

**University of Patras**



**Department of Mechanical and Aerospace Engineering**

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*Development of green composites with flax fibers and study of their fracture behavior.*

*Ανάπτυξη πράσινων σύνθετων υλικών με ίνες λιναριού και μελέτη της θραυστομηχανικής τους συμπεριφοράς.*

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## Abstract

Nowadays the humanity faces a big challenge for its prosperity and continuous development. This challenge is about the protection of the environment and the right utilization of the materials and their corresponding energy for their process. Thus, the idea of twisting to more environmentally friendly materials constitutes a necessary step for the protection of the resources of the planet and the saving of big amounts of energy.

Natural fibers constitute an interesting proposal for substituting harmful for the environment fibers (like aramid and glass fibers). Their biodegradability and their general low environmental impact are some interesting features, which make them an ideal environmentally friendly solution. Also, their low cost, low weight and relatively good mechanical properties are some other positive aspects of their use.

Moreover, concerning the resins, which are used in the modern composites, researchers have developed some ecofriendly solutions (biobased resins). These biobased resins have a content, which derives from renewable sources, while they can be degradable or not. The use of biobased resins constitutes an alternative for substituting petroleum-based resins, which degrade sluggishly and provoke pollution due to their toxicity.

However, research for the materials with natural fibers and not conventional resins must be carried out in order to understand the behaviour of these materials. This research will constitute the base for the potential future applications of these materials, and it is essential to be done in order to attract the interest of various industries (e.g., automotive, energy). Thus, the mechanical characterization of these materials and their overall behaviour is a key parameter for their future applications.

In this thesis, it is studied extensively the use of natural fibers and especially flax fibers in green composites. Also, it is researched the sector of the biobased resins and how they can be manufactured. However, the main scientific interest of this thesis is the characterization of the interlaminar fracture toughness of composites with natural fibers. Different parameters, which can affect the behaviour of the composites are presented, while an extensive bibliography research is cited in order to cover the scientific work of other researchers.

## Περίληψη

Στις μέρες μας η ανθρωπότητα αντιμετωπίζει μια μεγάλη πρόκληση για την ευημερία και την περεταίρω ανάπτυξή της. Αυτή η πρόκληση αφορά την προστασία του περιβάλλοντος και τη σωστή αξιοποίηση των υλικών και της αντίστοιχης ενέργειάς τους για τη δημιουργία τους. Έτσι, η ιδέα της στροφής σε πιο φιλικά προς το περιβάλλον υλικά αποτελεί απαραίτητο βήμα για την προστασία των πόρων του πλανήτη και την εξοικονόμηση μεγάλων ποσοτήτων ενέργειας.

Οι φυσικές ίνες αποτελούν μια ενδιαφέρουσα πρόταση για την υποκατάσταση επιβλαβών για το περιβάλλον ινών (όπως οι ίνες αραμιδίου και γυαλιού). Η βιοδιασπασιμότητά τους και το χαμηλό περιβαλλοντικό αποτύπωμα είναι μερικά ενδιαφέροντα χαρακτηριστικά, που τις καθιστούν φιλική λύση προς το περιβάλλον. Επίσης, το χαμηλό κόστος, το χαμηλό βάρος και οι σχετικά καλές μηχανικές τους ιδιότητες είναι μερικά άλλα θετικά χαρακτηριστικά τους.

Επιπλέον, όσον αφορά τις ρητίνες που χρησιμοποιούνται στα σύγχρονα σύνθετα υλικά, οι ερευνητές έχουν αναπτύξει κάποιες φιλικές προς το περιβάλλον λύσεις (ρητίνες βιολογικής βάσης). Αυτές οι ρητίνες βιολογικής βάσης έχουν συστατικά, τα οποία προέρχονται από ανανεώσιμες πηγές, ενώ μπορεί να είναι βιοδιασπώμενες ή όχι. Η χρήση ρητινών βιολογικής βάσης αποτελεί μια εναλλακτική λύση για την υποκατάσταση των συμβατικών ρητινών, οι οποίες βιοδιασπώνται αργά και προκαλούν ρύπανση στο περιβάλλον λόγω της τοξικότητάς τους.

Ωστόσο, πρέπει να διεξαχθεί έρευνα για τα υλικά με φυσικές ίνες και ρητίνες βιολογικής βάσης για να γίνει κατανοητή η συμπεριφορά αυτών των υλικών. Αυτή η έρευνα θα αποτελέσει τη βάση για τις πιθανές μελλοντικές εφαρμογές αυτών των υλικών και είναι απαραίτητο να γίνει προκειμένου να προσελκύσει το ενδιαφέρον διαφόρων βιομηχανιών (π.χ. αυτοκινητοβιομηχανία, βιομηχανία της ενέργειας). Έτσι, ο χαρακτηρισμός των μηχανικών ιδιοτήτων αυτών των υλικών και η συνολική τους συμπεριφορά αποτελεί βασική παράμετρο για τις μελλοντικές τους εφαρμογές.

Στην παρούσα σπουδαστική εργασία μελετάται εκτενώς η χρήση φυσικών ινών και ιδιαίτερα των ινών λιναριού σε πράσινα σύνθετα υλικά. Επίσης, ερευνώνται οι ρητίνες βιολογικής βάσης και πώς μπορούν να δημιουργηθούν. Ωστόσο, το κύριο επιστημονικό ενδιαφέρον της παρούσας σπουδαστικής εργασίας είναι ο χαρακτηρισμός της διαστρωματικής αντοχής σε θραύση των σύνθετων υλικών με φυσικές ίνες. Παρουσιάζονται διάφορες παράμετροι που μπορούν να επηρεάσουν τη συμπεριφορά των σύνθετων υλικών, ενώ παρατίθεται εκτενής βιβλιογραφική έρευνα προκειμένου να καλύψει το επιστημονικό έργο άλλων ερευνητών.

# Chapter 1: Composite materials

## 1.1 Introduction

Material science constitute a multidisciplinary field, which combines sectors like physics, chemistry, biology, mechanical, chemical, and structural engineering. The cooperation between scientists of different specialization is intended to obtain high-performance materials, which can substitute already existing materials with lower overall properties. In the following figure is shown the interaction of different science sectors with material science.

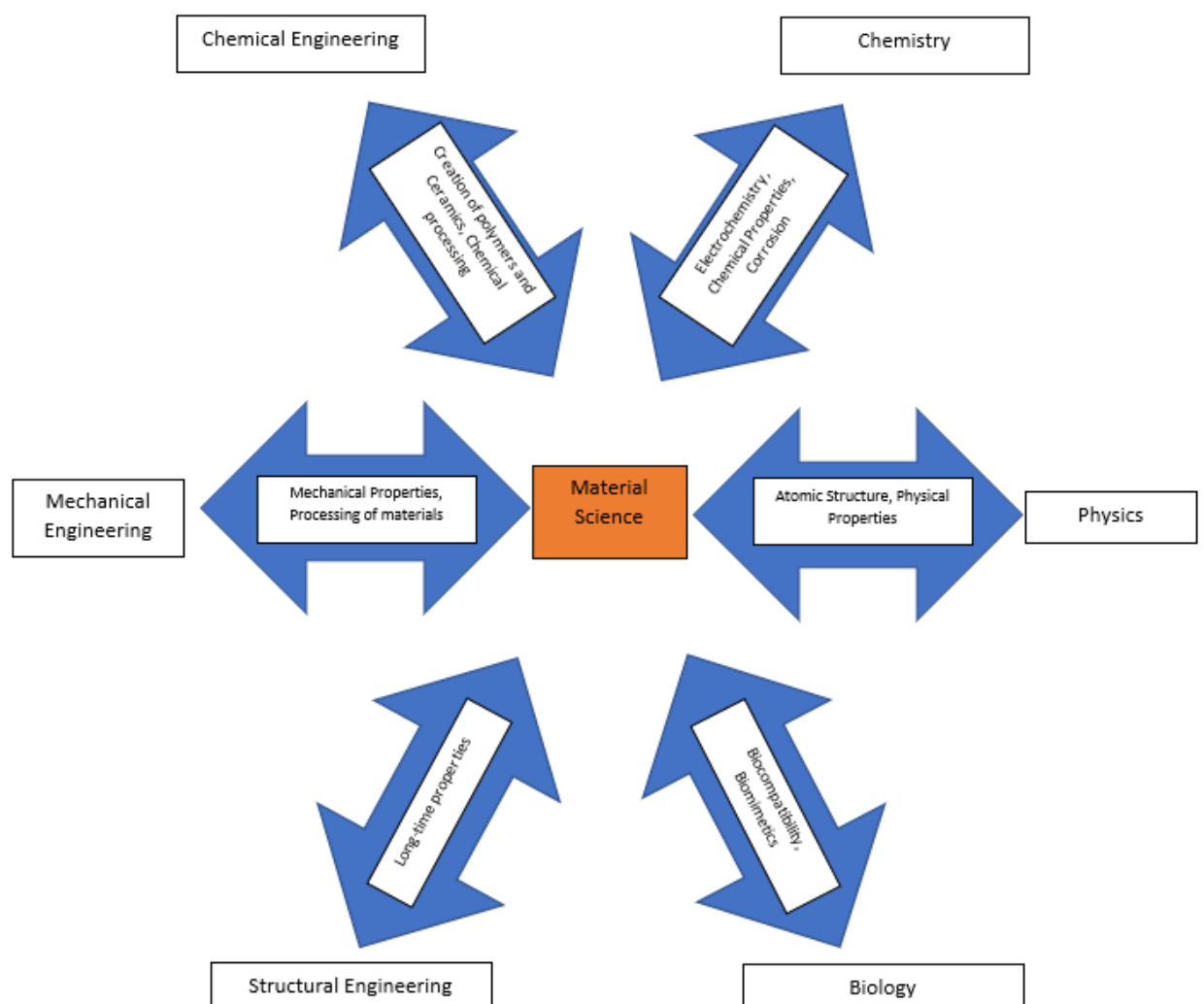


Figure 1. Interaction of different scientific fields with material science.

The new materials, which are used the recent years, are characterized for their simultaneously augmented strength and decreased weight. This aims in the overall energy saving and in applications of high-end performance. Indeed, these materials have influence on big high-tech structural sectors like automotive, aerospace and aeronautics.

In the category of new materials are subjected the composite materials. This category is interesting for the engineers due to their non-ending combinations. The intrinsic flexibility of composite materials is explained by the fact that they can be adjusted depending on the application, which are intended for. This major advantage is the reason, why composite materials have gained much popularity and can be applied in more and more constructions. Unfortunately, it is difficult to fully define the term composite materials, as it comprehends many concepts. Nevertheless, it is accepted that the main characteristic of composite materials is the anisotropy, which explains the different properties depending on the direction of the materials. This characteristic is the reason, why composite materials are so easily adjusted in each case scenario, and it gives major possibilities in design.

Composites could be defined by the combination of two or more different materials connected in macroscopic or microscopic way with the view of creating a multiphase system with dissimilar physical properties from these of the initial materials. The term phase involves any homogenous part of the composite material. The two easily distinct phases of the composite materials are the matrix and the reinforcement. The matrix has the biggest proportion in the system of composite material, and it is considered continuous, while the reinforcement is discontinuous and dispersed into the system.

Moreover, it is observed a region between the two phases of the composite materials, which is called interphase. This region appears to have different physical properties of the initial materials and it constitutes a transition zone between the matrix and the reinforcement.

In general, matrix and reinforcement have different responsibilities in the system of a composite material. The role of matrix is to keep the reinforcement and to provide the shape. Also, it protects the composite from the environment and handling, while it transfers the load to the reinforcement. Moreover, as a continuous phase, the matrix has influence on the transverse properties of the composite. On the other hand, the reinforcement has a dominating role in enhancing the strength and the stiffness of the composite, while it may also determine the thermal and electrical properties of the material.

## 1.2 Historic review of composite materials

From a historical point of view, composite materials are not considered new materials. On the contrary, humankind discovered these materials many years ago. Economic reasons, and the shortage of some resources have led to a higher demand of composite materials in the recent years. People have invented composite materials from the antiquity to facilitate their quality life. At the beginning, materials from the physical environment like wood, stone, clay and bones were used. The continuous experimentation of combining different natural materials, in time, has led to new composite materials, which have better properties and could cover new emerged needs.

The first composite materials known today, were constructed by the Babylons at the period of 4000-2000 B.C. The evidence for this is derived from the Bible in the chapters of Genesis and Exodus. Later in Egypt, around 300 B.C., many citations describe the construction of rafts from papyrus reeds immersed into tar. Also, Assyrians around 1000 B.C. used boards, which were immersed into waterproof asphalt, in order to construct boats (known as gufas). Similarly, the Greeks around 500 B.C. used reinforced materials to manufacture the famous triremes.

Beyond the marine field, composite materials were used in the construction field. Egyptians in 5000 B.C. reinforced the clay bricks with straw, aiming to the reduction of contraction stresses, which were provoked by the drying of the clay. Also, in Mesopotamia, around 1000 B.C., the coating of bricks and tiles was applied by restricting the surface wear, while during Romanian times ceramic frits were used for the reinforcement of roadworks.

Moreover, there are many citations throughout the human history concerning the construction of weapons, which were created with a combination of materials. Around 1000 B.C., an arc was constructed in west Asia with laminates of horns, resulting in a robust and lightweight arc, which could be used from riders. Furthermore, Mongolians created arcs with a wider variety of materials like wood, silk and tendon of animals, while a similar laminated technique was observed in the swords of Japan.

Concerning ancient Greece, citations about shields are made in Homeric epics. Specifically, in Iliad, the shield of Achilles is described as a very strong weapon. 5 laminates of metals were used to create the shield, while each layer of metal represented a different part of life. The parts of life were linked with the following metals: gold, silver, bronze, tin and iron. Also, the shield of Agamemnon is described in the Iliad of Homer. This shield is described as a beautiful full-body piece with fringes. The different layers were bonded with screws and hoops from copper. Overall, the Greek shields were known for their stiffness and strength against the penetration of hostile spears and arrows.

Additionally, special reference should be made for the evolution of paper. Papyrus was the most famous material for stationery in the Antiquity, until the end of Roman Empire. This material was flourishing at the Nile's riverside in Egypt and at the region of Syracuse in Sicily. After, parchment was used for the first time in 197 B.C. from the king of Pergamon, Eymenis the second. Parchment was fabricated by the leather of animals and thin sheets of them were created as a new version of modern paper. The discovery of the current paper was made in China, but the technique of fabrication was not known in Europe for centuries. Meanwhile,



Arabs changed the procedure of construction of paper concerning the raw material, as they used local resources like flax and hemp.

In general, the evolution of composite materials does not appear to have the same rate in time. Until the 19<sup>th</sup> century, this development was very restricted and the materials, which were used until then, were not very different from those of the Antiquity. The real progress was made in the 20<sup>th</sup> century with the parallel evolution of polymers.

In 1940s, due to the World War II, the FRP industry has implemented its knowledges from the research to production. Strong, lightweight, and weather resistant materials were used for the war industry. Then, chemists also made the important discovery that the fiberglass composites were transparent to radio frequencies, promoting to the use of these materials in radar domes and other electronic equipment. In 1942, US Navy took advantage of this discovery and substituted electrical terminal boards with the use of fiberglass-melamine composites. Furthermore, the emerging automotive industry, during that time, introduced two processes (compression molding of sheet molding compound-SMC and bulk molding compound-BMC). Also, the use of pre-impregnated sheets made the development of composites simpler.

In 1950s, the evolution of pultrusion process, vacuum bag molding and large-scale filament winding was made. The process of filament winding was essential for the cases of large-scale rocket motors, which were used in the aerospace industry. Huge effort was made to find materials that would allow spacecrafts to go to space and re-enter into the Earth. The heat, which was generated by this procedure could exceed 1500 °C, which was prohibitive for any material known these times. Also, in 1953, the first car made with fiberglass/polyester body panels appeared in the automotive industry.



*Figure 2. Chevrolet Corvette-1953, the first car made of fiberglass/polyester panels.*

In 1960s, carbon fibers and high stiffness and strength boron fibers were appeared. Carbon fibers, due to their lower cost and superior processing capabilities, had gathered the main scientific interest. Applications of these materials regarded the aerospace, the automotive, the sporting and the consumer goods.

In 1970s, the automotive market became the leader of using composite materials, leaving behind the marine market, concerning the use of composite materials, taking the first place. Also, sporting goods like tennis rackets were reinforced with carbon fibers more and more. The improved strength and lower weight of graphite permitted tennis rackets to increase the

velocity of the tennis ball. Also, in 1971, DuPont made the scientific discovery of Kevlar, an aramid-based fiber.

In 1990s, there was a major interest in extending the knowledge of materials to even smaller scale. Hybrid materials, which contain organic and inorganic components at molecular scale, were investigated. A new design strategy emerged at that time, which is called biomimetism. Hybrid materials tried to imitate the nature and replicate its characteristics. Moreover, nanocomposites gained ground from that time, which can offer improved mechanical strength, toughness and electrical or thermal conductivity.

In 2010s, the development of 3D printing enabled manufacturing objects into homes and small businesses. Thus, anyone could create any object with the only requirement of a CAD program on their desktop. With this convenience, emerging frontier materials were created, with a big range. Indeed, from toys and jewelry to aircraft apparel was made possible to be created. Also, in 2016, the development of 3D printed continuous fiber-based composites paved the way for 3D parts with enhanced material properties.

In the following figure is depicted the historic evolution of materials and their importance through time.

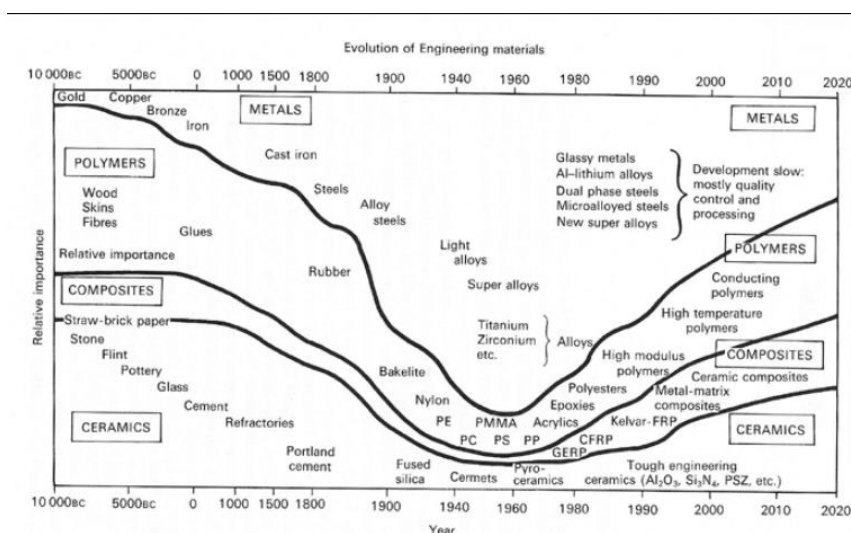


Figure 1.1 Schematic diagram showing the relative importance of the four classes of materials (ceramics, composites, polymers and metals) in mechanical and civil engineering as a function of time. The time scale is nonlinear. (Source: Ashby, 1987.)

Figure 3. Historic evolution of materials.

### 1.3 Classification of Composite Materials

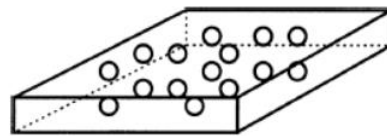
Composite materials can be classified into different categories depending on different parameters each time. The classification can be done concerning the nature of the materials used, the type of the reinforcement or the matrix and other characteristics.

