UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

DIPARTIMENTO DI INGEGNERIA CHIMICA, DEI MATERIALI E DELLA PRODUZIONE INDUSTRIALE

XXIX PhD PROGRAMME IN

INDUSTRIAL PRODUCT AND PROCESS ENGINEERING

CURRICULUM ON PRODUCTION TECHNOLOGY AND SYSTEMS

PhD PROGRAMME COORDINATOR: PROF. ING. GIUSEPPE MENSITIERI

On the manufacturing techniques of lightweight hemp-epoxy composites and improvement of their flame resistance

PhD PROJECT SUPERVISOR
PROF. ING. FABRIZIO MEMOLA CAPECE MINUTOLO

PhD CANDIDATE
LUCA BOCCARUSSO

PhD PROJECT CO-SUPERVISOR
PROF. ING. MASSIMO DURANTE

DOTTORATO IN INGEGNERIA DEI PRODOTTI E DEI PROCESSI INDUSTRIALI

PIAZZALE TECCHIO 80—80125 NAPOLI—ITALIA

TEL. (39 81) 7682512/7682552

XXIX PhD PROGRAMME IN

INDUSTRIAL PRODUCT AND PROCESS ENGINEERING

CURRICULUM ON PRODUCTION TECHNOLOGY AND SYSTEMS

PhD PROGRAMME COORDINATOR: PROF. ING. GIUSEPPE MENSITIERI

On the manufacturing techniques of lightweight hemp-epoxy composites and improvement of their flame resistance

PhD PROJECT SUPERVISOR
PROF. ING. FABRIZIO MEMOLA CAPECE MINUTOLO

PhD PROJECT CO-SUPERVISOR
PROF. ING. MASSIMO DURANTE

PhD CANDIDATE
LUCA BOCCARUSSO

THIS PAGE WAS INTENTIONALLY LEFT BLANK.

To my parents, Eugenio and Giustina.
Constant sources of inspiration and role
model.

List of Contents

Acknowledgements

This thesis would not have been possible without the support of my supervisors Prof. Fabrizo Memola Capece Minutolo and Prof. Massimo Durante. I would like to express to them my sincere gratitude for their significant suggestions, inspiring guidance and immense knowledge.

List of Tables

List of Figures

iv

Abstract

The thesis work has been focused on the study of manufacturing technologies used to produce lightweight hemp/epoxy composites for their future applications as lightweight components, such as in the transportation industry. In this field, apart from the mechanical properties, good flame resistance is also required and then to increase the flame resistance of these components was another goal of this thesis. For this purpose, woven hemp fabrics with large mesh were used to produce porous structures and then lightweight hemp/epoxy composites for their future application both as independent structural components and as core for sandwich structures.

The thesis work is structured in the following six sections.

The first one begins with an overview on the state of the art of the hemp/epoxy composites and the main concepts about the flame retardants and the flame resistance techniques was presented. In this section, the need to investigate the possible use of hemp/epoxy composite materials, the study of their manufacturing processes (easily applicable for the industrial production) to produce low density composites and the study of techniques able to improve their flame resistance are highlighted.

Therefore, an overview about biocomposites, their classification, their advantages and disadvantages, and their manufacturing technologies are reported in the second section.

The materials and the methods used to conduct the experimental campaign, both for the manufacturing of lightweight structures and for the improvement of their flame resistance, are presented in the third section, which is structured as follows:

- *Firstly, a detailed description on the materials and in particular on the hemp fibres is reported;*
- *Subsequently, in order to produce natural fibre reinforced composites with different density values the use of different processes, i.e. infusion, vacuum infusion, brushing hand lay-up and injection moulding were described. To achieve this goal, the section is divided in three sub-sections (Part 1, Part 2 and Part 3); each sub-section is focuses on one of the above-mentioned technologies;*
- *Finally, the methods used to improve the flammability resistance of hemp composites, mixing the epoxy resin with different percentage content of APP (ammonium Poly-phosphate), are described.*

The subsequent sections of the thesis (Section 4 and 5) focus on the results and the discussion on both the feasibility of the illustrated processes and on the properties of the obtained products. Therefore, a full characterization in terms of tensile, flexural, compression, impact and flame resistance properties are carried out and then discussed.

Conclusive remarks, where the main results are summarized, close the thesis work

.

Chapter 1: Introduction and Overview

1.1 Introduction

Due to the increasing environmental awareness, depletion of petroleum resources, disposal problems after use, and introduction of new rules and regulations by legislative authorities to satisfy the new demands of the society, the new products must minimize the environmental impact. This aspect is especially relevant in the composite manufacturing field, where petroleum polymers and synthetic fibres are still widely used. This concept is directly connected with an efficient use of the material and of the energy resources, waste management and with the use of products and technologies with less impact on the environment. It is also clear that the search of lightweight composites structures is increasing in different industrial fields, i.e. automotive components, building materials and aeronautic industry and in general in the transportation industry, where the drive for weight and costs saving is greatest. Indeed, the products required from this filed should be as light as possible as well as cheap, together with high mechanical properties. Considering that the use of bio-based materials matches very good both the environmental, the costs and the *lightweight requirements* and highlighting the tremendous advantages and opportunities associated with the use of these materials such as low cost, less tool wear during processing, high specific properties and their availability as a renewable resource, *there is still need to investigate and to increase their engineering application fields*. Under this point of view, the use of natural fibres as reinforcement in composite materials is attracting more and more interest [1, 2, 3] and a large amount of researches were conducted in order to study a range of recyclable materials based on natural fibres such as jute, oil, palm, coconut, flax, hemp, kenaf and many more [4, 5, 6, 7, 8, 9, 10]. Among various kinds of natural fibres, hemp is one of the most interesting plants, it can easily be grown around the world, it has low cost, low density, ability of extracting heavy metals from the soil makes, high specific strength when compared to glass or aramid fibers and it is available as a renewable resource. The hemp fibre had a considerable history in terms of providing high tensile strength, especially in the use for roping, and in being part of a large productive system [11]. After a few decades of oblivion, due to drug production-related issues, the availability of varieties with low tetrahydro-cannabinoids (THCs) content, allowed hemp production to resume [12]. It is therefore necessary in this moment to raise the profile of fibre use towards more engineered components, which may be of interest in several fields, including building, automotive and leisure sectors [13].

Regarding the matrix used for the composite manufacturing, its selection is limited by the temperature at which natural fibres degrade. Most of the natural fibres used for reinforcement in natural fibre composite are thermally unstable above 200 °C, although under some circumstances it is possible for them to be processed at higher temperature for a short period [3].

Due to this limitation, only thermoplastics that soften below this temperature and thermosets, which can be cured below this temperature, are useable as a matrix [14].

Thermoplastics are capable of being repeatedly softened by the application of heat and hardened by cooling and have the potential to be the most easily recycled, which has seen them most favoured in recent commercial uptake, whereas a better emphasis of the fibres mechanical properties are generally achieved by using thermosets as matrix.

In fact, thermoset polymers are particularly attractive as matrix materials for natural fibre reinforced composite production as they generally have reactive functional groups that make them compatible with hydrophilic fibre surfaces [15]. Among these, the epoxy is one of the most interesting polymer resins that used as matrix for the natural fibre composites shows very high mechanical properties of the final product [3].

However, as organic materials, the polymers and the natural fibres are very sensitive to flame, then the improvement of the flame resistance is becoming more and more an important topic for the use of natural fibre composites products in any application fields where fire problems can occur, such as in the transportation industry. Therefore, for these applications *an improvement of the flame resistance is strictly required* in order to allow the termination of the burning process before that the actual ignition occurs.

1.2 Literature Review

The main application fields where the use of hemp composites found success are in building and automotive applications because in this fields there are an enormous demand to decrease the energy consummation.

For example, in the building sector two main strategies have been followed for the energy efficient : (i) reducing energy consumption during the building service life, for instance by adopting the "Zero Energy Building" approach [16, 17]; (ii) reducing energy consumption also in the pre-service life, including raw materials extraction and manufacturing [16, 18], for instance by developing new building materials based on renewable resources (such as hemp) and/or involving less energy consuming manufacturing processes [19]. Following this latter approach, novel sustainable

composites for the building industry have recently been proposed [16, 20] and several studies are still in progress. However, the aim of these studies is to investigate on the durability of the hemp composites and to highlight their good thermal and sound insulation properties and then their use for both internal and external thermal insulating products but no applications for structural component was founded [16].

Recently, the automotive industry has begun to employ natural fibres in the manufacture of both interior and exterior vehicle components to reduce the overall weight of the car whilst increasing its fuel efficiency and sustainability [21]. Several multinational companies, such as Daimler Chrysler, Mercedes Benz and Toyota, have introduced natural fibre composites into their products and plan to further increase their use in future components [22]. Jaguar and Land Rover [23] developed a prototype car door from flax/polypropylene and reported that the natural fibre component offers an excellence performance compared to current parts. Their results showed that this prototype is approximately 60% lighter than the equivalent steel part for the same stiffness, while Jaguar's prototype is roughly 35% lighter than a glass filled polypropylene component with the same thickness. But in the last years several research was done, indeed the issue is still open, indeed in the last years many researchers showed that composites based on natural fibres can, if correctly designed, offer comparable properties to those based on conventional fibres. Mallaiah et al. [24] compared the properties of bio-based and synthetic fibre based sandwich structures and demonstrated that a hybrid structure based on bamboo and glass fibres offers higher values of core shear stress and face bending stress than those structures manufactured from either pure glass or bamboo fibres.

Recently, lightweight composite structures have seen dramatically increasing use in aircraft and satellites, where the drive for weight saving is greatest. Composite sandwich structures are recognised as offering a high strength to weight ratio as well as high specific bending stiffness and strength characteristics under distributed loads.

As known, these structures are composed of a core, which is light but thick with low strength, and two skins, that are stiffer and stronger [21]. A lot of alternative forms of sandwich panels can be accomplished by combing different core and skin materials combined with different geometries. Honeycomb, foam, truss and corrugated core are the most widely used cores in sandwich panels. Researchers proposed alternative forms for sandwich panels: Xu et al. [25] introduced a new idea that combined graded material and lattice core for forming the graded lattice core sandwich structures, which was different from the convectional truss core structures. Zuhri et al. [21] studied the properties of square and triangular honeycomb core materials based on co-mingled flax fibres reinforced polypropylene and polylactide polymers. Rao et al. [26] characterized the bond strength and energy absorption capabilities of recycled sandwich panels made from sawdust polypropylene composites.

Cicala et al. [27] showed the feasibility of using hemp/epoxy biocomposite materials as base for an hexarchiral auxetic truss-core made with RTM techniques.

Based on this overview, it is clear that there is still need to investigate the possible use of these materials and to study manufacturing processes that are in the same time no complex, easy to industrial scale-up and able to produce low density composites.

In addition, since the aim to extend the application fields of the natural fibre composites, there are a lot of applications in which fire problems can occur and then the improvement of the flame resistance can be deeply felt, considering that as organic materials, the polymers and the natural fibres are very sensitive to flame.

One of the most expeditious method used to improve the flame retardancy is the incorporation of additive that can interfere with the combustion during a particular stage of the burning process [28]. The most widely used additive types are inorganic compounds, halogenated compounds and phosphorous compounds [29, 30]. In addition, boric acid, ammonium phosphates and borates, ammonium sulphate and chlorides, zinc chloride and borate, antimony oxide, sodium borate and dicyanodiamide are also used [28].

An example of a widely used inorganic flame retardant is the ammonium polyphosphate (APP) which, unlike the other phosphorus-based additives, is not harmful to health.

The flame retardants can be used either by direct incorporation into polymer matrix during the process or by impregnation or grafting onto natural fibres. Several authors demonstrated the interest

to modify natural fibres surface using phosphorous compounds:

Dorez et al. [31] investigated the thermal degradation and fire behaviour of different natural fibres/PBS biocomposites additivated with APP. This addition was beneficial to the formation of a strong char barrier and for a significant decrease of the peak of heat rate release (PHRR); Shumao et al. [32] studied the influence of APP on the flame retardancy of a ramie fibres-reinforced poly (lactic acid). The authors obtained better flame retardancy with the incorporation of APP both in fibres and in matrix; Nie et al. [33] used microencapsulated APP as flame retardant in poly (butylenes succinate)/bamboo composites. The results of cone calorimeter showed that PHRR and the total heat release (THR) decrease substantially with the addition of the flame retardant;

Schartel et al. [34] studied the incorporation of APP in flax/PP biocomposites. They delivered a comprehensive characterization of the fire response for forced flaming combustion.

Generally, in these researches single fibres were employed with a good distribution into the matrix but, nowadays, *the fabrics represent the most widely used long fibres reinforcement that ensure good directionality with no filament winding technologies*.

Therefore, it is clear that the improvement of the fire resistance of the natural fibres reinforcement is deeply felt and then the study of technologies able to manufacture products with this property using fabric as reinforcement an open issue.

1.2.1 Sandwich Structures

Since the use of fabric characterized from an high value of the mesh could be used to produce porous structures, it is interesting to note that among different applications they can be used as core for sandwich structures. Indeed, an example of the use of natural fibre reinforcement composites (NFRCs) for these structures is presented. Therefore, in this section a short overview on the sandwich structure design is proposed.

Amongst all possible design concepts in composite structures, the idea of sandwich construction has become increasingly popular because of the development of man-made cellular materials as core materials. Sandwich structures consist of: (i) a pair of thin stiff, strong skins (faces, facings or covers); (ii) a thick, lightweight core to separate the skins and carry loads from one skin to the otherand (iii) an adhesive attachment which is capable of transmitting shear and axial loads to and from the core, Figure 1.2-1.
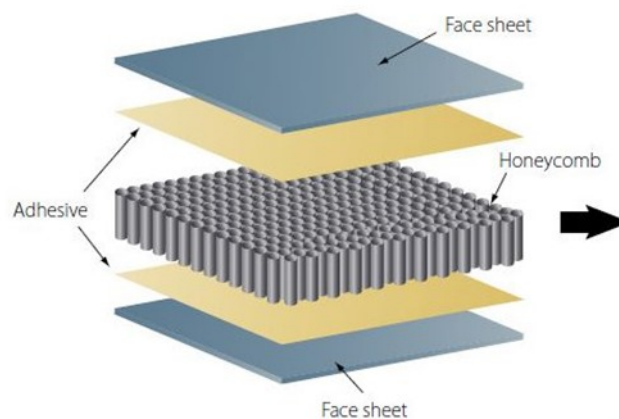
Figure 1.2-1 Sandwich construction with honeycomb core.

The separation of the skins by the core increases the moment of inertia of the panel with little increase in weight, producing an efficient structure for resisting bending and buckling loads. Table 1.2-1 shows illustratively the flexural stiffness and strength advantage of sandwich panels compared to solid panels using typical beam theory with typical values for skin and core density. By splitting a solid laminate down the middle and separating the two halves with a core material, the result is a sandwich panel.

	t	$2t$	$4t$
Relative Bending Stiffness	1	7.0	37
Relative Bending Strength	1	3.5	9.2
Relative Weight	1	1.03	1.06

Table 1.2-1 Example of structural efficiency of sandwich panels in terms of weight.

The new panel weighs little more than the laminate, but its flexural stiffness and strength is much greater; by doubling the thickness of the core material, the difference is even more striking.

Thus, sandwich panels are popular in high performance applications where weight must be kept to a minimum, for example for aeronautical structures, high speed marine craft and racing cars. In the most critical weight applications, composite materials are used for the skins cheaper alternatives such as aluminium alloy, steel or plywood are also commonly used. Materials used for cores include polymers, aluminium, wood, and composites. To minimise weight these are used in the form of foams, honeycombs or with a corrugated construction (see Figure 1.2-2).
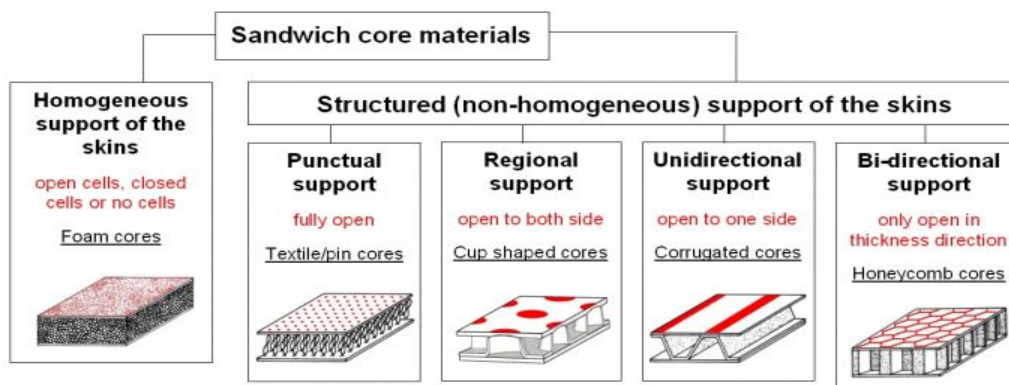
Figure 1.2-2 Example of sandwich core structures.

Due to the increase of the moment of inertia of the panel due to the separation of the skins by the core, these structures maximize their use under flexural loads.

Therefore, to produce lightweight hemp/epoxy laminates for future applications as lightweight component, such as cores for sandwich structures, an aim of this thesis is to present their production through different technological techniques, allowing to obtain laminates with different density values. Therefore, the feasibility of the processes was studied and a mechanical characterization of hemp composites in terms of tensile, flexural, compression and impact strength was carried out.

1.2.2 Flame Retardants and Flammability Testing Techniques

Because the thesis is also focused on the improvement of the fire resistance of NFCs, a brief introduction on flame retardants and on flammability testing technique is required and then it is proposed below.

