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Chapter 5

Thermoplastic Natural Fiber Based Composites

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Abstract:

This chapter is devoted to natural fiber reinforced thermoplastic composites. First, the various fibers used to prepare thermoplastic-based composites and their main properties are presented and analyzed. The problems to solve (fibers degradation, compatibility with the matrix) are discussed. Then, the methods of preparation of natural fiber-based composites are introduced. As it is the topic of Chapter 2, we focus mainly on the melt compounding by twin-screw extrusion and its specific difficulties: dispersion of the fibers, breakage mechanisms, and thermal degradation. Finally, an overview of the main properties of the natural fiber-based composites is included.

Key Words:

Lignocellulosic fibers, thermoplastic composites, mechanical properties, extrusion.

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Introduction

Thermoplastic composites reinforced with carbon or glass fibers have been used for a long time in the plastic industry, for applications in automotive, sport, aeronautics, and other fields [1-3]. However, the need to limit greenhouse gas emissions by reducing the weight of vehicles and the global trends towards a “greener” industry has led to the recent development of composites based on natural fibers. Indeed, these fibers are light, cheaper, have interesting mechanical properties, and are derived from renewable resources. They therefore appear as interesting potential candidates for the preparation of thermoplastic matrix composites. However, beside positive properties, natural fibers present also possess certain drawbacks that must be overcome to obtain satisfactory products. In this chapter, the main natural fibers used in the preparation of composites are presented, as well as their properties, and the main problems to be solved during composite preparation. Next, the processes used for this preparation, consisting essentially of compounding by twin-screw extrusion and shaping by injection molding, are considered. Finally, the main properties of these fiber-based composites are reviewed.

Presentation of natural fibers and fiber-based composites

Natural fibers have various origins. As shown in Figure 5.1, they may be mineral (asbestos, for example), animal (silk, wool, etc.) or vegetal. In this chapter, the focus is

on vegetal fibers, i.e. lignocellulosic fibers, which come from different products (wood, fruits, leaves, straw etc.) and different parts of plants. Some are specifically cultivated, like flax or cotton, while others are just waste resulting from agricultural activities, such as banana or pineapple leaf fibers (PALF). In this chapter, we pay attention to lignocellulosic fibers and we will not consider cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC), which are also used in composite preparation. We refer interested readers to specific reviews on this topic [4-7].

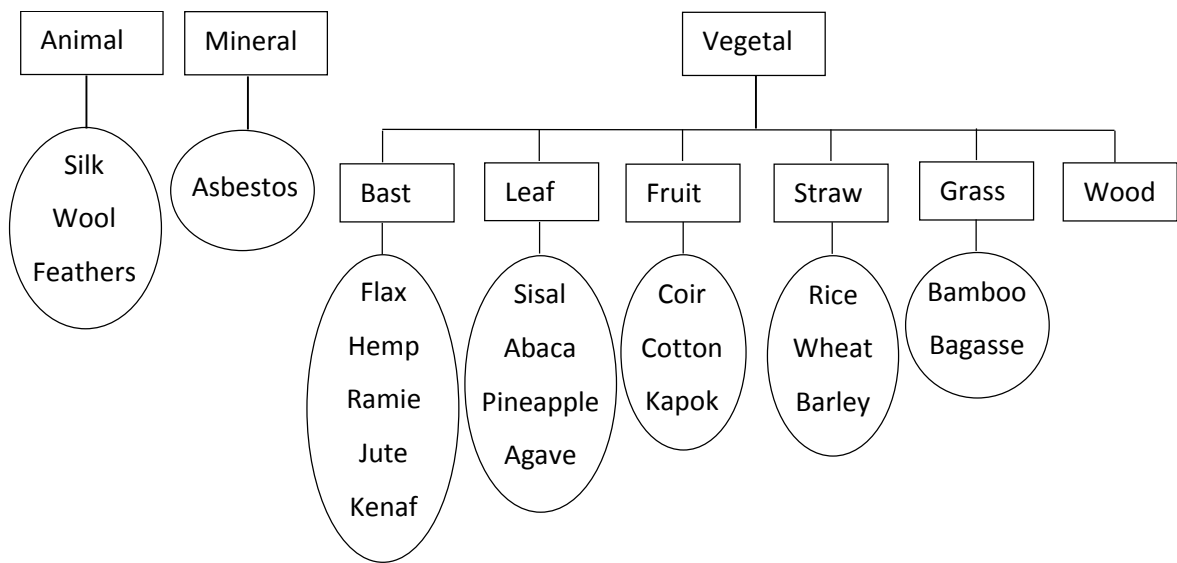


Figure 5.1: Classification of natural fibers (adapted from Zini and Scandola [8] and Gurunathan et al. [9])

Composition of natural fibers

Lignocellulosic fibers have a complex structure and can be themselves considered as composites [10]. They consist essentially of three components, namely cellulose, hemicellulose and lignin. Cellulose is the main component responsible for the mechanical properties of the fibers. Hemicellulose, lignin and pectin are the “cement” that binds

together fibers into bundles. Composition varies according to different factors [11], such as vegetal origin, age, climate, extraction technique etc. Typical compositions of the main lignocellulosic fibers are given in Table 5.1. These data were obtained from an extensive survey of the abundant literature on this topic [12-49]. It shows the large variability of fiber composition, even within the same species.

Table 5.1 Chemical composition of various lignocellulosic fibers according to the literature

Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Wax (%)
Flax	60-85	14-22	1-3	2-15	1-6
Hemp	55-90	10-22	2.5-6	1-3	1-2
Ramie	62-76	5-17	1-9	0.3-2	0.3
Jute	58-73	12-24	12-16	0.2-2	0.5
Kenaf	45-72	15-30	6-16	3-5	-
Sisal	53-78	6-26	8-14	10-14	1-2
Abaca	56-68	18-25	5-15	1-1.5	0.2
PALF	70-83	15-20	5-12	2-4	4-7
Coir	32-53	0.3-20	31-46	3-4	0.6
Cotton	83-98	4-6	0.7-2	0-4	0.6
Kapok	13-51	23-49	13-21	7-23	-
Bamboo	36-65	11-30	2-32	-	1-4

Properties of natural fibers

In addition to mechanical performance, the main attraction of lignocellulosic fibers as reinforcing agents for producing composites are its density and price. As the composition exhibit great variability, the same goes for mechanical properties. Moreover, the techniques of measurement play an important role (use of a stress gauge, slope of the stress-strain curve, true or apparent values, etc.). In addition, it is not always clear to

know if the results concern individual fibers or bundles. Nevertheless, a large review of the literature has allowed gathering the data presented in Table 5.2 [8, 16, 17, 20, 22, 23, 33, 35, 36, 44, 49-77].

