

# Chapter 2

## Fundamentals



This chapter focuses on the water diffusion process in composites materials. Special attention is given to vegetable fiber reinforced polymer composites. Herein, the main issues related to this important topic such as foundations, advantages and problems associated with the use of vegetable fibers as reinforcement in polymer composites are discussed, especially that caused by weak adhesion and exposure to the hot and humid environments, are presented and discussed.

### 2.1 Natural Fiber-Reinforced Polymer Composites

Currently, environmental issues are increasingly assuming a prominent role in our society, including conditioning technological development. In materials engineering, this role evidences the greater importance attributed to renewable and biodegradable materials whose manufacture involves low energy consumption. In this context, the evolution of different technologies has allowed the use of reinforced plastics with several productive, economic and ecological advantages.

More recently, environmental concerns as well as very stringent regulations and standards, have prompted the industries to research and use more eco-friendly and/or sustainable processing methods or products. In order to achieve this goal, available manufacturing processes are being modified or adapted to comply with these regulations, alternative technologies are developed and improved or else renewable biomaterials and biofibers are being used to generate eco-friendly composite materials. Broadly defined, biocomposites are composite materials made from natural/bio fibers; the polymer matrix may be petroleum based or naturally derived (biopolymer), and the former may be biodegradable or not. Biocomposites derived from plant fibers and biopolymers are likely to be more eco-friendly and such composites are termed green composites. While synthetic matrix/plant fiber composites are not as

ecofriendly, they are still more environmental friendly than an all-synthetic material. Natural fibers, both of animal and plant (lignocellulosic) origin, meet these requirements.

Vegetable fibers are biodegradable, sustainable and renewable, carbon dioxide neutral and have a positive environmental impact, as they are nontoxic and nonabrasive to mixing and molding equipment, leading to significant production cost reductions. Their major constituents are cellulose, hemicellulose, lignin, pectin, waxes and water-soluble substances.

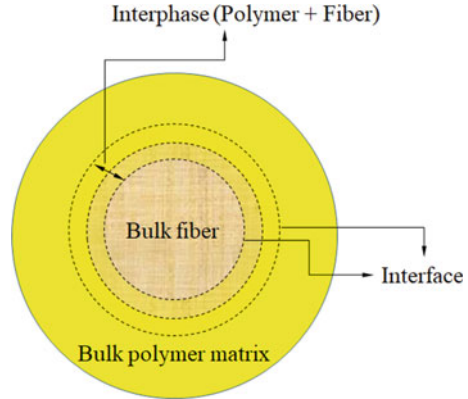
Plant fibers are a choice material for biocomposite production due to their worldwide availability, economical production, safer handling and working conditions compared to synthetic reinforcements, good set of mechanical properties, low cost per volume, low density and high relative strength and stiffness, which results in composites with specific strength and stiffness comparable to that of glass reinforced ones.

Strong arguments for encouraging the use of these materials include ecological, technological and economic advantages presented by vegetables fibers as well as social concerns since from an economical point of view, they generally originate from poor regions [1].

The main disadvantages presented by vegetable fibers for polymer composite applications are related to their high moisture sorption (hydrophilicity), relatively low processing temperatures ( $\leq 200$  °C (although it is possible to use higher temperatures for short periods), low resistance to microorganisms and poor fiber/polymer adhesion to most polymer matrices. All these factors ends up by compromising the composite's immediate and long-term mechanical performance [2]. Therefore, despite their attractiveness, natural fiber-reinforced polymer matrix composites are very sensitive to influences from external environmental agents such as water (in the liquid or vapor phases), humid air, temperature, radiation (X-rays,  $\beta$  and  $\gamma$  rays, ultraviolet rays), chemical agents or any combination between them [3–5]. They are also very sensitive to internal factors such as fiber volume fraction and orientation, for example. The different factors cited above justify the significant amount of effort and research on understanding vegetable fiber-reinforced polymer composites degradation under adverse operating conditions. These actions also contemplate many others types of polymer composites, such as those reinforced by metallic fillers.