1.2.2.1   Flame Retardants

The Flame retardants (FMs) impart flame retardancy character to materials such as coatings, thermoplastic or thermoset polymers, textiles and composite materials. These FRs can prevent, minimize, suppress or stop the combustion process of materials. They act to break the self-sustaining polymer combustion cycle shown in Figure 1.2-3, and consequently reduce the burning rate or extinguish the flame in several ways: (i) the modification of the pyrolysis process in order to decrease the quantity of evolved flammable volatiles, this normally involves in the formation of a char (less flammable) serving as barrier between the polymer and flame (stage 'a'); (ii) the isolation of the flame from the oxygen/air supply (stage 'b'); (iii) the introduction into the polymer formulations of those compounds that will release efficient flame inhibitors (e.g. chlorine andbromine) (stage 'c'); and (iv) the lowering of thermal feedback to the polymer to prevent further pyrolysis (stage 'd') [35, 36]. To protect polymer materials from fire, there are different approaches to be considered and of the most expeditious method is the use of flame retardant additives (FRAs).
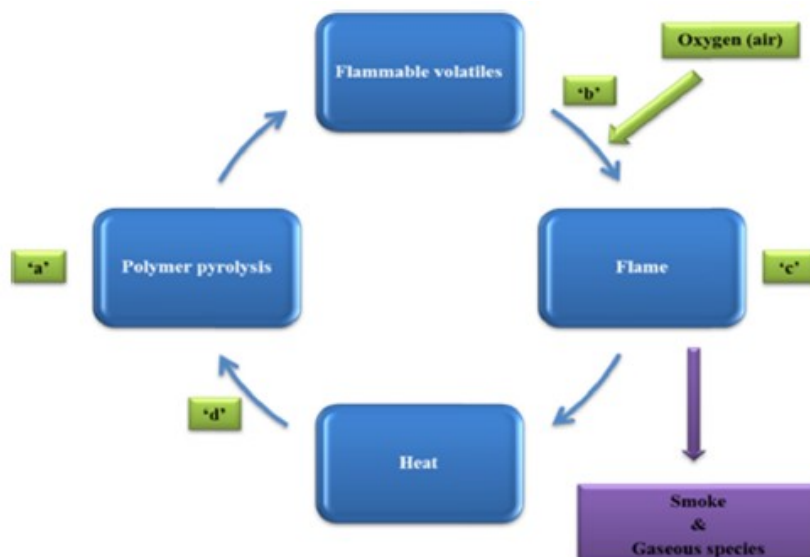
Figure 1.2-3 Demonstration of the self-sustaining polymer combustion cycle; a–d represent potential modes of flame retardants [35].

Flame retardant systems can act either chemically or physically in the solid, liquid or gas phase. Such actions do not occur singly but should be considered as complex processes in which various individual stages occur simultaneously, with one dominating. They are dependent on the nature of flame retardant system in place [35, 37].

The action mechanisms of flame retardants can happen both in the condensed phase, in which the degradation of the polymer occurs, and in the gas phase, in which the combustion of the volatile products occurs. In both cases, these mechanisms can be chemicals (blocking the radical process of combustion, dehydration process with char formation and intumescence resulting phenomenon, etc) or physical (cooling, dilution, coating, etc).

An example of a widely used inorganic phospurous flame retardant is the ammonium polyphosphate (APP) which, unlike the other phosphorus-based additives, is not harmful to health; it is a combination of polyphosphoric acid and ammonia.

The APP are stable and nonvolatile compounds. Those with long chains start decomposing at temperatures above 300 °C giving polyphosphoric acid and ammonia, whereas the short chain ones decompose at 150 °C. It is thus important to adapt a crystalline form of APP to the decomposition temperature of a polymer. When an APP is incorporated into a polymer that contains oxygen and/or nitrogen atoms, polymer charring occurs. Thermal degradation of APP creates free acidic hydroxyl groups that condense by thermal dehydration yielding a cross linked structure of ultraphosphate and polyphosphoric acid with a highly cross linked structure. Polyphosphoric acid reacts with oxygen and/or nitrogen containing polymers and catalyses their dehydration reaction and char formation.

However, the effectiveness of an APP is dependent on the loading concentration. In non-self-charring polymeric materials, the APP can modify the degradation mechanism of the polymer [38].

The APP interferes with the process of initiation and development of the flame through different processes:

- release of water and gas, which dilutes the gases produced by the flame;
- cooling of the material surface;
- production of a resistant and non-flammable layer on the material surface, that acts as insulator both for the heat and the volatile fuels.

1.2.2.2   Flammability Testing Techniques

Flammability of polymers and/or composites can be characterized by the ignitability, flame spread rate and heat release. Several small, intermediate and/or full scale flammability tests are used in industrial and/or academic laboratories. They are used for either screening materials during production or testing manufactured products. The most common flammability test techniques are: the cone calorimetry, the pyrolysis combustion flow calorimetry (PCFC), the limiting oxygen index (LOI) and the vertical burning test.

1.2.2.2.1   Cone Calorimetry

Cone calorimetry is a technique used to quantify the flammability of materials by determining various flammability parameters. It was first reported on by the National Bureau of Standards (NBS), now known as the National Institute of Standards and Technol-ogy (NIST), in 1982.

Cone calorimetry is one of the most effective medium sized fire behaviour tests used to study the rate of heat released by materials exposed to radiant heat flux. Its principle is based on the measurement of decreasing oxygen concentration in the combustion gases of the sample that is subjected to a given heat flux (10–100 kW m^{-2}). It has been standardized in the United States (ASTM E 1354) and now in an international standard (ISO 5660) [35, 37].

Figure 1.2-4 shows an experimental schematic representation of a cone calorimeter. A sample of 100×100 mm dimensions is horizontally (occasionally vertically) placed in a sample holder on a load cell for evaluation of the mass loss during the experiment. The sample is aluminium foil wrapped on

the sides and at the bottom. It is put in a retainer frame over low density ceramic wool and the retainer frame is secured to the specimen holder.
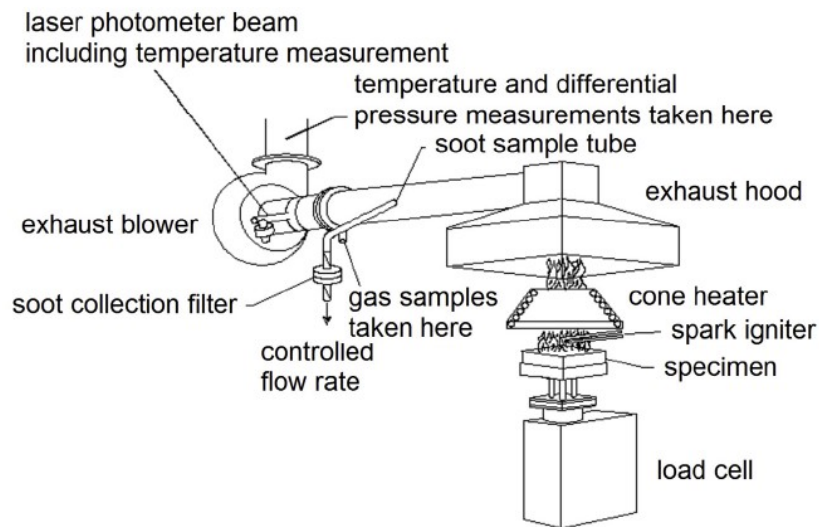
Figure 1.2-4 Schematic representation of an experimental set-up in a cone calorimeter.

A conical radiant electrical heater uniformly irradiates the sample from above, and the combustion is triggered by an electrical spark. The combustion gases that are produced pass through the cone and are removed by means of an exhaust duct system with a centrifugal fan and an extraction hood. The centrifugal fan is situated in the combustion gas line to set the flow rate of combustion products. Along the combustion gas line there is a gas sampling ring positioned before the fan. The gas sampled in the ring is first passed through two filters to remove particles. It is then passed through a cold trap and a drying agent to remove possible water. Finally, it reaches the gas analysers. Between the gas sampling ring and the fan there is also a smoke measurement system. This system determines the amount of smoke produced using a laser photometric beam [35, 39].

To perform the basic cone calorimeter experiments, only an oxygen analyser is required. Furthermore, to better understand the burning process and minimize the uncertainties in the results, additional analysers are usually fitted. These may be CO and CO_2 analysers. To further analyse combustion products and gaseous species, a Fourier transform infrared (FTIR) spectrometer can be coupled through a heated line [35, 40].

The measurements of gas flow and oxygen concentration are used to calculate the quantity of heat released per unit of time and surface area (heat release rate, *HRR*) expressed in kW m^{-2} and its mean value (*HRR$_m$*). The development of HRR over time i.e. the value of its peak maximum (*PHRR*) or *HRR* maximum is considered in order to assess the fire properties of materials, as well as the time to reach the peak (*TTP*). The calculation of HRR is based on Huggett's observation in a study of the

estimation of HRR via oxygen consumption measurements [41]. Huggett observed that most organic materials release an amount of heat that is practically proportional to the amount of oxygen consumed while burning. The proportionality factor is constant from one material to another and is equal to 13.1 kJ g^{-1} consumed oxygen, with an accuracy of approximately 5%. Integration of the heat release rate (*HRR*) versus time curve gives the total heat release (*THR*) expressed in MJ m^{-2} [35]. Cone calorimetry, in addition to the aforementioned parameters, enables also the characterization of time to ignition (*TTI*), time to flame out (TFO), mass loss rate, levels of oxygen, carbonmonoxide and carbon dioxide, and total smoke released (*TSR*). Furthermore, it provides more detailed fire characteristics, with *HRR* being the most widely used parameter for evaluating the fire properties. The cone calorimetry is regarded as the most versatile medium sized fire testing method ever invented.

1.2.2.2.2   Vertical burning test

According to FAR25.853A standard, the vertical burning test V12, the specimen was held vertically and a flame fuelled by natural gas was applied to the centre line of the lower edge of the specimen; this one must stay to 19 mm above the top edge of the burner (see Figure 1.2-5). The flame was applied for 12 s and removed, and the time required for flaming combustion to cease (after flame time) is noted as t_f. The distance between the burner and the specimen must remain constant during flame application. Instead, the length of the damaged area is noted as L_b. If some drops fall from the specimen, their burning time is known as t_d. Before the test, rectangular specimens, 310 mm x 75 mm, were conditioned for 24 h at 27 °C and with a humidity of about 50%. Methane 99% pure was employed for this type of test.
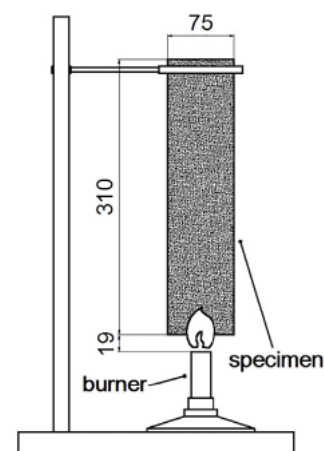
Figure 1.2-5 Schematic representation of set-up in vertical burning test.

The Vertical burning V12 test is widely used both in industry and academic research centres. It is intended to meet industrial requirements as well as classify polymeric materials hierarchically. The information obtained remains limited due to its basic and unrefined character. For specimens that flow, the test seems less appropriate than for more cohesive materials [37].

Therefore, on the base of the above considerations, in this thesis the epoxy resin was mixed with APP particles, to use this mixture in the infusion process and to study the technological feasibility of the process to manufacture hemp/epoxy composites with good mechanical and fire resistance properties.

1.3 Aim of the Thesis

After an overview on the state of the art of the hemp/epoxy composites discussed in this section, it was highlighted that there is still need to investigate on the possible use of these materials. The study on manufacturing processes, easily applicable for the industrial production, to produce low density natural composites and the study of techniques able to improve their flame resistance is still an open issue. Therefore, the thesis work has been focused on the study of manufacturing technologies used to produce lightweight hemp/epoxy composites for their future applications as lightweight components, such as in the transportation industry. In this field, apart from the mechanical properties, good flame resistance is also required and then to increase the flame resistance of these components was another goal of this thesis. Processes such as, vacuum infusion, brushing hand lay-up, injection moulding and continuous impregnation process were investigated and used both for the manufacturing of lightweight hemp structures and to produce hemp/epoxy composite with high flame resistance properties.

Therefore, the properties of the produced composite materials were widely investigated.

References

[1] K. Rohit and S. Dixit, "A Review - Future Aspect of Natural Fiber Reinforced," *Polymers from Renewable Resources,* vol. 7, no. 2, pp. 43-59, 2016.

[2] M. Garcia, I. Garmendia and J. Garcia, "Influence of natural fiber type in eco-composites," *Journal of Applied Polymer Science,* vol. 107, no. 5, pp. 2994-3004, 2008.

[3] K. Pickering, M. Aruan Efendy and T. Le, "A review of recent developments in natural fibre composites and their mechanical performance," *Composites: Part A,* vol. 83, pp. 98-112, 2016.

[4] M. R, K. V and N. YS, "Recent development in natural fiber reinforced polypropylene composites.," *J Reinf Plast Compos,* vol. 28, no. 10, pp. 1169-89, 2009.

[5] Z. L and M. M, "Commingled natural fibre/polypropylene wrap spun yarns for structured thermoplastic composites.," *Compos Sci Technol,* vol. 70, no. 1, pp. 130-135, 2010.

[6] B. B, S. M and B. L, "Manufacture and characterisation of thermoplastic composites made from PLA/hemp co-wrapped hybrid yarn prepregs.," *Composites Part A,* vol. 50, pp. 93-101, 2013.

[7] P. S, B. J, L. L, H. P and V. I, "Characterization of flax/epoxy prepregs before and after cure," *J Reinf Plast Compos,* vol. 32, no. 11, pp. 777-785, 2013.

[8] G. N and M. J, "A comparison of the mechanical characteristics of kenaf and lyocell fibre reinforced poly(lactic acid) (PLA) and poly(3-hydroxybutyrate) (PHB) composites.," *Composites Part A,* vol. 42, no. 12, pp. 2010-2019, 2011.

[9] R. AK, M. A, M. BC, J. R, R. R and B. AN, "Short jute fiber-reinforced polypropylene composites: effect of compatibilizer," *J Appl Polym Sci,* vol. 69, no. 2, pp. 329-338, 1998.

[10] S. M, S. P and B. A. Law S, "Interface modification and mechanical properties of natural fiber-polyolefin composite products.," *J Reinf Plast Compos,* vol. 24, no. 2, pp. 121-130, 2005.

[11] C. Hill and M. Hughes, "Natural fibre reinforced composites: opportunities and challenges," *J Biobased Mater Bioenergy,* vol. 4, no. 2, pp. 148-152, 2010.

[12] D. Lachenmeier, L. Kroener, M. F and B. Madea, "Determination of cannabinoids in hemp food products by use of headspace solid-phase microextraction and gas chromatography-mass spectrometry," *Anal Bioanal Chem,* vol. 378, no. 1, pp. 183-189, 2004.

[13] I. De Rosa, H. Dhakal, C. Santulli, F. Sarasini and Z. Zhang, "Post-impact static and cyclic flexural characterisation of hemp fibre reinforced laminates," *Composites: Part B,* vol. 43, no. 3, pp. 1382-1393, 2012.

[14] d. S. PA, G. JC, A. J and M. G., "Natural fibers plastic composites for automotive applications.," in *In: 8th Annual automotive composites conference and exhibition (ACCE 2008).*, Troy, MI: SPE Automotive & Composites Division, 2008.

[15] M. S. Islam, P. KM and N. Foreman, "Influence of alkali fiber treatment and fiber processing on the mechanical properties of hemp/epoxy composites," *Journal of Applied Polymer Science,* vol. 119, p. 3696–3707, 2011.

[16] E. Sassoni, S. Manzi, A. Motori, M. Montecchi and M. Canti, "Experimental study on the physical–mechanical durability ofinnovative hemp-based composites for the building industry," *Energy and Buildings,* vol. 104, pp. 316-322, 2015.

[17] A. Marszal, P. Heiselberg, J. Bourrelle, E. Musall, K. Voss, I. Sartori and A. Napolitano, "Zero energy building—a review of definitions and calculation methodologies," *Energy Build,* vol. 43, pp. 971-979, 2011.

[18] E. Franzoni, "Materials selection for green buildings: which tools for engineers and architects?," *Procedia Eng,* vol. 21, pp. 883-890, 2011.

[19] A. Korjenic, V. Petrànek, J. Zach and J. Hroudovà, "Development and performanc evaluation of natural thermal-insulation materials composed of renewable resources," *Energy Build,* vol. 43, pp. 2518-2523, 2011.

[20] E. Sassoni, S. Manzi, M. Montecchi and M. Canti, "Novel sustainablehemp-based composites for application in the building industry: physical, thermal and mechanical characterization," *Energy Build,* vol. 77, pp. 219-226, 2014.

[21] M. Zuhri, Z. Guan and W. Cantwell, "The mechanical properties of natural fibre based honeycomb core materials," *Composites: Part B,* vol. 58, pp. 1-9, 2014.

[22] J. Holbery and D. Houston, "Natural-fiber-reinforced polymer composites in automotive applications," *JOM,* vol. 58, no. 11, pp. 80-86, 2006.

[23] B. Weager, "High-performance biocomposites: novel aligned natural fibre reinforcments," *JEC Compos Mag,* vol. 55, pp. 36-47, 2010.

[24] S. Mallaiah, K. Sharma and M. Krishna, "Development and comparative studies of bio-based and synthetic fiber based sandwich structures," *Int J Soft Compos Eng,* vol. 2, pp. 232-235, 2012.

[25] G. XU, J. Zhai, T. Zeng, H. Wang, S. Cheng and D. Fang, "Response of composite sandwich beams with graded lattice core," *Composite Structures,* vol. 119, pp. 666-676, 2015.

[26] S. Rao, K. Jayaraman and D. Bhattacharyya, "Micro and macro analysis of sisal fibre composites hollow core sandwich panels," *Compos: Part B,* vol. 43, pp. 2738-45, 2012.

[27] G. Cicala, G. Recca, L. Olivieri, Y. Perikleus, F. Scarpa, C. Lira, A. Lorato, D. Grube and G. Ziegmann, "Hexachiral truss-core with twisted hemp yarns: Out-of-plane shear properties," *Composite Structures,* vol. 94, pp. 3556-3562, 2012.

[28] M. Sain, S. Park, F. Suhara and S. Law, "Flame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide.," *Polym Deg Stab,* vol. 83, pp. 363-367, 2004.

[29] M. Rigolo and R. Woodhams, "Basic magnesium carbonate flame retardants for polypropylene.," *Polym Eng Sci,* vol. 32, no. 5, pp. 327-334, 1992.

[30] M. Mngomezulu, M. John, V. Jacobs and A. Luyt, "Review on flammability of biofibres and biocomposites.," *Carbohydr Polym,* vol. 111, pp. 149-182, 2014.