The main criterion of classification of composites is the type of the matrix material. Thus, composites can be separated into the following categories:

- **Polymeric Matrix Composites (PMC)** are the materials which use as matrix a polymer and they are reinforced with any reinforcing phase. PMCs are the most famous composites with a big range of applications on different sectors. Their popularity is attributed to the low cost and the simplicity of fabrication methods. Moreover, it is not usual to see non-reinforced PMCs, because of their low mechanical properties. On the contrary, PMC materials can offer the following properties: high tensile strength, stiffness, fracture toughness, good abrasion resistance and good corrosion resistance. The main disadvantages are focused on the low thermal resistance and high coefficient of thermal expansion. They find applications on many sectors, including sport goods, secondary load-bearing aerospace structures and automotive parts.
- **Metal Matrix Composites (MMC)** are the materials which use as matrix a metal material. They are usually reinforced with ceramic (oxides, carbides) or metallic (lead, tungsten) reinforcement. Metallic matrices, versus polymeric, poses the asset of their application on cases which require long-term resistance to harsh environments. Also, the strength and modulus of the most metallic materials are higher in comparison to the polymers. The advantages that offer MMCs are the following: high compression strength, high specific strength and stiffness, fire resistance, operation in wider range of temperatures, better electrical and thermal conductivity, no absorption of moisture, low weight, and good damping. The drawbacks of MMCs concern their big density and their hardness to fabricate, leading to constructions of weight and cost respectively. Lastly, an additional classification can be made concerning the type of the metallic matrix. Thus, there are 4 categories: aluminum, magnesium, titanium, and copper matrix composites.
- **Ceramic Matrix Composites (CMC)** are the materials which use a ceramic matrix. These composites can use various types of materials for reinforcement like metals, polymers, glasses, and ceramics. Nevertheless, they are not usually reinforced with glass, organic or metallic fibers because ceramic matrix composites are often used at high temperatures and therefore a stability of the fiber at these temperatures is desired. Generally, the main reason to create CMCs is to enhance the toughness of monolithic ceramics because of their brittle nature. Whiskers and short fibers are used often as reinforcement to enhance the resistance of crack propagation, despite the fact that they can provoke a catastrophic failure. Also, it must be noted that long or continuous fibers are also used and they give better strength in comparison to the previous mentioned reinforcements. Moreover, they offer improved toughness due to the fact that they hold the ceramic matrix composites together. Generally, CMC composites reveal significant corrosion resistance, good compressive strength, and resistance at high temperatures. They are widely used in applications where high temperatures take place like pistons and rotors.

Another classification that can be made is based upon the type of reinforcement. According to this criterion, composite materials can be classified into the following categories:

- **Particulate Composites:** In this category, the reinforcement is in the shape of particulates. Particles can have virtually any shape, size or configuration. Particulate composites usually have less strength and stiffness than continuous fiber composites. On the other hand, they are usually gained at a lower cost. Also, particulate composites can achieve contents of reinforcement up to 40-50%, because of their difficult processability and brittle nature. Composites with particulates are usually isotropic because the particles are added randomly. The most widely used composites have a polymer matrix but there can be found particulate composites with metal or ceramic matrix. The most well-known particulate composite is considered the concrete.



*Figure 4. Particulate composite material.*

- **Fibrous Composites:** In this category, fibers which are characterized for their high strength and modulus are used in a matrix with a certain or not certain direction. Typical fibers are considered glass, aramid, and carbon fibers. Generally, fibers can be from ceramic, polymer, or metal material. A fiber is characterized by its aspect ratio (length/diameter) and due to its small diameter, it contains fewer defects compared to the corresponding bulk material. Continuous fibers (e.g., unidirectional, woven cloth and helical winding), normally with preferred orientation, have high aspect ratios, while discontinuous fibers (e.g., chopped fibers, random mat), usually random orientated, have low aspect ratios. Also, it must be noted that a general rule is that the smaller the diameter of the fiber, the higher is its strength, while the fibers with smaller diameter have greater flexibility and are more easily handled in fabrication processes. The chemical and physical properties of fibers and matrix are preserved. However, the resulting effects of their combination cannot be gained with either of constituents acting alone. Application of fibrous composites can be found in domestic appliances, electrical devices, athletic goods, structural components, parts of transport vehicles and in the aerospace industry.

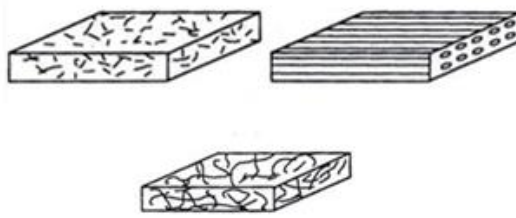


Figure 5. Types of fibrous composites.

- Laminated Composites:** In this category, the matrix material and the reinforcement are combined in a form of sheet. These composites are constituted by layers (plies) which are stacked to create a laminate sheet. A layer can use many types of reinforcement like UD fibers, short fibers, woven or braided fibers. The adjacent plies which have the same orientation are known as ply group. Finally, these composites have usually improved strength, stiffness, corrosion resistance, wear resistance, acoustic and thermal insulation.

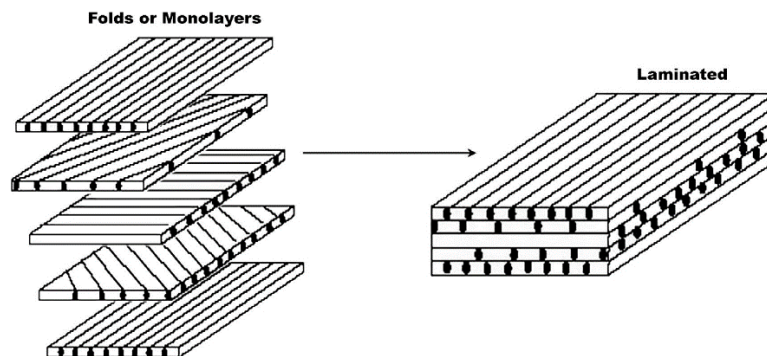


Figure 6. Typical laminated composite.

- Sandwich Composites:** A sandwich composite is a material with two thin, but stiff, skins and a lightweight, but thick, core. The most used core materials are honeycomb and foams. The skins are attached to the core using adhesives or by brazing together the parts in the case of metal components. The foam cores are used when the characteristics of waterproof, sound and heat insulation of cores are desired. The honeycomb has a higher stiffness to weight ratio in comparison with the foam core, but its intrinsic problem is that it has small adhesive area, which can occur debonding. Generally, the sandwich materials are used for improving the bending stiffness and for obtaining lightweight structure. Also, the impact energy and the absorption of mechanical oscillations are usually improved.

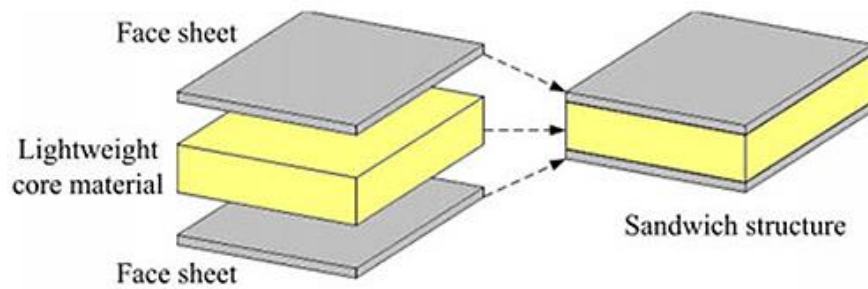


Figure 7. Sandwich composite.

- Natural Composites:** The composites, whose parts are already in nature and their structure and behaviour are similarly with the remaining composites, belong to this category. Typical natural composites are the following: wood, bones, bamboo and muscles. The cylindrical cells of wood, which have orientation parallel to the stem, are considered as reinforcement like the glass fibers in a composite, while the strength of the wood is related to on the orientation of the cells. Another natural composite is considered the bone. The organization and composition of the bone at different hierarchical levels (from the molecular level to the macrostructural level) affect its overall mechanical properties. In the following figure are shown the structure of bones at different scales.

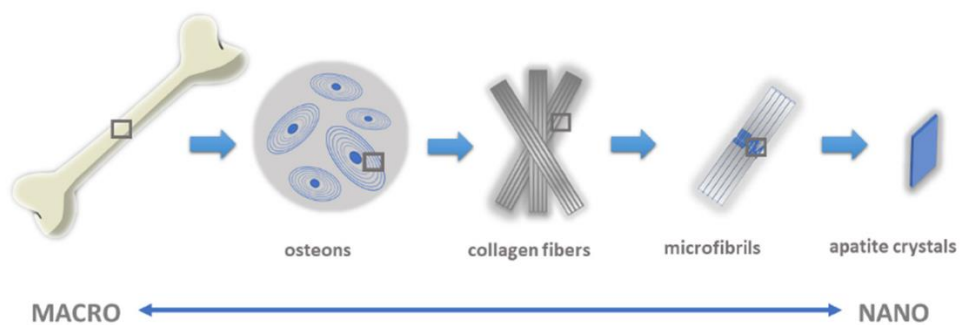


Figure 8 Structure of bones at different levels



Figure9. Wood.

- Green Composites:** In this category, composites, that are environmentally friendly, are included. The predominately green materials are those which come directly from nature, while there are others which are considered as green due to the fact that they are biodegradable. Therefore, there's the category of biobased materials (which come



from renewable resources) and the category of biodegradable materials (which come either from renewable or fossil fuel sources).  
In the following figure are shown some bioplastics which either belong to the biobased and/or biodegradable category.

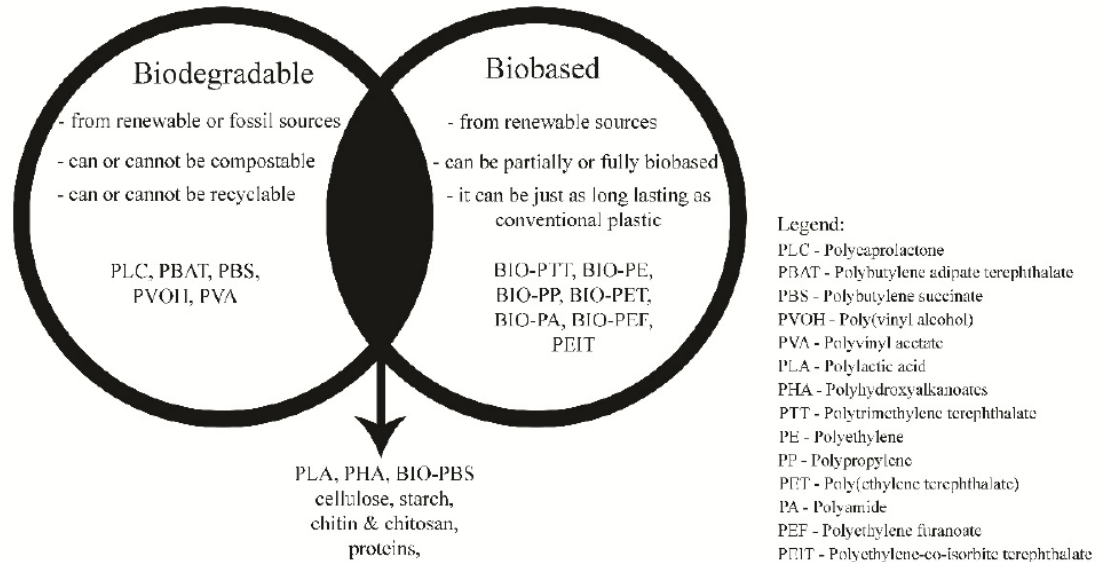


Figure 10 Bioplastic and differentiation between the groups of biobased and biodegradable polymers



Figure 11 Prepreg layers with PLA and flax fibers, as a green composite.

Another classification of composite materials concerns the shape and the size of reinforcement used. Therefore, the following categories are distinguished:

- Long-continuous fibers within the matrix, which can be parallel or randomly oriented.
- Short fibers within the matrix, which can be parallel or randomly oriented.
- Particulates, which can have any shape, size or configuration.
- Very tiny particulates, which have a diameter less than  $10^{-8}$ m.
- Reinforcement with lamina form.
- Interconnected networks.
- Hybrid composites with particulates and fibers.

Besides the shape of the reinforcement, the size can be a criterion for the classification of the composite materials. Thus, composite materials can be separated according to the order of magnitude of the reinforcement size:

- **Macro-composites:** This category includes composites, which have a reinforcement with a size ranging from a few millimeters to meters.
- **Micro-composites:** This category includes composites, which have a reinforcement with a size in the range of micrometer.
- **Nano-composites:** This category includes composites, which have a reinforcement with a size in the range of nanometer. Typical nanocomposites are the ones with carbon black, silicas, clays, carbon nanofibers and carbon nanotubes.

Moreover, depending on the material of the fiber, a classification of composites can be made.

- **Glass fibers:** are created by mixing materials like sand, silica, clay, calcite and colemanite. By changing the different contents of each material, different types of glasses can be formed. Thus, there are many types of glasses, which reveal different characteristics like alkali resistance or high mechanical properties. Generally, there are three well-known types of glass fibers:

1. **E-glass** (E for electrical) is the most well-know glass fiber type, which is used. It has big strength and modulus, while it displays good electrical properties.
2. **C-glass** (C for corrosion) is the most robust fiber against chemical corrosion. It reveals less strength compared to E-glass and it is the most expensive.
3. **S-glass** (S for stiffness) is more expensive compared to E-glass, but it displays bigger modulus of elasticity and high temperatures resistance. It is usually used in the aerospace industry.

In the following table is shown some typical properties of glass fibers:

Glass Fiber Type	Description	Density (g/cm <sup>3</sup> )	Tensile Strength (GPa)	Young's Modulus (GPa)
E-glass	E for good electrical insulation	2.54	1.7–3.5	69–72
S-glass	S for high silica, able to withstand high temperatures	2.48	2.0–4.5	85
C-glass	C for corrosion resistant	2.48	1.7–2.8	70
Cemfil	Alkali resistant glass fiber	2.70		80

*Figure 8. Typical properties of glass fibers.*

One of the principal advantages of using glass fibers for reinforcement in polymers is their high performance against low cost. However, the glass fibers suffer from a reduced tensile modulus (less than 100 GPa), which is one of the lowest among all the fibers and whiskers. In addition, the high density of the glass fibers (more than 2.4 g/cm<sup>3</sup>) prevents their uses from many applications, where light structures are needed. Other glass fiber shortcomings include low fatigue resistance, high sensitivity to abrasion during handling and high hardness.

- **Carbon fibers:** Carbon fibers have a relatively small diameter (5–10µm) and are mainly made of carbon atoms. They are characterized for their superior mechanical



properties (high strength and stiffness), their low thermal expansion and low weight. These assets made carbon fibers very attractive to the aerospace, military, motorsports, and sports industries. Nevertheless, they are considered an expensive solution in comparison to other fibers, like as glass or plastic fibers. Also, there can be a further classification based on modulus, strength and final treatment temperature.

- **Polymer fibers:** The most famous polymer fibers are considered nylon, polyethylene, and Kevlar. They do not reveal very high mechanical properties, but their low cost of production makes polymer fibers very famous. Aramid fibers (commercially known as Kevlar) belong to the aromatic polyamide class. There are many categories depending on their molecular structure (e.g., Kevlar 29, Kevlar 49, Kevlar 149). Generally, aramid fibers are known for their high stiffness and toughness properties. Also, they reveal good tensile properties and low compression properties., while they show a vulnerability to visible or ultraviolet light (it can lead to discoloration).
- **Metallic fibers:** In this category are included fibers, that are made of metal, plastic-coated metal, metal-coated plastic or a core completely covered by metal. They constitute an interesting category, because of their remarkable mechanical properties. Nevertheless, it cannot be omitted that the specific strength of metallic fibers is inferior to high performance carbon, polymer or ceramic fibers due to their higher density. Extra disadvantages can be considered the poor corrosion resistance and inferior bonding strength with matrix.
- **Ceramic fibers:** In this category are included fibers that are very robust to high temperatures. Despite this characteristic, all of these fibers are brittle and flaw-sensitive materials. As a result, they are susceptible to crack propagation.
- **Natural fibers:** These fibers are taken from sources which are considered biobased. These sources are including vegetables and animals. The most famous subcategory is the bast fibers, which belong to the vegetable fibers. Generally, bast fibers are a sustainable form of reinforcement in composite materials, while they are easily recyclable and are characterized for their no-toxicity. Also, they are cheaper, have lower density and lower energy of consumption in contrast to the synthetic fibers (like glass and carbon fibers). Moreover they have good fracture resistance, good sound absorption, good specific tensile properties, and low thermal expansion. Typical examples of natural fibers used are flax, hemp, jute, kenaf, sisal and banana fibers.

## 1.4. Interphase of matrix and fibers

Interphase is the region existing between bulk fiber and bulk matrix. In this region, fiber and matrix are chemically and/or mechanically combined or, otherwise indistinct. The term interface is used, respectively, for the two-dimensional border separating the distinct phases. The thickness of the interphase depends on different factors like the size of polymeric chains, the mobility of the chains, the strength of intermolecular bonds of molecules or group molecules of polymer and the bonds between the polymer and the reinforcement. Although, this region covers a very little area, it has big influence on the thermomechanical, chemical and electrical properties of the material. Generally, the interphase is crucial due to the fact that it transfers stress from the matrix to the reinforcement. Also, it controls the fracture toughness of the composite and has a big influence on the moisture absorption and the behavior of the composite in a corrosive environment. Weak interphase can cause weak strength and modulus, while a strong interphase can have the opposite effect. The experiment that is used to describe the bonding of the fiber-matrix is the pull-out test.

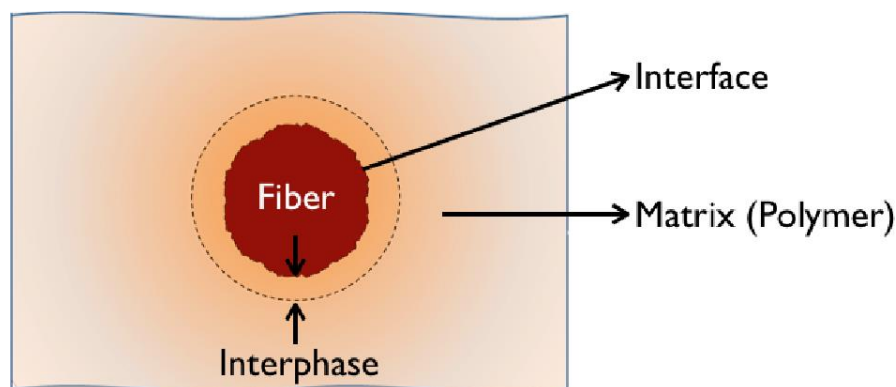


Figure 9 The interphase between matrix and the fiber

## 1.5 Advantages-Disadvantages of composite materials

A list of the advantages of composite materials can be summarized as following:

- Strength
- Stiffness
- Cost
- Thermal insulation
- Thermal conductivity
- Acoustic insulation
- Corrosion Resistance
- Wear Resistance
- Fatigue Behavior

All these advantages clearly cannot be obtained simultaneously, and each composite is designed specifically for each occasion, which is emerged.

Additional advantages of composites as structural components are the following:

- High-end mechanical properties
- Load transfer after material failure
- Small sensitivity to notches.
- Reduction of number of the constructed parts
- Improved aerodynamic surfaces.
- Corrosion Resistance
- Damping in oscillations
- High impact strength
- Low cost of production
- Reduction of weight of the construction

Besides the advantages, that can offer the composite materials, there may be listed some disadvantages. These are the following:

- Significant creep of the matrix
- Low resistance in mechanical wear
- Sensitive to extreme environmental conditions (sea environment, chemical environment, high temperatures)
- Often high initial cost
- Repeated crushes at the same point can result in debonding of fibers-matrix.
- Some composites, after their initial crack, lose their strength rapidly.
- After a failure in a composite, the composite must be reconstructed from the beginning.

## Chapter 2: Polymers

Polymers are large molecules that play an important role in our lives and prosperity. They can be found in many aspects of our lives, including food (protein), clothes (polyester, nylon) and houses (wood cellulose, alkyd paints). The polymeric materials created by human beings have been investigated since the nineteenth century and the polymer industry is now bigger than the copper, steel, aluminum and some other industries combined. A polymer consists a number of repetitive structural units called monomers, which form the chain. The chemical reaction for the creation of a polymer is called polymerization. Generally, the molecule of a polymer is known for its very high molecular weight (between 10000-1000000 g/mol) and it has several structural units usually bound together by covalent bonds.

