66 MPa, a 75.4% increase. In related work, the tensile, flexural and dynamic strength of Jute/PP composites were enhanced by approximately 50% when the jute fibers are treated with 0.1 wt% MAHgPP solution of toluene, although the impact strength was negatively affected [121, 122]. Li et al., investigated two different kinds of silanes as coupling agents to treat sisal fibers surfaces [15]. The coupling agents were diluted in acetone to 6% concentration before use. A 24 h immersion of the sisal fibers was done using the coupling solution after which it was washed with acetone and dried up in the oven for 4 h at 60°C. Their results showed that the sisal surfaces were etched and they were very rough, which led the unbundling of the fiber bundle into smaller fibers, as seen in **Figure 3**. This increased the operative surface area presented for contact with the polymer matrix. Although, it was reported that the interaction at the interface was more of mechanical interlocking with less of chemical bonding. Therefore, the observed increase in load was due to frictional shear stress transferal across interface. Other coupling agents which had performed relatively well, have also been reported by other researchers [11, 123, 124]. However, to chemically modify the surface properties of the cellulose fibers to the extent that they can in turn influence the polymer composites properties significantly, it is suggested that the fibers should be modified to its nanoscale [125, 126].

### 6.4.2 Nanocellulose and nanoparticles

Nanocellulose particles are derived from rigorous chemical modification of plant fibers using a combination of alkaline and acidic solution in phases. At the nanoscale chemical modification is relatively easier; large numbers of the OH groups at the surface are more exposed; the amorphous components of the fibers have been eliminated, leaving only the crystalline part of the cellulose material. The nanoscale cellulose fibers when modified have wide application [127, 128]. Filler or additives can be described as materials which are added to the matrix in low percentages ranging from 0.1 to 5 wt% in order to improve performance and impact some special properties [129]. Some of the fillers are low-cost, allowing for a cost effective measure for the enhancement of performance properties. In addition, they can improve the processing of the material by controlling the viscosity of the resin [130]. Common fillers used in NFPCs include metal particles, nanosize cellulosic materials (CNCs), silica, nano-clay, maleic anhydride (MA)

and carbon nano-tubes (CNT) [131]. Mohanty et al. showed that better interfacial adhesion existed amongst the fiber/matrix owing to filler addition in the NFPC as evident from the SEM micrographs of the fractured tensile samples; this resulted in the improvement of the mechanical properties [132]. Mechanical properties enhancement were resultant from the adding of fillers at low wt% which has led to the consistent assembly observed and enhanced stress transfer amongst the fiber and the matrix [1]. Meanwhile, at higher wt% of fillers, there was deterioration in the properties of the NFPCs, due to agglomeration of the fillers and the interfacial adhesion between the polymer matrix and fiber were noticed to be weak. Furthermore, it was suggested that the rise in tensile modulus and the fall in impact strength of the NFPCs with clay fillers were as a result of the polymer matrix improved cross-link density, which led to a decrease in the stiffness of the composite, hence reduced the impact strength [130, 133]. While in other studies, aluminum powder was used as fillers and in others, modified clay improved the impact strength of the composite, as the SEM micrographs revealed the existence of less voids and rise in density along with improvement in stiffness resultant from better interfacial adhesion amongst the fiber and the matrix in the presence of the modified clay [134, 135]. Other advantages of filler addition to sisal fiber reinforced polymer composites are increased moisture absorption or reduced water uptake as reported by [135, 136].

The addition of nanoparticles to NFPC to improve their interfacial properties has gained more popularity in recent time. Nanoparticles incorporation into polymer composites has been reported to improve their strength and young's modulus, as can be seen from earlier discussion. The addition of these nanoparticles at very low concentration of approximately 0.1–1.0% had influenced the mechanical properties of the NFPCs [137]. The modifications of the particles by some researcher have led to improved chemical interactions when added to the composites. Thereby improving interfacial bonding and by extension, mechanical and thermal properties [138–140]. Moreover, the addition of inorganic nanoparticles has helped to improve both thermal and mechanical [131]. This has influenced the crystallization process during processing of the composites. The improved crystallinity can encourage superior mechanical interlocking of the polymer-fiber interface.