[31] G. Dorez, A. Taguet, L. Ferry and J. Lopez-Cuesta, "Thermal and fire behavior of natural fibers/PBS biocomposites," *Polym Deg Stab,* vol. 98, pp. 87-95, 2013.

[32] L. Shumao, R. Jie, Y. Hua, Y. Tao and Y. Weizhong, "Influence of ammonium polyphosphate on the flame retardancy and mechanical properties of ramie fiber reinforced poly(lactic acid) biocomposites," *Polym Int,* vol. 59, no. 2, pp. 242-248, 2009.

[33] S. Nie, X. Liu, G. Dai, S. Yuan, F. Cai and B. Li, "Investigation on flame retardancy and thermal degradation of flame retardant poly(butylene succinate)/bamboo fiber biocomposites," *J Appl Polym Sci,* vol. 125, pp. E485-489, 2012.

[34] B. Schartel, U. Braun, U. Schwarz and S. Reinemann, "Fire retardancy of polypropylene/flax blends.," *Polymer,* vol. 44, no. 20, pp. 6241-6250, 2003.

[35] M. E. Mngomezulu, M. J. John, V. Jacobs and A. S. Luyt, "Review on flammability of biofibres and biocomposites," *Carbohydrate Polymers,* vol. 111, pp. 149-182, 2014.

[36] D. Price, G. Anthony and P. Carty, "Introduction: Polymer combustion, con-densed phase pyrolysis and smoke formation," in *Fire retardant materials*, Woodhead Publishing Limited, 2001, pp. 1-30.

[37] F. Laoutid, L. Bonnaud, M. Alexandre, J. M. Lopez-Cuesta and P. Dubois, "New prospects in flame retardant polymer materials: From fundamen-tals to nanocomposites," *Materials Science and Engineering R,,* vol. 63, pp. 100-125, 2009.

[38] S. Bourbigot and G. Fontaine, "Flame retardancy of polylactide: An overview," *Polymer Chemistry,* vol. 1, p. 1413–1422, 2010.

[39] R. Carvel, T. Steinhaus, G. Rein and J. L. Torero, "Determi-nation of the flammability properties of polymeric materials: Anovel method," *Polymer Degradation and Stability,* vol. 96, pp. 314-319, 2011.

[40] J. Lindholm, A. Brink and M. Hupa, "Cone calorimeter – A tool for measur-ing heat release rate," 2009. [Online]. Available: http://www.ffrc.fi/FlameDays 2009/4B/LindholmPaper.pdf.

[41] C. Huggest, "Estimation of rate of heat release by means of oxygen consump-tion measurements," *Fire and Materials,* vol. 4, no. 2, pp. 61-65, 1980.

Chapter 2: Biocomposites

2.3 Introduction to Biocomposites

The fibre-reinforced composites market is a multi-billion euro business with applications in the automotive, construction, marine, electronics, sporting goods, appliance, aerospace, and consumer product industries. These materials are attractive due to their unique ability to combine the properties of various materials to produce a high-performance, easily tailored and efficient system. Thus, the market for composite materials is fast growing and lucrative. The establishment of the fibre reinforced polymer (FRP) composites industry dates back to the early 1900s when fibres were first combined with phenolic resins and later reached commodity status during the 1940s with the development of glass-fibre reinforced unsaturated polyester [1]. Since then, the FRP industry has seen a steady increase with glass-fibres being the dominant reinforcing material in use. Not surprisingly, the demand for composite materials continues to grow as new applications are found.

In recent years, there have been growing economic concerns regarding the depletion of petroleum resources as well as an increased awareness of the environmental effects of producing, using and disposing of synthetic materials. Additionally, in the past decade several government based initiatives such as the Energy Policy Act of 2005, Biomass Research and Development Act of 2000, and the Farm Security and Rural Investment Act of 2002 (U.S. Public Law 107-17), have offered economic incentive to consider biobased alternatives to petroleum based materials [1].

Economic and environmental concerns coupled with these government initiatives have encouraged research into more environmentally benign alternatives to common glass and petroleum-derived composites. Many of these researches focused on the development of biocomposites and other natural renewable materials.

Biocomposites can be broadly defined as a composite material that makes use of one or more environmentally friendly materials such as natural fibre reinforcements or biopolymers, so biocomposites have various levels of environmental friendliness based on their constituent materials and their ability to biodegrade. A schematization of these composites categories under the current definition of biocomposites is shown in Figure 2.3-1.
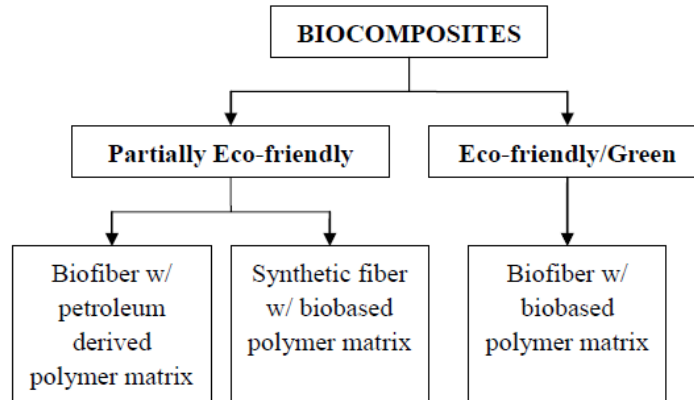
Figure 2.3-1 Classification of biocomposites based on material constituents.

Depending on the type of polymer used, these composites can also be entirely biodegradable, suggesting the highest level of economic and environmental benefits. For the class of biocomposite materials to be successful and long-lasting, it is important that their development follow a promising economical route.

For both glass fibres and petroleum-derived polymers the manufacturing processes were well developed which ensure that the resulting GFRPs are produced at relatively low cost. Although most biopolymers currently cost more than traditional petroleum-based polymers, it is expected that increased demand and further technological developments will reduce the cost of these biomaterials. Furthermore, the low cost of natural fibre reinforcements can help to bring down the overall composite costs.

Several researchers showed that the energy consumption required to produce a natural fibre mat (9.7 MJ/kg), including cultivation, harvesting, and fibre digestion, is less than a quarter of the energy required to produce a comparable glass fibre mat (54.8 MJ/kg) [2]. Furthermore, the density of most plant fibres is also around 40 percent lower than that of glass fibres. This allows for additional cost savings in different application fields such as in transportation applications (automotive, aeronautic). From the above reasons, it is clear that biocomposites offer many potential advantages over traditional synthetic composites.

Considering the definition of biocomposite reported in the Review *"Biocomposites: technology, environmental credentials and market forces"* [3] in which a biocomposites is defined as a composite material when one or more phase(s) derives from a biological origin, the composite considered in this study and manufactured by using hemp fibres and epoxy resin can be considered as a biocomposite.

2.4   Natural Fibres Composites (NFCs)

Glass is the most common reinforcing fibres for use in polymer (thermoset and thermoplastic) matrix composites. The major advantage of glass fibre includes low price, high tensile stress, high chemical resistance and relative ease of processing. However, it is characterized by several disadvantages. It has low yield modulus, relatively high specific gravity among other conventional fibres, sensitivity to abrasion with handling, relatively low fatigue resistance, and high hardness which causes excessive wear on moulding dies and cutting tools [4]. The biggest problem with glass and other conventional fibres is that they are not biodegradable or easily recyclable and their disposal is difficult. Alternative synthetic fibres such as aramid and carbon are limited to industrial applications such as aerospace and ballistics, where cost of the product is less important than maximising the performance (high strength, stiffness and low density) to an extremely higher level.

The use of natural fibres as reinforcement in polymer matrix composites (PMCs) to replace conventional fibres like glass is currently receiving more increasing attention because of the growing environmental awareness and advantages (low cost, low density, high specific properties, abundant availability) they possess. The annual agricultural crop fibres (e.g. hemp, flax) have higher mechanical strength as compared to commonly used wood based fibres (e.g. wood flour, wood fibre) and the PMCs produced using these fibres as reinforcements can result in significant property improvements. Recent research on the use of annual growth agricultural crop lignocellulosic fibres suggests that they have the potential to be used as reinforcement both in thermoset and thermoplastic matrices. Of these fibres, hemp and flax are the least used fibre in the production of PMCs, they have the best mechanical and thermal properties. However, there are many problems associated with incorporating natural fibre into polymer matrices, namely: (i) poor compatibility of a hydrophilic fibre and a hydrophobic matrix that results in poor mechanical properties of the composites, (ii) high sensitivity of natural fibre towards moisture that results in composite dimensional instability and loss in mechanical properties through swelling [5], and (iii) relatively poor thermal stability. Both thermoset and thermoplastic polymers are used as matrix for NFCs:

Thermoset resins (e.g. epoxy, polyester, phenolic, and polyurethane) are used for natural fibre composites (NFCs) in applications where higher performance is required. These thermoset polymers contain reactive functional groups that aid the development of an interface with the natural fibres. Thermoset composites have superior thermal stability and lower water absorption compared to thermoplastic composites. Epoxy and phenolic are known to possess the ability to form covalent bonds with plant cell walls through -OH groups [6]. Moreover, composite products can be achieved using low viscosity epoxy that cure at room temperature and the polymerisation of epoxy (curing

reaction) is carried out by addition reaction without evolution of volatiles which is a desirable property to prepare void-free products. Therefore, although epoxy resins are relatively expensive than polyesters, they have good potential for the development of NFCs [7].

Thermoplastic composites can be recyclable, have low processing costs and the ability to be moulded into complex parts when compared to thermoset composites. Composites based on petroleum originated thermoplastic matrices such as PP and PE are very common today and are being extensively used in automotive applications, building materials, and household products. However, growing environmental awareness is forcing the industries to find more environmentally friendly materials for their products. Therefore, materials derived from natural resources of plant origin (e.g. cellulose and starch), synthetic polymers from natural monomers (e.g. PLA), and polymers from microbial fermentation (e.g. PHB) are being assessed by researchers [8, 9] for use as potential matrices in biodegradable and ecologically friendly composites. The study of PLA and especially of natural fibre/PLA composites is very limited [10, 11]. However, Bodros *et al.* [12] showed that the tensile strength and the young modulus of PLA/flax composites are higher than PP/flax composites and that the specific tensile strength and modulus of flax/PLA composite are very close to glass/polyester composites.

For natural fibres to be able to compete with synthetic fibres, improvement of the mechanical and thermal properties of the composites is necessary. This can be achieved by obtaining better adhesion between fibre and matrix and by using better composite processing conditions.

2.4.1 Matrix selection

The matrix is an important part of a fibre-reinforced composite. It provides a barrier against adverse environments, protects the surface of the fibres from mechanical abrasion and it transfers load to fibres. The most common matrices currently used in NFCs are polymeric as they are light weight and can be processed at low temperature. Both thermoplastic and thermoset polymers have been used for matrices with natural fibres [13].

Matrix selection is limited by the temperature at which natural fibres degrade. Most of the natural fibres used for reinforcement in natural fibre composite are thermally unstable above 200 °C, although under some circumstances it is possible for them to be processed at higher temperature for a short period of time [14].

Due to this limitation, only thermoplastics that soften below this temperature such as polyethylene (PE), PP, polyolefin, polyvinylchloride and polystyrene and thermosets (which can be cured below this temperature) are useable as a matrix [15]. However, it can be noted that the thermoplastics named

constitute the most common thermoplastics consumed by the plastics industry and outweighs the use of any other thermoplastic matrices generally used. Indeed, PP and PE are the two most commonly adopted thermoplastic matrices for NFCs. The main thermosets used are unsaturated polyester (UP), epoxy resin, phenol formaldehyde and VE resins. Thermoplastics are capable of being repeatedly softened by the application of heat and hardened by cooling and have the potential to be the most easily recycled, which has seen them most favoured in recent commercial uptake, whereas better realisation of the fibre properties are generally achieved using thermosets [15].

Replacement of petroleum-based with bioderived matrices has been explored. Of these, PLA is the clear front-runner from a mechanical property perspective, and has been shown to give higher strength and stiffness with natural fibres than PP.

2.4.2 Bio-derived Thermoplastic as Matrix

Cellulose fibres (e.g. hemp, flax, jute) are widely used with conventional thermoplastic polymers (e.g. PP, PE) as reinforcement in composite production to improve mechanical properties. In fact, the history of composites from renewable resources is far longer than conventional polymers. The study and utilization of natural polymers is an ancient science. Typical examples, such as paper, silk, skin, and bone arts, can easily be found in museum around the world. In the biblical
Book of Exodus, Moses's mother built the ark from rushes, pitch and slime, a kind of fibre reinforced composite, according to the current classification of material. During the opium war, more than 1000 years ago, the Chinese built their castles to defend against invaders using a kind of mineral particle reinforced composite made from gluten rice, sugar, calcium carbonate and sand [16].
However, the availability of petroleum at a lower cost and the bio-chemical inertness of petroleum based products have proven disastrous for the market of natural polymers. It is only about last two decades when the significance of eco-friendly materials has been realized. Now polymers from renewable resources have started drawing an increasing amount of attention. The two main reasons for that are the environmental concerns [17], and the realization that the petroleum resources are limited. Generally, polymers from renewable resources can be classified into three groups: (i) natural polymers such as starch, protein, and cellulose (ii) synthetic polymers from natural monomers, such as PLA and (iii) polymers from microbial fermentation, such as polyhydroxy butyrate (PHB). Like numerous other petroleum based polymers, many properties of polymers from renewable resources can be improved through composite production [16]. The development of synthetic polymers like PLA using monomers from natural resources has been a driving force for the development of biodegradable polymers from renewable resources. Therefore, in today's world PLA is the most promising among bio-derivable polymers [16]. PLA can be processed (e.g. compression moulding,

pultrusion, extrusion and injection moulding) like petroleum based polyolefins and its mechanical property is better than the widely-used polymer PP [18]. On the degradation, PLA does not emit any carbon dioxide to the environment like other biodegradable materials from renewable resources. The degradation occurs by hydrolysis to lactic acid, which is metabolized by micro-organisms to water and carbon dioxide. If PLA is comprised together with other biomass, the biodegradation occurs within a couple of weeks and the material can fully disappear within a month [16]. Chemically, it is a linear aliphatic polyester of lactic acid which can be obtained by fermentation of renewable agricultural materials like corn, sugarcane and sugar beets. Lactic acid is converted to a cyclic lactide dimer which is then polymerised to PLA through a ring opening reaction.

The major applications of PLA products are in household wastes as plastic bags, barriers for sanitary products and diapers, planting, and disposable cups and plates. However, many authors reported the possibilities of developing fully bio-degradable composite products by using biodegradable polymers as matrix and natural fibres as reinforcements [17, 18]. Keller et al. [19] reported that PLA should produce fibre reinforced composites with high mechanical properties for

light weight construction materials. Oksman et al. [15] observed that PLA had good potential as a polymer matrix in flax fibre reinforcement for composites production. They reported that the composite strength produced with PLA/flax was about 50% better than that of PP/flax composites. Due to the increasing commercial interest for natural fibre reinforced polymer composites for use in automotive applications and building constructions as well as demands for environmentally friendly materials, the development of fully biodegradable composites for many applications could be an interesting area of research.

2.4.3 Thermoset Polymers as matrix

Much of the early work used thermosetting resins as matrix material for composite production. Products like tufnol which is made from cotton fibres and epoxy resin, have been available for some time, having good stiffness and strength [20]. In the last few years there has been renewed interest in these products for use in automotive applications. To achieve reinforcing effects in composites it is necessary to have good adhesion between the fibres and resins. Epoxy and phenolic thermosetting resins are known to be able to form covalent cross-links with plant cell walls via -OH groups [6]. Composite manufacture can be achieved using low viscosity epoxy and phenolic resins that cure at room temperature. In addition, epoxy resin does not produce volatile products during curing which is most desirable in production of void free composites. Therefore, although epoxy resins are relatively more expensive than polyester, they have potential for the development of high added value plant fibre composites, where long fibres at a high content are required. In fact, generally the

highest tensile and flexural properties for NFCs are achieved with thermoset matrices for which the highest values in descending order are for epoxy, vinyl ester then unsaturated polyester, relating to the order of expected degree of adhesion with the fibre and hence stress transfer capability [15].

2.4.4 Process Techniques

Normally, natural fibre polymer composites are fabricated by using traditional manufacturing techniques that are designed for conventional fibre reinforced polymer composites and thermoplastics. These techniques include resin transfer moulding (RTM), vacuum infusion, compression moulding, direct extrusion, compounding and injection moulding. Nevertheless, such techniques have been well developed and accumulated experience has showed their success for producing composites with controllable quality [21]. However, their suitability for natural fibre reinforced polymer composites is still unsure due to the materials, geometrical, mechanical, thermal and structural properties of the natural fibres and biodegradable polymers are somehow, different with synthetic fibres and petroleum-based plastics, respectively. For example, chemical treatments on the fibre surface are normally required to compensate its incompatible bonding effect at the interface between the hydrophilic fibre and hydrophobic matrix. Other technical problems such as the uniformity of fibre distributed inside the composites, thermal degradations and weathering effect of fibre and matrix, water absorption of both fibre and matrix, wettability of resin impregnated into spaces between fibrils and the breakage of fibres during mechanical stirring/mixing stages during the manufacturing processes also limit the use of natural fibres and biodegradable polymers for new composite development. *Recently, seeking for technologies for developing fireproof natural fibre reinforced polymer composites is also one of key topics worldwide to apply them for aircraft interior components*. Therefore, the resultant properties of composites in relation to the selections of right materials, pre-processing methods and manufacturing process are inextricably intertwined [21]. *Suitable manufacturing processes must be utilised to transform the materials to the final shape without causing any defect of products*.

For the selection, a suitable process to fabricate biodegradable polymer-related composites, design and manufacturing engineers would mainly focus on numbers of criteria including desired properties, size and shape of resultant composites, processing characteristics of raw materials, the production speed and the manufacturing cost. The size of the composites is a dominating factor for the preliminary assessment on a suitable type of manufacturing processes to be used. For small to medium sized components, injection and compression mouldings are preferred due to their simplicity and fast processing cycle. However, for large structures, they are typically manufactured by open moulding

and autoclave processes. Like other plastic products, the complexity of shape of a product also influences the type of manufacturing processes to be used.