### 2.1 Production of polymers

It is important to highlight the stage of polymerization, because polymerization reaction conditions affect the polymer properties through altering the molecular weight distribution, branching distribution and composition distribution (for copolymers), number of terminal bonds, etc. Also, it is important to be sited that once a polymer is formed, some of its properties can rarely be altered. Because of this, the polymer synthesis stage, during which polymerization reaction takes place, is the most important step in polymer production.

The following types of synthesis can be distinguished:

- a) Step-growth or polycondensation polymerization
- b) Chain growth or addition polymerization

1) In the **polycondensation**, there is normally an employment of two di-functional monomers that can go through typical organic reactions. The monomers are transformed to molecules with low weight (dimers, trimers, tetramers, etc.). These molecules, also known as oligomers, have the ability to interact with each other with their free functional groups. With this type of polymerization chains of moderate molecular weight can be achieved, while in chain-reaction polymerization, chains of higher molecular weight can be created. This fact can be attributed to the reduction of the free functional groups with the increase of the molecular weight. Also, another reason is that the different groups are linked to the end of the chains and consequently they have no capability to move freely through the viscous medium.

Some features of this type of polymerization are the following:

- a. The concentration of the growing chains is high, due to the fact that monomers are easily transformed into oligomers.
- b. The creation of the polymer chains takes several time, sometimes demanding several hours to several days.
- c. Because of the relatively high value of activation energy of the chemical reactions, the mixture is at an environment with high temperature.
- d. Moderate molecular polymers can be created with step-reaction polymerization.
- e. Branching or crosslinking generally cannot appear except the case of the use of a monomer with three or more functional groups.

In this category, some important polymer that can be produced are:

- Polyethylene
- Polypropylene
- Polystyrene
- Poly (vinyl chloride)
- Poly (methacrylate)

2) In the **chain growth polymerization**, monomers, which contain a carbon-carbon double bond, have the ability to take place in a chain reaction. Generally, this type of polymerization contains three distinct steps. In the first step (initiation step) the formation of a reactive particle is made. More precisely, a molecule is thermally decomposed or goes through a chemical reaction with the aim of generating an "active species". This "active species" (which may be free radical, cation, anion or a coordination complex) react with the monomer's carbon-carbon double bond and thus the initiation step of the polymerization is achieved. With this reaction, there are provoked new free radical, cation, anion or complex, which will be used later. At the end of the initiation step, the first structural unit of the polymer chain is created. At the next step (propagation step), it is taken place the growing of the polymer chain with the new 'active species' linking to monomers with the same way as previously mentioned. The growth of the polymer chains is happening until the termination step. In this last step, the creation of the polymer chain is completed through reaction either with other molecules found in the polymerization mixture, with a connection with another growing chain or with the destruction of the active site.

Some features of this type of polymerization are the following:

- a. The procedure of creating polymers is very quickly once the initiation step is completed.
- b. It is observed that the 'active species' are rare in the mixture. As a result, the mixture has mainly newly formed polymers and unreacted monomer.
- c. This type of polymerization is an exothermic procedure, and it is expected to reach high temperatures.
- d. As compared to step-growth polymerization, there are created polymers with high molecular weight.
- e. With this type of polymerization, secondary chains can be connected to the main chain.

Some basic polymers of this type of polymerization are the following:

- Nylon 66
- Polyester
- Polyurethane
- Polycarbonates

Also, there are 5 basic industrial processes for the production of polymers. These are the following:

- a. Bulk polymerization
- b. Precipitation polymerization
- c. Solution polymerization
- d. Suspension polymerization
- e. Emulsion polymerization

The choice of the industrial scale polymerization process is a multi-factorial procedure, in which should be taken many parameters. From the point of the manufacturer, his main concerns are about the production rate and the properties of the end-product. By extension, these parameters will influence the molecular weight and the distribution characteristics of the polymer chains.

## 2.2 Classification of polymers

There are several classifications, that can be made concerning the polymers. One classification criterion is that one based on the architectural form of polymer chains. Thus, three types are distinguished:

- **Linear**: the molecules have the form of a plain chain and are formed into one dimension.
- **Branched**: the molecules have the form of branches of a tree. A main chain is distinguished, and side chains are developed upon the main chain. These polymers are formed into two dimensions.
- **Crosslinked or network**: the molecules of the chains are connected together, creating a network. These polymers are formed into three dimensions.

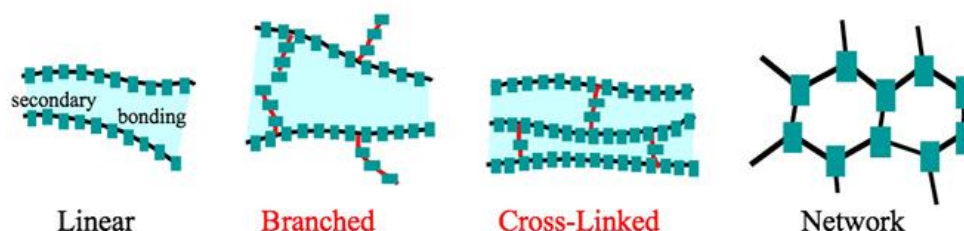


Figure 10. Classification of polymers based on the polymer chain.

Depending on the type of the atoms, which constitute the main chain, another classification can be made:

- **Homochain polymers**: the main chains are made from atoms of a single element.
- **Heterochain polymers**: the main chains are made from atoms of two or more elements.

Depending on the structure of the main chain, the following categories can be distinguished:

- **Homopolymers**: the molecules of chains are constructed from one type of structural unit.
- **Copolymers**: the molecules of chains are constructed from two or more structural units.

Copolymers can be further classified into the following categories:

1. Random copolymer: the structural units are randomly located along the polymer chain.
2. Alternating copolymer: the structural units are found in alternating positions along the backbone.
3. Block copolymer: the structural units are found in long alternating segments.
4. Graft copolymer: is a polymer comprising molecules with one or more species of block (branches) connected to the main chains.
5. Periodic copolymer: the structural units are arranged in a repeating sequence.
6. Aperiodic copolymer: the monomer sequence distribution is not regular but follows the same arrangement in all chains.
7. Gradient copolymer: the monomer composition shifts in a gradually manner along the polymer chain.

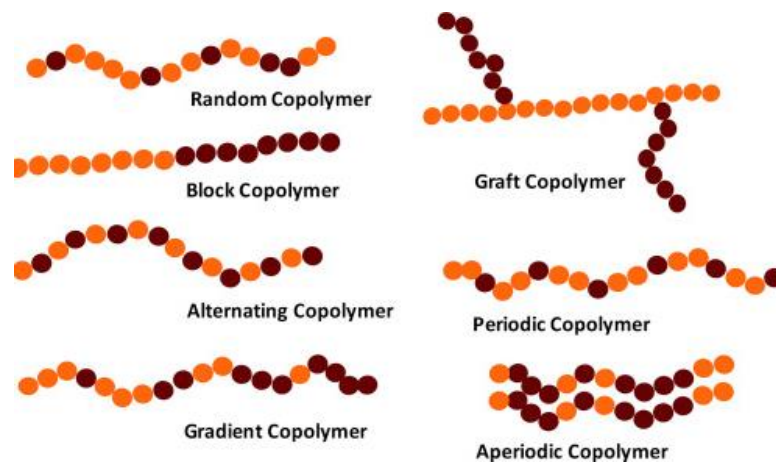


Figure 11. Classification of copolymers.

Also, depending on the tacticity (term used to define how the pendent groups on polymers are placed on the polymer backbone) polymers can be distinguished in the following categories:

- **Isotactic:** the substituents are all located on the same side of the main chain.
- **Syndiotactic:** each successive substituent is connected on opposite side of the main chain.
- **Atactic:** the attachment of substituents is completely random.

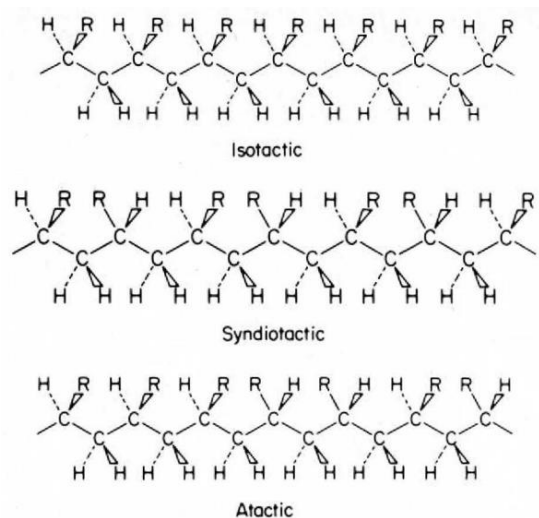


Figure 12. Stereochemical configurations of monosubstituted vinyl polymers.

Depending on their origin and their chemical composition, polymers are distinguished in the following categories:

- **Natural:** these polymers are originated from nature (wool, silk, cellulose, proteins).
- **Semi-synthetic:** these polymers are emerged from chemical modifications of natural polymers (rayon, cellulose nitrate, cellulose acetate, cellophane).
- **Synthetic:** the monomers that constitute these polymers are not in the nature (PVC, nylon, teflon, bakelite terylene).

Depending on the thermomechanical properties, another classification can be made (3 categories).

- **Thermoplastics:** In these polymers, the macromolecules are linked together with weak intermolecular forces van der Waals. The structural units have an arrangement that looks like the molecules are strands of pearls mixed together. When these polymers are heated, the intermolecular forces are restrained, and the material becomes soft and flexible. Also, in higher temperatures, the material is transformed into a viscous fluid. After the cooling of the heated material, the material returns to its initial state (solid). This cycle of heating and cooling can theoretically be done infinite times without any consequence, and it constitutes an advantage of this category. Despite this theoretical assumption, the cycle of heating-cooling provokes a reduction on the overall properties of the material. Thermoplastics may be in the form of liquid or solid. They reveal great strength and have the ability to oppose to shrinking. Nevertheless, they have high production costs, and they are inappropriate for some high temperature applications. Typical thermoplastic materials are considered:
  - i. Polyethylene (PE)
  - ii. Polypropylene (PP)
  - iii. Polystyrene (PS)
  - iv. Polyacrylonitrile (PAN)
  - v. Poly (methyl methacrylate) (PMMA)



- vi. Poly (vinyl chloride) (PVC)
- vii. Polycarbonate (PC)
- viii. Acrylonitrile butadiene styrene (ABS)

- **Thermosetting:** These polymers are produced from a chemical reaction in two stages and all thermosetting polymers are created by condensation polymerization. In the first stage, macromolecule chains are produced, like in thermoplastics, with the difference that take place in further reactions. In the second stage, under the pressure and temperature crosslinks are formed. These bonds are created between the macromolecules, and this results in creating a material, which is solid and rigid. The structure of the thermosetting is considered as a network of molecules, in which limited movement can be observed. Also, the most interesting feature of the thermosets is that they do not liquidize with reheating. On the contrary, if we apply high temperatures on thermosets, then these materials are decomposed. Thus, recycling of thermosets is not possible, and it constitutes the main problem of these materials. Despite this fact, their use is extensive due to their cost efficiency, low weight, and durability. Typical thermosetting materials are considered:

- i. Polyester resin
- ii. Phenol-formaldehyde resin
- iii. Epoxy resin
- iv. Polyurethane
- v. Polyimides

- **Elastomers:** The common elastomers have macromolecular chains that are tangled together. They can perform large elongations and after these elongations, chains cannot return fully to their initial state. For this reason, vulcanization process is done to make crosslinks and make these polymers return to their initial state after elongations. Generally, the loosely crosslinked materials have stretching properties and they are able to come back at the initial shape after the release of the stress. A large number of crosslinks would make the material rigid, hard and closer in properties to a thermoset. Typical elastomer materials are considered:

- I. Natural rubbers
- II. Styrene-butadiene block copolymers
- III. Polyisoprene
- IV. Polybutadiene
- V. Ethylene propylene rubber
- VI. Ethylene propylene diene rubber
- VII. Silicone Elastomers

Generally, the structure of polymers is determined from the following parameters:

- Constitution
- Configuration
- Conformation
- Orientation
- Crystallinity

The constitution and the configuration are considered as the chemical structure, while the orientation and crystallinity determine the natural structure of the polymer. The

conformation belongs both to the natural and chemical structure because it is a consequence of configuration and determines the orientation and the crystallinity of the macromolecular chain.

The chemical structure includes the structure of the macromolecule and influences the chemical reactivity, while the natural structure includes the structure of molecule units and influences the properties of the material. The two types of structures with the combination of the mobility of the parts of chain and macromolecules determine the properties and the fields of application of polymer materials.

Generally, polymers can be divided into two classes: in the first are subjected those which are totally amorphous under all conditions and in the second belong those which are semicrystalline. Completely amorphous polymers (like atactic polystyrene) are generally considered to have randomly coiled and entangled chains. On the contrary, in the case of semicrystalline systems, the crystallinity is found in crystalline domains known as crystallites or lamellae. These crystalline regions have around amorphous matrix. Also, crystallites have not the usual form compared to organic crystals, while they are smaller in size. Moreover, the molecules are orientated randomly but with a specific pattern when observed. The chains mainly are parallel to the crystalline regions and when they reach the amorphous region, they make a turn to the crystalline region. In some cases, it is observed that chains enter in another crystalline region by penetrating the amorphous region. Also, there is the case that the chains enter the amorphous region and create structures called spherulites. The semicrystalline polymers are characterized for their stiffness and strength, when compared to amorphous polymers.



*Figure 13. Representation of a semicrystalline polymer.*

## 2.2 Properties of polymers

### **Mechanical Properties**

Some important mechanical properties, that are taken as parameters for the study of polymers, are:

- a. Young's modulus
- b. Yield strength
- c. Tensile Strength
- d. Elongation at break

The Young's modulus reflects the rigidity of the polymer, while the yield strength reflects the strength, when the elastic region finishes, and the plastic begins. The tensile strength signifies the strength at failure in a tensile experiment, while the elongation at break reflects the percentage of elongation of the polymer until the moment of failure. The tensile experiment is used to find these mechanical properties and to determine the relationship of stress-strain. The engineering stress is defined by the following relationship:

$$\sigma = \frac{F}{A_0}$$

*Equation 1 Definition of engineering stress*

The stress is measured in MPa and F is the force, which is applied in a surface  $A_0$ . For small strains in tensile experiment, the stress and the strain are correlated with the following relationship (Hooke's law):

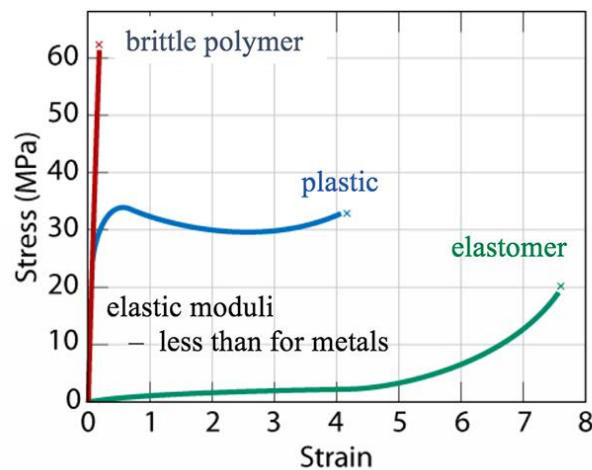
$$\sigma = E * \varepsilon$$

*Equation 2 Hooke's law*

, where E is the Young's modulus (measured in GPa or psi). When the stress is proportional to strain, the strains are considered linear elastic.

Generally, the mechanical properties are influenced from a series of parameters, like the nature of load and its time of application, temperature, moisture and the crystallinity of polymer.

The increase of temperature and moisture have a negative impact on mechanical properties, reducing the Young's Modulus and the strength, while the ductility of the polymer is increased. Moreover, the increase of crystallinity of a polymer, increases the strength of a material and it makes the material more brittle.



*Figure 14. Stress-strain behavior of different polymers.*

Generally, polymers have a range of properties depending on different parameters. There are many categories of polymers by taking into consideration the toughness, the deformation, and the strength. There are polymers with high toughness and large permanent deformations, while there are others with high strength and stiffness, but without large deformations. Moreover, these properties are not correlated with the monomer, which was used to create

the polymer. Nevertheless, they are linked with how they chains interact with each other. The bonds and the physical entanglement play an important role in the characterization of the polymer.

Some mechanical properties of basic polymers are mentioned below:

Polymers	Density (g/cm <sup>3</sup> )	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength
Epoxies	-	55-130	2.7-4.1	110-150	3-4	-
Phenolic	-	50-60	4-7	80-135	2-4	-
Polyesters	-	34-105	2.1-3.5	70-110	2-4	-
Vinylesters	-	73-81	3-3.5	130-140	3	-
Polylactide	1.24	56.3	3.6	-	-	-
Polyester	1.2	61	4	-	-	-
Polyvinyl chloride (PVC)	1.35	48	3.300	-	-	0.32 J/cm
Polystyrene	-	46	2.9	-	-	0.17 J/cm
Polypropylene (PP)	0.899 - 0.920	26 - 41.4	0.95 -1.776	55.2	0.83-1.73	21.4 -267 J/m
Low density polyethylene(LDPE)	0.910 - 0.925	4-78.6	0.055 -0.38	-	-	>854 J/m
High density polyethylene (HDPE)	0.941-1	14.5- 38	0.413- 1.490	-	0.41-1.07	26.7 J/m

*Εικόνα 1 Mechanical properties of basic polymers*

Moreover, the relation of polymers with temperature is essential for understanding an important part of the behavior of the polymers. It is described mainly by two values, the glass transition temperature  $T_g$  and the melting temperature  $T_m$ . Generally, the glass transition temperature is related with the amorphous region of the polymer, while the crystalline region is related with the melting temperature. Below the glass transition temperature  $T_g$  the polymer segments do not have the adequate energy to greatly move. At this point segmental motion pauses and the material shifts from a rubbery solid to a brittle glass-like state. The  $T_g$  is observed both to amorphous and semicrystalline polymers. The glass transition affects only the amorphous region, whereas crystalline region doesn't change in the semicrystalline polymer. Moreover, the  $T_g$  is greatly influenced by the intermolecular forces, chain stiffness, crosslinking, pendant groups, plasticizers, molecular weight and the rate of change of temperature. Generally, this value of temperature is important, while it is taken into consideration to determine the handling temperature range of the polymer.

The melting temperature  $T_m$  is called the temperature at which the solid polymer with regular structure of molecular chains is transformed into a viscous liquid with random structure. In other words, it is the critical temperature, above which the crystalline regions in a semicrystalline polymer are able to flow and the ordered phase turns to disordered. Above  $T_g$ , semicrystalline polymers start to soften. Nevertheless, they do not reveal fluid behavior, until the  $T_m$  range is reached.

The degree of crystallinity of the polymer plays an important role for the melting temperature. With increasing the degree of crystallinity, increasing energy is demanded for the separation of molecules. As a result, higher melting temperature is observed with increasing degree of crystallinity.

In the following table the glass transition temperature and the melting temperature of some basic polymers are shown.

<i>Material</i>	<i>Glass Transition Temperature [°C (°F)]</i>	<i>Melting Temperature [°C (°F)]</i>
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Poly(ethylene terephthalate) (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

Figure 15. Glass transition temperature and melting temperature for basic polymers.

The  $T_g$  of a polymer can be determined with various ways. Some of the most well-known are considered:

- Dilatometry
- Differential scanning calorimetry (DSC)
- Dynamic mechanical analysis (DMA)

Dilatometry: is a method that measures changes in specific volume in relationship with the temperature of the polymer. Through this method both  $T_g$  and  $T_m$  can be determined. Generally, specific volume increases with increasing temperature, while there are different curves for amorphous and semicrystalline, polymers. As a semicrystalline polymer is cooled from its liquid state until the  $T_m$ , its specific volume drops rapidly, mirroring the crystallinity structure, which appears. In the case of amorphous polymer, there is no sharp reduction of the specific volume at the  $T_m$ . On the contrary, a linear decrease is expected until the glass transition temperature. In the rigid glassy state, the specific volume of both amorphous and semi-crystalline polymers still reduces, but at a slower rate. This difference on the rate constitutes the indication for the glass transition temperature.