#### *6.4.3 Hybrid fibers*

Hybrid fibers are a combination of two or more different fibers to make a composite. The addition of glass and/or carbon fibers to form hybrid fibers has also contributed to improving the composite properties. Allamraju et al., reported an increase in the compression and tensile strength of Jute/glass hybrid fibers epoxy composite, as a result of percentage increase in mass fraction of jute fibers [141]. Their results showed that the measured strengths increased as the fiber load increases from 6 to 9%, after which there was a decrease. The 9 wt% jute fibers that was reported as the optimal loading was attributed to higher stiffness of the composites and an improved fiber-matrix adhesion.

Hybrid composites are prepared by the combination of two or more different type, shape or size of reinforcement [142]. The crossbreed composite properties is completely dependent on many elements such as, extent of intermingling of fibers, fibers orientation, fiber surface roughness, compatibility between the fibers and their matrix, and the property of the individual fibers [143]. Recently, investigations on the properties of the crossbreed composites were centered on the natural/synthetic fibers, natural/natural fiber and natural/synthetic/additive modified reinforced polymer composites. Essentially for applications that required such

hybrid/crossbreed composites with stiffness and high strength, but the employment of pure natural fiber polymer composites is difficult.

The popularity of these crossbreed types of composites is increasing rapidly owing to their capability to provide freedom to tailor the composites and achieving properties that cannot be acquired in composite encompassing only one kind of material [13, 144]. One of the major reasons for creating crossbreed NFPCs is to utilize the pluses of the fibers and lessen some drawbacks [145]. Another reason is based on economy, which is to decrease the cost of the finished composite product. Even though the usage of natural fibers in composites is less costly in comparison to the orthodox reinforcements, there are significant differences in the costs of natural fibers. Therefore, partially substituted cotton fibers in a composite made with wood fibers could offer very huge benefits in terms of the performance of the composite and also in the manufacture prices. The hybridization of wood flour- polypropylene composites with waste cone flour (20–40 wt%) was reported the composite was said to have been negatively affected in terms of their flexural properties and water resistance of the composite [146]. However, adding pine cone flour (10 wt %) to the composite revealed no substantial consequence on the measured properties, i.e. water absorption and flexural strength properties. This means it is economically advantageous. Further research showed that reducing the amount of pine cone flour added to the composite lead to positive improvement.

#### *6.4.3.1 Natural/natural hybrids*

Hybrid composites of sisal fibers and short banana fibers were also prepared using a polyester [147, 148]. From the result obtained, the tensile strength of the polyester composite was observed to rise as the volume fraction of the banana fiber was increased. On the other hand, the impact strength of the composites was affected negatively with increasing volume fraction of the banana fibers. Nevertheless, the impact strength improved with rise in total content of the fibers used. The observed properties were ascribed to two factors: (i) the lower microfibrillar angle of the banana fibers ( $11^\circ$ ) as compared to that of sisal ( $20^\circ$ ) and (ii) the better compatibility between the polymer matrix and banana fibers, which decreased the possibility of fiber pullout.

In the same vain, Venkateshwaran et al., prepared the same hybrid of banana and sisal fibers using epoxy resin in order to determine the optimal quantity of banana fibers with regard to its tensile properties [149]. The results revealed that about 50% of the complete fiber content added was good enough to impact significantly on the tensile strength of the composite. The differences in the morphologies of the different fibers have been shown to be of significant advantage when used as hybrid in a composite [142].