Table 5.2 Properties of various lignocellulosic fibers according to the literature

Fiber	Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Price (\$/kg)
Flax	1.4-1.5	320-2000	10-103	1.2-3.6	1.7-2.7
Hemp	1.4-1.6	270-1110	14-70	0.8-4.0	0.7-1.7
Ramie	1.4-1.5	400-1000	24-128	1.2-4.0	0.5-1.1
Jute	1.2-1.5	114-800	8-78	1.2-1.5	0.5-1.1
Kenaf	1.2-2.7	223-930	14-60	1.6-6.9	0.4-0.6
Sisal	1.2-1.5	347-885	3-98	1.2-1.5	0.6-1.8
Abaca	1.5	270-900	17-90	1.0-6.2	0.5-1.3
PALF	0.8-1.6	170-1627	60-82	0.8-1.6	0.4-0.6
Coir	1.2-1.3	131-343	3-17	1.2-1.3	0.4-0.7
Cotton	1.2-1.6	287-800	6-13	1.2-1.6	0.6-2.2
Kapok	1.3	45-93	2-19	1.0-4.0	-
Bamboo	0.6-1.4	140-1610	11-89	1.3-8	0.3-0.5

Despite the large variations in properties, especially mechanical, lignocellulosic fibers present some common peculiarities. First, they are light (density typically in the range 0.6-1.6 g/cm³) compared to glass fibers (density 2.6 g/cm³). Second, they are cheap. Specific technical fibers of flax and cotton can reach 2-3 \$/kg, but the more common fibers remain below 1 \$/kg, whereas glass and carbon fibers are around 3-5 and 15-20 \$/kg, respectively. For all vegetal fibers, the elongation at break is limited (in the range 0.8-8%), similar to the values of glass (2.5%) and carbon (1.4-1.8%) fibers. In contrast, tensile strength (100-2000 MPa) may seem low compared to glass (2000-3500 MPa) and carbon (4000 MPa). For the most resistant fibers (hemp, flax, PALF), the Young's

modulus is close to or even higher than that of glass (around 70 GPa), but obviously lower than that of carbon (230-240 GPa). Generally speaking, the mechanical properties of lignocellulosic fibers are thus promising for their use as reinforcing agents, but they are even better if specific values are considered. The specific values are the actual values divided by the density. For example, the specific modulus is equal to 29 GPa.cm³/g for glass, similar to ramie, while it is much higher for flax (34-48 GPa.cm³/g) or for PALF (42-57 GPa.cm³/g). In the same way, the specific tensile strength of flax (220-1380 MPa.cm³/g) is comparable to that of glass (770-1340 GPa.cm³/g).

To summarize, the main advantages of vegetal fibers are their low density and high specific strength and stiffness. They are a renewable resource, the production of which requires little energy and can be obtained at low cost. However, they also present certain disadvantages. Compared to glass or carbon fibers, they have less durability and high moisture absorption. There is a great variability in the properties, due to weather or harvest conditions. They also have limited temperature of degradation, typically below 200°C, which reduces the possibilities of choice of the matrix and processing conditions [78, 79].

Thermoplastic matrices

Natural fiber reinforced elastomers are mentioned in Chapter 7 and thermosets in Chapter 8. The present chapter is focused on thermoplastic matrices. They can be divided into oil-based and bio-based or biodegradable materials. The oil-based matrices are typically polyolefins (polyethylene, polypropylene), polystyrene (PS) and poly(vinyl chloride) PVC. Among the bio-based ones, the most common are poly(lactid acid) (PLA) and polyesters such as poly(hydroxyl alcanoate) (PHA), poly(butylene succinate) (PBS), or

poly(butyrate adipate terephthalate) (PBAT). In fact, beside the mechanical or barrier properties of the selected matrix, two criteria must be considered for developing natural fiber-based composites. The first is the processing temperature. Indeed, most natural fibers begin to degrade above 200°C [80, 81]. Therefore, the melting and processing temperatures of the selected matrices should be low enough to avoid thermal degradation. The second criterion is the compatibility between fiber and matrix. Indeed, natural fibers are hydrophilic while main polymers are hydrophobic in nature, which leads to poor compatibility and limited interfacial adhesion, resulting in low mechanical properties. This problem can be partially solved by chemically or physically modifying the surface of the fibers. This is described in details in Chapter 3. Another solution, which will be used in this chapter, is to add a compatibilizer to the matrix, usually a polymer grafted with maleic anhydride [82-84].

Composite processing

The various manufacturing methods used for natural fiber reinforced composites are detailed in Chapter 3. Different types of composites can be prepared with natural fibers. For continuous filaments and long fibers, impregnation, lamination, pultrusion, and compression molding are commonly used. However, these techniques are mainly encountered in the case of thermoset matrices. For short fibers and thermoplastic matrices, the preferred process is melt mixing, i.e. extrusion and injection molding. In a first step, the fibers are mixed with the polymer matrix, generally using a twin-screw extruder, in order to obtain composite pellets. In a second step, these pellets are processed by injection molding, sometimes by thermoforming, to obtain a final shape. During the compounding step, the main problems to be solved are the homogeneous dispersion of

the fibers into the matrix and the breakage of the individual fibers or bundles. Indeed, the mechanical properties of a composite strongly depend on the filler aspect ratio, i.e. the length L divided by the diameter D [85]. When subjected to high stresses and strains, not only the length, but also the diameter, of the bundles can be greatly reduced and it is very important to understand and to limit these mechanisms. In the following section, we will thus focus on the compounding step, in particular on the mechanisms of breakage of the lignocellulosic fibers.

Preparation of natural fiber-based composites by twin-screw compounding

As explained above, the compounding of natural fibers into a thermoplastic matrix presents many challenges: the fiber attrition must be minimized, the temperature must be kept below 200°C, and the fibers must be homogeneously dispersed into the matrix. Among the various extrusion and mixing processes, co-rotating twin-screw extrusion is often preferred as it is a continuous process, very flexible, and with important mixing capacities. It is more and more used, as shown by the recent review of Gallos et al. [86].

Short presentation of the twin-screw extrusion process

A co-rotating twin-screw extruder is composed of two adjacent screws, rotating in the same angular direction into an eight-shaped barrel [87]. The screws and the barrels are modular, which makes it possible to define a screw profile adapted to each specific application. The screw profile consists of different elements, typically right-handed screw elements for conveying and restrictive elements (blocks of kneading discs or left-handed

screw elements) for mixing. The feeding is provided by volumetric or gravimetric feeders, allowing independence between the feed rate and the screw speed. A typical screw profile used for the preparation of natural fiber-based composites is shown in Figure 5.2.