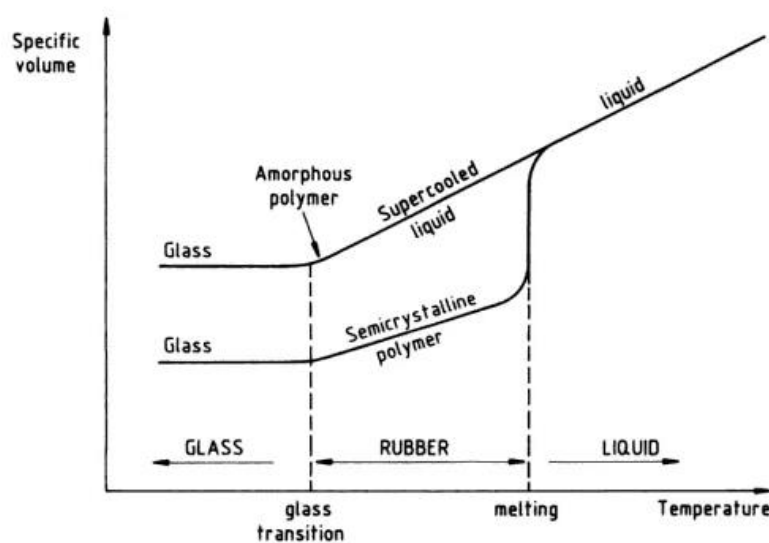


Figure 16. Variation of specific volume with temperature for an amorphous and a semicrystalline polymer.

DSC: the experiment of differential scanning calorimetry is founded on the principle that, as a material undergoes different phase transitions, thermal energy is either absorbed (endothermic) or emitted (exothermic). Considering that in the  $T_g$  a structural alteration at the molecular level takes place, there is an anticipation to observe a shift in enthalpy ( $\Delta H$ ). Consequently, the  $T_g$  can be determined from this change of heat flow, which indicates the change of enthalpy.

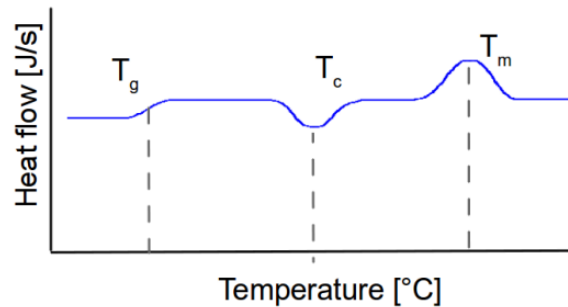


Figure 17. Example plot of heat flow versus temperature for a polymer that undergoes a glass transition, crystallization and melting.

DMA: in this technique a sinusoidal straining and relaxing of a material at a given frequency as the temperature raises is made. There are 2 commonly used approaches to determine the  $T_g$ . These are:

- a. Onset of the storage modulus curve
- b. Peak of the tan delta curve

A dramatic decrease in storage modulus signifies the onset of the glass transition and the peak of the tan delta is often used to represent the glass transition temperature, even though the glass transition occurs over a temperature range. It is considered the most sensitive technique for the  $T_g$  analysis and the most expensive, while it demands bigger quantity of material in comparison with the DCS method.

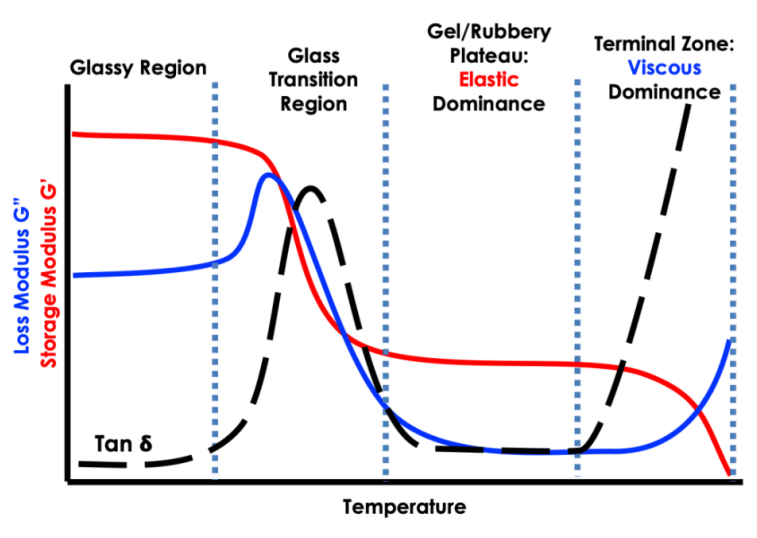


Figure 18. A plot of storage modulus (red), loss modulus (blue) and tan delta (black dashed) as a function of temperature.

## **Thermal Properties**

Polymers reveal low thermal conductivity ( $0.1 - 0.3 \text{ Wm}^{-1}\text{K}^{-1}$ ) and for this reason are often used as insulators. Furthermore, polymers display high thermal expansion coefficient due to their weak intermolecular bonds. Finally, the specific heat is relatively high in polymers due to the increased vibrations of atoms, which are in the chain of macromolecules.

## **Electrical Properties**

Electrical properties are linked with dielectric and electrical conductivity. The majority of polymers are insulators (impede the flow of current), due to the existence of covalent bonds and the lack of ionic or electronic pathway.

## **Optical Properties**

The optical properties of polymers are connected to the degree of crystallinity and the polymer structure. Most polymers are considered transparent and colorless, whereas there are others like phenolic resins and polacetylenes that are colored, translucent or opaque. In amorphous polymers, there are no crystals, which can scatter the incident light and thus these polymers are transparent. The crystalline polymers, that do not have oriented crystals, are considered semitransparent, due to the scattering of the crystals. In the case of orientated crystals, these polymers are considered transparent. Also, polymers that show transparency to visible light may be colored with colorant, while some others may become opaque due to the addition of additives, fillers and flame retardants. Moreover, the refractive index  $n$  (a measure of the bending or refraction of a ray of light, when passing from one medium into another) is about 1.5 for many polymers, while this value is high for crystals and it is dependent on the wavelength of the incident light and the temperature.

## **Acoustic properties**

The absorption of sound in polymers can reach elevated levels. Indeed, there are cases that they achieve a performance up to 4 orders of magnitude higher than metals. For this, responsible are the mechanisms of various molecular structural relaxation processes, concerning the motion of the entire long molecular chains or of selected short molecular segments. The average time (relaxation time  $\tau$ ) which is needed for the specific molecular motion is an essential parameter of the relaxation process and the sound absorption. At low frequencies  $f \leq 1/\tau$ , the molecules have time to respond and therefore sound absorption is high. On the contrary, at high frequencies  $f \geq 1/\tau$ , the molecules have no time to respond, leading to the opposite effect. Also, generally the sound speed through the polymers is considered low, while for higher frequencies an augmentation of the sound speed is observed, because of the increased stiffness of the polymer (no molecular relaxation). Finally, acoustic experiments are conducted to find properties of a material like modulus of elasticity, wave propagation speed and damping.

## 2.3 Advantages and disadvantages of polymers

Polymers have attracted the researchers, because of their many advantages over their limited disadvantages. The interest of scientists is focused on restricting the disadvantages of polymers with various ways. These ways are in the center of material science, which shows a promising scientific future concerning the optimization of polymer materials.

A list of advantages of polymers can be summarized as following:

- High resistance to chemicals
- Lightweight materials
- Radar absorbent, and thermally and electrically insulating.
- Comparable structural strength with lower weight
- Inexpensive to make.

Also, a list of disadvantages is cited below:

- Low temperature resistance and low heat capacity
- Limited machining especially at high speeds
- Low structural rigidity
- Low recyclability and biodegradability



## Chapter 3: Epoxies

### 3.1 Introduction

Epoxy resins are made of chains, which contain the epoxy(oxirane) group. In this group are found two carbon atoms and an oxygen atom. The structure of this group makes epoxy resins highly reactive (due to the compressed internal angle of epoxide ring and subsequently large ring strain) and creates diverse epoxy resins. Also, this group may lie within the body of the molecule, but it is usually terminal. Generally, in the monomer of the resins are found two or more epoxy groups.

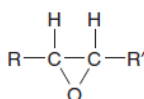


Figure 19. General structure of an epoxy resin.

The functional groups of epoxies can be created by:

1. The reaction between olefins and oxygen-containing compounds (like peroxides)
2. Dehydrohalogenation of chlorohydrines
3. The reaction of epichlorohydrin with a suitable di- or poly-hydroxy compound or other active hydrogen-containing compounds.

A classification of epoxy resins that can be made is the following:

1. Cycloaliphatic resins (R and R' are a piece of a six membered ring)
2. Epoxidized oils (R and R' are parts of an unsaturated fatty acid)
3. Glycidated resins (R is hydrogen and R' can be polyhydroxyphenol, polybasic acid or polyamine).

The last category has the largest portion of the market with the most characteristic resin, the bisphenol-A based epoxy resin.

Generally, epoxy resins, which are a blend of oligomeric materials, are “cured” or cross-linked by chemical reaction into a three-dimensional infusible network using a cross-linking agent (curing agent). In this way, the resins are converted easily from the liquid (or thermoplastic) state to hard thermoset solids. There are two main categories of curing agents. In the first, the curing agents catalytically promote curing, while in the second they are directly involved in the reaction, and they are connected with the resin. Also, there is a third category, in which the curing agents can combine these two mechanisms. Curing can be carried out at room temperature with the use of the heat from the exothermic reaction or with the aid of external heat. The epoxy group has two possible ways of reaction, either anionically or cationically. When it reacts anionically, the epoxy ring opens with various ways to produce an anion, while in the cationic case, the epoxy groups open by acids. Generally, the choice of the curing agent is largely related to the requirements of properties of the final product and the limitations of the method of fabrication. There are three major categories of curing agents, and these are:

- Amines
- Acid anhydrides
- Lewis bases and acids.

Further classification can be made concerning the amines category. There can be distinguished into aliphatic, cycloaliphatic and aromatic.

The basic concept of the amine and the acid anhydrides curing agents can be displayed in the following figure:

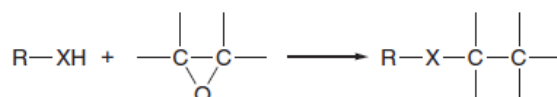


Figure 20. Reaction of epoxide ring with amines or acid anhydrides.

In the cases of amines and acid anhydrides, a reaction occurs in the epoxy group (nucleophilic addition) to the terminal or  $\alpha$ -carbon atom of the epoxide. This reaction produces respectively, the  $\beta$ -hydroxyamine or  $\beta$ -hydroxyester. X in the above figure can be NH, NR' or COO.

Concerning the Lewis acids and bases, the homopolymerization of the epoxide is responsible for the cure of epoxy resins.

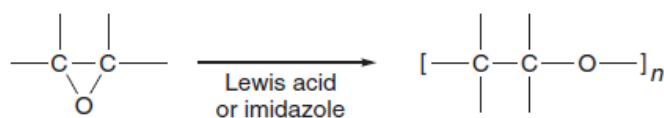


Figure 21. Homopolymerization of epoxide via Lewis acids and bases or imidazoles.

A more detailed review of the curing agents is cited below:

### Amines

It is the most popular category of curing agents, comprising over the half of the market. Generally, amines can create cross-linked epoxy resins either by catalytic or by bridging across epoxy molecules. So, two categories of curing agents can be identified, catalytic agents and polyfunctional cross linking agents that connect the epoxy resin molecules together. Also, there are cases that there are taken place both the catalytic and the cross-linking mechanisms. It is observed that usually primary and secondary amines act as reactive molecules, while tertiary amines are catalytic.

Concerning the cross-linking mechanism, a display of this effect is shown in the following figure. Generally, for this aim, reactions can be done via the epoxy ring or through the hydroxyl groups. A typical example is shown below.

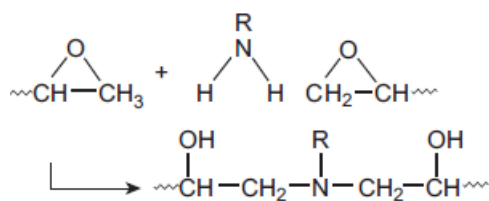


Figure 22. Cross-linking with the aid of amines.

Generally, all amines (aliphatic, cycloaliphatic, aromatic) can have a reaction with the epoxide ring forming simultaneously by-products. Especially, aliphatic amines due to their bigger nucleophilic nature (affinity to bond with positively charged atomic nuclei) compared to aromatic amines, have more quick reactions. Generally, linear aliphatic amines have the ability of curing epoxy resins very quickly at ambient temperature (~30 min), whereas in the case of cycloaliphatic amines, it is observed a slow reaction and an external source of heat is needed. Also, concerning aromatic amines, they surely cannot react with epoxy resins at ambient temperatures and their use is found mainly at cases which demand high temperatures. The pot life of aliphatic amine system is 30-40 min, while for cycloaliphatic and aromatic systems are respectively 1-3h and 10-40h.

Aliphatic polyamines are popular curing agents, because as previously mentioned they are able to cure at room temperature. They have relatively short pot life, while they can reach full cure in about 7-10 days at ambient temperature. Also, they are used usually only with liquid resins and common curing agents of this category are: diethylenetriamine (DETA) and triethylenetetramine (TETA).

Moreover, aliphatic polyamines can provoke some difficulties due to their high reactivity and their big potential of allergenic activity. Derivatives like polyamide curing agent improve these restrains and for this reason they are used extensively in many applications. Also, polyamide enhances the adhesion of glass, metal and other substances, while it exhibits low shrinkage.

Concerning cycloaliphatic amines, they produce cured resins with significantly higher  $T_g$  in comparison with linear aliphatic amines, while they are considered less carcinogenic in comparison to aromatic amines. Therefore, there is a trend to replace aromatic amines in open resin processes with cycloaliphatic amines. Applications of cycloaliphatic curing agents have a wide range and some of them are the creation of high solid coatings and adhesives. The most widely used cycloaliphatic diamines are considered the isophorone diamine and 1,2-diarninocyclohexane.

Aromatic amines are used as curing agents, and they create materials that have much better overall properties in comparison to those which contain aliphatic amine curing agents. Indeed, products with this type of amines have significantly higher Heat Distortion Temperature than those which are obtained from aliphatic amines. Also, a positive characteristic of aromatic amine systems is that they have the ability to create a thermoplastic (B) stage, providing useful life and time in the procedure of the creation of the material. This feature gives several advantages like the possibility to cure the product at another time or location. A drawback of this category is that most of aromatic amine curing agents exhibit relatively viscous behaviour at room temperature for most processes. They react slowly with epoxy resins at room temperature, and for this reason they are used at elevated temperatures. Some common

aromatic curing agents are considered: m-phenylenediamine (MPDA), 4,4- Methylenediamine (MDA), 4,4- Diaminodiphenyl sulfone.

### **Acid Anhydrides**

Acid anhydrides are considered the second most significant category of curing agents for epoxy resins. Practically, they are preferred against acids, because the latter releases more water on cure, a fact which is unwanted for the cured products. Also, similarly to aromatic amines, acid anhydrides demand high cure temperatures, while a catalyst is desired in order to have the best mechanical properties. Moreover, a drawback of this category is the high reactivity of acid anhydrides with water, which restrain their applications. However, generally, they show long pot life, low viscosity and low exotherm behaviour during curing. Their applications include filament winding, pultrusion, VARTM and RTM. Moreover, some acid anhydride systems show good physical, electrical and chemical properties. However, acid anhydride cured systems reveal less resistance to alkalis compared to the amine-cured systems. Some basic acid anhydrides curing agents are considered: nadic methyl anhydride (NMA), hexahydrophthalic anhydride (HHPA) and methyl tetrahydrophthalic anhydride (MTHPA).

### **Lewis Acid Systems**

The last category of curing agents is the Lewis acid cured resins and the most commercialized curing agent is the boron trifluoride- monomethylamine (BF<sub>3</sub>-MEA) complex. In this category, the curing agents are not coreactants, but they act for the homopolymerization of the epoxy resin.

## **3.2 Properties of epoxies**

Several advantages have made epoxy resins very popular in the industry. They have an uncommon combination of properties, in comparison to other liquid resins, such as phenolics, polyesters, acrylics, which can be summarized as following:

- Low viscosity: The liquid resins combined with their curing agents are usually low viscosity systems.
- Easy cure: Epoxy resins cure quickly and easily in a wide range of temperatures depending on the curing agent.
- Partially cured: Epoxy resins can be partially cured and stored in this state.
- Low shrinkage: Epoxy resins reveal low shrinkage behavior, while they do not provoke volatile by-products.
- High adhesive strength: Due to the existence of polar hydroxyl and ether groups, the epoxies are considered brilliant adhesives.
- High electrical insulation: Epoxy resins are considered exceptional electrical insulators.
- High mechanical properties: The strength of the epoxy resins is usually superior in comparison to other types of resins.
- Versatilities: Epoxy resins have a huge diversity, due to the fact that can have many modifications (mixing of different resin types, selecting curing agents, use of modifiers or fillers).

Nevertheless, there are some drawbacks, which can be summarized as following:

- Brittle nature
- Poor thermal conductivity
- High cost
- Difficulty in the recycling

Often it is needed expertise for selection of the suitable resin system.

### 3.3 Applications of epoxy resins

In the following subsection are presented some applications of epoxy resins.

#### **Paints and surface coating**

In order to create coatings, epoxies can be mixed with other types of resins (like alkyds and amino resins). Generally, the coatings of epoxy resins found applications in the anti-corrosion industry, due to their high chemical and corrosion resistance. For this reason, the marine industry makes an extensive exploitation of these coatings. Besides the anticorrosive applications, epoxy coating systems are widely used for flooring and decorative reasons.

#### **Electrical and electronic systems**

Epoxy resins have applications on personal electronic devices and domestic electrical equipment. An example of this field is the printed circuit boards (PCBs), which are created with the combination of glass fibers and epoxy resins. The reason why they are so attractive to these industries is attributed to the fact that they have excellent electrical insulation. Moreover, epoxy molding compounds (EMCs) are widely exploited as encapsulation materials for semiconductors devices.

#### **Composite materials**

Epoxy resins are able to have a good bonding with fibers (like glass, carbon, aramid fibers) and thus they produce composite materials with good properties, which are characterized as the best of the thermoset's category. The processes of manufacturing composite materials can be divided into 2 categories: wet resin and prepreg processes. In the case of wet resin procedures, there is a direct mix of the epoxy resin and the reinforcement by the fabricator, while prepregs are composite materials, which have already impregnated fibers and they are partially cured. Also, epoxy composite laminates are widely exploited for the repair of both composite and steel structures, mainly in marine applications (boat repair due to impact damage or osmosis effect).

Process
<b>Wet Resin Processes</b>
Contact molding (hand laminating)
Resin transfer molding
Resin infusion
Filament winding
<b>Prepreg Processes</b>
Press molding
Vacuum bag oven processing
Vacuum bag autoclave processing

Figure 23 Processes for the production of composite materials

## Wind Energy

Glass-epoxy composites have applications on wind energy industry for the turbine blades. Also, carbon-epoxy composites are placed for added reinforcement in the spar caps for longer blades. Generally, there has been a movement the last years to epoxy resins due to their superior behavior to fatigue and impact resistance.