Depending on the performance of composites products, suitable raw materials (thermosets/ thermoplastics, high/low viscosity, processing temperature) should be chosen with an appropriate composite fabrication technology. However, in certain extent, the criteria of selecting the right manufacturing processes for natural fibre composites are different with the one used for traditional polymers. The properties of natural fibre composites are highly dependent on the length, orientation, diameter and content of fibre. The surface condition of the fibre also plays a key role as it would affect the bonding interface between the fibre and surrounding matrix. Removal of a surface coating of fibre (like silk and coir fibres) or pre-treatment of fibre (like hemp) by using chemical process may be required to ensure a good adhesion as result. Theoretically, high tensile strength could be achieved by increasing the amount of fibre used. However, it may not be done by using injection moulding process as the expansion of fibre in wet condition could cause a sucking effect. Therefore, compression moulding may be used for a simple form of composites products.

The most common methods used for NFCs are extrusion, injection moulding (IM) and compression moulding. Resin transfer moulding (RTM) is also used with thermoset matrices and pultrusion has been successfully employed for combined flax /PP yarn composites and thermoset matrix composites [25, 26]. Factors determining properties include temperature, pressure and speed of processing. It is possible for fibre degradation to occur if the temperature used is too high, which limits the thermoplastic matrices used to those with melting points lower than the temperature at which degradation will occur. In extrusion, thermoplastic, usually in the form of beads or pellets, is softened and mixed with the fibre transported by means of a single or two rotating screws, compressed and forced out of the chamber at a steady rate through a die. High screw speed can result in air entrapment, excessive melt temperatures and fibre breakage [15]. Low speeds, however, lead to poor mixing and insufficient wetting of the fibres. This method is used on its own or for producing pre-cursor for IM. Twin screw systems have been shown to give better dispersion of fibres and better mechanical performance than single screw extruders [27]. IM of composites can be carried out with thermoset or thermoplastic matrices, although is much more often used for thermoplastic matrices. Variation of fibre orientation occurs across the mould section with shear flow along the walls due to friction resulting in fibre aligned along the mould wall whilst a higher stretch rate at the centre produces fibre that is more transversely aligned to the flow direction, a structure referred to as skin core structure [15].

Alignment is more significant with higher fibre contents. Residual stress in thermoplastic matrix composites due to pressure gradients, non-uniform temperature profiles, polymer chain alignment

and differences in fibre and matrix thermal expansion coefficients can reduce composite strength [24]. Due to the viscosity requirements, IM of such composites is generally limited to composites of less than 40 m% fibre content. Fibre attrition in IM as for extrusion reduces the length of the fibre during processing. Compression moulding (CM) is generally used for thermoplastic matrices with loose chopped fibre or mats of short or long fibre either randomly oriented or aligned, but can also be used with thermoset matrices. The fibres are normally stacked alternately with thermoplastic matrix sheets before pressure and heat are applied. The viscosity of the matrix during pressing and heating needs to be carefully controlled, in particular for thick samples to make sure the matrix is impregnated fully into the space between fibres. Good quality composites can be produced by controlling viscosity, pressure, holding time, temperature taking account of the type of fibre and matrix [24]. Film stacking was recommended as it limits natural fibre degradation due to involvement of only one temperature cycle [12]. Temperature still needs to be carefully controlled as commonly there is little difference in temperature between that at which a particular matrix can be processed and that at which fibre degradation will occur. Reduction of fibre strength has been shown to occur at temperatures as low as 150 °C and at 200 °C, with strength reducing by 10% in ten minutes [15]. Overall, there is a compromise between obtaining good wetting and avoiding fibre degradation that leads to an optimum temperature for a particular composite material/geometry. This has been explored with film stacking of flax reinforced poly(ester amide) composites, with an optimum temperature for composite tensile properties found to be 150 °C [20]. Flexural properties were found to be less dependent on temperature below 150 °C, but reduced significantly at higher temperatures. For composites made from jute yarn and the bacterial copolyester Biopol the optimum compression temperature for a range of mechanical properties was found to be approximately 180 °C [15]. The highest strength was obtained at 200 °C for non-woven mat reinforced PP. Alternatively to film stacking, sheet moulding compounds have been used in CM [15].

In RTM, liquid thermoset resin is injected into a mould containing a fibre preform. The main variables with this process are temperature, injection pressure, resin viscosity, perform architecture and mould configuration [24]. Advantages compared with other processes include lower temperature requirements and avoidance of thermomechanical degradation [28]. Compaction in this process is affected by the structure of natural fibres including the effect of lumen closing and due to lower degrees of fibre alignment, natural fibre composites are less compactable than glass fibre composites [28]. Good component strength can be achieved with this process which is suitable for low production runs [15].

2.5   Natural Fibres: Source and Classification

Natural fibres can be sourced from plants, animals and minerals. An overview of natural fibres is presented in Figure 2.5-1. Generally, plant or vegetable fibres are used to reinforce polymer matrices and a classification of vegetable fibres is given in Figure 2.5-2 [30]. Plant fibres are a renewable resource and have the ability to be recycled. The plant fibres leave little residue if they are burned for disposal, returning less carbon dioxide (CO_2) to the atmosphere than is removed during the plant's growth.
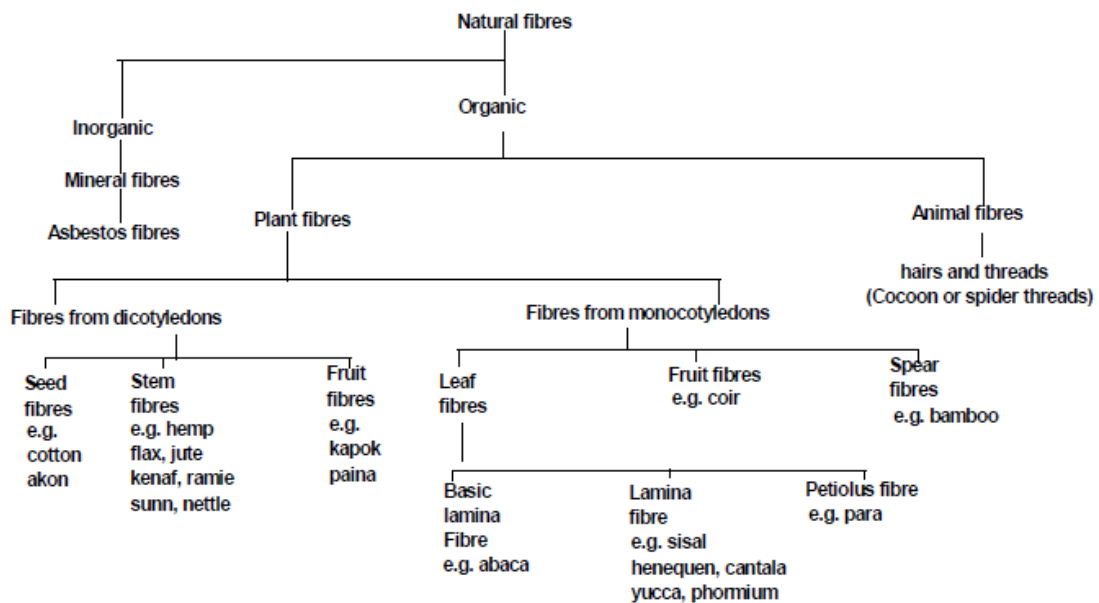
Figure 2.5-1 Overview of natural fibres.
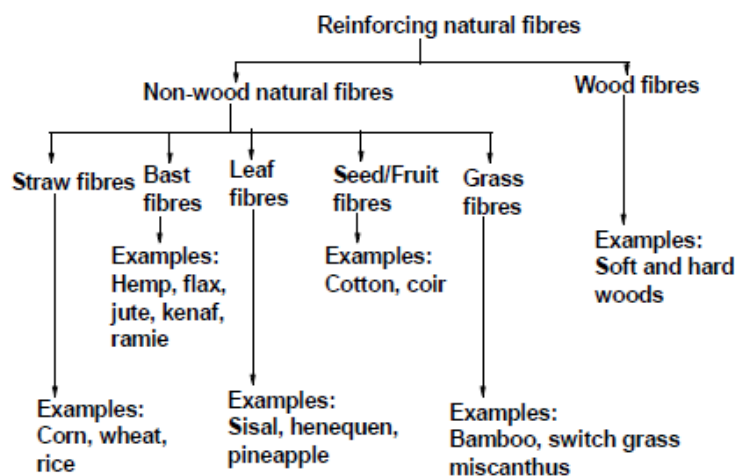
Figure 2.5-2 Classification of natural fibre that can be used as reinforcements in polymers.

The leading driver for substituting natural fibres for glass is that they can be grown with lower cost than glass. The price of glass fibre is around 1.96 € per Kg and has a density of 2.5 g/cm³. On the other hand, natural fibre costs 0.2 - 0.5 € per kg and has a density of 1.2-1.5 g/ cm³. As can be seen from Table 2.5-1 the tensile strength of natural fibres is substantially lower than that of glass fibres though the modulus is of the same order of magnitude. However, when the specific modulus of natural fibres (modulus per unit specific gravity) is considered, the natural fibres show values that are comparable to or even better than glass fibres. Material cost savings, due to the use of natural fibres and high fibre filling levels, coupled with the advantage of being non-abrasive to the mixing and moulding equipment make natural fibres an exciting prospect. These benefits mean natural fibres could be used in many applications, including building, automotive, household appliances, and other applications.

Properties	Fibre						
	E-glass	Hemp	Flax	Jute	Sisal	Coir	Ramie
Desnity [g/cc]	2,55	1,48	1,4	1,46	1,33	1,25	1,5
TS [MPa]	2400	550-900	800-1500	400-800	600-700	220	500
YM [GPa]	73	70	60-80	10-30	38	6	44
Specific modulus	29	47	31	7-21	29	5	2
FS [%]	3	1,6		1,8	2-3	15-25	2
Moisture absorption	-	8	7	12	11	10	12-17

Table 2.5-1 Properties of glass and natural fibres.

2.5.1 Comparison of Cellulose Fibres

Chemical composition, surface characteristics, structural defects, strength, stiffness, and costs are some of the important parameters in selecting natural cellulose fibres for use in polymer composites. The price of natural fibres fluctuate considerably depending on a number of factors like supply, quality, demand, and exchange rate [30].Table 2.5-2 [31] shows a comparison of prices for commonly used fibres.

Fibre	Price (USD/Kg)
Juta	0,4-0,7
Hemp	0,5-1,5
Flax	0,4-0,8
Sisal	0,6-1,0
Wood	0,2-0,4
Glass	1,5-2,5
Carbon	10-100

Table 2.5-2 The prices of some fibres.

Wood is the most abundantly used natural cellulose fibre because of its extensive use in pulp and paper industries. However, for better strength and stiffness cellulose fibres like hemp, flax, jute, kenaf and sisal are becoming increasingly important in composites production. Commercially available cellulose fibres and their sources are listed in Table 2.5-3 [23].

Fibre source	Species	World Production (10^3 tonnes)	Origin
Wood	(>10,000 species)	1.750.000	Stem
Bamboo	(>1250 species)	10.000	Stem
Cotton Lint	Gossypium sp.	18.450	Fruit
Jute	Corchorus sp.	2.300	Stem
Kenaf	Hibiscas cannabinus	830	Stem
Flax	Linum usitatissimum	830	Stem
Sisal	Agave sislana	378	Leaf
Roselle	Hibiscus sabdariffa	250	Stem
Hemp	Cannabis sativa	214	Stem
Coir	Coco nucifera	100	Fruit
ramie	Boehmeria nivea	100	Stem
Abaca	Musa textitles	70	Leaf
Sunn hemp	Crotolaria juncea L.	70	Stem

Table 2.5-3 Commercially available fibre sources and their production.

Hemp, flax, jute and kenaf are called bast fibres, as they develop in the inner bark (phloem) of the stem of dicotyledonous plants. Some physical characteristics of bast fibres are given in Table 2.5-4 [29].

Fibre	Length of textile fibre (mm)	Length of ultimate fibre (mm)	Diameter (µm)	Weight per length	Density (g/cc)
Hemp	1000-3000	5-55	16-50	3,20	1,4
Flax	300-900	13-60	12-30	1,7-17,8	1,4
Jute	150-360	0,8-6	5-25	13,27	1,4
Sisal	600-1000	0,8-8	100-400	9-400	1,2-1,45
Ramie	1500	40-250	16-125	4,6-6,4	1,4
Kenaf	900-1800	1,5-11	14-33	50	-

Table 2.5-4 Physical characteristics of bast fibres.

Hemp, flax, and jute have similar morphologies and can have similar functions in composite materials. Cellulose, hemicelluloses, and lignin are the basic components of natural fibres and govern the physical properties of fibres. Gassan and Bledzki [31] reported that cellulose, lignin, hemicelluloses, and pectin cell walls differ in their composition and structure depending on the climatic conditions and age. The chemical composition of some cellulose fibres is given in Table 2.5-5 [22].

Fibre	Cellulose	Hemicelluloses	Lignin	Pectin	Water solubles	Fat and wax	Moisture
Hemp	67,00	16,10	3,30	0,80	2,10	0,7	10,00
Flax	64,10	16,70	2,00	1,80	3,90	1,5	10,00
Jute	64,40	12,00	11,90	0,20	1,10	0,5	10,00
Sisal	65,80	12,00	9,90	0,80	1,20	0,3	10,00
Ramie	68,60	13,10	0,60	1,90	5,50	0,3	10,00
Sunn	67,80	16,60	3,50	0,30	1,40	0,4	10,00
Abaca	63,2	19,6	5,1	0,5	1,4	0,2	10,00

Table 2.5-5 Percentage chemical composition of cellulose fibres.

The chemical constituent of plant fibres is important, since it can affect their ultimate utilisation. Robson [23] reported that the chemical constituents of plant fibres have specialised functions in the cell wall. Cellulosic microfibrils form crystalline regions and impart enormous strength and stiffness, cellulose and hemicelluloses form semi-crystalline and amorphous regions which provide necessary flexibility while the amorphous regions of lignin give rigidity and a degree of hydrophobia [29].

2.6   Historical background of Natural Fibres Composites (NFCs)

The production and use of composite materials can be traced back to early human existence. Composites produced with natural plant matter and its constituents like stem and fibre were used to make shelter, tools, clothes, and weapons. In ancient Egyptian times, some 3000 years ago, straw was used to reinforce clay bricks to build walls. These composites were produced by placing the structural elements on top of one another to produce the desired design.

Later on, natural fibre composites (NFCs) lost much of their interest, due to the introduction of more durable construction materials like metals and ceramics. The history of modern composites can be considered to begin in 1937 (when salesmen from the Owens Corning Fibreglass Company began to sell fibreglass to interested parties around the United States). The pace of composites development accelerated during the World War II, when the United States Government became concerned that the supplies of metals for aircraft might not be available and instructed the engineers to try to determine the current best practices in composites production. However, the spur to the rapid development of large scale production of composite materials began in the early 1960s, due to the development of carbon fibres in the UK and boron fibres in the USA. These fibres used to reinforce both thermoset and thermoplastic polymer matrices for use in automotive applications [32].

Over the last few years, natural fibres have attracted attention as substitutes for synthetic fibres in composites production largely due to increased emphasis on sustainability. These natural fibres are low in cost and in density, and have high specific properties. They are renewable, nonabrasive, and their specific properties are comparable with the most commonly used reinforcing glass fibres.

About seventy years ago, natural fibres such as hemp and flax started to be used mostly in textile and paper industries. Currently, the market for natural fibres has expanded to the extent that most European car producers now use natural fibres for interior components (see Figure 2.6-1) because of their low density, acceptable mechanical properties, low wear on tools, and low processing costs.

Figure 2.6-1 Automobile components based on polymer composites reinforced with lignocellulosic fibres [33].

Indeed, since 1941, natural fibres and polymers were also used in the automotive industry by Henry Ford in the soybean car, more recently referred to as the hemp body car (see Figure 2.6-2). Its body was made partially from soybeans and hemp. The body was lighter and therefore more fuel efficient than a normal metal body. It was designed to run on hemp fuel.
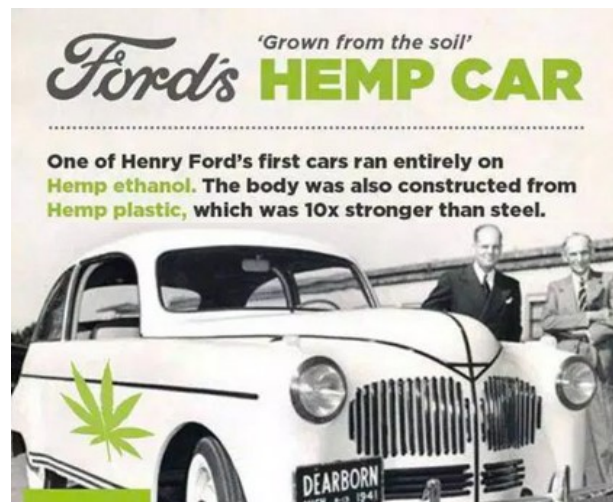
Figure 2.6-2 Car from hemp by Henry Ford [34].

However, the first car maker to use polymers filled with natural fibre was Mercedes-Benz in the 90s, by manufacturing door panels containing jute fibres. Indeed, the market for natural fibres has been growing at an increasing rate, especially for automotive applications [33]. For instance, the German automotive industry increased its usage of natural fibres from 4,000 tons in 1996 to 18,000 tons in 2003. From 1996 to 2002, there was almost a linear increase in quantities used, with yearly

growth rates of between 10 and 20% [36]. Many research projects showed that natural fibres have very good sound absorption efficiency and are high impact strength [1, 26, 28, 29, 30, 31]. The energy management during impact (such as in the case of a car accident) for natural fibres is better in comparison to the use of glass fibre in automotive parts. The mass of the car using natural fibre composites is lower and thus it reduces the energy needed for production by of the material by 80 % and the energy (fuel) needed to run the car is proportional to the weight savings [37] .

Nowadays, almost all the major car companies (Audi Group, BMW, Mercedes, Volkswagen, Ford and Opel) now use bio-based composites in several applications such as interior trim components like dashboards and door panels (see Figure 2.6-1). For example, in 2000, Audi launched the A2 midrange car in which door trim panels were manufactured from flax/sisal mixture mat reinforcing polyurethane.