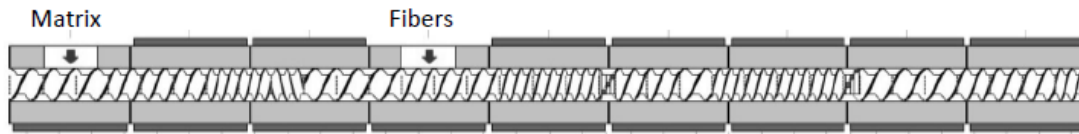


Figure 5.2: Example of screw profile used for the preparation of natural fiber-based composites. The flow goes from left to right.

The matrix in solid form, generally in pellets, is fed at the entry of the extruder. It is melted in the first restrictive element (here, a left-handed screw element) and the fibers are thus introduced into the molten matrix. Several blocks of kneading discs are then used to properly disperse the fibers. The composite finally flows through the shaping die and is cooled and pelletized after the die exit. The various barrel elements and the die are thermally regulated, according to the characteristics of the matrix. It is important to note that the fibers can also be premixed with the matrix pellets and introduced simultaneously into the main hopper but, in this case, the fiber degradation is largely aggravated [88-90]. Compared to solid pellets, the feeding of natural fibers may be more difficult. Indeed, the apparent density is very low and, as the fiber loading is typically between 20 and 50wt%, the volume to be introduced into the extruder can be very large. Therefore, fibers are sometimes compressed into pellets before being fed [91-92], but their dispersion is more difficult thereafter. In addition, fibers are flexible and can become entangled and form clusters that can sometimes block the feeders.

Breakage mechanisms

As shown by many authors, the strong thermomechanical conditions encountered during the extrusion process lead to the breakage of the lignocellulosic fibers [93-96]. As the fibers are usually assembled into bundles, the breakage induces a reduction in the length L but also in the diameter D , by fibrillation of the bundles and individualization of the fibers. Therefore, the aspect ratio L/D , which partially controls the mechanical properties, varies with the processing conditions. The breakage mechanisms of rigid fibers, like glass fibers, are well known and correctly modeled [97, 98]: in a shear flow, the fibers are aligned in the flow direction and, from time to time, rotate. During this rotation, they are subjected to compressive forces which, when exceeding a critical value, lead to a buckling and an immediate rupture. For the vegetal fibers, the mechanisms are different because these fibers are flexible. As deduced from rheo-optical observations [99, 100], the fibers break essentially by fatigue, after many bending. Unlike glass fibers, the breakage is not instantaneous and occurs preferentially at the level of fiber defects. To illustrate this mechanism, Figure 5.3 shows the fibrillation of a flax bundle and the breakage of an individual flax fiber in a shear flow.

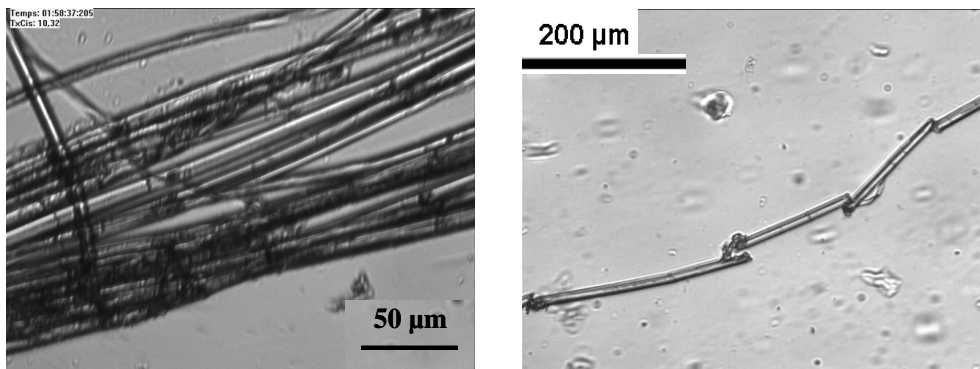


Figure 5.3: Rheo-optical observations of (a) the fibrillation of a flax bundle and (b) the rupture of an individual flax fiber (adapted from Le Duc et al. [99]).

To characterize the thermomechanical treatment applied to the fibers during the compounding process, several parameters have been used in the literature [88, 95, 99].

The first one is the specific mechanical energy (*SME*), which is expressed as:

$$SME = \frac{C}{C_{\max}} \frac{N}{N_{\max}} \frac{P}{Q} \quad [1]$$

where C is the torque, C_{\max} is the maximum torque, N is the screw speed, N_{\max} is the maximum screw speed, P is the motor power, and Q is the flow rate.

The second parameter is the cumulative strain, which can be written as:

$$\Gamma = \sum \dot{\gamma} t \quad [2]$$

where $\dot{\gamma}$ is the local shear rate and t the local residence time. The summation indicates that the local strain is cumulated all along the screw profile. *SME* can be measured experimentally on an extruder, but not Γ , which can only be calculated from theoretical considerations. Since the shear rate is proportional to N and the residence time to $A/Q + B/N$ where A and B are geometrical parameters [87], it can be deduced that the cumulative strain is proportional to N/Q . Γ can also be calculated more accurately using dedicated software allowing to define the flow conditions along the twin-screw extruder [101]. Anyway, by comparing the results obtained with an internal mixer under constant *SME* or constant strain conditions, it was recently shown by Di Giuseppe et al. [102] that the changes in the fiber dimensions were controlled by the cumulative strain and could be defined according to exponential functions:

$$L_w = L_\infty + (L_0 - L_\infty) \exp(-k_L \Gamma) \quad [3]$$

$$D_w = D_\infty + (D_0 - D_\infty) \exp(-k_D \Gamma) \quad [4]$$

where L_w (respectively, D_w) is the actual fiber length (respectively, diameter), L_0 (resp., D_0) is its initial length (resp., diameter), L_∞ (resp., D_∞) is its ultimate length (resp., diameter), and k_L (resp. k_D) is a breakage constant, quantifying the breaking kinetics. k_L and k_D obviously depend on the type of fiber considered.