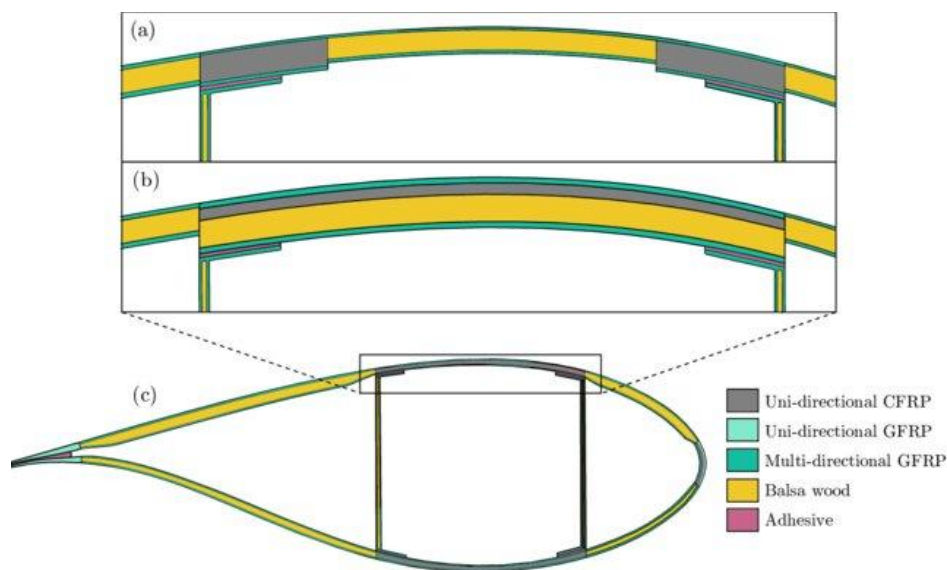


Figure 24. Blade of a wind turbine with different spar cap topologies: (a) split spar cap (b) continuous spar cap.(c) baseline of the blade.

## 3.4 Bioresins

### 3.4.1 Introduction

With the continuous growth of plastic production at the recent years, environmental concerns are aroused concerning the usage of petroleum-based resins. These resins degrade sluggishly and provoke pollution because of their toxicity. Biobased polymers constitute an alternative solution due to the origin of them, restricting the usage of the harmful resins. Bioresins come from renewable resources, while they can be degradable or not. Moreover, biodegradable resins have a promising role in replacing the traditional resins, focusing respectively on the

end-of-life issues aroused from the environmentally detrimental resins. They come both from renewable and fossil sources, while they can be both recyclable and unrecyclable.

Generally, biobased resins can be thermoplastic or thermoset. Biobased thermoplastics (like poly(lactic acid), polyhydroxyalkanoates and poly( butylene succinate)) are widely spread commercially. On the contrary, biobased thermosetting resins are limited commercially, although steps are made for their evolution. The most commercially available resins are mainly epoxy resins, unsaturated polyester resins and polyurethane. Also, it is a usual practice to mix biopolymers and oil-based plastics, in order to enhance properties like heat resistance and poor impact resistance of biobased resins. Thermoset bio-derived resins, which are commercially available have a bio-content of 20 and 50% and are not biodegradable.

On the contrary, among thermoplastics, we can find biodegradable resins and the most well-known are:

- Poly(lactic acid) PLA
- Poly(butylene succinate)
- PHAs
- TPS (thermoplastic starch)

, while some non-biodegradable thermoplastic resins are:

- bio-polyolefin
- bionylons
- cellulose and lignin-based polymers

### 3.4.2 Properties of bioresins

#### Mechanical properties

Biopolymers, which produce the biobased resins, have generally stiffness and strength, as shown in the following figures, that are close to those of PE and PP. Their intrinsic disadvantage is that they are heavier, resulting in reduced specific stiffness and strength. Also, they reveal poor thermal resistance and impact properties. Moreover, there are restrictions concerning their processability and their use for molds, because there is a narrow space between the processing temperature and the decomposition point.

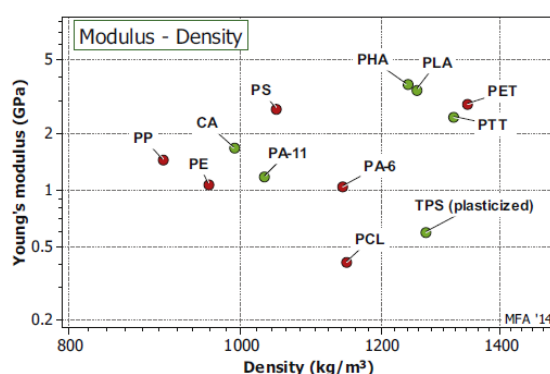


Figure 25. Young's modulus versus density of oil-based polymers (red) and biopolymers (green).

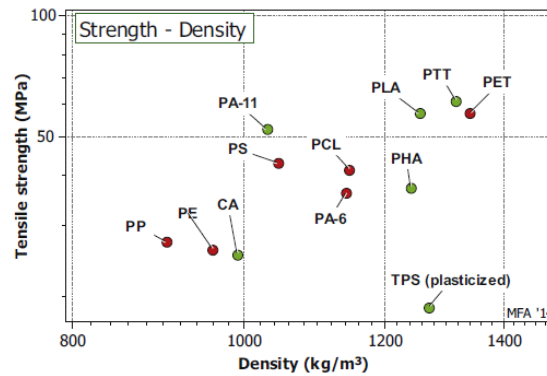


Figure 26. Tensile strength versus density of oil-based polymers (red) and biopolymers (green).

## Energy

Although it is expected that biopolymers require much less energy for production compared to oil-based products, it is not scientifically proved. In reality, there are no big differences except for the case of TPS (starch-based polymer). This similarity in the embodied energy is attributed to the fact that bioresins require heat and thus there is a demand of energy which was not seen at first sight. In the following figure is shown the embodied energy for different oil-based polymers and biopolymers.

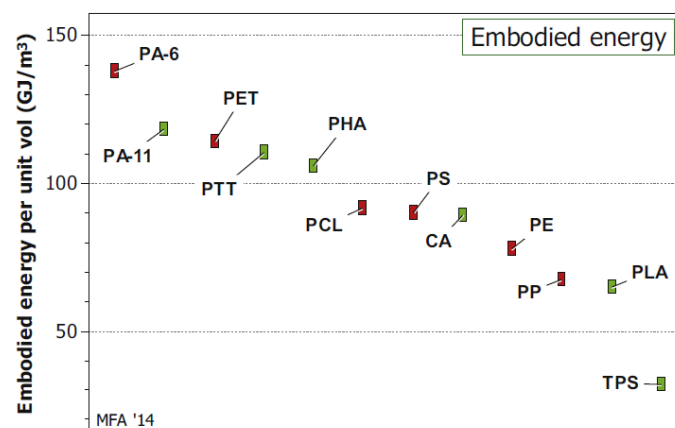


Figure 27. The embodied energy of petroleum-based polymers (red) and polymers from renewable resources (green).

## Environmental properties

Also, biopolymers are considered to be more environmentally friendly compared to oil-derived polymers. This fact is not totally accepted, because their water requirement is high due to the need of plant or animal feedstock. Also, as previously mentioned, not all biopolymers biodegrade, and this affects in a negative way the environment. The following figure illustrates the carbon footprint and water demand of biopolymers and oil-based polymers respectively.



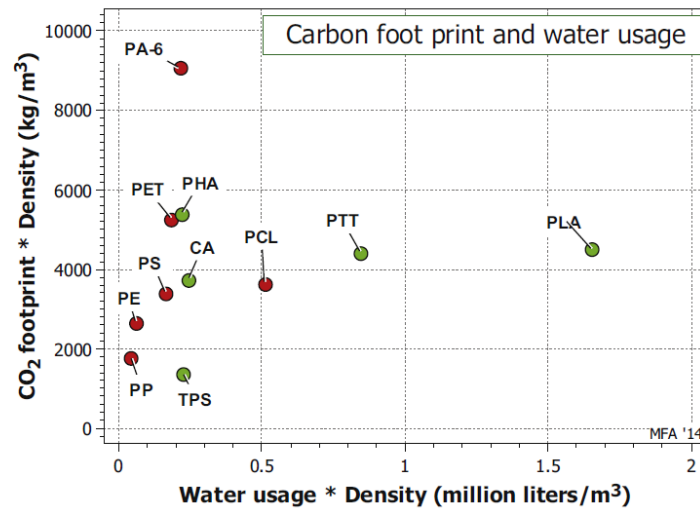


Figure 13 The carbon footprint and water usage of oil-based polymers (red) and biopolymers (green).

### 3.4.3 Manufacturing of bioresins

Despite the increasing interest towards these resins, it should be noted that unlike petrochemical research, plant chemistry has been little developed and great research should be made in the future. A big effort is made on creating chemically robust resins, which have a similar performance with those that are derived from petrochemicals. In the following figure, it is shown that few bioresins are commercially available in a large scale.

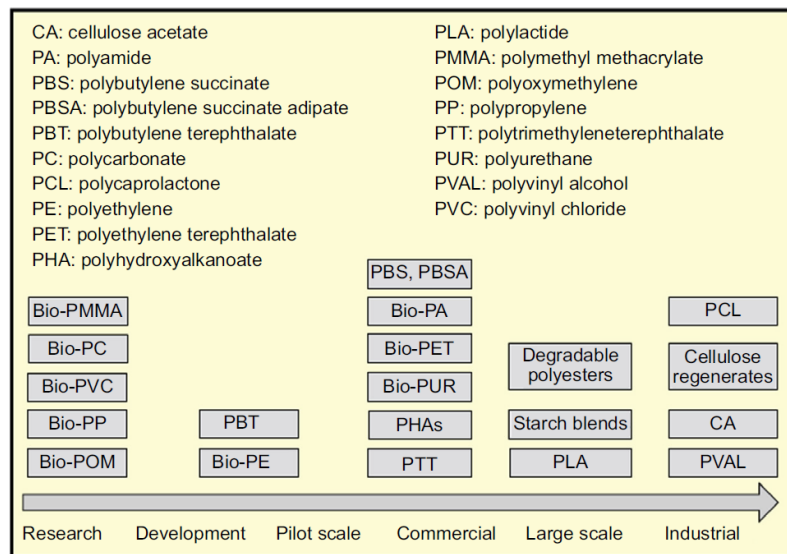


Figure 28. State of development of thermoplastics biopolymers.

Generally, biobased polymers are made from biomass, which comes from renewable resources. Corn, soya, cellulose and polysaccharides are sources, which can provide various polymers. Two big categories of substances for the creation of bioresins are widely used: the category of natural oil polyols and that one of sugar alcohols-carbohydrate.

## Natural Oil Polyols

Natural oil polyols derive usually from vegetable oils, which contain triglycerides. The principal constituents of triglyceride vegetable oils are considered the saturated and unsaturated fatty acids, which are chemicals for polymer synthesis. The triglycerides offer several reactive sites, which can undergo various chemical reactions and synthetic transformations. Generally, the modified fatty acids are the key concept for the synthesis of new bio-based sustainable polymers like epoxy resins, polyurethanes polyester and polyamides.

The fatty acids from vegetable oils consist of 8 to 24 carbon atoms and have a range of double bonds from 0 to 7. This is related on the plant type and climatic conditions of growing. For the majority of vegetable oils, naturally existing carbon-carbon double bonds are located between the 9<sup>th</sup> and 16<sup>th</sup> carbon atom. Moreover, the most natural carbon-carbon double bonds are not conjugated and thus they show low chemical reactivity. Nevertheless, some vegetable oils have conjugated double bonds and they demonstrate high polymerization activity. The structures of the most frequent fatty acids which exist in vegetable oils are depicted in the following figure.

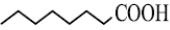
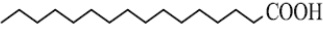




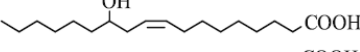


Fatty acids	Formula	Structure
Caprylic	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	
Palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	
Stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	
Oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	
Linoleic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	
Linolenic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	
Ricinoleic	C <sub>18</sub> H <sub>34</sub> O <sub>3</sub>	
α-Eleostearic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	
Vernolic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	

Figure 29. Structure of the most common fatty acids in vegetable oils.

Moreover, the iodine value is an important characteristic of potential conversion of oils (due to their double bonds), because it is a measure of their unsaturation. Higher iodine values mean greater presence of unsaturation and a higher potential for conversion of unstaurations. Also, there are distinguished three categories depending on the iodine value:

- Drying oils (>130mg/100g)
- Semi-drying oils (90-130 mg/100g)
- Semi-drying oils (<90 mg/100g)

Generally, linseed oil has the highest amount of iodine value, because it contains the highest amount of α-linolenic acid, which has three double bonds in its fatty-acid chain. In the following figure are cited the iodine values for various vegetable oils.

	Iodine value (mg/100 g)
Castor	81–91
Corn	118–128
Linseed	>177
Olive	76–88
Palm	50–55
Soybean	123–139
Rapeseed	100–115
Sunflower	125–140
Canola	100–115
Cottonseed	98–118
Peanut	84–100

Figure 30. Iodine values of various vegetable oils.

Although some vegetable oils contain some reactive sites like hydroxyls or epoxies in their chains of fatty acids, which can be directly used for polymerization, applications tend to be restricted. Most vegetable oils require modification before they can be used as monomers. These modifications can be made by chemical change of the reactive sites. Generally, three approaches are used to polymerize vegetable oils and create thermosetting materials:

- Direct polymerization of the C=C bond in the vegetable oil structure.
- Functionalization of the triglyceride C=C bond and creation of a crosslinked structure.
- By producing monomers derived from vegetable oils through chemical transformation.

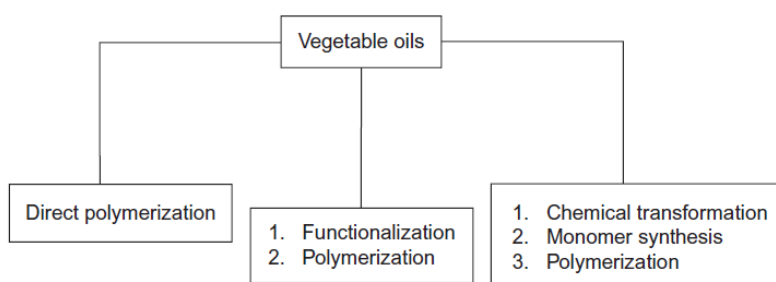


Figure 31. Schematic representation of three approaches to synthesize biopolymers from vegetable oils.

Moreover, some of the most used oils are analyzed below:

#### Soybean oil

Epoxidized soybean oil (ESO) is an economical alternative for the replacement of petroleum-based polymers. It is used for resins for green composites and adhesives, while it can be used for lightweight rigid foams. Thermoset resins can be created by functionalizing the triglycerides of epoxidized soybean oil with methacrylic acid, acetyl anhydride and methacrylic anhydride.

#### Linseed oil

It is considered one of the most widely used epoxidized oil, since it has additional double bonds, which are found in linolenic acid chains. Indeed, linseed oil owns the highest unsaturation (~6.6 units double bond per triglyceride) and because of that, the high epoxy value after epoxidation, the storage modulus, the thermal stability and the  $T_g$  of cured systems

are much higher than those of other vegetable oil counterparts. However, it should be highlighted that compared with petroleum-based epoxy resins, linseed oil polymers exhibit similar thermal properties, but lower mechanical properties.

### **Sugar Alcohols- Carbohydrates**

Sugar alcohols are another source for creating bioresins. They are a class of polyols with polymeric polyols starting from monomeric polyols such as glycerin, ethylene glycol and sucrose. Sucrose is a disaccharide, while polysaccharides are long, complex chains of carbohydrates, such as cellulose, hemicellulose and starch. In this category, the most well-known sources are:

#### Starch

Bioresins can be created from nonedible and edible starches (corn, potato, etc.). Through destructure with the aid of mechanical and heat energy or with the incorporation of a plasticizing agent (water, amide, and/or polyols), thermoplastic starch can be created (TPS). However, it is observed that TPS has a tendency to aging and to change its structure, which makes it fragile. Generally, starch-based materials are characterized for their low mechanical strength, brittle behaviour and moisture absorption.

#### Lignin

It is considered a natural polymer which is located in the cell walls of dry land plants. It reveals aromatic functionality, while it is rich in phenolic hydroxyl groups along with its derivatives. Although, lignin could be considered structurally as bio-based substitutes of aromatic compounds, complex structure and low reactivity of lignin limit its directly utilization and application. Therefore, depolymerization or fragmentation is considered to be a promising method to generate phenolic compounds for high value-added applications. Generally, lignin shows impressive properties such as low weight, environmentally friendly and biodegradable nature.

Poly(Furfuryl) Alcohol (PFA) has received attention due to its fire resistance behaviour and high chemical resistance. They are privileged resins because of their aromaticity and availability. Furfuryl Alcohol (FA), the precursor of PFA, is an aldehyde that can be gained from hydrolysis of pentosan-rich biomass (like rice hulls, wheat and corn). The PFA resins find application areas such as wood adhesives and binders, foundry industry, polymer concretes.

## Chapter 4: Reinforcement-fibers

### 4.1 Natural fibers

#### 4.1.1 Introduction

Twisting to more environmentally friendly composites, natural fibers constitute a promising proposal, in order to substitute harmful for the environment fibers (e.g., aramid, glass fibers). They are biodegradable and they show low environmental impact with creating natural fiber reinforced polymer composites (NFRPCs), which consume lower energy (~9.55 MJ/kg) compared to the conventional fiber reinforced composites e.g., glass (~54.7 MJ/kg). Also, they reveal some attractive features including low cost, low weight, flexibility during processing, resistance to corrosion and fatigue. Moreover, some natural fibers can have comparable or quite near stiffness to this of glass fibers, but without reaching the corresponding tensile strength. On the other hand, natural fibers are competitive with synthetic fibers, because they have low density, which results in relatively high specific strength and modulus. In the following figure, the densities and the mechanical properties of natural and synthetic fibers are presented.

Fibre type	Main chemical component	Density (g/cm <sup>3</sup> )	Stiffness (GPa)	Strength (MPa)
Biobased fibres				
Flax	Cellulose, in a matrix of hemicellulose and lignin	1.5	50–90	500–900
Hemp		1.5	30–60	300–800
Jute		1.4	20–55	200–500
Bamboo		1.4	27–40	500–575
Synthetic fibres				
Glass	Silicon oxide	2.6	70–87	2500–4700
Carbon	Graphite	1.8	240–830	3500–4400

Figure 32. Properties of various natural and synthetic fibers.

#### 4.1.2 Classification of natural fibers

A classification can be made concerning the origin of natural fibers. Specifically, 3 categories are distinguished: plant fibers, animal fibers and mineral fibers. In plant fibers mainly five types of fibers are distinguished:

- seed fibers: the fibers are gathered from seeds or seed cases.
- leaf fibers: the fibers are gathered from leaves.
- bast fibers: the fibers are gathered from the skin or bast, which surround the stem of the plant.
- fruit fibers: the fibers are gathered from the fruit of the plant.
- stalk fibers: the fibers are actually the stalks of the plant.

In animal fibers mainly animal hairs and silk fibers (particular of certain spiders) are used, while in mineral fibers are acquired from minerals, creating, amosite, crocidolite, tremolite, actinolite and anthophyllite fibers. Both mineral and animal-based fibers are rarely applied as

reinforcement medias in composites as compared to plant-based fibers due to their unavailability and high price. Moreover, animal fibers show inferior stiffness and tensile strength compared to plant fibers, while they exhibit inferior hydrophilic properties, highly sensitivity to some alkalis and bad conductivity of heat. In this chapter, plant fibers are mainly analyzed, because of their good properties and their extensive use in natural reinforced composites.

In the following figure are displayed the categories of natural fibers as mentioned before.

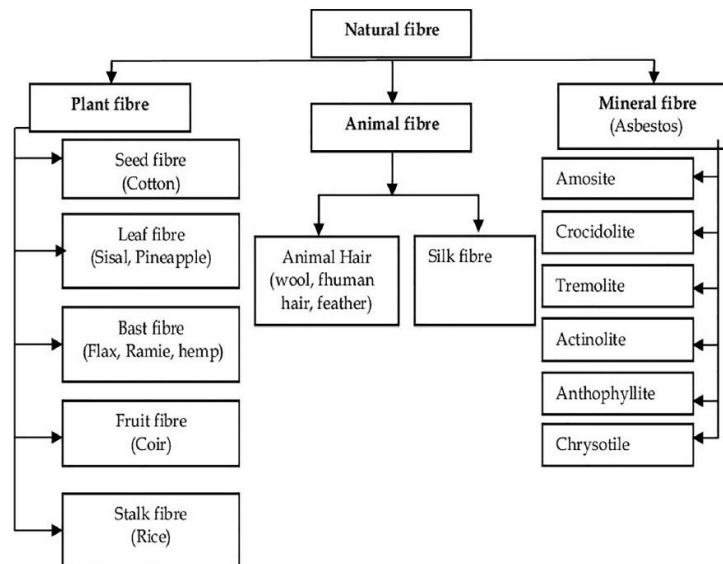


Figure 33 Classification of natural fibers

A special reference must be made for the following categories, because they contain some of the most widely used natural fibers.