As showed in Figure 2.6-3, NFCs can also be very cost effective materials for applications in building and construction (e.g. walls, ceiling, partition, window and door frames), storage devices (e.g. bio-gas containers, post boxes), furniture (chairs, stools, tables), electronic devices (outer casing of mobile phones), automobile and railway coach interior parts (inner fenders and bumpers), window and door frames, furniture, railroad sleepers, packaging, toys and other miscellaneous applications (helmets, suitcases), shelves and in general those application which do not require very high mechanical resistance but, instead low purchasing and maintenance costs [38, 39, 40].
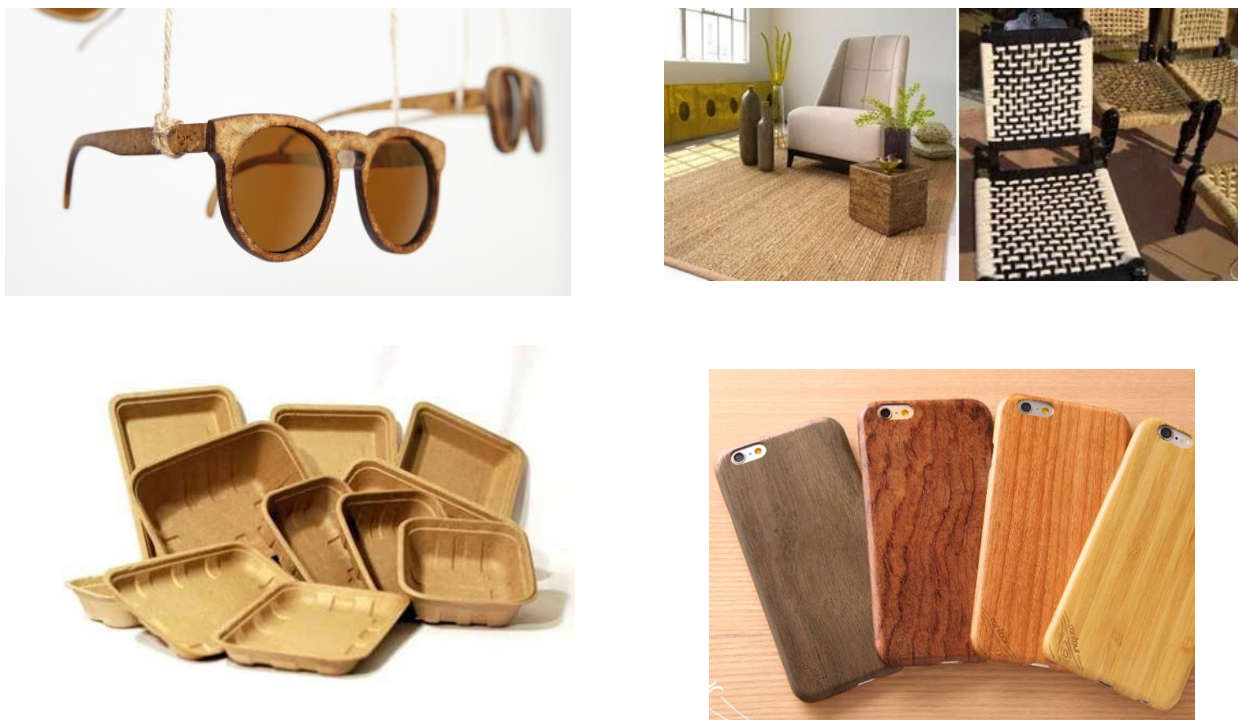
Figure 2.6-3 Some Applications of natural fibres.

Considerable research has also been carried out in the field of bio-based plastics and biocomposites, which demonstrates their significance. Nevertheless, part of product life cycle is research and development. The actual engineering process begins when the developed science is applied to a specific application. Bio-based composites offer great opportunities for an increasing role as alternate material. The use of biocomposites has extended to almost all fields including packaging, biomedical, building, civil, construction and automotive industry, etc. [41].

Some of the building and construction applications where bio-based composites are potentially used include window frames, framing, fencing, walls, doors, flooring and ceiling panels. Roof structures form biocomposites were manufactured from soy oil-based resin and cellulose fibres in the paper sheets form, being made from recycled cardboard boxes [42]. Pulp from residual sisal and coir fibres and eucalyptus waste has also been used as a replacement for asbestos in roofing components [43]. The use of bamboo fibre as reinforcement in structural concrete elements has also been studied [44]. Building temporary housing can be another potential application of biocomposites. Usually, temporary housings from wood plastic composites are set-up whenever a catastrophe occurs. When the situation recovers to normalcy the temporary housings are disassembled and the waste is put in landfills. Thereby, to reduce this type of landfill waste, such applications necessitate to apply the biocomposites and more definitely green composites, which can possibly be composted or recycled by energy recovery after their service life [41].

2.6.1 Natural Fibre Composites Market

The use of NF in composite materials is predicted to be a growing market. According to Lucintel's report [45] etiolated "Natural Fibre Composites Market Trend and Forecast 2011–2016: Trend, Forecast and Opportunity Analysis in 2010" (Figure 2.6-4), the global natural fibre composites market has reached US $289.3 million in 2010, with compound annual growth rate (CAGR) of 15% from 2005. By 2016, NFCs market is expected to reach US $531.3 million with CAGR of 11 % over the next five years. NFCs have experienced healthy growth in last six years. NFCs market is divided into two segments: wood fibre and non-wood fibres. Wood fibre is most used for building and construction, whereas non-wood fibres, such as flax, kenaf, hemp, were the main materials of choice for automotive and in general for the transportation industry.

North America is the largest region for building & construction applications and Europe is the largest region for automotive applications. Europe is the top continent in terms of total NFCs consumption; Asia is emerging as a big market for NFCs due to the rapidly increasing demand in China and India.

In the future, Lucintel expects a higher market fragmentation due to emerging economies. Future markets are anticipated to be highly competitive and companies with innovative capabilities can thrive and gain market share. Several automobile models, first in Europe and then in North America, featured natural fibre reinforced thermosets and thermoplastics in door panels, package trays, seat backs and trunk liners.
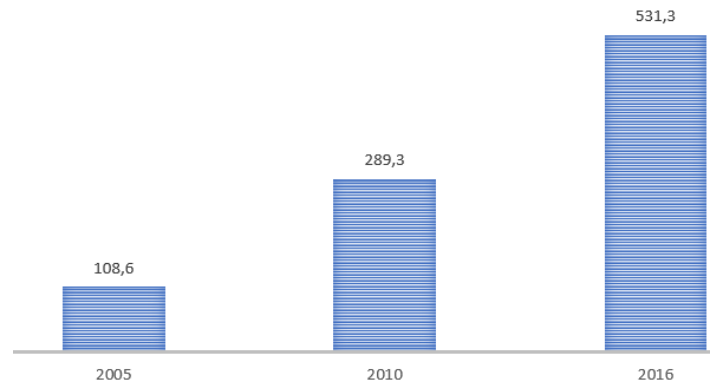
Figure 2.6-4 Natural Fibre Composites Trend

2.7 Natural Fibres Composites: Advantages and Disadvantages

2.7.1 Advantages

Most of natural fibres that have been investigated for composite reinforcement are lignocellulosic materials, or those derived from plants. The strengths of plant fibres have long been recognized and utilized. Roping, textiles, tools, and even housing materials are just some of the past and present applications that take advantage of the unique mechanical properties of plant fibres. In addition to their good mechanical properties, there are several other advantageous qualities that plant fibres have over traditional composite fibre reinforcements. These fibres are typically derived from fast-growing renewable plants and therefore are not only significantly cheaper and much less subject to economic fluctuations, but also reduce environmental concerns associated with the depletion of natural resources. Additionally, the density of cellulose based fibres can be as much as half that of traditional reinforcing fibres such as those made from glass [46]. The resulting natural fibre reinforced polymer (NFRP) composites can therefore be lighter than traditional composites allowing for more efficient systems and reduced costs associated with material transportation. Natural fibres are also non-toxic materials making them occupationally safer than glass fibres which produce glass particles during processing that can cause allergic reaction, skin irritation, or irritation to the respiratory system if inhaled. Plant fibres are also known to be less abrasive than traditional fibres allowing for less damage to the equipment required to process them.

Composites made with natural fibres are alleged to have considerably improved life cycle assessments (LCA) as they require less energy and have a lower carbon footprint than those made with glass fibres. This is in part due to the fact that only the amount of carbon dioxide that a plant assimilates during its growth phase is released during its degradation or combustion, thereby making plant fibres a carbon neutral material. Additionally, the energy consumption to produce a natural fibre mat (9.55 MJ/kg), including cultivation, harvesting, and fibre digestion, is less than a quarter of the energy required to produce a comparable glass fibre mat (54.7 MJ/kg). Patel et al. [47] performed LCAs for several current biocomposite systems and determined that the potential environmental benefits of biocomposites are significant and can be expected to be a valuable contributor toward a more environmentally friendly and sustainable world. Additionally, Joshi et al. [48] defined four general drivers for the superior environmental performance of natural fibre reinforced composites as compared to glass fibre reinforced composites for automotive applications; (i) the production of natural fibres has lower environmental impact, (ii) substitution of base polymers by higher volume of natural fibres, (iii) lower energy use during lifecycle as a result of reduced material weight, (iv) biodegradation or energy and carbon credits from end life incineration. This study determined that in most cases natural fibre composites are likely to be environmentally superior to glass fibre composites. Table 2.7-1 [49] highlights some of the main beneficial characteristics of natural fibres as compared to glass fibres.

	Natural fibres	Glass fibres
Density	Low	Twice than natural fibres
Cost	Low	Low to high
Distribution	Wide	Wide
Energy Consumaption	Low	High
Renewable	Yes	No
Recyclable	Yes	No
CO2 Neutral	Yes	No
Abrasion to machines	No	Yes
Health risk	No	Yes
Disposal	Biodegradable, energy harveating	Inceniration, land-filled

Table 2.7-1 Comparison between natural and glass fibres.

2.7.2 Disadvantages

The transition from conventional fibres like glass, carbon, and aramid to plant based fibres for composite reinforcement faces some difficulties. It is due to the below-reported factors that affect the use of natural fibres in composites.

Mechanical properties variability

The processing and manufacture of natural fibres is different from the one of traditional fibre reinforced polymers (FRP). This can act as an obstacle for widespread implementation of natural fibre reinforced composite technology as it may require companies to develop new machines and methods for manufacture of broad goods and fabrics. Additionally, conventional fibres can be repeatedly produced with a defined range of properties. In contrast, the properties of natural fibres are subject to a higher level of variability. A large variation in the properties of natural fibres is found.

Their properties are affected by several factors such as type of fibres, moisture content and form of fibres (yarn, woven, twine, chopped, felt, etc). Moreover, the properties are also affected by the place where the fibres are grown, cultivation condition, the part of the plant they are harvested from, growing period and retting or extracting process.

Wettability and Interfacial Bonding

Interfacial bonding largely depends on the adhesion between the reinforcement and the matrix. The adhesion plays an important role to transfer the stress from the matrix to the fibre and thus contributes towards the properties of the composites. Poor surface adhesion due to insufficient wetting is the principal reason for the formation of a weak or ineffective interface between the fibre and the matrix. Most thermoplastics (e.g. PP and PE) are generally non-polar (hydrophobic) in nature, which makes them incompatible with polar (hydrophilic) natural fibres and thus results in an inefficient fibre matrix bonding. On the other hand, thermosets like epoxy and phenolic are known to be able to form covalent cross-links with plant cell walls via -OH groups. However, due to the presence of unstable noncellulosic components like hemiclluloses and lignin, untreated natural fibre has performed well below their potential abilities. Therefore, to increase long term stability of the composites, surface treatment of untreated fibre is necessary, such as the alakalization, the acetylation, and the silane treatement. Normally, alkalization with sodium hydroxide (NaOH) solution is the most widely used process for the surface treatment of natural fibers due to its low cost, effectiveness, and convenience of use [50, 51].

Thermal Stability and Flame Resistance

Natural fibres have low thermal stability that results in the exclusion of some manufacturing processes, and also limits the use of the composites to low temperature applications. The low thermal stability increases the possibility of cellulosic degradation and possibility of emissions of volatile materials that could adversely affect the composite properties. Processing temperatures are thus limited to about 200 °C, although it is possible to use higher temperature for short periods of time. This apparently limits the type of thermoplastics that can be used with natural fibres. In addition, as organic materials, the natural fibers are very sensitive to flame; then, the improvement of flame retardant requirement of the composite materials has become more and more important in order to comply with the safety requirements of the natural fibre/composite products.

Biodegradability

Natural fibres degrade easily when exposed to nature environment. Some methods for degradation include biological, chemical, mechanical, thermal, photochemical and aqueous. The biodegradability of natural fibre is often put forward as a positive advantage justifying the use of these fibres. However, for many outdoor applications it is necessary for composites to be serviceable for several years.

In order to increase their service life, it is necessary to control this natural degradation. One way of preventing or slowing down the natural degradation process is by modifying the cell wall chemistry. Undesirable natural fibre properties such as dimensional instabilities, flammability, biodegradability, and chemical degradation can be eliminated or slowed down in this manner.

Chemical treatments can reduce the water uptake in the fibres, and can therefore reduce the amount of fibre swelling and biological degradation by blocking the available –OH group on the fibre surface.

Effect of Fibre Orientation

Natural fibre reinforced composites are made with random and oriented fibres. Composites made with oriented fibre in the test direction are generally stronger and stiffer than randomly oriented fibre. Both the failure strain (FS) and the maximum stress of fracture decrease with increasing angle of the fibre orientation axis with the test direction. The composite tensile strength decreases by four times when the angle between the fibre orientation axis with the test direction increases by about 26° while the composites yang's modulus decreases by only two times.

Influence of Humidity

Water on the fibre surface and on the matrix, can act like a separating agent between the fibre and matrix during the formation of the fibre/matrix interface. Therefore, fibre and matrix drying is

necessary prior to processing. On top of that evaporation of the water during composites processing over 100 °C leads to the formation of voids, the most undesirable phenomenon of composite production. Thus, reduces the mechanical properties of composites. Bledzki et al. [52] reported an increase of TS of 10% and YM of 20% for jute/epoxy composites when they dried the fibre to minimise the humidity content of jute fibre from 10 to 1 prior to the composites processing. The hydrophilic fibres also absorb moisture during the service life of composites. Moisture absorption leads to fibre swelling which causes micro-cracking of the composites, resulting in degradation of mechanical properties. Joseph et al. [5] showed that moisture absorption of NFCs can be reduced significantly by improving the interfacial bonding through chemical treatment of the fibres and/or matrices.

References

[1] A. K. Mohanty, M. Misra and L. T. Drzal, Natural Fibers, Biopolymers, and Biocomposites, CRC Press - Taylor & Francis Group, 2005.

[2] F. T. Wallenberger and N. E. Weston, Natural Fibers, Plastics and Composites, Springer Science+Business Media, LLC ed., 2004, pp. 275-285.

[3] P. A. Fowler, J. M. Hughes and R. M. Elias, "Biocomposites: technology, environmental," *Journal of the Science of Food and Agriculture,* vol. 86, p. 1781–1789, 2006.

[4] P. K. Mallik, Fiber-reinforced composites: materials, manufacturing, and, New York: Marcel Dekker, 1993.

[5] P. V. Joseph, M. S. Rabello, L. H. C. Mattosoc, K. Joseph and S. Thomas, "Environmental effects on the degradation behaviour of," *Composite Science and Technology,* vol. 62, pp. 1357-1372, 2002.

[6] K. Joseph, S. Varghese, G. Kalaprasad, S. Thomas, L. Prasannakumari, P. Koshy and C. Pavithran, "Influence of interfacial adhesion on the mechanical properties and fracture behaviour of short sisal fibre reinforced polymer composites," *European Polymer Journal,* vol. 32, no. 10, pp. 1243-1250, 1996.

[7] I. K. Varma, S. R. A. Krishnan and S. Krishnamoorthy, "Effect of chemical treatment on mechanical properties and moisture regain of jute fibers," *Textile Research Journal,* vol. 58, no. 9, pp. 537-543, 1998.

[8] A. P. Mathew, K. Oksman and M. Sain, "Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC)," *Journal of Applied Polymer Science,* vol. 97, pp. 2014-2025, 2005.

[9] S. J. Eichhorn, C. A. Baillie and e. al., "Review: Current international research into cellulosic fibres and composites," *Journal of Materials Science,* vol. 36, no. 9, pp. 2107-2131, 2001.

[10] T. Kasuga, Y. Ota, M. Nogami and Y. Abe, "Preparation and mechanical properties of polylactic acid composites containing hydroxyapatite fibers," *Biomaterials,* vol. 22, no. 1, pp. 19-23., 2001 .

[11] J. H. Lee, T. G. Park, H. S. Park, D. S. Lee, Y. K. Lee, S. C. Yoon and J.-D. Nam, "Thermal and mechanical characteristics of poly(l-lactic acid)," *Biomaterials,* vol. 24, pp. 2773-2778, 2003.

[12] E. Bodros, I. Pillin, N. Montrelay and C. Baley, "Could biopolymers reinforced by randomly scattered flax fibre be used in structural applications?," *Composites Science and Technology,* vol. 67, no. 3-4, pp. 462-470, 2007.

[13] J. Holbery and D. Houston, "Natural-fiber-reinforced polymer composites in automotive applications," *JOM,* vol. 58, no. 11, pp. 80-86, 2006.

[14] J. Summerscales, N. Dissanayake, A. Virk and W. Hall, "A review of bast fibres and their composites. Part 1 – fibres as reinforcements.," *Composites Part A,* vol. 41, no. 10, pp. 1329-35, 2010.

[15] K. Pickering, M. Aruan Efendy and T. Le, "A review of recent developments in natural fibre composites and their mechanical performance," *Composites: Part A,* vol. 83, pp. 98-112, 2016.

[16] L. Yu, K. Dean and L. Li, "Polymer blends and composites from renewable resources," *Progress in Polymer Science,* vol. 31, pp. 576-602, 2006.

[17] B. Bax and J. Müssig, "Impact and tensile properties of PLA/Cordenka and PLA/flax composites," *Composites Science and Technology,* vol. 68, no. 7-8, pp. 1601-1607, 2008.

[18] K. Oksman, M. Skrifvars and J. F. Selin, "Natural fibres as reinforcement in polylactic acid (PLA) composites," *Composites Science and Technology,* vol. 63, pp. 1317-1324, 2003.