Experimental observations of fiber breakage during twin-screw compounding

Many authors have reported the effect of extrusion conditions (screw profile, screw speed, feed rate, regulation temperatures, and sequence of introduction) on the final dimensions of the fibers in the composite [82, 89, 93-95, 103-107]. The fiber dimensions are generally characterized by 3D-microtomography [108, 109] or by 2D image analysis after dissolution of the matrix. Different techniques may be employed, which are more or less accurate depending on the case considered [110-112]. Usually, size distributions of length L , diameter D and aspect ratio L/D are measured over a population of at least a few hundred fibers, and average values are derived from these distributions. For example, for the length:

$$L_n = \frac{\sum_{i=1}^{Nc} n_i L_i}{\sum_{i=1}^{Nc} n_i}, \quad L_w = \frac{\sum_{i=1}^{Nc} n_i L_i^2}{\sum_{i=1}^{Nc} n_i L_i} \quad [5]$$

where Nc is the number of classes and n_i is the number of fibers of length L_i in class i . L_n and L_w are the average values in number and weight, respectively. In the following, the values in weight will be preferred because they give more importance to long fibers.

To better understand what happens during the compounding process, the best solution is to characterize the fiber dimensions not only at the die exit, but also all along the screws.

This can be achieved by stopping the extruder under steady state conditions, and by

rapidly cooling and extracting the screws or the barrel to collect samples. Such experiments have been performed by Berzin et al. [88, 113-116], El Sabbagh et al. [96], and Gonzalez-Sanchez and Gonzalez-Quesada [110]. As an example, we consider the screw profile of Figure 5.2, used to compound flax fibers of initial length 4 mm with a matrix of polypropylene (PP) and polypropylene grafted with maleic anhydride (PP-g-MA). The chosen composition is as follows: 78wt% PP / 2wt% PP-g-MA / 20wt% fibers. Different experiments have been carried out by varying screw speed and feed rate, and collecting samples all along the screws. An example of result is shown Figure 5.4.

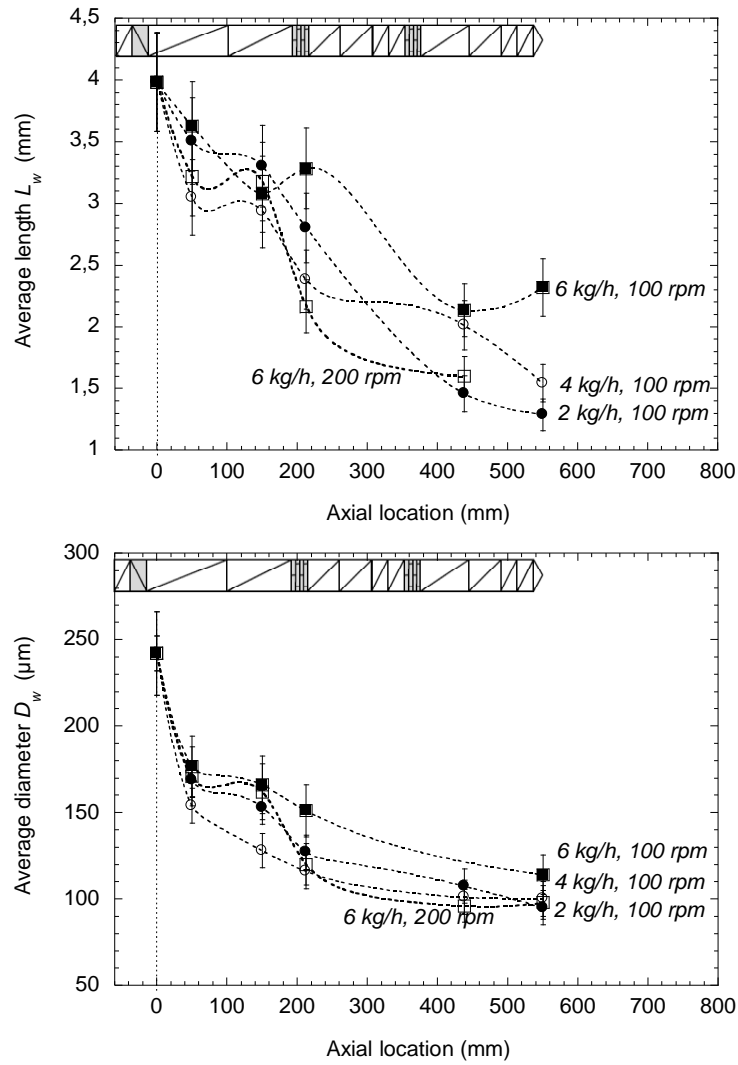


Figure 5.4: Change in weight average length (a) and weight average diameter (b) of flax fibers along the screw profile for various processing conditions: ■: 6 kg/h, 100 rpm; □: 6 kg/h, 200 rpm; ●: 2 kg/h, 100 rpm; ○: 4 kg/h, 100 rpm. The dotted lines are just to guide the eyes.

As soon as the fibers are introduced, they undergo a rapid decrease in length and diameter, even in screw conveying elements where flow conditions are mild. The decrease in dimensions goes on until the screw end, more or less rapidly depending on the location and the processing conditions. At the die exit, the fibers are shorter and thinner when the feed rate is reduced at constant screw speed, which can be explained by a longer residence time. The same observations can be made when the speed is increased at constant feed rate, which is related to a higher shear rate. In fact, as explained in the previous section, these changes are controlled by the cumulative strain supported by the fibers. This strain was calculated for the various locations and processing conditions using the Ludovic[®] software, developed by Vergnes et al. [101] and marketed by SCC company (SCC, Saint Etienne, France, <https://www.sccconsultants.com>). The results are shown in Figure 5.5.