### Leaf fibers

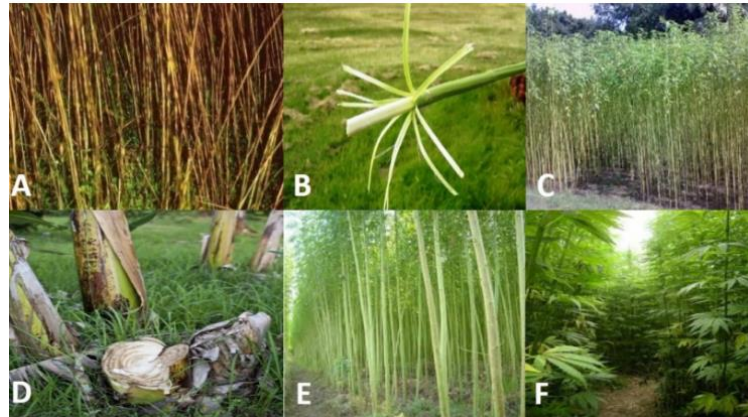
Sisal, abaca and manila leaf fibers are representative types of natural fibers of this category. From sisal and abaca can be obtained some of the longest fiber lengths of plant fibers (1-4m) and generally leaf fibers are characterized for their superior impact properties. Also, they have generally higher thickness compared to bast fibers.



Εικόνα 2 Sisal plant

## Bast fibers

Flax, hemp, jute, nettle, okra and ramie belong to this category. They display good flexural strength and modulus of elasticity, while they often reinforce polymer composites. They have diameters ranging from 12  $\mu\text{m}$  to 17  $\mu\text{m}$  and they can reach lengths of 20mm (hemp).

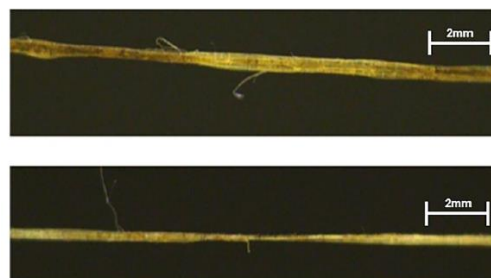


*Εικόνα 3 Different types of bast fibers (A) Flax (B) Hemp (C) Jute (D) Banana (E) Kenaf and (F) Ramie*

Moreover, it is important to be noted that plant fibers show great variability concerning their mechanical properties. For this, several factors play a role and the main four are listed below:

- Plant anatomy: the internal organization of the plant structure
- Growth conditions: e.g., soil quality, fertilization, field location, climate, weather conditions
- Fiber processing conditions
- Experimental characterization methods

The first three factors can cause true variability in fiber properties. They can cause variability between the batches of fibers e.g., because of the inevitable changes in growth conditions from year to year (or from field to field). They can cause variability within batches of fibers e.g., because of the inherent spread of differently matured fibers from different plants, and because of the non-uniform processing conditions. Moreover, an important emphasis must be made for the morphological scattering of the bundles of fibers, which is one of the reasons for variability of mechanical properties. There is a high intra-bundle and inter-bundle scattering of the cross-section of the natural fibers, unlike man-made fibers whose dimensions can be standardized during their industrial production. In the following figure, are shown the strong lengthwise variations of flax fibers.



*Figure 34 Two different flax fibre bundles section seen in profile*

Lastly, the fourth factor causes artificial variability due to measuring errors from experimental characterization methods.

#### *4.1.2.1 Comparison of natural fibers*

The selection process of the ideal natural fiber for a composite has 5 general phases. Phase 1 includes the screening and choosing the options from the rich variety of natural fibers. Then it is essential to choose the criteria of selection based on the application which the composite is designed for. In the phase 2, collection of data about the options which were selected is made. Then, in the third phase, a comparison of the criteria is made in order to evaluate their significance (weightage of criteria). In the fourth phase, respectively, an assessment of the options with various Multi- Criteria-Decision-Making techniques (MCDM) is made. Finally, the ranks derived from different MCDM are compared and the best option is chosen.

##### **Choosing criteria**

First of all, the mechanical properties of natural fibers must be considered the most important parameter, because it directly affects the performance of the composite. So, specific strength, specific modulus and strain at break are three major criteria, which can be used in MCDM techniques. Also, due to the high tendency of natural fibers to absorb moisture and its negative effects on the mechanical properties, the moisture absorption should be considered a criterion. Moreover, another critical parameter that influences the mechanical properties is the aspect ratio (length to diameter). It is known, that there is an ideal value of aspect ratio for each natural fiber, which optimizes their properties. Generally high aspect ratios are desired because better fiber interaction with the matrix is made. Lastly, the criterion of cost should not be neglected, because it plays a vital role in the material selection.

##### **Weightage calculation**

Each criterion carries a weight, which mirrors its importance in the decision-making process. A slight change in criteria weight can cause different results and lead to other conclusions. So, the selection of the method for determining the weight of the different criteria is an essential step, which should not be overlooked rapidly. Three categories are distinguished concerning the weighting methods: subjective, objective and integrated weighting methods. In subjective methods, experts' opinion determines the criteria weights with usually setting some questions in the process. In this procedure, conflicts often appear, because no unanimity may appear between the colleagues. Generally, the main drawback of this category is that the possibility of determining freely the weights may lead to false results. A representative technique for subjective weighting methods is called Analytical Hierarchy Process (AHP). It uses a pairwise evaluation for determining the significance of every criterion in comparison to the other, by using the Saaty's comparison scale. In the following figure is shown the Saaty's scale.



For any pair of objectives $i, j$ :	
Score	Relative significance
1	Objectives $i$ and $j$ are of equal significance
3	Objective $i$ is weakly more significant than $j$
5	Objective $i$ is strongly more significant than $j$
7	Objective $i$ is very strongly more significant than $j$
9	Objective $i$ is absolutely more significant than $j$

Figure 35 Saaty's comparison scale

On the contrary, in the objective weighting methods, weights are emerged using mathematical computation without the opinion of experts. The drawback of this method is that the outcome of this procedure may not coincide with the real weights. In this category belong the methods of Entropy and Criteria Importance Through Intercriteria Correlation (CRITIC method).

Respectively, the integrated weighting methods combine both subjective and objective information. Indeed, this approach takes into account a mathematical model and objective factors. In the following figure are cited some of the most well-known methods for each category.

Weighting methods		
Subjective weighting methods	Objective weighting methods	Integrated weighting methods
Point allocation Direct rating	Entropy method Criteria Importance Through Inter-criteria Correlation (CRITIC)	Multiplication synthesis Additive synthesis
Ranking method	Mean weight	Optimal weighting based on sum of squares
Pairwise comparison (AHP)	Standard deviation	Optimal weighting based on relational coefficient of graduation
Ratio method Swing method Delphi method Nominal group technique Simple Multi-attribute Ranking Technique (SMART)	Statistical variance procedure Ideal point method	

Figure 36 Classification of weighting methods

Suitable objective weighting methods for the evaluation of natural fibers are considered the Entropy and the CRITIC method.

In the following figure are shown the results of a study, which compared natural fibers using entropy and CRITIC method.  $E_j$  and  $C_j$  are parameters, which are essential for determining the weights  $w_j$ .

	Aspect Ratio	Strain at break	Specific strength	Specific modulus	Moisture Absorption	Cost
$E_j$	0.81	0.92	0.97	0.95	0.86	0.88
$w_j$	0.31	0.13	0.06	0.08	0.23	0.19

Figure 37 Entropy values and criterion weights as per entropy method

Criterion	Ranking based on entropy method
Aspect ratio	1
Strain at break	4
Specific strength	6
Specific modulus	5
Moisture Absorption	2
Cost	3

	Aspect Ratio	Strain at break	Specific strength	Specific modulus	Moisture Absorption	Cost
$C_j$	1.461	1.503	1.805	1.960	1.520	1.321
$w_j$	0.15	0.16	0.19	0.20	0.16	0.14

Figure 38C\_j values and Criterion weights as per CRITIC method

Criterion	Ranking based on CRITIC method
Aspect ratio	4
Strain at break	3-4
Specific strength	2
Specific modulus	1
Moisture Absorption	3-4
Cost	5

Generally, there is not a clear ranking for each criterion, and this can be seen for example from the criterion of specific modulus, which takes the 5<sup>th</sup> place based on entropy method and the 1<sup>st</sup> place based on the CRITIC method.

### MCDM techniques

MCDM techniques have been created in order to determine the most beneficial solution based on some models, which use the weighing criteria. Based on the decision-makers inclinations and design requirements, the elected option can be a group of non-inferior solutions or a comprised one. Various types of MCDM have been developed and utilized in several domains of mathematical optimization, computer science etc Some MCDM forms are mentioned below:

- TOPSIS: it is based on the principle of finding a comprising solution, which is nearest to the positive ideal solution (PIS) and distant from the negative ideal solution in terms of the Euclidean distance.
- VIKOR: it is a technique, which provides the compromise solution to the MCDM problem having conflicting criteria. The solution is the option, which is nearest to the ideal solution.
- PROMETHEE II: it is based on the concept of pairwise comparison of the alternatives. Various relation degrees are used to get results

In the following figure are displayed the rankings for each natural fiber. E stands for entropy-based calculations, while C for CRITIC based-calculations.

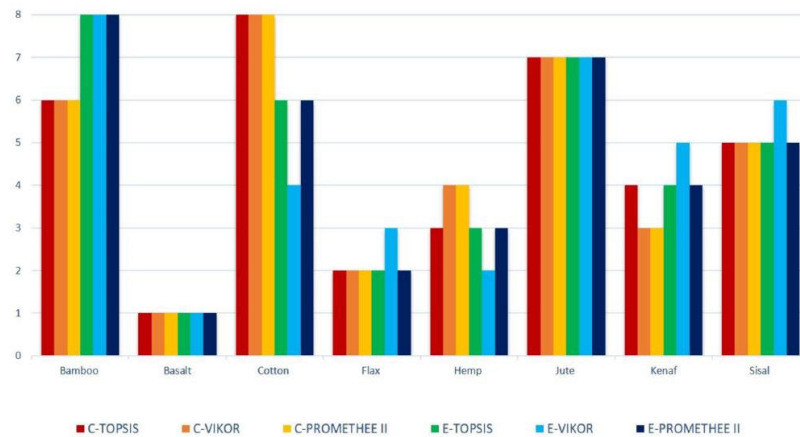


Figure 39 Ranking of natural fibers given by different MCDM methods.

From the above figure, it is clear that basalt fiber is at the first place for all the MCDM methods. This can be attributed to its lowest moisture absorption, highest aspect ratio and good mechanical properties. Despite the higher specific strength and specific modulus of flax fibers in comparison to basalt fibers, they have taken mainly the second position. That's because, flax fibers reveal much higher moisture absorption and are more expensive compared to basalt fibers. However, flax fibers reveal lower moisture absorption compared to the classic natural fibers of jute and hemp. These observations can be seen from the following figures.

Fiber	Aspect Ratio ( $\mu\text{m}$ )	Strain at break (%)	Specific Strength (MPa/g/cm <sup>3</sup> )	Specific Modulus (GPa/g/cm <sup>3</sup> )	Moisture Absorption (%)	Cost (US \$/ton)
Bamboo	48.67	1.73	383.10	22.10	14.00	500.00
Basalt	1760.56	3.56	787.50	24.18	0.10	1000.00
Cotton	1510.64	6.50	264.90	8.00	33.50	2850.00
Flax	1744.19	1.40	832.50	36.00	7.00	3150.00
Hemp	983.61	1.60	360.00	47.30	8.00	1550.00
Jute	226.67	1.80	411.00	14.00	12.00	950.00
Kenaf	258.33	1.60	641.00	36.55	9.10	400.00
Sisal	162.96	2.5	426.30	29.00	11.00	650.00

Figure 40 Criteria values of the natural fibers

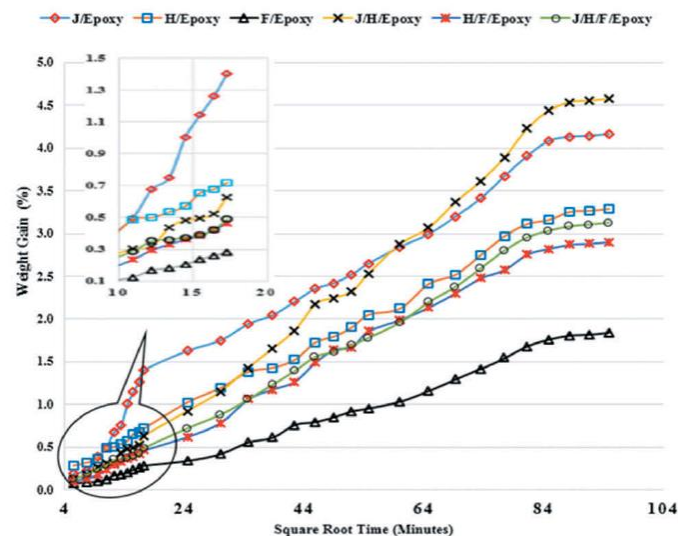


Figure 41 Percentage weight gain during water uptake (J-jute, H-Hemp, F-Flax)

Generally, it is important to point out that no MCDM technique gives the perfect ranking, because each MCDM approach has its own advantages and limitations.

#### 4.1.3Properties of natural fibers and their influence on composites

As discussed above, natural fibers are an eco-friendly solution for their introduction in composites, because of their biodegradability and low energy consumption. Other advantages that can be added are their low weight, good thermal and sound insulation. However, concerns are aroused regarding their high moisture absorption, low fire resistance and low durability. Indeed, moisture absorption is a major challenge because it has a negative impact on the mechanical properties of the composite. Various methods are researched with the aim of restricting these unwanted characteristics. In the following figure, a more detailed analysis of advantages and disadvantages of natural fibers is displayed.

Advantages	Disadvantages
It has lower weight	These have higher moisture absorption
These are less expensive	Have lower durability
These are renewable	These have poor fire resistance
Have higher flexibility	Have lower mechanical properties
These are renewable	Variation in quality exist
Have eco-friendly nature	Have low thermal resistance
Have good thermal and sound insulation	Poor microbial resistance exists
These ae nontoxic	Demand and supply cycles exist
Biodegradable in nature	
Have lower energy consumption	

Figure 42 Advantages and Disadvantages of natural fibers

Generally, various factors can influence the properties of the natural reinforced composites, Typical parameters for this influence may be considered the type of the matrix, the reinforcement type and the manufacturing technique. An overview of the tensile strengths and moduli of composites with natural fibers can be seen from the following figure.

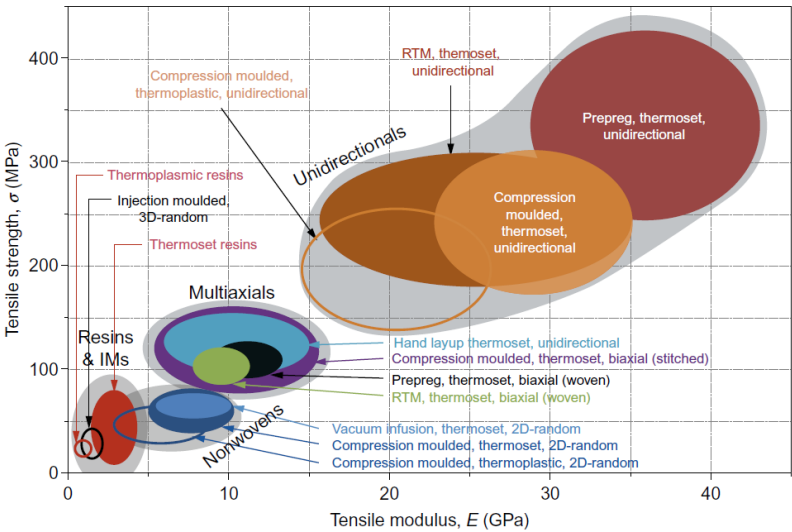


Figure 43 Tensile strength versus stiffness of natural fiber composites

#### 4.1.4 Chemical and physical modification of natural fibers

It has been observed that most of natural fibers do not bound well with the polymer matrix. This is explained by the fact that polymer matrix displays a hydrophobic nature, while natural fibers have a hydrophilic nature. For that reason, natural fibers are treated before they are incorporated as reinforcements. Plant fibers are mostly comprised of cellulose which has open hydroxyl groups in its structures. These hydroxyl groups form a polar bond with neighboring hydroxyl groups from other molecules and moisture in the air. With the chemical treatments, these hydroxyl groups are restrained by replacing the active hydroxyl groups with chemical reagents. Thus, lower moisture absorption and improved stress transfer capabilities are observed. In the following section are summarized some of the widely used chemical treatments.

- **Alkali treatment:** The alkali treatment is considered a complex, economical and powerful technique applied for enhancing the attachment of natural fibers especially with epoxy resins. Various parameter like the type of alkali used, the concentration of the alkali solution, time for which it is dipped in the solution, temperature have influence on the fiber surface morphology. This treatment disrupts the hydrogen bonding in the surface of natural fiber, while there are removed substances such as pectin, hemicellulose, lignin, waxes and impurities covering the cellulose fibrils. The rougher fiber surface, which is created, leads to increased surface contact between the fiber and the polymer matrix, enhancing their interfacial interaction. The reaction, which takes place is the following:  $\text{Natural fiber-OH} + \text{NaOH} \rightarrow \text{Natural fiber-O}^-\text{Na}^+ + \text{H}_2\text{O}$ . After chemical treatment NFs are washed with dilute acetic acid so that extra NaOH is removed and then it is cleaned with distilled water. In the following figure are shown SEM micrographs of untreated and alkali treated flax fibers. As previously mentioned, the destruction of hydrogen bonding found in the fibers causes a surface with increased roughness and this can be observed from the following figure.

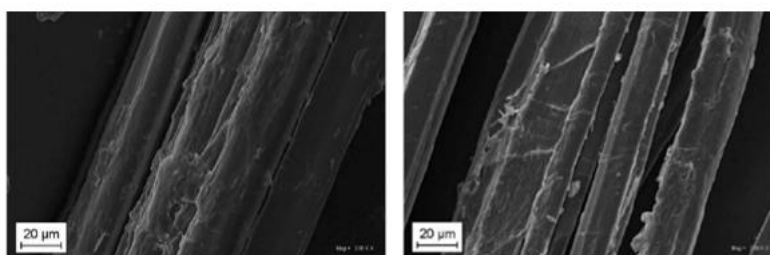
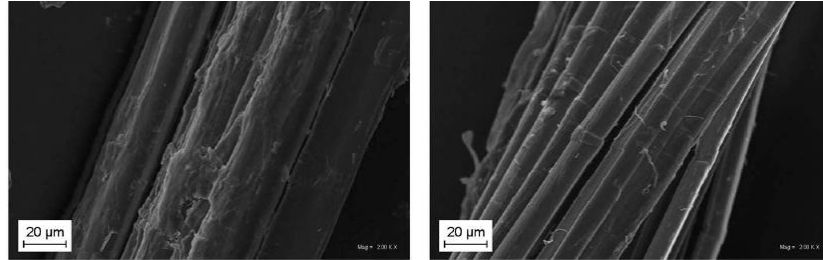


Figure 44 SEM micrographs of untreated (left) and alkali treated (right) flax fibers

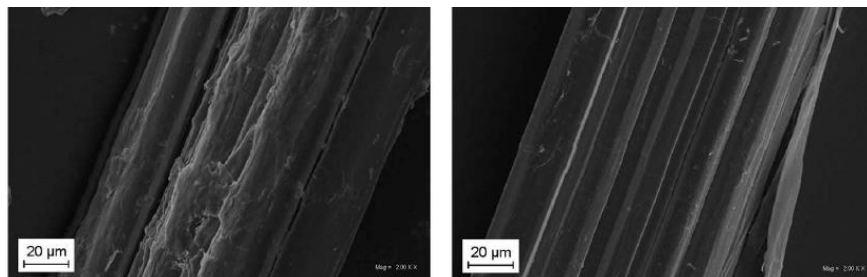
- **Silane treatment:** silane ( $\text{SiH}_4$ ) has a multivalent role and its introduction as a coupling agent enhances the fiber and by extension the fiber matrix interaction. There are considerable number of steps that go through the fibers with this technique. These are the hydrolysis, condensation and bond formation during the treatment of the natural fibers. In the presence of moisture silanol is formed. During condensation, one end of silanol connects

with the cellulose hydroxyl group of the fiber while the other end is connected with the matrix, creating a chemical bond between these two. The chemical reaction is the following:  $\text{CH}_2\text{CHSi}(\text{OH})_3 + \text{Fiber-OH} \rightarrow \text{CH}_2\text{CHSi}(\text{OH})_2\text{O-Fiber} + \text{H}_2\text{O}$ . With silanization an additional layer is created, eliminating microfibrils defects. Generally, the modified fibers with silane treatment interact better with the matrix than alkaline-treated fibers, leading to higher tensile strength, tensile modulus, flexural rigidity and thermal stability. In the following figure are shown SEM micrographs before and after silane treatment.