Furthermore, Fernandes et al., prepared hybrid composites of cork and coir fiber using high density polyethylene (HDPE) matrix [150]. With a coupling agent present, adding 10 wt% coir fibers to the composite caused a 30% rise in tensile maximum strength and a 39% rise in the tensile modulus. The overall effect of the coir fiber on the hybrid composites was very evident when compare to the single fiber composite, even with the coupling agent. Therefore, it can be said that the hybridization of NFPCs, most especially with natural/natural fibers, presented an efficient, sustainable and high economical way of improving the performance of the composites at a reduced cost. Also the addition of compatibilizers is still a necessity in order to create the needed covalent interactions required to enhance the performance characteristic property [151].

#### 6.4.3.2 Natural/synthetic hybrid fibers

Natural fibers mixed with synthetic fibers hybridization could provide the desirable strength of a composite due to their synergistic effects [152]. Conversely, as a result of environmental impacts and disposal issues relating to the synthetic fibers in addition to hybrid strength requirements for specific applications, the final fiber ratio would be a 50:50 ratio (natural: synthetic). This ratio, offers a balance and intermediary mechanical properties in comparison to mechanical properties of either the synthetic or sisal fiber composites. Natural/natural fibers hybridization in a composite could be beneficial as a result of the possible disparity in cellulose quantity of the natural fibers used. This has a substantial effect on the composites mechanical properties and individual fibers have their distinctive characteristics which can be tailored for defined applications. A combination of such fibers together can bring about the needed properties for such application and still remain environmentally friendly. These biocomposites could be used in secondary/tertiary structures and other applications that require low stiffness and strength. Senthilkumar et al., highlighted that the enhancement in the mechanical properties of the hybrid composites was due to the strong impact from the type of polymer matrix used, fiber treatment technique, individual fiber loading and fiber choice [153]. Additionally, the enhancement in mechanical properties for natural/synthetic hybrid fiber reinforced composites was more significant than that of natural/natural hybrid fiber reinforced composites. It is the fiber/matrix interface adhesion that is responsible for the significant disparity observed in their mechanical properties for natural/synthetic fiber reinforced composites when compared to that of natural/natural hybrid fiber reinforced composite which displayed weak interfacial adhesion, more fiber pull out when under stress and uneven natural fiber distribution in the developed hybrid composites [153].

The general resolve for combining any two fiber kinds together in a single composite is to preserve the advantages of the two fibers in the new material and eliminate to the barest minimum their individual drawbacks [145, 154–157]. The synthetic fibers are known to possess good mechanical properties and thermal stability. They also lead to increase in overall weight of the composite, thereby eliminating the light weight advantage a complete natural fiber composite bears. However, the idea of combining natural fibers and synthetic fiber is influenced by the following parameters [152, 158, 159].

- i. Relative amount of fiber
- ii. Elastic properties of the fiber
- iii. Failure strain ratio
- iv. Fiber strength distribution
- v. Degree of dispersion and uniformity
- vi. Matrix properties

In summary, the addition of other component to NFPCs has led to reduction in some of the problems associated to their fiber-matrix interface. Compatibilization have helped reduce fiber agglomeration, water absorption and improved dispersity in the matrix.

## 7. Possible applications of NFPCs with improved fiber-matrix adhesion

The application of NFPCs comes with different requirements. These requirements are specific to application demands which include mechanical properties, thermal stability, transparency, conductivity and operational temperature. These factors are not unconnected to the factors considered before processing. For mechanical and thermal stability, the design of the NFPCs are considered from the point of improved interfacial interaction, using compatibilizers, fiber surface modification, addition of other chemical components and lastly reducing the fibers to nanosizes.