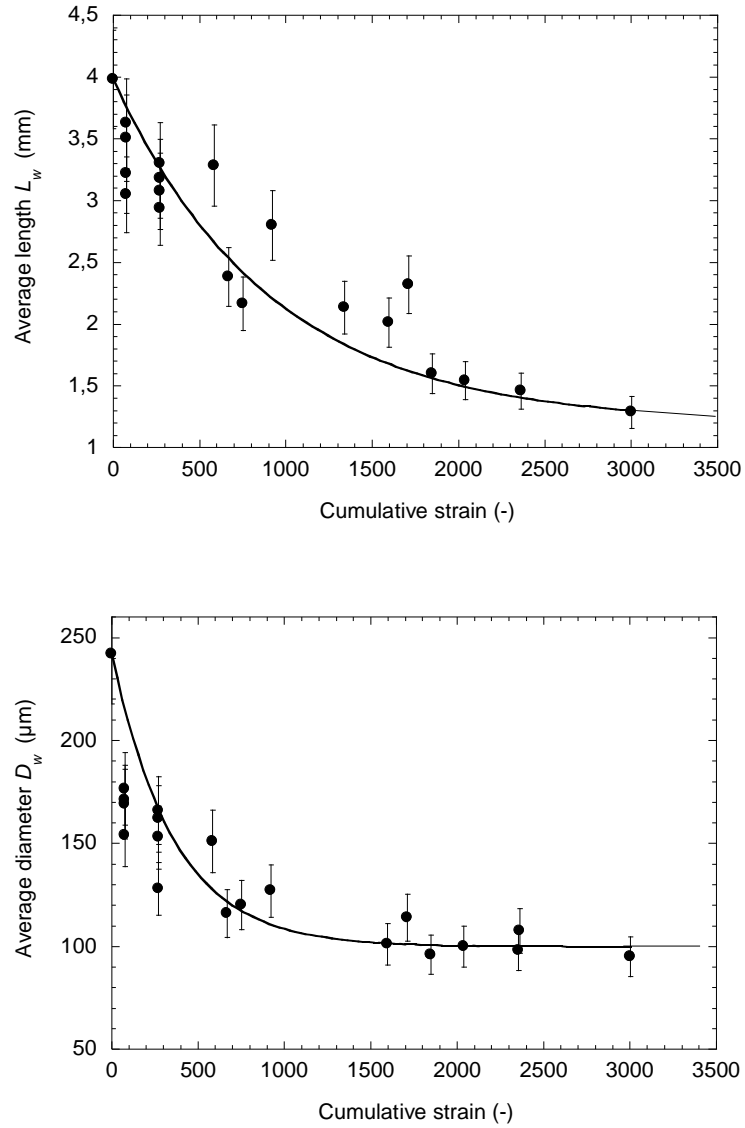


Figure 5.5: Change in weight average length (a) and weight average diameter (b) of flax fibers with the cumulative strain for various locations and processing conditions. The full lines are the fits obtained by using Eqs. 5.3 and 5.4.

A correct mastercurve is obtained whatever the conditions, confirming the validity of Eqs. 5.3 and 5.4 to describe the breakage mechanisms. The values of the breakage constants (1.1×10^{-3} and 2.8×10^{-3} for k_L and k_D , respectively) indicate that, for this particular fiber, fibrillation (separation of the bundles) is faster than breakage.

If the global trends presented here remain valid, whatever be the fiber and the thermoplastic matrix, the nature of the fiber and the matrix obviously plays an important role. For example, Figure 5.6 compares the behavior of flax and sisal fibers of the same initial dimensions ($L_0 = 12$ mm and $D_0 = 250$ μm).

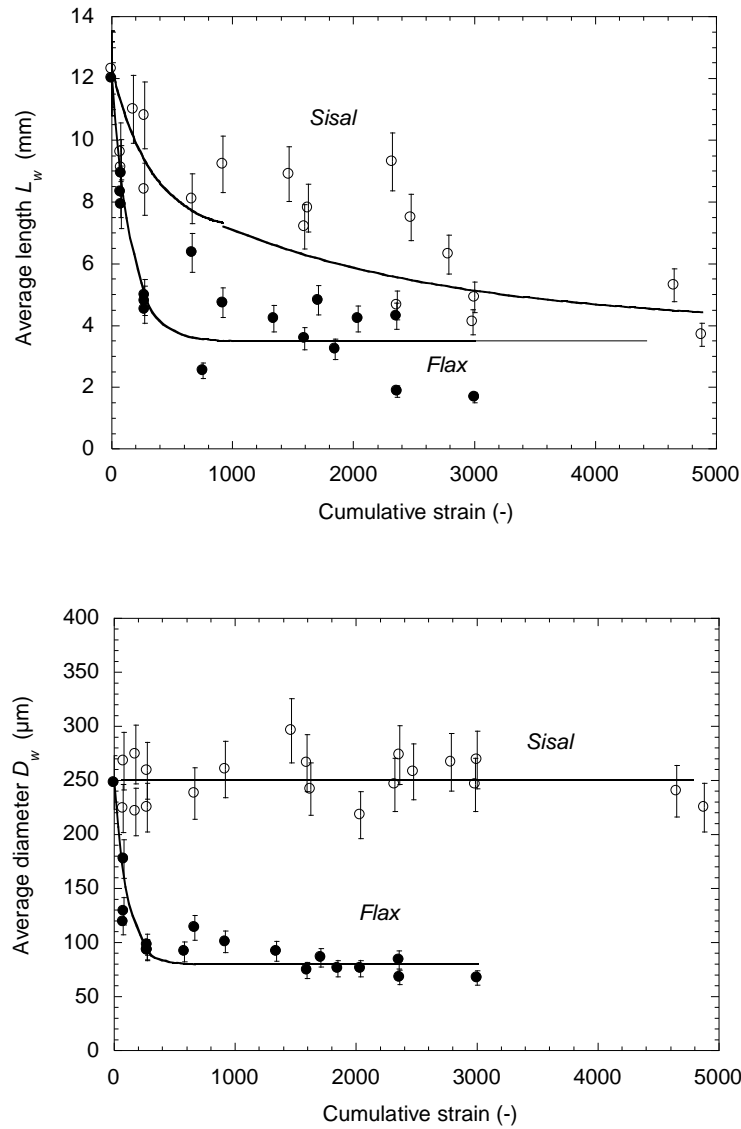
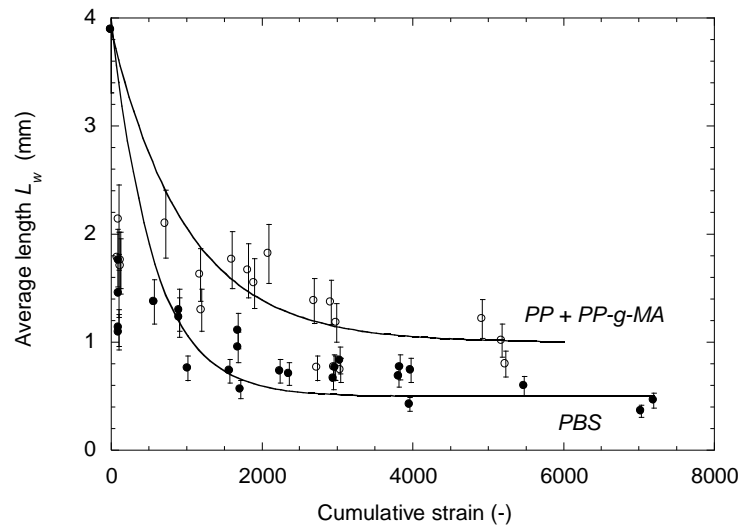


Figure 5.6: Change in weight average length (a) and weight average diameter (b) with the cumulative strain for various locations and processing conditions. Comparison between flax and sisal. The full lines are the fits obtained by using Eqs. 5.3 and 5.4.