*Figure 45 SEM micrographs of untreated (left) and silane-treated (right) flax fibers*

- **Acetylation treatment:** this method is known as the esterification strategy for strengthening regular or natural filaments. Acetyl gathering ( $\text{CH}_3\text{CO}$ ) reacts with the cellulose fibers, followed by the discharge of hydroxyl groups ( $\text{OH}$ ), hence reducing the moisture absorption capacity. While other chemical treatments leave more voids after the reaction, acetylation provides a rough surface topography with a smaller content of voids, establishing a more intimate contact between fibers and matrix and promoting interatomic fiber/matrix adhesion by van der Waals forces. In the following figure are shown SEM micrographs of treated with the acetylation treatment and untreated flax fibers. The surface of the acetylated fibers was smoother compared to the untreated fibers and the esterification process has led to an increase of the surface area.



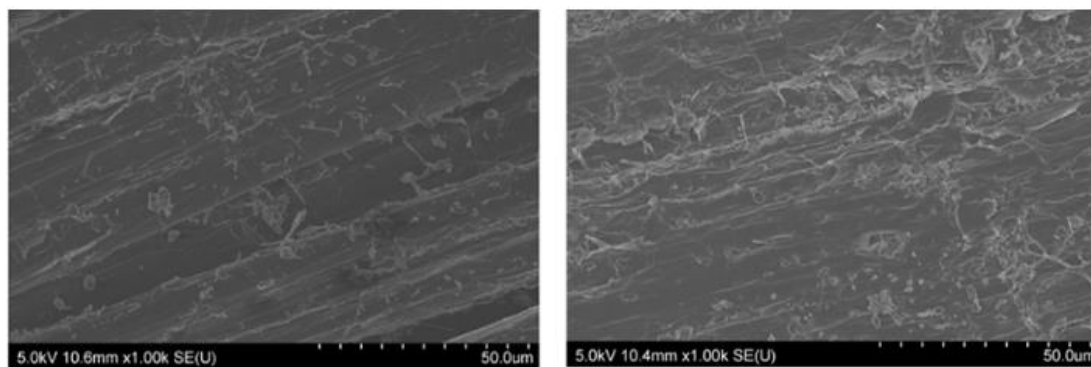
*Figure 46 SEM micrographs of untreated (left) and treated with acetylation treatment(right) flax fibers*

Other chemical treatments and their effects are displayed in the following figure:

Chemical Treatments	Functional Groups/ Coupling Agent	Specific Effects on Natural Fibers
Benzoylation treatment	Benzoyl chloride	Makes fibers hydrophobic
Peroxide treatment	Polyethylene	Improve the adhesion of fibers with a matrix Remove moisture from fiber
Sodium Chlorite treatment	Sodium Chlorite (NaClO <sub>2</sub> )	
Acrylation and acrylonitrile grafting	Acrylic Acid (CH <sub>2</sub> =CHCOOH)	Bonding capacity and stress transfer of the interface increases
Oleoyl Chloride treatment	Oleoyl Chloride	Improves wettability and adhesion properties
Triazine treatment	Triazine (C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> )	Improves the adhesion of the fibers
Permanganate treatment	Potassium Permanganate (KMnO <sub>4</sub> )	Improves the thermal stability of the fibers
Fungal treatment	Specific Enzymes	Enhance the linking/meshing of fibers in the matrix

*Figure 47 Chemical Treatments and their effects on natural fibers*

In physical treatments are changed the structural and surface properties of the fiber. In this way, fiber-resin adhesion is improved. Two widely used methods are the corona and plasma treatment, which make use of electric discharge. Indeed, the electrical energy modifies the fibers and better surfaces of the fibers are created. The main difference of plasma and corona treatment is that plasma has a narrower treating area but forces larger energy to the fibers, while corona treatment affects bigger areas with smaller enforcement of energy. Moreover, plasma leaves no ozone gas, which is released in the corona procedure. In the following figures are displayed SEM images of untreated and treated fibers with corona and plasma treatment.



*Figure 48 Effect of corona treatment on the surface of miscanthus fibers, left is depicted the untreated fibers and right the corona treated fibers.*



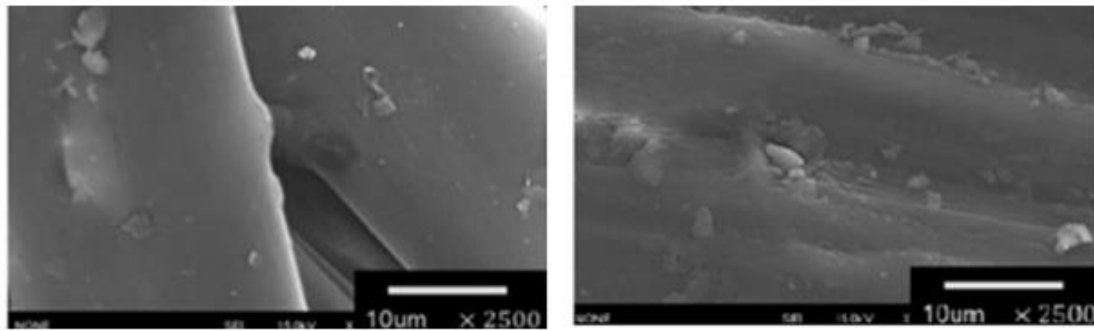


Figure 49 Effect of plasma treatment on the surface of jute fibers, left is depicted the untreated fibers and right the plasma treated fibers.

As seen above, the untreated fibers have smoother surface, while the surfaces of treated fibers are quite damaged. These mechanical defects can be explained by the energetic particles, which provoke the bombardment of the surface.

#### 4.1.5 Applications of natural fibers

Applications of natural fibers can be found in several industries like construction, automobile, aircraft components, electrical goods and biomedical industries. The main motivations of using NFRP in industries are the weight reduction and cost reduction. Generally, NFRPs can have non-structural and moderate load bearing interior applications, while their use to primary structural components is limited. They are mainly used for interior parts like door panels of automobiles, parcel shelves, seat cushions, cabin linings and dashboards. In the following figure are displayed the main applications of various natural fibers.

Natural fibers	Applications
Bast fibers (kenaf, hemp, jute, sisal, etc.	It is mainly used in instrument panels for covered components, door panels, seat back panels, door bolsters, pillars, centre consoles, and in load floors.
Banana	It is mainly used for wrapping paper.
Coir	Coir fibers are used for doormats, rugs, mattresses and car seat covers.
Cotton	Cotton is mainly used in insulation, soundproofing and trunk panels.
Coconut	It is used in back cushions and head restraints, seat bottom and seat cushioning and also in seat surfaces.
Flax	Flax fibers are used in rear parcel shelves, seatbacks, pillar panels and floor panels
Kenaf	Kenaf fiber is used in the inner panel of doors.
Wood	These fibers are used in covered seat back panels, inserts, spare tyre covers, door panels
Wool	It is used in seat coverings and upholstery
Wood flour	Wood flour is used in as a carrier for covered inserts and armrest and also in covered door panels.

Figure 50 Applications of various natural fibers based on their properties

Also, natural fiber reinforced composites have some ballistic applications, because of their high impact properties. They can be incorporated as a second layer in Multilayer Armor Systems (MAS). In a study, NFRPCs by pineapple leaves (PALF) were used as an extra protection to vests made with Kevlar. As a result, a higher level of protection was achieved.



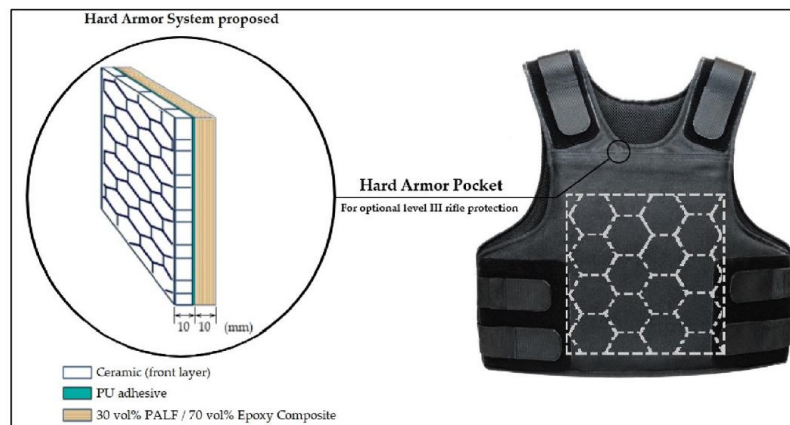


Figure 51 Schematic diagram of the hard armor system for ballistics protection

## 4.2 Flax fibers

Generally, lignocellulosic fiber is another way of describing plant fibers. The reason behind of this is that all plant fibers are mainly constructed of cellulose, hemicellulose and lignin. The majority of the fibers have a percentage of 50-70% cellulose, which is responsible for the high performance of the fibers. For this high performance of the plant fibers, the microfibrillar angle (MFA) plays also an important role. MFA is defined as the angle microfibrils (found in the S2 layer cell wall of the fiber) make in comparison to the fiber axis.

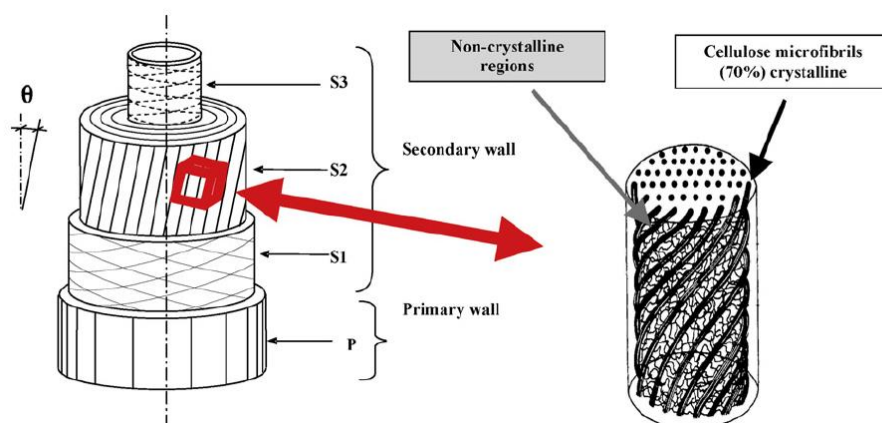


Figure 52 Schematic representation of flax fiber showing helix arrangement of cellulose fibrils

Generally, lower MFA and higher cellulose content provides higher ultimate strength and modulus, while higher MFA and lower cellulose content imparts ductility to the fibers. In the following figure are presented the percentage of components and the microfibrillar angle of various plant fibers.

Fiber	Origin	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Wax (%)	Ash (%)	Microfibrillar Angle (°)
Hemp	Bast	70–74	3.5–5.7	15–20	0.8	1.2–6.2	0.8	2–6.2
Jute	Bast	61–72	12–13	18–22	0.2	0.5	0.5–2	8
Sisal	Leaf	78	8	10	-	2	1	-
Flax	Bast	64–72	2–2.2	18–20	1.8–2.3	-	-	5–10
Ramie	Bast	69–91	0.4–0.7	5–15	1.9	-	-	7.5
Harakeke	Leaf	56–64	7.8	23–31	-	-	-	-
Coconut Coir	Fruit	36–43	0.15–0.25	41–45	3–4	-	-	30–49
Kenaf	Bast	45–57	22	8–13	0.6	0.8	2–5	2–6.2

Figure 53 Percentage of components and microfibrillar angle of various plant fibers

As seen above flax fibers have a relatively low microfibrillar angle and a relatively high content of cellulose. Thus, flax fibers reveal great mechanical performance, and it is the reason why they are often chosen as reinforcement in composites.

#### 4.2.1 The flax stem

The most important areas inside the flax stem are considered the fibre bundles, which are at the periphery of the stem and the woody core (xylem), which is located between the fibers and the central cavity. In a flax stem, there are about 10000-40000 fibers. These fibers find applications not only in textile industry but also in composite materials. Moreover, interestingly there is a form of composite material inside the stem because the fibers are connected via pectic junctions. Thus, the matrix of this 'composite' is considered the pectic polymers and the reinforcement the flax fibers. This results in the possibility of stress transfer and to a behavior of a composite. The pectic junctions which link the flax fibers have two types: homogalacturonan and rhamnogalacturonan, while they appear in two morphological forms. In the following figure is shown a transverse section of a flax stem and a detailed representation of the different parts.

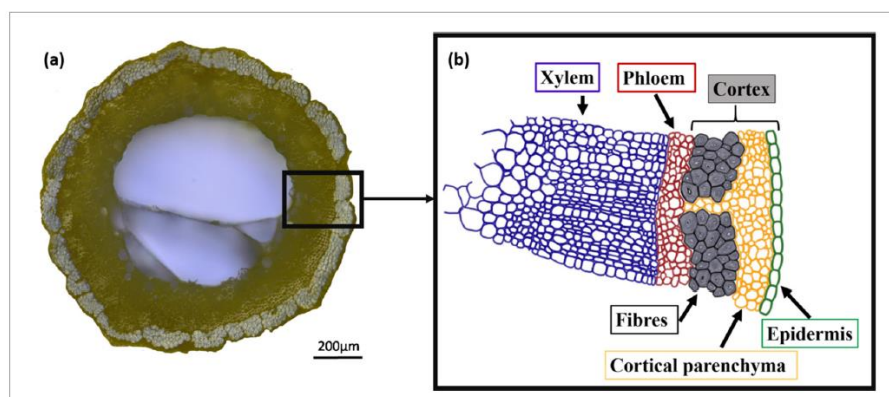
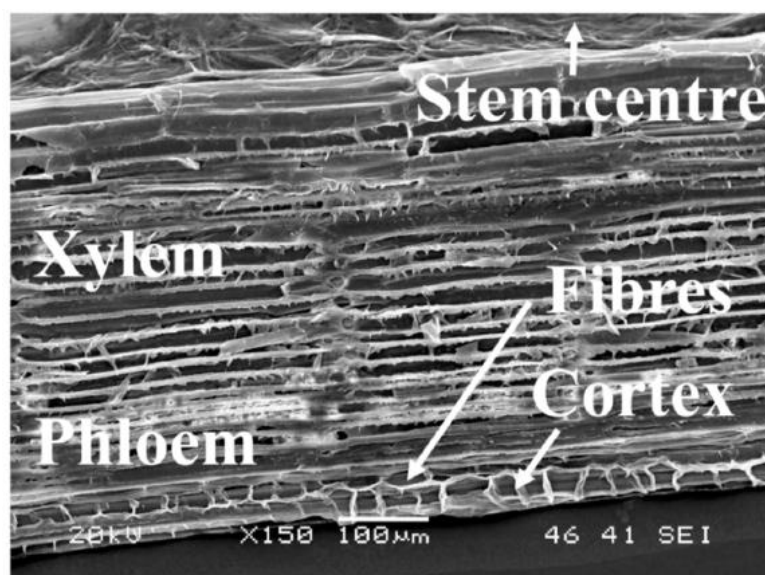


Figure 54 Transverse section of a flax stem (a) and a detailed representation of the different parts (b)

Xylem and phloem, which from them are derived the shives (also deployed in composite materials) are found in the inner part of the stem and they are characterized for their porosity. They contribute to the vascular system of the plant, while they play a significant role to the flexural strength of the stem (xylem account up to 30% of a dry flax stem bending stiffness). Their porous structure can be observed from the following figure, while a SEM image of flax shives is also cited.



*Figure 55 Longitudinal flax stem section showing the porous structure of phloem and xylem*

Moreover, there are some differentiations of the transverse cross-sections depending on the height of the stem, despite the fact that there is a similar architecture along the stem. As first observations that should be noted are that the diameter of transverse cross-sections in the lower part is bigger, while the central cavity increases till the middle of the stem. Also, there is a decrease of the xylem surface with increasing stem height. The fibre richness at different heights is also different. More precisely, it is observed that at middle height are found the most fiber-rich sections in contrast to other parts. Indeed, in the middle of the stem are observed an increased relative surface-area of the fibers and an increased number of fibers. Generally, the fibers taken from the middle are longer and this is correlated with better mechanical properties. In the following figures are shown the transverse sections at different heights of the stem and a table of mechanical properties along the stem length is cited.

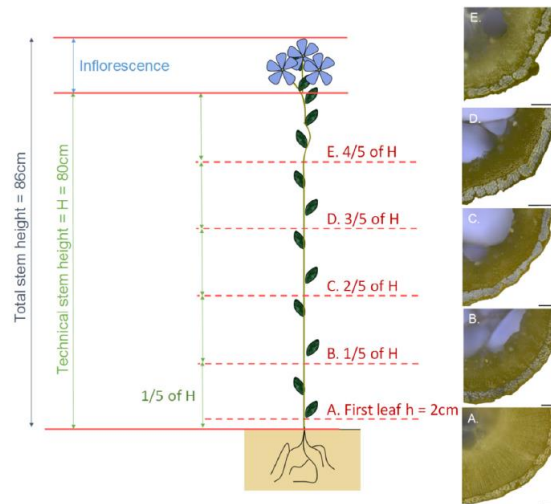


Figure 56 Transverse sections of flax stem at different heights

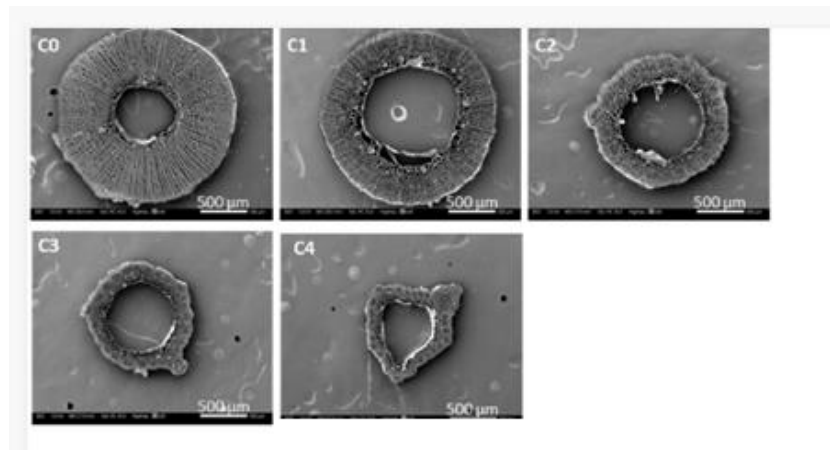


Figure 57 Evolution of the xylem and pith surface with increasing height (it has been done a bast fiber removal)

Localization of fibres along the stem		Bottom	Middle	Top
Length of elementary flax fibres $L_f$ (mm)	$L_f$ mean	$15.9 \pm 5.4$	$35.5 \pm 16.3$	$17.2 \pm 5.8$
	$L_f$ min	5.4	11	9.2
	$L_f$ max	27.3	87	31.3
Number of studied fibres for length measurements		26	51	32
Tensile mechanical properties of elementary flax fibres	Young's modulus (GPa)	$47.2 \pm 18.1$	$58.7 \pm 21.3$	$50.1 \pm 22.7$
	Tensile strength (MPa)	$872 \pm 437$	$911 \pm 422$	$768 \pm 363$
	Ultimate elongation (%)	$2.1 \pm 0.8$	$1.8 \pm 0.6$	$1.8 \pm 0.8$
Number of studied fibres for mechanical evaluations		46	45	57

Figure 58 Average lengths and tensile properties of fibers

Generally, the flax fibers are characterized for their polygon cross-sections and the fact that they have tapered ends. The different fiber ends are randomly distributed within the bundle, and this restricts the strain concentrations.