[19] K. Meinander, M. Niemi, J. S. Hakola and J. F. Selin, "Polylactides- degradable polymers for fibres and films," *Macomolecular Symposia,* vol. 123, pp. 147-154, 1997.

[20] L. Jiang and G. Hinrichsen, "Flax and cotton fiber reinforced biodegradable polyester amide composites," *Die Angewandte Makromolekulare Chemie,* vol. 268, pp. 18-21, 1999.

[21] U. Riedel and J. Nickel, "Natural fibre-reinforced biopolymers as construction materials - new discoveries," *Die Angewandte Makromolekulare Chemie,* vol. 272, pp. 34-40, 1999.

[22] A. Keller, D. Bruggmann, A. Neff, B. Müller and E. Wintermantel, "Degradation Kinetics of Biodegradable Fiber Composites," *Journal of Polymers and the Environment,* vol. 8, no. 2, pp. 91-96, 2000.

[23] D. Robson, Survey of natural materials for use in structural composites as reinforcement and matrices, Bangor, Gwynedd : Biocomposites Centre, University of Wales, 1993.

[24] M. P. Ho, H. Wang, J. H. Lee, C. k. Ho, K. T. Lau, J. Leng and D. Hui, "Critical factors on manufacturing processes of natural fibre composites," *Composites: Part B,* vol. 43, pp. 3549-3562, 2012.

[25] I. Angelov, S. Wiedmer, M. Evstatiev, K. Friedrich and G. Mennig, "Pultrusion of a flax/polypropylene yarn.," *Composites Part A,* vol. 38, no. 5, pp. 1431-8, 2007.

[26] E. Rodriguez, R. Petrucci, D. Puglia, J. Kenny and A. Vazquez, "Characterization of composites based on natural and glass fibers obtained by vacuum infusion.," *J Compos Mater,* vol. 39, no. 3, pp. 265-282, 2005.

[27] R. Malkapuram, V. Kumar and Y. Negi, "Recent development in natural fiber reinforced polypropylene composites," *J Reinf Plast Compos,* vol. 28, no. 10, pp. 1169-89, 2009.

[28] G. Francucci, E. Rodriguez and A. Vazquez, "A. Experimental study of the compaction response of jute fabrics in liquid composite molding processes.," *J Compos Mater,* vol. 46, no. 2, p. 155–67, 2012.

[29] R. R. Franck, Bast and Other Plant Fibres, Cambridge: Woodhead Publishing Limited, 2005.

[30] D. Robson and J. A. Hague, "Comparison of wood and plant fibre properties," in *Third International Conference on Woodfibre-plastic composites*, Madison, Wisconsin, USA: Forest Products Society., 1995.

[31] A. K. Bledzki and J. Gassan, "Composites reinforced with cellulose based fibres," *Progress in Polymer Science,* vol. 24, pp. 221-274, 1999.

[32] N. E. Zafeiropoulos, D. R. Williams, C. A. Baillie and F. L. Matthews, "Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part I. Development and investigation of surface treatments," *Composites: Part A,* vol. 33, pp. 1083-1093, 2002.

[33] A. K. Bledzki, V. E. Sperber and O. Faruk, "Natural and wood fibre reinforcement in polymers," *Rapra Review Reports,* vol. 13, no. 8, p. 152, 2002.

[34] M. Karus, S. Ortmann, G. C. Gahle and C. Pendarovski, Use of natural fibres in composites for the German automotive production from 1999 till 2005, Hürth: nova-Institut, December 2006.

[35] A. K. Bledzki, O. Fauruk and V. E. Sperber, "Cars from bio-fibres," *Macromolecular Materials and Engineering,* vol. 291, no. 5, pp. 449-457, 2006.

[36] M. Garcia, I. Garmendia and J. Garcia, "Influence of natural fiber type in eco-composites," *Journal of Applied Polymer Science,* vol. 107, no. 5, pp. 2994-3004, 2008.

[37] A. K. Mohanty, M. Misra and L. T. Drzal, "Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world," *Journal of Polymers and the Environment,* vol. 10, no. 1-2, pp. 19-26, 2002.

[38] J. Rout, M. Misra, S. S. Tripathy, S. K. Nayak and A. K. Mohanty, "The Influence of Fiber Surface Modification on the Mechanical Properties of Coir-Polyester Composites," *Polymer Composites,* vol. 22, no. 4, pp. 468-476, 2001.

[39] K. Rohit and S. Dixit, "A Review - Future Aspect of Natural Fiber Reinforced," *Polymers from Renewable Resources,* vol. 7, no. 2, pp. 43-59, 2016.

[40] Y. Cao, S. Shibata and I. Fukumoto, "Mechanical properties of biodegradable composites reinforced with bagasse fibre before and after alkali treatments," *Composites Part A: Applied Science and Manufacturing,* vol. 37, no. 3, pp. 423-429, 2006.

[41] S. Pilla, Handbook of Bioplastics and Biocomposites Engineering Applications, John Wiley & Sons Inc, 2011.

[42] M. A. Dweib, B. Hu, H. V. Shenton Iii and R. P. Wool, "Bio-based composite roof structure: Manufacturing and processing issues," *Composite Structures,* vol. 74, no. 4, pp. 379-388, 2006.

[43] V. Agopyan, H. Savastano Jr, V. M. John and M. A. Cincotto, "Developments on vegetable fibre–n cement based materials in São Paulo, Brazil: an overview," *Cement and Concrete Composites,* vol. 27, no. 5, pp. 527-536, 2005.

[44] K. Ghavami, "Bamboo as reinforcement in structural concrete elements," *Cement and Concrete,* vol. 27, no. 6, pp. 637-349, 2005.

[45] Lucintel, "businesswire," [Online]. Available: http://www.businesswire.com/news/home/20111013005534/en/Research-Markets-Natural-Fiber-Composites-Market-Trend.

[46] A. K. Mohanty, M. Misra and G. Hinrichsen, "Biofibres, biodegradable polymers and biocomposites: An overview," *Macromolecular Materials and Engineering,* vol. 276, no. 1, pp. 1-24, 2000.

[47] M. Patel and R. Narayan, "How Sustainable are Biopolymers and Biobased Products? The Hope, the Doubts, and the Reality," in *Natural Fibers, Biopolymers, and Biocomposites*, CRC Press, Boca Raton, 2005.

[48] S. V. Joshi, L. T. Drzal, A. K. Mohanty and S. Arora, "Are natural fiber composites environmentally superior to glass fiber reinforced composites?," *Composites Part A: Applied Science and Manufacturing,* vol. 35, no. 3, p. 371, 2004.

[49] P. Wambua, J. Ivens and I. Verpoest, "Natural fibres: can they replace glass in fibre reinforced plastics?," *Composites Science and Technology,* vol. 63, no. 9, pp. 1259-1264, 2003.

[50] A. Shahzad, "Effects of alkalization on tensile, impact, and fatigue properties of hemp fiber composites," *Polymer Composites,* vol. 33, pp. 1129-1140, 2012.

[51] L. Hongling, Y. Lingling, J. Hongbin and Y. Weidong, "Influence of alkali treatment on the structure and properties of hemp fibers," *Fiber Polymers,* vol. 14, no. 3, pp. 389-395, 2013.

[52] A. K. Bledzki and J. Gassan, "EFFECT OF COUPLING AGENTS ON THE MOISTURE ABSORPTION OF NATURAL FIBER-REINFORCED PLASTICS," *Die Angewandte makromolekulare Chemie,* vol. 236, pp. 129-138, 1996.

Chapter 3: Materials and Method

3.3   Materials Selection

The level of environmental friendliness of biocomposites ranges from those with small portions of renewable resource based materials to those that are not only entirely based on renewable resources, but are also entirely biodegradable; the latter of which is optimal. Although biocomposites show great promise in achieving the goals of a more environmentally friendly world, widespread application and use of these materials has been limited by their relatively low properties in comparison to traditional composite materials. The goal of the thesis was, as highlighted in the Chapter 1, to manufacture lightweight hemp composites for their further applications such as in the automotive field. A part from the lightweight required from the components used in this filed, a good flame resistance is also a property required and then it was also studied in this thesis.

Among various kinds of natural fibres, the hemp ones were chosen because hemp is one of the most interesting plants, it can easily be grown around the world, it has low cost, low density, ability of extracting heavy metals from the soil makes, high specific strength when compared to glass or aramid fibres and it is available as a renewable resource.

The hemp fibre had a considerable history in terms of providing high tensile strength, especially in the use for roping, and in being part of a large productive system [1]. After a few decades of oblivion, due to drug production-related issues, the availability of varieties with low tetrahydro-cannabinoids (THCs) content, allowed hemp production to resume [2]. *It is therefore necessary in this moment to raise the profile of fibre use towards more engineered components, which may be of interest in several fields, including building, automotive and leisure sectors* [3]. For this reason, different manufacturing technique are presented to produce hemp composites with different density values.

As matrix, an epoxy resin was used. This resin is the most commonly used thermoset plastic in polymer matrix composites and it is suitable to produce advanced composites for structural parts with high mechanical characteristics. Epoxy resins are characterized from low cure shrinkage, good chemical and environmental resistance, good chemical properties and good insulating properties but *the properties of flame resistance are low*. Due to this latter disadvantage, a method to increase the flame resistance properties of the hemp/epoxy composite is described.

3.3.1 Hemp as Reinforcement for composites

The use of hemp fibres as reinforcement in polymers does not only increase the mechanical properties over those of neat resin, but can also reduce the cost of the resulting product. Over the course of the last two decades, the hemp composites industry has experienced continual growth because of technological advancements and increased applications for these materials.

In this paragraph a brief overview on the evolution of the use of hemp fibres in composite from 1941 to nowadays is reported.

In 1941, hemp fibres (and flax) were firstly used in resin matrix composites for the bodywork of a Henry Ford car which could withstand ten-times the impact on an equivalent metal panel. Unfortunately, the car did not make into general production due to economic limitations at the time together with the great interest on the use of glass fibres.

However, the ecological concerns of society in issues such as sustainability, recyclability, and environmental safety in 1990s resulted in renewed interest in natural fibre composites and one of the most interested industrial fields that showed their possible applications was the automotive one.

Indeed, Germany has been at the forefront of using natural fibres in composite materials for automobile applications. A recent survey [4, 5] found that the use of natural fibres (excluding wood and cotton) in automotive composites almost doubled from 9,600 tons in 1999 to 19,000 tons in 2005. Flax fibres had the biggest market share at 65%, followed by hemp fibres at 10%. According to authors the market share of hemp fibres can be increased by establishing further processing capacities or by reduction in hemp insulation material market. Similarly, the use of natural fibre reinforced composites doubled from 15,000 tons in 1999 to 30,000 tons in 2005. On average the 5.4 million passenger cars produced in 2005 used 3.6 kg of natural fibres per car. The consumption of hemp fibres in European Union also increased in this time. Another survey found the market share of hemp fibres in automotive industry in EU countries increased from 1% in 1996 to 15% in 2002 [6].

In 2008, the British company Lotus (www.lotuscars.com) unveiled its environment friendly car Elise Eco [6]. The car uses hemp, sisal, and wool fibres in the manufacture of interior trim, roof, seat covers, and hard top. Window frames and floor coverings made of hemp fibre reinforced polymer composites were used during the 2008 Beijing Olympics [7, 6]. Sustainable Composites Ltd (www.suscomp.com) is a British company that was established in 2003 to develop a range of eco-friendly manufacturing materials made from sustainable crops such as hemp and castor oil. The company has successfully made surfboard and a dinghy from these materials. They have also developed a linseed oil based resin that contains 96% vegetable oil [6]. A Dutch company NPSP Composieten BV (www. npsp.nl) is manufacturing diverse products using hemp and flax fibers. Examples of products are mushroom-

shaped guideposts for bicycle paths, housings of radar units (glass fibers disturb the radar rays), boats, furniture, and loudspeakers [6]. The 4th International Conference of the European Industrial Hemp Association (EIHA), held in November, 2006 in Germany, revealed a globally increasing interest in hemp raw materials due to worldwide raw material shortages [7]. It was also pointed out that because of increasing wood prices worldwide, manufacturers have started to use hemp as a replacement material in lightweight chip boards. The conference concluded that the demand of hemp fibre was bound to increase in coming years [6]. Nowadays, the hemp fibres are also used a lot in different applications such as in sporting goods, in the mobility, in music industry and for furniture and interiors components.

The first highly visible application of hemp fibres in composites for sporting goods was realised in the 'Le Ventoux' bike where both hemp and flax fabrics were used in combination of carbon prepregs [8].

The abovementioned bicycles are the first example of how flax and hemp composites can be used in mobility related applications. Several applications are showed in Figure 3.3-1.

a

b

c

d

Figure 3.3-1 Hemp composites in mobility applications [9, 10, 11].

Hemp composites have also permeated to the sound industry to create new original products which combine good mechanical properties and ingenious design. Hybrid flax/glass woofer cones (see Figure 3.3-2) are used by FOCAL [12] in the production of automotive speaker kits since 2013, providing better dynamics and a more homogeneous sound in a richer range.

a   b

Figure 3.3-2 (a) Aria column speaker 900 from FOCAL [12] and (b) El Capitan Blackbird Guitar BLACKBIRD [13].

Designing furniture with bio-based composites occurs within a technological context. At the same time, it is a key dimension of a broad cultural domain meeting a diversity of needs and expectations. In fact, these properties create the opportunities to design in a new way, with bio-based composites as a next step in the composites technology [8]. The hemp chair (see Figure 3.3-3) is an example of the use of hemp as furniture. The hemp chairs shown in Figure 3.3-3 were presented by Werner Aisslinger and by Ko-Ho.

a   b

Figure 3.3-3 a) The Hemp Chair by Werner Aisslinger [14] and (b) the Geometric Hemp chair by Ko-Ho. Photo by Samuel Hoisko [15].

3.3.1.1   Industrial Hemp Fibres

Industrial hemp (cannabis sativa L.) is one of the oldest crops known to humans, and there is evidence of its use by ancient and modern civilizations. Many hemp fibre products (dating back to around 600-800 BC) were discovered commonly in the forms of rope, canvas and cordage. The earliest discovered application is found in a stone age village unearthed on the island of Taiwan over 10,000 years old, it represents the earliest evidence of Hemp to date [16]. Although the Chinese were probably the first to domesticate and use hemp extensively, the most noted euphoric users were the Hindu's and Scythians. The Scythians, who roamed the Asian continent and ruled ancient Russia during the days of the Greeks, used Hemp for utilitarian and euphoric purposes. They were among the finest craftspeople, artists and warriors the world has ever known [16]. Due to the similar leaf shape, hemp is frequently confused with marijuana. Although both plants are from the same species, cannabis, industrial hemp can be grown with little or none of the psychoactive properties of marijuana by utilizing low-THC (delta-9-tetrahydrocannabinol) varieties.

Hemp is a bast fibre plant like flax, kenaf, jute and ramie. Long slender primary fibres on the outer portion of the stalk characterise bast fibre plants. The primary hemp fibre is attached to the core fibre by pectin—a glue-like soluble gelatinous carbohydrate. This fibre can be used for production of composites ropes, textiles specialty pulp and paper. The fibre from the wood-like core can be used for animal bedding, garden mulch, fuel and an assortment of building materials. The seed contains

between 25-35% oil by weight, which is rich in essential fatty acids considered to be necessary to maintain health [17] and cannabinoids for medical, spiritual and recreational purposes.

Hemp in the world

The commercial production of hemp originated in Central Asia but was cultivated from the Equator to the polar circle. The Spaniards brought hemp to the Western Hemisphere in 1545. In 1645 it was introduced in the USA by the Puritans in New England as a fibre source for household spinning and weaving.

At the end of the 18th century, Australia and New Zealand were considered as ideal places by England to grow hemp, reducing their dependency on Russian hemp. The start of hemp's decline was in the early 1800s when cheaper alternative fibres such as jute and sisal became more readily available from India, Bangladesh and China. Hemp's popularity was also affected by technological breakthroughs in the late 1800s such as the cotton gin. Around this time, methods for creating paper from trees allowed new products that were cheaper or more desirable than hemp to be produced [16]. The rise of the petrochemical industries at the start of the 20th century brought further competition while the final nail in hemp's coffin came in 1937 when the United States Government's Marijuana Tax Act was introduced. The act required the registration and licensing of all hemp growers with the federal government to restrict production of marijuana. Many other countries followed the USA's lead and made hemp production and possession illegal. Production restrictions were slightly lifted to support the war effort from 1943-1945. However, it was not until 1992 that several countries started officially passing legislation allowing restricted cultivation of low-THC industrial hemp.

It was not until late 2001, that a new bill was passed to allow the cultivation of industrial hemp under licence with levels of no more than 0.3% THC. Where hemp has become legal again a dramatic increase in industrial hemp growth has occurred. Therefore, now is the right time for several countries to get the benefits from the rising popularity of hemp.

Hemp in Italy

The history of hemp cultivation in Italy goes back a long way. In the 16th century, Italian hemp was considered the best in the world, and in the early 1900's, Italy was second only to Russia in its hemp production. More than 100,000 hectares of agricultural land were used to grow hemp. For many years, hemp (Cannabis sativa, L.) was a traditional crop in Italy, but at present time it almost disappeared from Italian farmland, mainly because of economic reasons. There was a gradual decline in hemp production after 1914, culminating in an economic crisis in the late 50's and early 60's when hemp, a crop that had largely been taken for granted, became a less profitable proposition, forcing farmers

to turn to other crops in order to survive. Nevertheless, it cannot be denied that the problems due to the cannabinoid content in hemp plants played a major role in the negative attitude of the Italian Administration towards this crop. In fact, in 1980 hemp cultivation was prohibited in Italy, except in a very few and strictly controlled cases. Unfortunately, this fact caused the loss of the germoplasm of some old Italian hemp varieties, along with a stop in the development of new machinery for the cultivation and processing of hemp [18]. In the 90's eco-friendly movements promoted the cultivation of hemp, and its cultivation was re-started on a small scale only to meet with seemingly insurmountable obstacles. These were predominantly associated with anti-drug laws, with EC regulations demanding a maximum of 0.2% THC down from the 0.3% previously accepted. Since the 'drug' varieties usually have at least 10% THC and often more, this new regulation seemed unnecessary, and it served to deter farmers from rekindling hemp as an important crop. An EC list of accepted varieties listed only three Italian variants, and none of these was available any longer.