One of the most important factors in composite materials, manufactured by one or more continuous phases, is the region of interactions between the reinforcement and the matrix. It encompasses two sub-regions: the interface and the interphase. The interface is the boundary of contact (contact surface) between composite components (reinforcement and matrix) and has null thickness. In contrast, the interphase is a volumetric region where matrix and reinforcement are mixed and the chemical, physical and mechanical properties changes continuously from those of the matrix to reinforcement. Thus, its thickness is not null. The interphase is generated by the interdiffusion of atoms and molecules of the matrix across the interface, to inside the reinforcement. This phenomenon is more intense in situations involving polymer

**Fig. 2.1** A schematic illustration identifying the interface and interphase regions inside a polymer composite



matrices in the liquid state and vegetable fiber as reinforcement. Based on these definitions, two contact interfaces constitute the interphase. Figure 2.1 illustrates the physical representations of the interface and interphase inside a fiber-reinforced polymer composite.

The final properties of the composites depend fundamentally on how the individual components interact with each other, that is, they depend on the interface and interphase regions between the discontinuous and continuous phases. These regions are mainly responsible to transfer the mechanical load from the matrix to the reinforcement. Inadequate adhesion between the phases involved in the interface may lead to premature failures, compromising the performance of the composite. Therefore, in addition to the individual properties of each component of the composite, the interface should be as suitable as possible to optimize the combination of the properties involved [6–13]. The adhesion between reinforcement and matrix characterizes the physical and mechanical behavior of a composite.

In polymer composites, the failure should occur in the matrix. In practice, the adhesion between the constituents isn't perfect and the process of rupture is generated at the interface. Therefore, in most cases, failure of reinforced polymers occurs by shearing in the interfacial region. The failure occurs due to the weakness of the atomic or intermolecular bonds between the surface of the matrix and the surface of the reinforcement in the composite. The following types of failures can be cited: matrix cracking, local deterioration, delamination, fiber debonding, and pull-out.

One of the factors that favor interfacial interaction is the contraction undergone by the polymer matrix during its curing (crosslinking and solidification). In order for a better stress distribution to occur on the reinforcement surface during matrix contraction, a perfect wetting of the reinforcement by the resin is necessary [9].

## 2.2 Water Absorption in Natural Fiber-Reinforced Polymer Composites

Despite their strongly hydrophobic characteristic, polymers can absorb water when immersed in aqueous media or exposed to moisture. The intensity of this phenomenon is dependent on factors such as: polymer polarity, hydrogen bonding ability, crystallinity (thermoplastic polymers), degree of crosslinking (thermoset polymers) and manufacturing process. Thus, moisture in any form is deleterious to polymer composites, especially to those reinforced by natural fibers, which are highly hydrophilic materials.

There are two modes of moisture absorption in vegetable fiber reinforced polymer composites: (a) hydrogen bonds between the polymer and the hydrophilic groups of the filler and (b) through surface microcracks which are responsible for water transport and deposition inside the material [14].

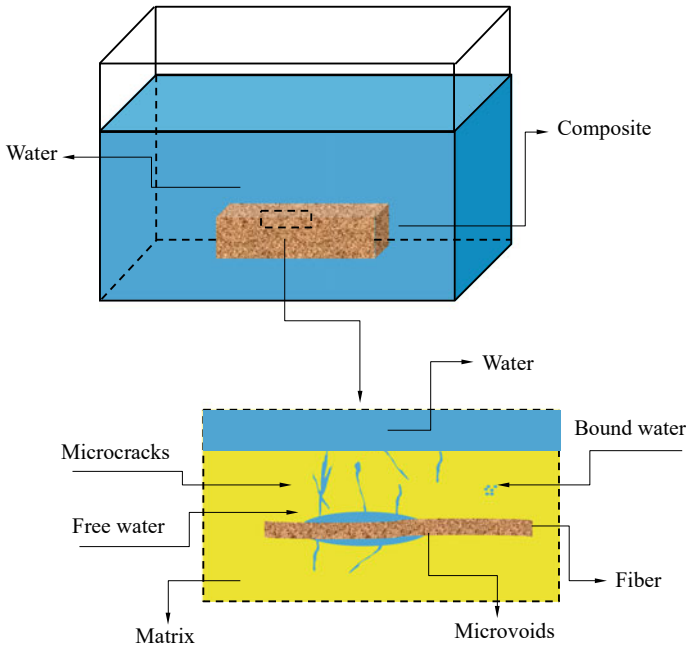
The water absorbed by polymers consists of both free water and bound water [15]. The free water are water molecules with the ability to move independently through the void spaces, while bound water are water molecules that are attached to polar groups of the polymers [16].