Moreover, as previously mentioned, the mechanical properties of flax fibers can be related to their growing conditions. The most significant parameter concerning the growth of the flax fibers is the accumulated temperature. It is identified that the optimum fiber richness is

reached around an accumulated temperature of 850-1100°C, which is a favorable condition for harvest. Also, the procedure of retting (spreading the fibers on the ground) has an important influence on the mechanical properties of flax fibers. Excessive retting can lead to the degradation of the fibers.

#### 4.2.2 The influence of the twist angle

In the textile industry, there are desired fibers which are characterized for their stability and finesse. Therefore, it is a common practice to twist the fibers and have yarns, which are known for their strength. This increase in strength is attributed to the increased friction of the fibers and their entanglement. The amelioration of the mechanical properties of dry yarn flax fibers can be seen from the following figure. Yarn 1 (Y1) corresponds to high twist, Yarn 3 (Y3) to a low twist and Yarn 2 (Y2) corresponds to low twist and has shorter fibers.

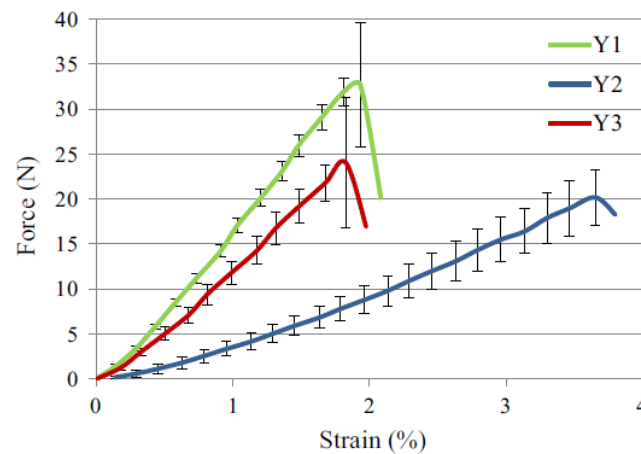


Figure 59 Force vs strain curves of three different yarns obtained by tensile tests

Nevertheless, for composite applications with flax fibers, the strategy of twisting the fibers is not ideal. In fact, this twist of the fibers has an effect as a misorientation in the composites and in combination with the fiber anisotropy are expected to appear reduced tensile strength and stiffness. Also, it should be noted that a high twist will be a barrier of the permeability of the fiber, and this can provoke voids and lower mechanical properties. In the following table is depicted that higher twist angles provoke lower mechanical properties of UD composites (an increasing twist angle have the composites with the following row: hackled flax, roving and yarn).

Fibre bundle type	Production method	$V_f$ (%)	Strength composite (MPa)	Stiffness composite (GPa)
Hackled flax	Prepregger	$42 \pm 2$	$378 \pm 38$	$28.2 \pm 2.6$
Roving	Drumwinder	$48 \pm 1$	$377 \pm 24$	$26.2 \pm 1.6$
Yarn	Drumwinder	$50 \pm 1$	$315 \pm 46$	$23.1 \pm 1.2$

Figure 60 Strength and stiffness of composites with different types of bundle types

An explanation of the lower stiffness of the composites as the twist angle increases can be attributed to the fact that the fibers when they are not twisted are longer. The shorter fibers result in a lower strain and by extension to a lower stress buildup. Thus, the stiffness of the composite is reduced.

Also, it is a point of interest, that a stiffness increase of composites can be observed at high strains. This can be seen from the following figure.

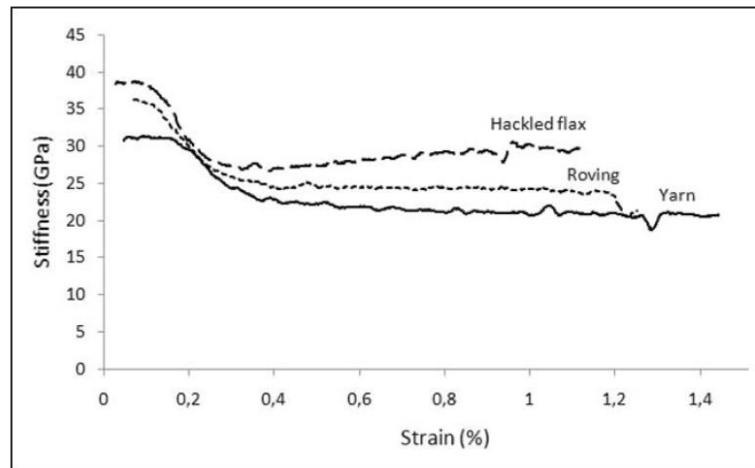


Figure 61 The change of the stiffness in relationship with strain for composites with different bundle types

This can be explained at two different scales. On a large scale, the fibres are adjusted and make a rotation in order to be more aligned to the load. On a smaller scale, the microfibrils make also a rotation in order to respond to the stresses.

## Chapter 5 Interlaminar fracture toughness of natural fiber composites

### 5.2.1 Introduction

The main failure mode of laminated composites can be considered the delamination. This failure mode has big influence on the stiffness of the composite and on its load-bearing capacity. It doesn't necessarily happen during the in-service of the composite, but it can also occur through the production process as a defect or in machining operations like drilling. Moreover, the hydrophilicity of natural fibers and the hydrophobicity of the matrix, impairs low interfacial adhesion between them, increasing the chances of delamination. Also, residual stresses, which originate from the sensitivity of natural fibers to moisture and temperature can enhance the delamination process. The interlaminar fracture mechanics of various fracture modes (Mode I, II, III or any combination of them) can light up the delamination processes.

The Linear Elastic Fracture Mechanics approach is used to describe the interlaminar fracture toughness. In this theory, the whole body can be considered to have an elastic behavior, except for a restricted zone (damage zone) near the crack tip. Generally, two indicators can be used to describe the interlaminar fracture toughness, the Stress Intensity Factor, and the Critical Strain Energy Release Rate. The first one is referred to the stress intensity level and the second to the energy, which is required for the growth of the crack. Generally, for fiber reinforced composites, the second indicator is used, because the stress field of these composites is more complicated due to various types of energy losses (like fiber pull-out and fiber-matrix debonding).

### 5.2.2 Parameters and mechanisms affecting the IFT

Some of the parameters of interlaminar fracture toughness can be summarized in the following list:

- Matrix type
- Fibre type and architecture
- Fibre orientation
- Interphase of fiber-matrix
- Thickness of the laminate
- Stacking sequence of the laminate

Generally, the interlaminar fracture toughness has many mechanisms. The main toughening mechanism can be considered the crack deflection. The fibers constitute an obstacle for the crack, and they contribute to the deviation from its path. Thus, a new and/or larger crack area is provoked, and energy is dissipated at a larger extent. The second of importance toughening mechanism can be considered the pull-out of the fibers from the matrix. With pulling out the fibers, energy is dissipated, because of the friction between the fibers and the matrix. The third mechanism can be considered the fiber bridging mechanism. In this mechanism the fibers link the surfaces of the fractured composite after their debonding. This way, part of the stress is carried by the fibers, hindering the crack propagation.

The above-mentioned mechanisms can be observed both to the Mode I and Mode II experiments. Additionally, for the Mode II, other significant absorbing mechanisms can be considered the shear cusp deformation, plastic deformation at the crack tip, shear friction and transverse shear deformation.

### **UD vs woven**

The woven fabrics have an additional resistance to crack propagation compared to the UD reinforcements, because they offer an irregular path for the crack growth. Thus, an increased interlaminar fracture toughness is observed, because of the higher consumption of energy of the longer paths. Also, they reveal better inter-ply interaction in comparison with UD preforms and this can be connected with the fiber bridging toughening mechanism.

### **Yarn linear density**

The yarn linear density can affect the interlaminar fracture toughness, because thinner yarn creates less crimp and by extent a less crack deviation from the predicted path. Moreover, for the Mode II, the presence of crimp constitutes an obstacle for the sliding motion of the adjacent plies. Thus, the crack propagation is hindered and improved interlaminar fracture toughness  $G_{IIC}$  is observed.

### **Length of the fibers**

It is observed that the fracture toughness is highly related to the length of the natural fibers. Short fibers provoke reduced fracture toughness, while medium and high length fibers at high loadings give composites with enhanced fracture toughness. The enhanced fracture toughness of longer fibers is attributed to the higher energies required for the matrix-fiber debonding and fiber pull-out.

### **Fiber treatment**

The fiber treatment (like alkaline treatment) may provoke a decrease in the interlaminar fracture toughness of composites. The improved adhesion of the fibers into the matrix can restrict some toughening mechanisms like fiber pull-out and fiber-matrix debonding, which may be dominant ways of dissipation of energy in a composite. However, in the case of the domination of other toughening mechanisms like fiber bridging, the fiber treatment may offer improved interlaminar fracture toughness.

### **Out of plane reinforcements**

Stitching is a technique, in which the composite is reinforced in the out of plane direction. With this technique, an increased mode I and mode II fracture toughness are observed, because the crack propagation is restricted. However, reduced tensile strength and modulus are expected to show up. The stitching density and the type of the stitch fiber play a significant role on the magnitude of the reduction of the in-plane mechanical properties.



## Chapter 6 Bibliography research

### 6.1 State of the art

#### 6.1.1 Interlaminar fracture toughness of composites with natural fibers and biobased resins.

Concerning the study of the fracture toughness of composites with biobased matrices and natural fibers, the scientific literature doesn't provide enough information. However, some papers can highlight some aspects of this topic. R.V. Silva and coworkers[1] investigated the effect of alkaline treatment of sisal and coconut fibers on the fracture toughness of composites with castor oil polyurethane matrix. This treatment for sisal fibers led to stronger adhesion, but simultaneously to decreased fracture toughness due to the restriction of energy absorption mechanisms like debonding and pull-out. On the contrary, for coconut fibers, the treatment led to the fibrillation process (breaking down the fiber bundle into smaller fibers), which enhanced the fracture toughness. Respectively, Moyeenuddin A. Sawpan, Kim L. Pickering, Alan Fernyhough, [2] showed that alkali and silane treatment on fiber hemp reinforced PLA composites, led to reduction of fracture toughness. Moreover, they revealed that short fiber hemp reinforced PLA composites have lower fracture toughness compared to those with long fiber hemp, due to the higher stress concentration in the fiber ends and poor matrix bonding. Additionally, V. Alvarez, and his team[3] showed in short sisal fibers reinforced starch-based composites that the fracture toughness is related to the fiber alignment.

Furthermore, Sateeshkumar Kanakannavar and Jeyaraj Pitchaimani[4] noticed the improvement of fracture toughness of flax braided woven PLA composites with the increase of fabric content. Also, they pointed out the architecture type of the reinforcement, indicating that braided composites in comparison to standard fabric composites need more strain energy to begin crack propagation. Moreover, Kim L. Pickering and coworkers[5], showed the influence of crystallinity of PLA composites reinforced with short hemp fiber. The fracture toughness is decreased with the increase of crystallinity due to the creation of an easier path for crack propagation.

#### 6.1.2 Interlaminar fracture toughness of composites with flax fibers and biobased epoxy

Concerning flax fiber reinforced petroleum-based epoxy composites, various studies have been made for their interlaminar fracture toughness. Yousef Saadati and coworkers [6] investigated the Mode I, II and mixed mode I/II of UD flax-epoxy composites. For mode I, results of  $G_{IIC}$  (574) and  $G$  propagation ( $G_{IC} = 903 \text{ J/m}^2$ ) occurred, while for Mode II,  $G_{IIC} = 612 \text{ J/m}^2$  occurred respectively. For the mixed mode, MMB tests resulted in  $G_{(I/II)C} = 414.4 \text{ J/m}^2$ . Similarly, Thamilarasu S. Rajendran and coworkers[7] investigated the Mode I and Mode II of twill weave 2/2 flax epoxy composites. The results were  $485 \text{ J/m}^2$  and  $962 \text{ J/m}^2$  for Mode I and II respectively[7]. Moreover, a different approach of investigating the Mode I fracture toughness was made by El Hadi Saidane and coworkers [8] who used acoustic emission. They created flax, glass and hybrid flax-glass woven composites and studied their behaviour. By creating classes depending on acoustic parameters and linking them with respective failure mechanisms, it was studied the behavior of the composites, showing that hybridization of glass fibers with flax fibers is an interesting solution for increased toughness.

With the aim of improving the fracture toughness, there are cited in literature some techniques, which can be used. For example, the team of M. Ravandi and coworkers [9] noticed the amelioration of Mode I toughness with stitching through the thickness of UD and woven flax epoxy composites. Nevertheless, with this technique a change in crack growth behavior from stable to stick-slip unstable fracture for higher stitch aerial fractions was observed. Additionally, it was noticed that the woven laminated composites showed better energy dissipation than UD, due to the larger fibre bridging and the larger plastic yield zone at the crack tip. Another way of improving the fracture toughness was achieved with the aid of interleaving of chopped flax yarn in UD flax fiber/epoxy composites [10]. It was concluded that this modification can contribute to higher fiber bridging phenomena and that the tortuous path, which was created by the chopped flax yarn, played a significant role for the improvement of the fracture toughness. Nevertheless, it was observed that high chopped yarn length and content could result to unstable crack propagation.

Concerning the effect of the architecture type and other parameters of the reinforcement on the fracture toughness was also examined by some authors. For example, F Bensadoun and coworkers [11] investigated the fracture toughness (both for Mode I and Mode II) of different flax epoxy architectures. They concluded that woven textile composites improve much more the toughness in comparison to the UD [0,90] cross-ply lay-ups, due to the yarn crimp and irregular surface of the layers, which create a more tortuous path of crack propagation. Also, Q. Liu and M. Hughes [12] examined the influence of varying weft yarn density, weave configuration and stacking sequence on fracture toughness. However, the team concluded that the fibre volume fraction dominates the toughness instead of the microstructural arrangement, while it was observed strong anisotropy in the weft and warp directions.

Summarizing tables of the most significant results for the Mode I and Mode II interlaminar fracture toughness of flax reinforced petroleum-based epoxy are cited below:

Πίνακας 1 Mode I Fracture Toughness of flax reinforced petroleum based epoxy composites

	YousefSaadatiet al[6]	Thamilarasueta[7]	Ravandietal[9]	Ravandietal[9]	Ravandietal[9]	LiYanetal[10]	Bensadoun[11]	Bensadoun[11]	Bensadoun[11]	6)ElHaidi[8]
<b>Reinforcement</b>	UD flax (200g/m <sup>2</sup> ) [0]12	twill weave 2x2 flax, 10 plies	woven 4x4 flax (500g/m <sup>2</sup> ) [0]4	woven 4x4 plain weave flax (500g/m <sup>2</sup> ) 4 plies	UD flax (110g/m <sup>2</sup> ) [0]16	UD flax [0]24	plainweave flax, 4 plies	twill weave 2x2 flax 4 plies	UD flax [0,90]2s	twillweave 2x2,10 plies
<b>Matrix</b>	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy
<b>Special Modification</b>	-	-	-	Flax Stitching(1,38*10 <sup>-2</sup> aerialfraction)	-	interleaving with chopped yarn (10mm and 20g/m <sup>2</sup> ), 3 plies	-	-	-	-
<b>Stiffener</b>	-	-	CFRP	CFRP	CFRP	-	GFRP	GFRP	GFRP	-
<b>CompositeFabrication</b>	RTM	Vacuumbaggingmethod	VARI	VARI	VARI	Hotcompactionprocess	RTM	RTM	RTM	Compressionmoulding
<b>Vf (%)</b>	0.41	-	0,31	0,31	0,4	~0,6	0,4	0,4	0,4	0,4
<b>DataReduction Method</b>	MBT	DCB/ECM	DCB/MBT	DCB/MBT	DCB/MBT	DCB/MBT	DCB/MBT	DCB/MBT	DCB/MBT	DCB/MBT
<b>Gic/ initiation (J/m<sup>2</sup>)</b>	574	-	~2000	~2400	~800	-	457	754	655	1079
<b>Gic/ propagation (J/m<sup>2</sup>)</b>	903	-	~3200	~4000	~1250	-	1158	1597	1086	~2400
<b>Gic (J/m<sup>2</sup>)</b>	-	485	-	-	-	1840	-	-	-	-

*Πίνακας2 Mode II Fracture Toughness of flax reinforced petroleum based epoxy composites*

	YousefSaadatietal[6]	Thamilarasuetal[7]	F Bensadoun[11]	F Bensadoun[11]	F Bensadoun[11]
<b>Reinforcement</b>	UD flax (200g/m <sup>2</sup> )	twillweave 2x2 flax	flaxplainweave, 4 plies	Flax twill weave 2x2 4 plies (low twist)	UD flax [0,90]2s
<b>Matrix</b>	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy
<b>Stiffener</b>	-	-	GFRP	GFRP	GFRP
<b>CompositeFabrication</b>	RTM	Vacuum bagging method	RTM	RTM	RTM
<b>Vf (%)</b>	0.41	-	0,4	0,4	0,4
<b>DataReduction Method</b>	CC/GBT	ENF/ECM	ENF/GBT	ENF/GBT	ENF/GBT
<b>G<sub>IIc</sub> (J/m<sup>2</sup>)</b>	378/612	962	1872	1315	1006

### 6.1.3 Tensile and flexural properties of composites with flax fibers and biobased epoxy

Concerning the tensile and flexural properties of flax fibers reinforced biobased epoxy, numerous studies have been made. Forkan Sarkar and coworkers [13] showed that UD flax reinforced bio epoxy composites and respective conventional epoxy composites have comparable tensile and flexural properties. However, some differentiated failure modes were observed in these experiments. Similarly, J. Schuster and his team [14] showed that the UD flax reinforced biobased epoxy composites have similar stiffness and tensile strength, but lower ultimate elongation compared with the composites with the conventional epoxy.

Generally, biobased epoxy resins can be emerged with various ways. Two different types of biobased epoxy resins be seen from Christopher Taylor and his team [15], who used epoxidized sucrose soyate (ESS) resin for UD flax reinforced composites and from Corentin Musa and her coworkers [16], who used isosorbide-based epoxy resin. The first team made tensile and flexural experiments showing that the composites meet requirements for structural quality composites, while the second showed the similarity of the tensile properties with the respective petroleum-based epoxy composites.

Also, concerning the reinforcement type and its modification in biobased epoxy composites have been made some studies. C. Avril et al [17] studied the tensile properties of different flax reinforcements (non-woven, balanced fabric and UD) in biobased epoxy resins. The UD composites revealed the highest tensile strength and stiffness, while the balanced fabric and the thick mat showed similar performance. Additionally, Marc Li Loong et al [18] investigated the effect of acetylation (1, 2, 3 and 4%) on the tensile properties of UD flax fiber reinforced bio-epoxy composites. It was concluded that the concentration for the best tensile strength and modulus is 2%. Respectively, D. Perremans and coworkers [19] described the effects of the APS and alkali treatments on the tensile behaviour of flax UD bio-epoxy composites. Improved interphase of fiber and matrix was obtained but the embrittlement of the fibers lead to a lower strength of the composites. Indeed, the treatments didn't change the dynamics of the stress-strain curve but affected slightly its form.

Lastly, an interesting study was made by Gaston Francuccu and his team [20], who investigated UD flax reinforced bio epoxy composites manufactured by the combination of vacuum bagging and compression molding stage. It was shown that the tensile and flexural performances were higher with the increase of the external pressure, mainly due to the better fiber to resin ratio.

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