The automotive industry is one of the major end user playing a key role in the utilization of NFPCs. In the early '90s, Mercedes-Benz was the first, as a carmaker, to use NFPC, by building panels for doors with jute fibers [160]. This resulted in other car makers following suite, utilizing natural fibers comprising polymer composites for parcel shelves, headrests, upholstery, door panels, etc. The widespread adoption can be linked to the advantages of NFPCs, relating to the impact on the environmental, cost, elastic modulus and weight. No matter the applications, it was always a necessity to increase the mechanical properties of the composites via pre-treatment techniques (as discussed earlier). The fibers which have been treated were used in several ways, in order to obtain non-woven structures, mats, etc. [9]. Researchers have shown that subjecting natural fibers to some form of distinct treatment could lead to the development of high-quality composites with mechanical properties which are similar to those of glass fiber composites [160]. An outcome that would have ordinarily been very difficult to achieve because of natural fibers' hydrophilic nature which encourages water molecule absorption and agglomeration with no adhesion to the polymer matrix; This is the challenge and much works is ongoing to overcome this challenges [160, 161].

For conductivity, the addition of inorganic nanoparticles has been used and this has served a dual purpose of also improving the mechanical and thermal properties. Transparency is best impacted on NFPCs by the use of nanocellulose modified or not, with careful selection of the matrix. Some of the biodegradables are considered as having transparent properties including PLA. For water and gas permeability, applications are numerous with good water permeability. Such composites can be applied in water filtration processes, while for low water permeability composites; can be applied in packaging.

Researchers have reported positive impact of cellulose fibers on moisture and gas barrier performances for biodegradable polymers after modification with nanosize celluloses [162, 163]. Ambrosio-Martin and his colleagues prepared biodegradable composites of PLA using CNCs [164]. They reported improvements of barrier properties of oxygen and water which was due to the addition of well-dispersed OLLA-BCNCs. The researchers hypothesized that the nanofillers were able to make a tortuous path for the permeation of gas and water, thereby acting as blocking agents inside the polymeric matrix and hence, causing an increase to the barrier properties of the material. In these materials, the CNCs good level of dispersion within the polymer matrix, the morphology and its orientation led to enhanced tortuosity effects, thereby, heightening the barrier properties of the materials [165, 166]. Sanchez-Garcia and co-workers did similar work on PLA biodegradable materials and reported a decrease in the water permeability capacity and oxygen of approximately 82 and 90% respectively on addition of CNC to the PLA matrix [167]. In contrast, Espino-Pérez et al., highlighted results that were entirely opposite after compounding PLA with n-octadecyl-isocyanate-grafted-CNCs [168]. In their publication, it was clear that there was no reduction in oxygen permeability on



adding CNCs into PLA. Apart from investigations about the tortuosity effects and barrier properties, researchers have tried to relate the improvement observed for the barrier properties to the materials crystallinity changes on addition of the nano-fillers to the polymer matrix [169]. Fortunati et al, highlighted the improvements in barrier properties of PLA/CNC nanocomposites as well as increased crystallinity simultaneously, which was attributed to the addition of CNCs [170]. Espino-Pérez and co-workers investigated CNC/PLA nanocomposites using a high D-lactic acid content (a material which under normal processing conditions cannot crystallize) as matrix [171]. In conclusion, they indicated that the tortuosity effect of CNC on the oxygen barrier properties is limited. Although, after addition of modified CNS, significant improvement in the water vapor barrier properties was observed. They reported the swelling of unmodified CNCs due to absorption of water as a result of their hydrophilicity, which encouraged the pathway for mass transport and this property was not demonstrated when modified CNCs were employed because the surface modification caused the reduction in the hydrophilicity of the nanoparticles [172]. Follain et al., also reported that other elements can be considered to be significant in moisture and gas barrier performances of CNC-based nanocomposites [173]. They indicated that the formation of a 3D network and close interfacial adhesion between PCL chains and CNC can result in the matrix having structural defects, which encourage transfer of gas. Hence, their results highlighting the barrier properties of CNC-based nanocomposites allow for the conclusion that the tortuosity effect is influenced by CNCs, CNC surface chemistry, the structure of the nanocomposite. Also, that change(s) in crystallinity of the host matrix play a vital role on moisture and gas barrier performances of the material.