It can be observed that the flax fibers break and fibrillate very quickly, while those of sisal break more slowly and do not fibrillate: their diameter remains fairly constant, even for large strains. These differences are related to the chemical composition of the fibers and their structure, inducing a different flexibility and cohesion of the bundles [100]: the sisal bundles are more cohesive than the flax because of their higher lignin content (see Table 5.1).

Similarly, for the same fiber and the same processing conditions, the properties of the matrix are also significant. A more viscous matrix has been shown to induce a more severe breakage [90, 117]. But, for similar viscosities, the polarity of the matrix is also crucial. Figure 5.7 shows the effect of the matrix (polar PBS and less polar PP+PP-g-MA) on the fibrillation and breakage of flax fibers. Under the same conditions, PBS leads to shorter and thinner fibers compared to PP+PP-g-MA. It has been proved by AFM measurements that it resulted from a better adhesion between flax fibers and PBS [116].



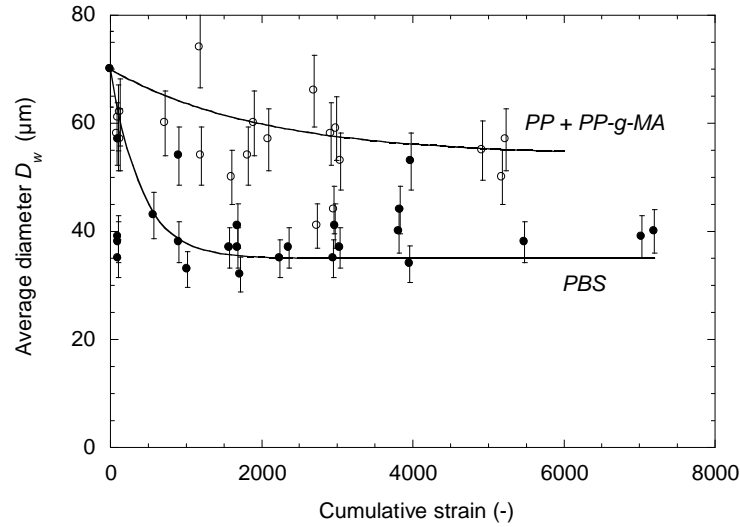


Figure 5.7: Change in weight average length (a) and weight average diameter of flax fibers (b) with the cumulative strain for various locations and processing conditions. Comparison between two matrices of similar viscosity. The full lines are the fits obtained by using Eqs. 5.3 and 5.4.

After compounding, the composite pellets are transformed into final objects during a second processing step, generally by injection molding. This process was much less characterized than the previous one. However, the few results of the literature show that fiber breakage is much smaller in this second step, probably because it is more difficult to break already shortened fibers [103, 114, 118-121]. Compared to extrusion, new problems arise in injection molding. The first is to properly fill the mold. The flowability of the composite is thus an important parameter, which can be tested using a spiral mold [122-123]. The flowability decreases as the fiber loading is increased. Moreover, it has been shown by El Sabbagh et al. [122] that the fiber content may change along the flow path, resulting in inhomogeneity of mechanical properties. As in extrusion, fiber dispersion and thermal degradation are important issues. For PP-based composites, they

can be improved by the addition of PP-g-MA, which “lubricates” the fibers and helps to decrease the injection temperature [117, 124, 125]. Finally, in the injected part, the orientation of the fibers directly controls the mechanical properties [126-127]. The flow conditions in the mold cavity can induce not only fiber orientation, but also high anisotropy. As the molten composite is injected into a cold cavity, a skin-core structure is usually observed [128-130]. The difference in flax fiber orientation between the center and the skin in an injected plate is shown in Figure 5.8. In the center, the fibers are nicely aligned in the flow direction, while, under the skin, the orientation is isotropic.

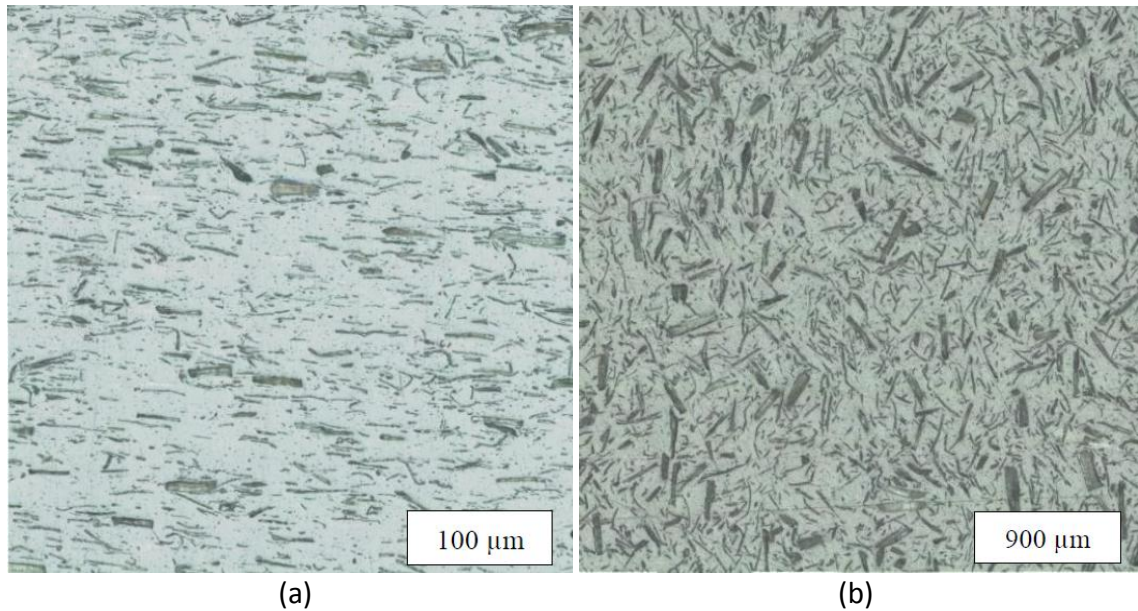


Figure 5.8: Orientation of flax fibers in an injected plaque (a) in the center, (b) under the skin. Flow direction is from left to right. (adapted from Abdennadher [129]).

Properties of natural fiber composites

Natural fibers are essentially used as reinforcing fillers to improve the mechanical properties of the matrices. But they can also lead to other interesting properties, such as thermal stability or enhanced matrix crystallinity.