Moisture diffusion in polymeric composites is governed by three different mechanisms. The first involves the diffusion of water molecules within micro gaps between polymer chains. The second involves moisture transfer through gaps and faults at the interface between fiber and matrix. This is a result of poor wetting and impregnation during the manufacturing process. The third involves the transport of water molecules through micro cracks in the matrix originated during manufacture [17–19].

When natural fiber-reinforced polymer composites are exposed to moisture, free water penetrates and binds with hydrophilic groups of the fiber, establishing intermolecular hydrogen bonds with the fiber and reducing interfacial adhesion between fiber and matrix. This leads to swelling of the cellulose fibers, which promotes an increase in the stress at the interfacial regions resulting in its embrittlement and thus, leading to formation of micro cracks inside the matrix around the swollen fibers [20–22]. This promotes capillarity and transport of moisture via micro cracks, causing deterioration of the fibers, which eventually lead to the definitive debonding between fibers and matrix. After long time periods, biological activities such as fungal growths eventually degrade the natural fibers [15, 16] compromising the mechanical performance of the composite. Thus, water absorption is one of the limiting factors that reduce the applicability, physical and mechanical properties of the composite [23]. Figure 2.2 illustrates the moisture types (Free water and bound water) and the effect of water migration on the fiber—matrix interface.

Considering that these materials may be exposed to moisture or even submerged in water during their use, water absorption studies are of great academic interest, especially when heated environments are involved [17, 24].

Vegetable fibers are hydrophilic and fiber moisture not only acts as plasticizer but makes polymer impregnation more difficult, causing weak adhesion on the polymer matrix-fiber interface, which leads to internal stresses, void formation and premature failure of the fiber-polymer system [25–27].



**Fig. 2.2** Water migration mechanisms in vegetable fiber-reinforced polymer composite

This weak interfacial adhesion is associated with low polarity and low chemical affinity between the matrix and the fiber, which causes the formation of voids at the interface, initiation of faults and interfacial degradation that compromise the mechanical performance of the composites.

Effectively, vegetable fiber-reinforced polymer composites display lower mechanical properties than synthetic fiber-reinforced composites. However, as previously exposed, water sorption adversely affects the mechanical performance and physical integrity of natural fiber-reinforced polymer composite; so, the differences in mechanical properties between the natural and synthetic fiber-reinforced polymer composites can be even greater. Thus, knowing the effect of moisture on the composite properties is crucial for outdoor applications. The incompatibilities between natural fiber reinforced composites and water may be diminished by surface modification (chemical treatment) of the fiber or the matrix. In general it is the fiber, not the matrix, that is treated [28].

Several studies show that the mechanical properties of vegetable fiber reinforced composites significantly improve at high fiber content [29–31]. However, when fibrous polymer composites absorb moisture effects such as swelling, plasticizing, dissolving, leaching and/or hydrolyzing, result in discoloration, embrittlement, lower resistance to heat and weathering, and lower mechanical properties.

Due to their importance, several works on the water sorption kinetics of vegetable fiber reinforced polymer composites are reported in the literature [32–50]. In general,

the amount of water absorbed by a sample varies as a function of its composition, dimensions, void fraction (available free volume), temperature, surface area, surface protection, and exposure time. In this context, the effects of moisture and temperature of composites on several performance parameters, such as tensile and shear strengths, elastic moduli, fatigue behavior, creep, rupture stress, response to dynamic impact, and electrical parameters (electrical resistance and dielectric constant, for example), have been regularly investigated [3].

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