Biodegradation has been described as a vital prerequisite for biomedical materials, agricultural mulches and the packaging industry, as a result of the high level of consumption of these materials. Thus, the preparation of biodegradable polymers with improved properties is necessary but not without its own challenges. However, it will be exceptional to alleviate the concerns of landfills, chiefly in countries which are yet to adopt the technique of composting. A lot of research output has shown enhanced biodegradation for a number of polymer matrices when cellulosic fibers are added to them [174, 175]. However, the surface modification of the cellulose fibers negatively influences the matrix degradation because it reduces the number of OH group on the cellulose surface and so decreases the hydrophilicity [176]. Pinheiro and co-workers prepared poly (butylene adipate-co-terephthalate) PBAT-based composites with modified and unmodified cellulose fibers [174]. They presented from their results that the addition of unmodified cellulose fibers caused more weight reduction and this was attributed to the hydrophilic properties of the nanocrystals that hastened the hydrolysis of PBAT. In another related work, Monhanty et al, reported similar findings and also highlighted that the hydrophilic properties of the reinforcement encourages the degradation of the polymer [177]. The crystal size [178] and crystallinity of the polymer matrix [179, 180] have also been reported to playing a vital role in the degradation degree of the matrix, considering that regions which are crystalline are relatively unaffected by hydrolysis [178–182].

The use of other methods such as micro-fibrillation, laser, and ionomer to enhance the mechanical properties of materials have been reported. Choudhury and co-workers highlighted the capacity to improve the tensile and flexural properties of NFPCs by ionomer treatment of natural fibers [183]. The improvement was as a result of uniform stress dissemination and good dispersion of the fibers inside the matrix. This enhancement in mechanical properties by the microfibrillation was largely ascribed to the larger interaction observed between the polymer and fibers after the treatment by micro-fibrils and aggregates.

The selection of polymer matrix in all these areas of application becomes very important and sensitive. Although there are general purpose polymers with little or no health concerns for examples PP, PE, HDPE. When these polymers are compounded with NFs, their composites become more susceptible to microorganism attack, thereby making them biodegradable.

## 8. Conclusion

The dependence of performance properties on a strong fiber-matrix interface cannot be over emphasized. Fiber-matrix interfacial interactions are very important properties of all polymer composites. The performance properties are highly dependent on the kind of fiber-matrix interfacial bonds formed. These bonds can be physical or chemical in nature. The physical interaction includes interlocking between the matrix and the fibers, which is as a result of the rough edges of splits caused by the various surface treatments subjected to the fibers. While chemical interactions include the formation of bonds from the weak Van der Waal force to a strong covalent bond. The chemical bonds can be induced by (i) the type of surface treatment given to the fibers, which be either be a chemical or biological treatment and (ii) the deliberate addition of selected compatibilizers which confer specific functionality on either the fibers or the polymer matrix. Furthermore, the addition of nanoparticles has been reported to help improve interfacial interactions through the direct participation in the crystallization processes which increases rigidity of the polymer matrix and thus enhances the physical interlocking at the interface. The use of hybrid fibers of polymer blends is another way of improving the interfacial interaction in NFPCs. Hybrid fibers can be natural/natural or natural/synthetic. While the natural/synthetic hybrid fibers clearly have better thermal and mechanical properties, their effect on the environment will always be of great concern. With appropriate surface treatments, natural/natural hybrid fibers have been reported to display improved thermal stability and good mechanical properties. Also, the use of polymer blends has resulted in improved interactions. The choice of processing methods and conditions can undermine the kind of and extent of interaction formed. While the in-situ polymerization is used for thermosets, it mostly leads to the formation of covalent interactions. The thermoplastics are prepared using melt blending which mostly gives rise to interlocking or at most Van der Waal force types of interaction at the interphases, although compatibilizer can be added to form covalent interactions. However, melt blending processes are more prone to thermomechanical degradation, which is likely to affect the blends performance properties. In conclusion, to ensure that the materials with the required properties are developed, it is necessary that the factors discussed above are properly considered.

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