Mechanical properties

Recent reviews on the mechanical properties of natural fiber composites have been proposed by Faruk et al. [131] and Pickering et al. [77]. The abundant literature on this topic focuses on tensile, flexural and impact properties. It is not obvious to draw general conclusions because these properties depend on many factors, related to fibers, matrix, and fibers in the matrix. The fiber is involved not only through its specific properties (strength, stiffness, flexibility, composition, structure, etc. See Tabs. 5.1 and 5.2), but also through its dimensions, specifically the aspect ratio L/D . Indeed, to efficiently transmit the stresses and reinforce the matrix, the fiber must have an aspect ratio higher than a critical value, expressed by:

$$\left(\frac{L}{D}\right)_{crit} = \frac{\sigma_f}{2\tau_i} \quad [6]$$

where σ_f is the tensile stress of the fiber and τ_i is the interfacial strength.

This critical value obviously depends on the selected materials, fiber and matrix. The mechanical properties of the matrix also play a great role. Finally, the last essential factors are the following: first of all, the amount of fibers, typically between 20 and 50wt%, and then, the state of dispersion of these fibers. Due to the strong hydrogen bonding between the fibers, their dispersion in a non-polar matrix is difficult and agglomerates of fibers with millimetric size may exist in the composite. The level of

dispersion can be estimated by measuring the relative surface area of these agglomerates on sample pictures [104]. In addition to dispersion, the fiber orientation is also an important factor, which depends mainly on the process used to prepare the composite. By using compression or hand lay-up and lamination techniques, it is possible to perfectly orient the long fibers in a certain direction. In contrast, by injection molding, only short fibers with a less controlled orientation can be obtained (see Fig. 5.8). Composites with long oriented fibers will obviously present better mechanical properties, but we focus here on the composites prepared by extrusion/injection, which are better suited to large industrial productions. For semicrystalline polymers, the degree of crystallinity, which can be increased by the nucleating effect of the fibers, is another important factor [132]. Finally, one of the most important parameters is the compatibility between the fiber and the matrix, i.e. the interfacial properties. Indeed, since the lignocellulosic fibers are hydrophilic while most of the thermoplastic matrices are hydrophobic, the adhesion between them is usually poor, which leads to inefficient reinforcement. To seek remedy to this problem, the fibers can be chemically or physically modified. This is explained in detail in Chapter 5.3. Another solution, which has become customary in compounding, consists of adding to the fiber/matrix composition a compatibilizer which will improve the interactions. The most common is a polymer grafted with maleic anhydride, since the hydroxyl groups of the cellulose tend to form covalent bonds with the maleic anhydride groups [133, 134]. An illustration of the role of compatibilizer is shown in Figure 5.9. It represents the fractured surface of PP-based composites filled with 30wt% ramie fibers, in presence or not of PP-g-MA (3wt%) [106].

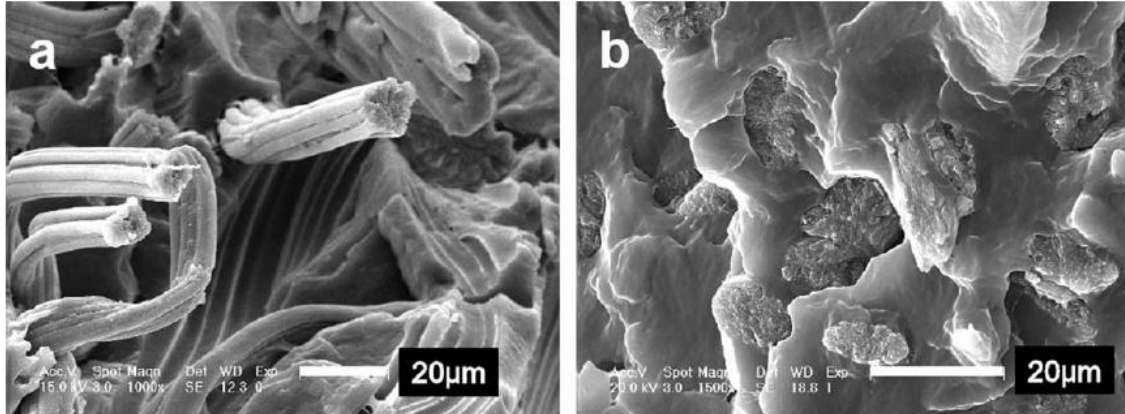


Figure 5.9: Fractured surfaces of PP-ramie composites, with (a) and without (b) PP-g-MA. (reprinted from Feng et al. [106], with permission).

Without PP-g-MA, most fibers are pulled out from the matrix and their surfaces are very smooth, indicating a poor adhesion. In contrast, with PP-g-MA, most fibers are fully embedded, confirming a strong interaction with the matrix.

Despite the huge variability of mechanical properties for the reasons exposed above, we will summarize below the main qualitative results we can draw from the literature.

Tensile properties

For PP-based composites, tensile strength and Young's modulus increase with the amount of PP-g-MA [135-137]. It has been reported that the optimal amount of PP-g-MA is around 5-10wt% based on the fiber content and 1.5-2.5wt% based on the matrix. However, this optimum value depends on the MA content and the melt flow index (MFI) of the compatibilizer, which influences the wettability of the fibers and the possibility to create entanglements with the matrix chains. Regardless of matrix and fiber, tensile strength and Young's modulus also increase with the fiber content [106, 115, 138-142]. The increase is more or less linear, as shown in Figure 5.10, with a maximum reached around 40-50wt%.

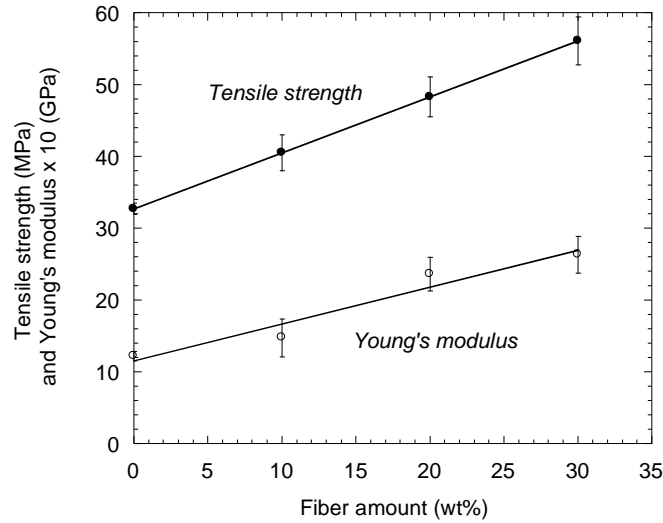


Figure 5.10: Changes in tensile strength and Young's modulus with fiber amount for PALF-PP composites. Young's modulus values have been multiplied by ten for a clearer presentation (adapted from Berzin et al. [115]).