3.3.1.2 Plant and Bast Fibre Morphology

Industrial hemp is an annual plant and normally dioecious, meaning the species has separate male and female plants. A female hemp plant can be seen in Figure 3.3-4. However, monoecious varieties (male and female parts on the same plant) can also be grown through breeding and selection. Hemp is sensitive to day length and the plant matures as days get shorter. Its growing season is from the middle of April to the middle of September and it can be grown as a fibre, seed, or dual purpose crop.

Figure 3.3-4 Female hemp plant.

The cross-section of hemp is almost orbicular at the bottom and angular at the top. The stalk is generally 4-10 mm thick and 1.5-2.5 m high. The interior of the stalk is hollow, surrounded by woody

cores called hurds, as shown in Figure 3.3-5. The hurd fibres are very thin walled, weak, brittle, and comparatively shorter than bast fibre and therefore are not considered for composite production. Outside the cambium layer where cells grow and differentiate there is the phloem or parenchyma layer, which contains the valuable long cells known as bast fibre.
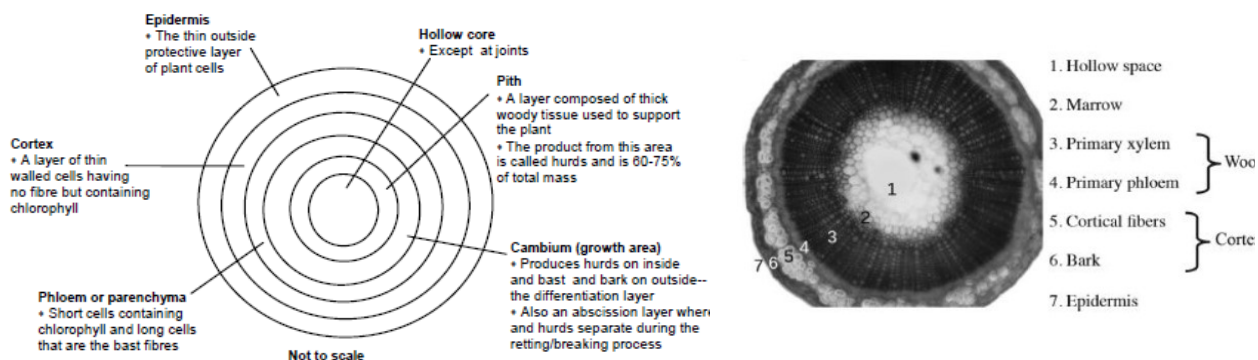
Figure 3.3-5 Cross section of a hemp stem [19, 20].

Hemp seeds are smooth and about 3.17 to 6.35 millimetres long. The seeds usually contain from 29 to 34% of oil. The oil is similar in composition to drying oils such as linseed and consists primarily of three fatty acids: linoleic (54-60%), linolenic (15-20%), and oleic (11-13%). Both the fibre and seed can be used in a wide range of applications. Industrial hemp can be grown in a variety of soils, but it does best in loose, well drained loam soils with high fertility and abundant organic matter. Plants require plentiful moisture throughout the growing season, especially during the first 6 weeks. Hemp also needs substantial amounts of nutrients to produce high yields.

Hemp diseases are not widespread and occur sporadically. They are usually caused by seed- and soil-borne fungi, which can be controlled by seed treatment before planting or by rotation. Under favourable conditions, hemp is very competitive with weeds, so herbicides are generally unnecessary in hemp fibre production. The hemp fibres can be considered as composites as they consist of cellulose microfibrils wound in amorphous materials like lignin and hemicellulose. The primary cell of the fibre cell wall is located on the outside of the fibre and it is relatively thin consisting of pectin, lignin and cellulose. The secondary cell wall is composed of two or three layers that make up most of the fibre diameter, and consists of highly crystalline cellulose microfibrils and amorphous celluloses. The technical fibre is simply a smaller part of a bast fibre bundle. The elementary fibre, also called ultimate or single fibre, is one cell of the bast fibres. The principle of the different levels of fibres in the plant is described in Figure 3.3-6.
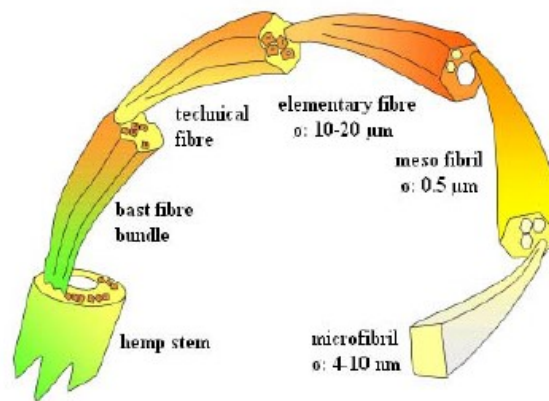
Figure 3.3-6 Composition of hemp stem.

3.3.1.3   Factors Affecting Fibre Mechanical Properties

Several structural aspects like crystallinity and amorphousness, orientation of molecular chains and imperfections (e.g. pits and nodes) affect the mechanical strength of hemp fibres like other natural fibres. The variation in chemical composition and structural imperfections develops in hemp fibres due to growth conditions and harvest procedures. Therefore, a large variation in mechanical strength occurs in fibres and differs between different parts of a plant as well as from one plant to another.

There are other factors that may also affect the fibre properties including, maturity of the plants, fibre separation process, type of soil and the climate under which they were grown. The crystalline structure of cellulose makes the fibres stiff and strong in tension but also susceptible to kink band formation under compressive loading which significantly reduces fibre strength [21]. Table 3.3-1 [6] shows typical physical and mechanical properties of hemp fibre and Table 3.3-2 [6] the tensile properties of hemp fibres as reported by different authors.

These are representative values for these properties with considerable scope for variation. Apart from their high tensile strength and stiffness, their high aspect ratio (length/diameter ratio) and lower density make hemp fibres a good material to be used as reinforcements in composite materials. Their disadvantages for use in composite materials, like most other natural fibres, are their non-uniform and non-smooth surfaces, variability of properties, and low resistance to water absorption and decay.

Properties	Values
Ultimate length (mm)	8,3-14
Ultimate diameter (mm)	17-23
Aspect ratio (length/diameter)	549
Specifi apparent desnity (gravity)	1500
Microfibil angle (°)	6,2
Moisture content (%)	12
Cellulose content (%)	90
Tensile strength (MPa)	310-750
Specific Tensile strength (MPa)	210-750
Young's modulus (GPa)	30-60
Specific Young's modulus (GPa)	20-41
Failure strain (%)	2-4

Table 3.3-1 Typical physical and mechanical properties of hemp.

Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
690		1,6
1235		4,2
310-750	30-60	2-4
550-900	70	1,6
690		1,6
895	25	
500-1040	32-70	1,6
920	70	
690-1000	50	1,0-1,6
920	70	1,7
270-900	20-70	1,6

Table 3.3-2 Tensile properties of hemp fibers as reported by different authors.

Growing Conditions

Hemp is a high yield commercial fibre crop that flourishes in areas with moderately cool climates. It can be grown on a wide range of soils, but tends to grow best on soil that is well drained, high in organic matter and non-acidic. The plants are distinctly male or female and they generally flower between June and October. Hemp requires limited pesticides as it grows quickly, attracting few pests. Hemp's extensive root system is very beneficial, as it is effective in preventing erosion, aiding in the removal of toxins and improving the soil structure by aerating the soil for future crops. Another remarkable environmental benefit of growing hemp is that it consumes carbon dioxide and it is an

ideal rotation crop. Hemp grows successfully at a density of up to 150 plants per square meter and reaches a height of between two and five meters in a three-month growing season.

Harvesting

Hemp crops are harvested at different times; for example, harvesting stalks for high quality primary fibre occurs as soon as the crop flowers, and harvesting for seed production and stalks occur 4–6 weeks after flowering, when male plants begin to shed their pollen [22]. Harvesting hemp for paper pulp and textiles occurs as the female plant is in flower and before seed formation, utilising specialised cutting equipment. The moisture content at the time of harvest is about 54%. For storage of dry hemp, the moisture content must be less than 15% to avoid fibre decay by microorganisms.

The crop is cut, and then the stalks can ret in the field to loosen the fibres. During this process, most of the nutrients extracted by the plant are returned to the soil as the leaves decompose. The stalks are turned and then baled with hay harvesting equipment.

Hemp grown for fibre is harvested at early to mid-flowering stage using specialised equipment. Liu et al. [23] reported that early harvesting of hemp is beneficial, resulting in stiffer composites. This is because of the fibre bundles in the tissue which are stuck to the epidermis and these tissue strips result in a single large fibre. The important reduction in hemp bast mechanical properties with plant maturity may be attributed to the combined effect of the noticeable decrease in cellulose deposition, and the formation and the increase in proportion of secondary fibres that caused deterioration of primary fibre quality regarding morphological and chemical characteristics.

Highly lignified fibres are not desirable and favourable for retting. Considering the mechanical performance of hemp bast fibres, hemp harvested at the beginning of flowering is therefore recommended for use in strong composites. In addition, if hemp is harvested late in the season for bast fibre production, drying conditions are often poor, with subsequent loss of fibre yield and quality in the drying swath.

3.3.1.4   Hemp Fibre Constituents

The constituents of hemp fibre vary with origin, area of production, variety, and maturity of the plant. The major constituents of fully developed hemp fibre cell walls are cellulose, hemicelluloses, lignin, and pectin, as reported in Table 3.3-3 [6].

Fibres have a complex multi-layer structure consisting of the primary wall around a secondary wall as shown in Figure 3.3-7. The secondary layer has three distinct layers (S1, S2 and S3). These layers consist of cellulose, hemicellulose and lignins in varying amounts to form of microfibrils. The S2 layer is usually the thickest layer and determines the mechanical properties of the fibres.

The pectin occurs in most mature plant cell walls except for hurd fibres, wherein extensive secondary cell wall thickening replaces almost all the pectin with lignin.

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Other (%)
67,0	16,1	0,8	3,3	2,8
74,4	17,9	0,9	3,7	0,8
74,0	18,0	1,0	4,0	
55,0	16,0	18,0	4,0	7,0
76,0	11,5	1,3	3,2	
57-77			9-13	
75,1	<2		8,0	
70-74	17,9-22,4	0,9	3,7-5,7	0,8
75,6	10,7		6,6	
78,3			2,9	
76,1	12,3	1,6	5,7	3,3

Table 3.3-3 Chemical composition of hemp fibres as reported by different authors.
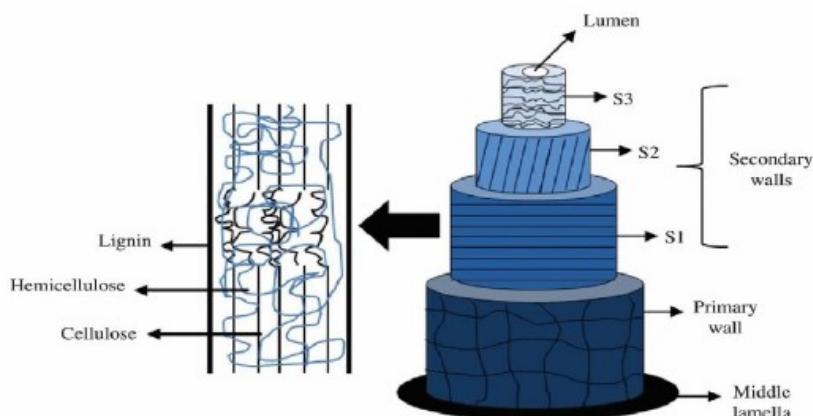
Figure 3.3-7 Schematic representation of plant fibre structure: S1-external secondary wall, S2-middle secondary wall and S3-internal secondary wall.

3.3.1.4.1   Cellulose

The long thin crystalline microfibrils in the secondary cell wall are made of cellulose. It is the reinforcing material and is responsible for the high mechanical strength of fibres. It consists of a linear polymer of D-anhydroglucose units where two adjacent glucose units are linked together by β-1,4-glycosidic linkages with elimination of one water molecule between their -OH groups at carbon atoms 1 and 4 (see Figure 3.3-8).

Chemically, cellulose is defined as a highly crystalline segment alternating with regions of non-crystalline or amorphous cellulose [25].
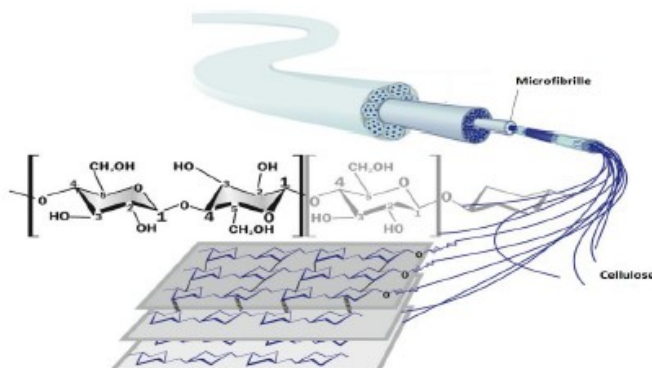
Figure 3.3-8 Structure of cellulose [26].

The glucose monomers in cellulose form hydrogen bonds both within its own chain (intramolecular) forming fibrils and with neighbouring chains (intermolecular), forming microfibrils. These hydrogen bonds lead to formation of a linear crystalline structure with high rigidity and strength. The amorphous cellulose regions have a lower frequency of intermolecular hydrogen bonding, thus exposing reactive intermolecular -OH groups to be bonded with water molecules. Amorphous cellulose can therefore be considered as hydrophilic in nature due to their tendency to bond with water. On the other hand, very few accessible intermolecular –OH are available in crystalline cellulose and it is far less hydrophilic than amorphous cellulose. Crystalline microfibrils have tightly packed cellulose chains within the fibrils, with accessible –OH groups present on the surface of the structure. Only very strong acids and alkalis can penetrate and modify the crystalline lattice of cellulose.

3.3.1.4.2 Hemicelluloses

Hemicelluloses in hemp fibres are polysaccharides (excluding pectin) bonded together in relatively short and highly branched chains. Hemicelluloses differ from cellulose in three different ways. Firstly, unlike cellulose (containing only 1,4-β-D-glucopyranose units) they contain several different sugar units. Secondly, they exhibit a considerable degree of chain branching, whereas cellulose is a linear polymer. Thirdly, the degree of polymerization of native cellulose is ten to hundred times higher than that of hemicelluloses. Unlike cellulose, the constituents of hemicelluloses differ from plant to plant. Hemicelluloses contain substituents like acetyl ($-COCH_3-$) groups and glucoronic acid.

By attaching ferulic acid and p-coumaric residues, hemicelluloses can form covalent bonds to lignin. Due to this linking ability of hemicelluloses, degradation of it leads to disintegration of the fibres into cellulose microfibrils resulting in lower fibre bundle strength [27]. Mainly the acid residues attached to hemicelluloses make it highly hydrophilic and increase the fibres' water uptake, which increases the risk of microbiological fibre degradation. It has been found that hemicelluloses thermally degrade more at lower temperatures (150-180°C) than cellulose (200-230°C).

3.3.1.4.3 Lignin

Together with cellulose, lignin is the most abundant and important polymeric organic substance in the plant world. Lignin increases the compression strength of plant fibres by gluing the fibres together to form a stiff structure, making it possible for trees of 100 meters to remain upright. Lignin is essentially a disordered, polyaromatic, and cross-linked polymer arising from the free radical polymerisation of two or three monomers structurally related to phenylpropane [28]. Free radical coupling of the lignin monomers gives rise to a very condensed, reticulated, and cross-linked structure. The lignin matrix is therefore analogous to a thermoset polymer in conventional polymer terminology. When exposed to ultraviolet light, lignin undergoes photochemical degradation [29]. Since hemp belongs to the angiosperm phylum, it contains hardwood lignin of coniferyl alcohol, sinapyl alcohol and a minor content of p-coumaryl alcohol [25]. It was shown by treatment of hemp with P-radiata-cel that the degradation of lignin and pectin (presumably) reduces the fibre bundle tensile strength slightly. Therefore, lignin seems to act like a matrix material within the fibres, making stress transfer on a micro-fibril scale and single fibre scale possible.

3.3.1.4.4 Pectin

Pectin is a complex branched structure of acidic structural polysaccharides, found in fruits and bast fibres. Much of the structure consists of homopolymeric partially methylated poly-α-(1-4)-D-galacturonic acid residues, but there are substantial 'hairy' non-gelling areas of alternating α-(1-2)-L-rhamnosyl-α-(1-4)-Dgalacturonosyl sections containing branch-points with mostly neutral side chains (1-20 residues) of mainly L-arabinose and D-galactose (rhamnogalacturonan I).
Pectin is the most hydrophilic compound in plant fibres due to the carboxylic acid groups and is easily degraded by defibration with fungi [25]. Tests on hemp fibres (single fibres as well as fibre bundles) show that treatment with pectinase enzymes can result in pectin degradation which might lead to a

slight reduction in fibre strength [25]. Pectin along with lignin and hemicelluloses present in natural fibres can be hydrolysed at elevated temperatures.

3.3.1.5   Used Hemp Reinforcement

In order to understand how to manufacture lightweight hemp components and how to increase their flame properties in a way industrially viable, both a bidirectional and a unidirectional woven hemp fabric (see Figure 3.3-9) were used in this work.

The choose to use fabrics as reinforcement is because of nowadays, they represent the most widely used long fibre reinforcement that ensure good directionality without using filament winding technologies. In addition, in some cases the use of these fabrics can represent an advantage when the production of porous structures is required. This point will be more clear in the next chapter.

The woven hemp fabrics used in this work provided by Fidia [30] and their properties are reported in Table 3.3-4 and Table 3.3-5.
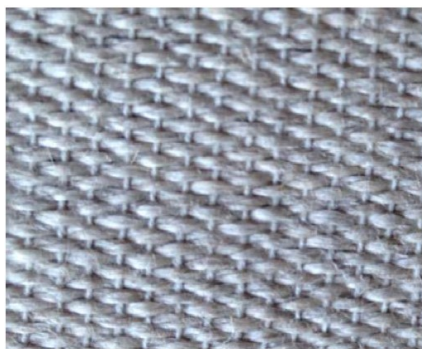
a   b

Figure 3.3-9 Unidirectional (a) and bidirectional (b) woven hemp fabric used.