Above this threshold, the dispersion and wetting of the fibers become difficult, which induces a decrease in the mechanical properties. Other parameters such as the orientation or the aspect ratio of the fibers are barely mentioned.

Flexural properties

As with the tensile properties, flexural strength and modulus are improved by the presence of a compatibilizer [143]. Both parameters increase with fiber content [91, 106, 119, 141, 142, 144].

Impact properties

In contrast to the tensile and flexural properties, the results on the impact properties are more subject of debate. The fracture behavior of natural fiber-based composites depends not only on the fiber properties, but also on their length, adhesion, orientation, dispersion and distribution. Moreover, the methods to characterize the impact strength are numerous

(Charpy, Izod, with samples notched or not), which leads to a sometimes difficult interpretation of the literature data. Anyway, some global trends can be derived. For natural fiber-based composites, the impact strength is in the range 5-29 kJ/m², and seems highly dependent on the matrix. If the matrix is ductile, the introduction of fibers tends to reduce the impact strength because the fibers create regions of stress concentration that require less energy to initiate cracks. The opposite effect is observed when the matrix is fragile. For example, a systematic reduction in impact strength compared to the matrix is observed with PP when filled with flax [93, 135, 143, 145], hemp [145, 146], kenaf [121], and cellulose fibers [91]. An increase in impact strength has only been reported by Bledzki et al. [119], but with long fibers (initially 15 mm, reduced to 2 mm after extrusion), and by Mihai et al. [92], but with very low values (around 3 kJ/m²). In contrast, with PLA, a systematic increase in impact strength is obtained by adding kenaf [147], hemp [146], jute [148], and abaca [119]. Surprisingly, Oksman et al. [149] are the only ones to report a decrease of impact strength for flax/PLA composites. Polystyrene (PS) also presents an increase in impact strength when reinforced with agave [150].

Since impact properties are highly dependent on the fiber/matrix adhesion, better results are obtained in the presence of PP-g-MA for PP-based composites [145, 146]. Moreover, the impact strength increases with the PP-g-MA content, with an optimal value around 5wt% (based on the fiber amount). The influence of the fiber content seems to depend on the type of fiber. For PP-based composites, the impact strength increases with the fiber content for flax [92] and sisal [143], but decreases for cellulose fibers [91], jute [143], and hemp [146]. It decreases for PHBV/hemp [103] and increases for polyamide 10-10/cellulose fibers [107].

Other properties

Thermal stability

Here also, the results of the literature are contradictory. The temperature of onset of degradation, detected by Thermogravimetry Analysis (TGA), is reported to decrease in the presence of fibers by some authors (Frollini et al. [151] for PBS/sisal, Lee et al. [152] for PP/kenaf and PBS/kenaf, Feldmann et al. [107] for PA10-10/cellulose), and to increase by others (Joseph et al. [132] for PP/sisal, Singha and Rana [150] for PS/agave). The reasons for this discrepancy are unclear. Nevertheless, Subasinghe et al. [121] indicate a lower combustion rate for PP/kenaf composites compared to pure PP.

Crystallinity

For PP-based composites, except Lee et al. [152], the majority of authors reports an increase in crystallinity with the presence of natural fibers (ramie, flax, sisal, kenaf, bamboo), which act as nucleating agents [92, 106, 132, 152, 153]. Moreover, the crystallinity increases with the fiber content [92, 106, 132].

Water uptake

One of the disadvantages of using lignocellulosic fibers as reinforcing fillers is their hydrophilicity, which leads to a high capacity of water absorption. Therefore, if a composite based on these fibers is subject to some water uptake, this can adversely affect mechanical or aging properties. All studies prove that water uptake is much greater in the presence of natural fibers [92, 117, 154-156]. This depends among other on the type of fiber, the type of the matrix, and the fiber content. Typical values are in the range 1-12wt%, for immersion periods in water between 15 and 330 days. For the same matrix and 20wt% fiber, Frollini et al. [151] have shown that water uptake is more important for

coconut, followed by sisal and curaua. Similarly, for the same kenaf fiber at 30wt%, Lee et al. [152] reported higher water uptake for PP compared to PBS. Regardless of the fiber and matrix, water uptake increases with fiber content [135, 157, 158] and, for PP-based composites, it is reduced by the introduction of PP-g-MA [135, 152, 159, 160].

Conclusions

Studies on natural fiber composites began in the early eighties. To our knowledge, one of the first papers on this subject was published by Belmares et al. in 1981 [161], on a thermoset resin reinforced by palm, sisal and henequen fibers. Since that date, interest in these materials has grown significantly. Searching on Google Scholar with “natural fiber composites” leads to about 10 200 references, including all kinds of fibers and matrices. In fact, by looking at the number of publications per year (Figure 5.11), it can be seen that these studies were principally developed after 2000, following an exponential growth, to reach more than 1300 publications in 2018.

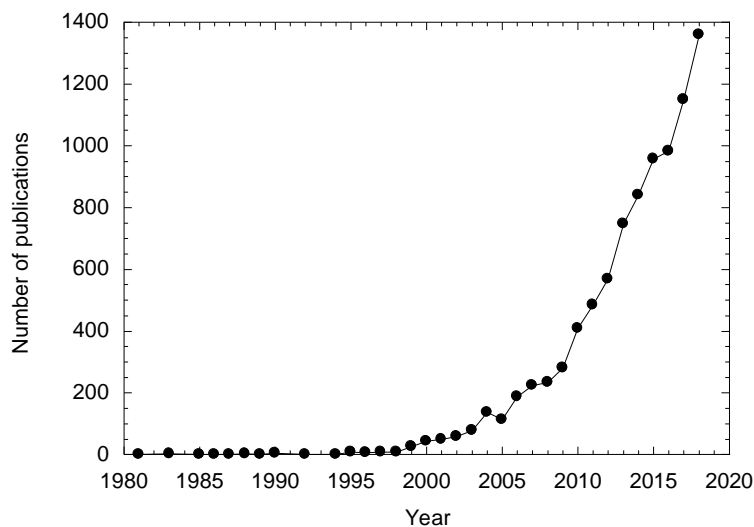


Figure 5.11: Number of publications by year on “natural fiber composites” since 1980 (data from Google Scholar).

Beside this scientific interest, concrete applications have been developed and, for example, it is now common to find natural fiber-based composites in automotive parts: for example, door panels for Audi, Peugeot, BMW, seat backs for Toyota, Volkswagen, instrumental panels for Mitsubishi, Opel, etc. With the huge problem of global warming, the trend towards using lightweight but strong materials is becoming increasingly crucial and it is likely that natural fiber composites will continue to improve and develop in the next future.

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