Properties	
Single yarn (un-impregnated)	
Tensile strength [MPa]	507
Tensile modulus [GPa]	18.4
Elongation at breaking [%]	3.27
Density [g/cm^3]	1.5
Fabric	
Tex	334
GMS [g/m^2]	340
Equivalent thickness [mm]	0.155

Table 3.3-4 Properties of the unidirectional woven hemp fabric [30].

Properties	
Single yarn (un-impregnated)	
Tensile strength [MPa]	507
Tensile modulus [GPa]	18.4
Elongation at breaking [%]	3.27
Density [g/cm^3]	1.5
Fabric	
Tex	334
GMS [g/m^2]	380
Equivalent thickness [mm]	0.155

Table 3.3-5 Properties of the bidirectional woven hemp fabric [30].

## 3.3.2 Epoxy Resin as Matrix

Epoxy resins are the most commonly used thermoset plastic in polymer matrix composites.
These resins are a family of thermoset plastic materials which do not give off reaction products when they cure and so have low cure shrinkage. They also have good adhesion to other materials, good chemical and environmental resistance, good chemical properties and good insulating properties [31]. Epoxy is a very versatile resin system, allowing for a broad range of properties and processing capabilities. It exhibits low shrinkage as well as excellent adhesion to a variety of substrate materials. Indeed, they are the most widely used resin materials used in many applications, from aerospace to

sporting goods. There are varying grades of epoxies with varying levels of performance to meet different application needs. They can be formulated with other materials or can be mixed with other epoxies to meet a specific performance need. By changing the formulation, properties of epoxies can be changed; the cure rate can be modified, the processing temperature requirement can be changed, the cycle time can be changed, the drape and tack can be varied, the toughness can be changed, the temperature resistance can be improved, etc. Epoxies are cured by chemical reaction with amines, anhydrides, phenols, carboxylic acids, and alcohols.
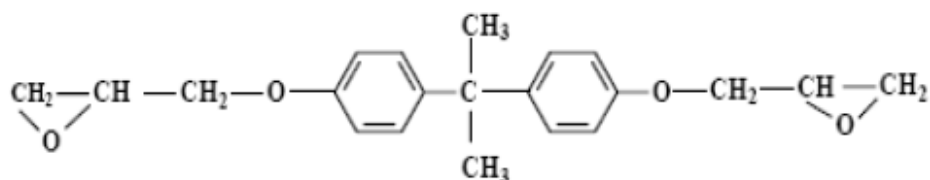
3.3.2.1 Epoxy Resins

Epoxy resins are characterised by the presence of more than one 1, 2-epoxy group per molecule. The three-membered ring structure is also known as the epoxide, oxirane, or ethoxyline group (Figure 3.3-10). This group may lie within the body of the molecule but is usually terminal. The three-membered epoxy ring is highly strained and is reactive to many substances, particularly proton donors.
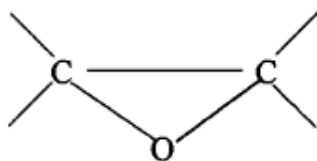
Figure 3.3-10 Epoxy ring [32].

Epoxy resins, depending on their backbone structure, may be low or high viscosity liquids or solids. In low viscosity resin, it is possible to achieve a good wetting of fibres by the resin without using high temperature or pressure. The impregnation of fibres with high viscosity resins is done by using high temperature and pressure. A wide range of starting materials can be used for the preparation of epoxy resins thereby providing a variety of resins with controllable high performance characteristics. These resins generally are prepared by reacting to a polyfunctional amine or phenol with epichlorohydrin in the presence of a strong base. The commercially available diglycidyl ether of bisphenol-A (DGEBA), Figure 3.3-11, is characterised by epoxy equivalent weight, which can be determined either by titration or quantitative infrared spectroscopy. The presence of glycidyl units in these resins enhances the processability but reduces thermal resistance.

Figure 3.3-11 Chemical structure of DGEBA [33].

There are many epoxy resins in use. High molecular weight resins are prepared by reducing the excess of epichlorohydrin and reacting under strongly alkaline conditions. The nonepoxy part of the molecule may be aliphatic,cyclo-aliphatic or aromatic hydrocarbon. It may be non-hydrocarbon and polar also. Treatment with curing agents gives insoluble and intractable thermosets.

To facilitate processing and modify resin properties other constituents may be included in the compositions; e.g., solvents, diluents, plasticizers flexibilizers and accelerators. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Hardeners include anhydrides (acids), amines, polyamides, dicyandiamide etc.

The advantages of epoxy resins are low polymerisation shrinkages unlike polyesters during cure, good mechanical strength, excellent resistance to chemicals and solvents, and excellent adhesion to fibres. The epoxy molecule also contains two ring groups at its centre, which are able to absorb both mechanical and thermal stresses better than linear groups, giving epoxy resin very good stiffness, toughness and heat resistance. The primary disadvantages of the epoxy resins are that they require long curing times and, in general, their mould release characteristics are poor. The epoxy resins are characterised by their high adhesive strengths. This property is attributed to the polarity of aliphatic -OH groups and ether groups that exist in both the initial resin and cured system. The polarity associated with these groups promotes electromagnetic bonding forces between epoxy molecules and the polar fibres [33].

3.3.2.2   Used Epoxy Resin

The epoxy resin used in this work is the SX10 EVO provided by Mates [34]. This resin was chosen because of its interesting properties below reported (from Table 3.3-6 to Table 3.3-9).

1	Low Viscosity	The SX10 is an epoxy resin of modified bisphenol with variable reactivity possibility of acceleration it has low viscosity that ensures excellent impregnation of the reinforcements also in the case of multi-axial or high GMS reinforcement.
2	Low Toxicity	Its special formulation makes it one of the least toxic epoxy resins on the market, with a significant reduction on the risk of sensitization phenomena for the users. The absence of smell due to the absence of volatile solvents allows its use without requiring expensive facilities of room ventilation.
3	Great Versatility	With the ability to accelerate the polymerization and with the possibility of processing both at room temperature and at average temperature, the resin SX10 shows a high flexible in its applicability.
4	High Glass Transition Temperature	With 7 days of hardening cycle at 25 ° C, values of 55-63 °C are reached for the glass transition temperature while with a cycle of 8 hours at 25 ° C + 24 hours at 60 ° C the mean value of the glass transaction temperature reaches 83-89 °C. The maximum reachable value is 91 °C.
5	Excellent Mechanical Properties	The mechanical properties in the two above mentioned cases of the curing cycle (7 days at 25 °C or 8 hours at 25 °C + 24 hours at 60 °C) show that the SX 10 is a resin suitable for the manufacture of products for advanced composite for structural applications where high mechanical properties are required.
6	Careful Mixing	As all the epoxy resin systems to respect the more precisely as possible mixing proportions of resin and hardener is strictly necessary. An error greater than 5% involves a lowering of the final characteristics of the resin. For this epoxy system, the ratio between the resin and the hardener weigh must be 100:26.
7	Plot - Life	This time, variable with the room temperature and with the presence of accelerator, is called pot life. Keep in mind that it is good practice to distribute the mixed product in large and shallow containers that facilitate the dissipation of the heat produced by the exothermic reaction. Smaller the amount of resin in the trays of application and higher will be the time of applicability.
8	Use of Fillers	To change the thixotropy and the density of a product can be useful to add inert fillers to the resin, according to the proportions in large and shallow containers that facilitate heat dissipation.

Table 3.3-6 Highlight points of epoxy resin SX10.

Technical data

Resin

Type	Epoxy resin of modified bisphenol
Physical State	Liquid
Gardner index	≤ 3
Viscosity at 25 °C [mPa·s]	1200 ÷ 250
Volatile Substances at 100 %	> 0,3
Density at 20 °C [g/cm^3]	1,1 ÷ 1,15
Flash Point [°C]	> 100

Hardener			
	Middle (M)	**Slow (S)**	**Extra - Slow (ES)**
Type	Modified cycloaliphatic polyamine		
Physical State	Liquid		
Gardner index	≤ 4	≤ 8	≤ 3
Viscosity at 25 °C [mPa·s]	30 ÷ 10	40 ÷ 10	40 ÷ 10
Volatile Substances at 100 %	> 0,5	> 0,5	> 0,5
Density at 20 °C [g/cm^3]	0,95 ± 0,05	0,95 ± 0,05	0,95 ± 0,05
Flash Point [°C]	98	104	100

Table 3.3-7 Technical data sheet.

Suggested curing cycles

Curing in 5 ÷ 7 days at 25 °C	With hardener type M or S + acc
Curing in 24 ÷ 48 h at 30 °C	With every hardener type
Curing in 8 ÷ 24 h at 40 °C	With every hardener type

Table 3.3-8 Suggested curing cycles.

Mechanical Properties		
Curing cycles	7 days at 25 °C	8 hours at 25 °C + 24 hours at 60 °C
Tensile strength (UNI 5819) [Mpa]	55 ÷ 65	60 ÷ 70
Breaking point (UNI 5819) [%]	2,0 ÷ 3,0	3,5 ÷ 5,0
Tensile modulus (UNI 5819) [Mpa]	2800 ÷ 3300	2700 ÷ 3200
Flexural strength (UNI 7219) [Mpa]	85 ÷ 95	105 ÷ 120
Flexural elongation (UNI 7219) [mm]	7,5 ÷ 8,5	9,5 ÷ 10,5
Flexural Modulus (UNI 7219) [Mpa]	2500 ÷ 3000	2400 ÷ 2900
Compression strength (UNI 4279) [Mpa]	105 ÷ 120	100 ÷ 120
Glass Transition temperature [°C]	50 ÷ 58	75 ÷ 85
Maximum reachable Glass Transition temperature [°C]	82 ÷ 89	91

Table 3.3-9 Mechanical Properties data sheet.

3.4   Experimental Procedure

In this section, will be described the experimental procedure adopted in the experimental campaign both for the manufacturing of lightweight hemp composites and for the improvement of their flame resistance property.

3.4.1 Lightweight Hemp Manufacturing

Because of the main intent was to manufacture lightweight hemp composites, different technique was used and to make the reading as flow as possible this paragraph is divided in three parts:

- **Part 1 - Use of an Innovative Infusion Process:** The aim of this part is to present a new natural core based on woven hemp fabric and epoxy matrix produced by a new infusion process; in addition, sandwich structures with skin of hemp/epoxy composites were manufactured. Therefore, a mechanical characterization of the hemp core in term of compression, tensile, flexural and shear strength was carried out. Finally, a comparison among sandwiches with hemp core and the ones with other types of core materials was carried out.

- **Part 2 - Conventional and Un-conventional Processes:** The aim of this part is to show other manufacturing processes for producing lightweight hemp/epoxy laminates for future applications, for example as a core for sandwich structures.

In this part the main goal is to decrease the minimum value of density, of the hemp composites, reached in the Part 1.

Therefore, their production through three no-complex processes was illustrated and laminates with three different density values were obtained. Therefore, the feasibility of the processes was studied and a mechanical characterization of hemp core in terms of tensile, flexural and impact strength was carried out.

- **Part 3 – Continuous Impregnation Process:** This part is directly connected with the previous two and based on their results, this part is focused on the manufacturing of lightweight hemp/epoxy composites by using a process easy for an industrial scale-up and allowing a low density with a good repeatability. This was done by using two hemp fabric types and composites with different density and thickness values were obtained. To assess the mechanical performances of the produced composites, bending, compression, tensile and impact tests were performed according to related ASTM standard.

3.4.1.1   Part 1: Use of an Innovative Infusion Process

An epoxy resin (details reported above) and a woven hemp fabric of 380 g/m^2 (details reported above), were used to produce the core material investigated by resin infusion process. Before impregnation, the fabrics were soaked in 2% NaOH solution at room temperature for 30 min. After treatment, fibres were copiously washed with water to remove any traces of alkali on the fibres surface and subsequently neutralized with 1% acetic acid solution. Then, the treated fibres were dried in an oven at 60°C for 12 h. The impregnation of the reinforcement with epoxy resin, was obtained by using vacuum, a close mould constituted by a glass plane and a polymeric bag and the use of a peel-ply layer on the laminates surface; no polymeric net was employed as resin distributor because of the high values of permeability characterizing the fabric.

Since the core of a sandwich structure should be as lightweight as possible and should have to provide shear and compression capacity and the integrity of the structure [28, 29], the mesh of the fabric was enlarged in order to have its lightening, to increase its permeability allowing a freely flow of the resin during the infusion process. For this purpose, from the hemp fabric one alternative tow in weft and wrap direction is manually removed; therefore, a woven hemp fabric of around 190 g/m^2 was used, Figure 3.4-1.
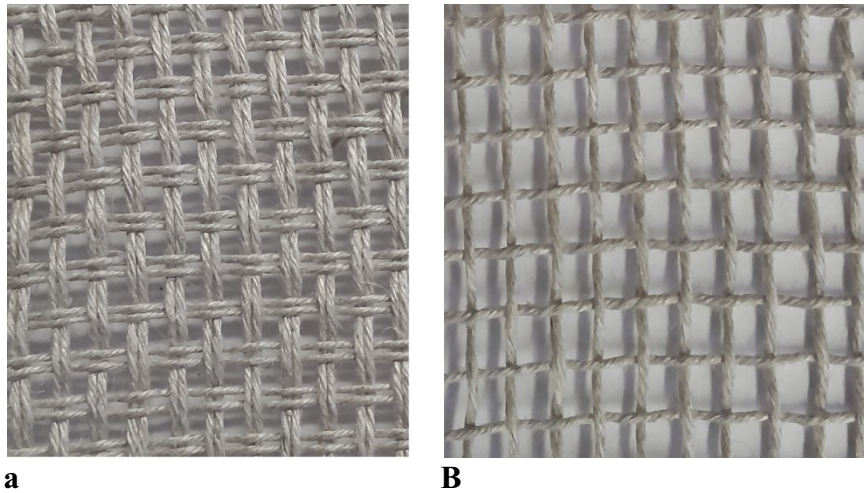
Figure 3.4-1 Woven hemp fabric before (a) and after (b) the enlargement of the mesh.

During the infusion process, air/resin mix was used in order to make a porous structure [30]. To do this, the core laminates were manufactured by using a modified infusion technique in which both a resin and an air inlet tube were used. For each laminate ten hemp fabric layers was used and the following steps were followed and summarized in Figure 3.4-2.

- The process starts as the conventional one: the resin inlet is open whilst the air inlet is close. This configuration is called ''configuration number I''.

- When the length of the impregnated zone reaches half of the total fabric length, the resin input is stopped, closing its inlet, and the air inlet is opened to allow the entry of air in to the mould. This configuration is called ''configuration number II''. Although, passing from configuration number I to number II the pressure drop is equal to 10%, the correct impregnation for the total fabric length was obtained. The air input is allowed until the gelation time of the resin was reached.

- Subsequently, the air inlet is closed and the process was conducted as the conventional one until the complete resin polymerization occurred. This step, called as ''configuration number III'' is necessary in order to confer the correct compaction of the laminate.

a	b	C
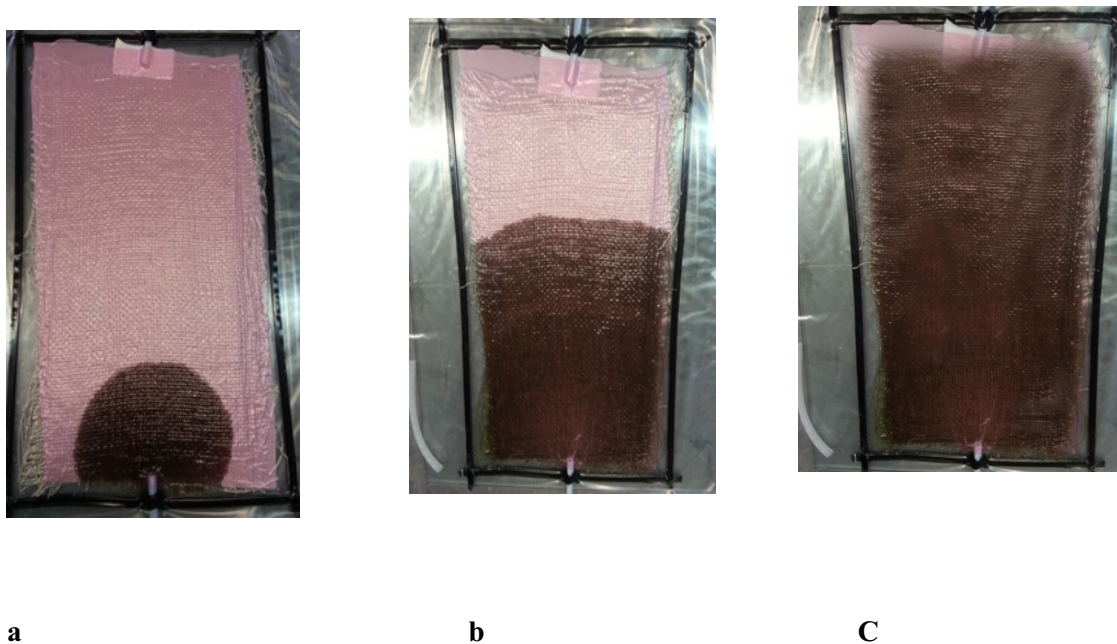
Figure 3.4-2 Steps of the proposed infusion process: Configurations number I (a), number II (b) and number III (c).

The laminates produced by means this technique had a density of about 0.6 g/cm^3, a thickness of 10 mm and the content of fibre was about 31 wt.%.

Separately from the core, the skins composite materials were also made by vacuum infusion process. Unlike the previous cases, in this case the porosities were not desired, therefore a classic vacuum-assisted resin infusion process was used. For this purpose, the same resin used for the core was used, whilst as reinforcing material of the face sheets, a woven hemp fabric (supplied by maekotessuti [34]) of 190 g/m^2 was used. The same soaked and dried treatment of the core reinforcement fabric was done for this fabric. The skin laminate was around 1.60 mm thick using four fabric layers.

Therefore, the skin laminate was glued on the core laminate using the araldite as glue.

The nominal thickness of all sandwich composites samples was around 13.2 mm. In addition, to compare the aforesaid sandwich structures with the ones having more known materials as core, an aluminium foam (aluligth supplied by eckagranules [35] with a density equal to 0.6 g/cm^3) and a divinycell foam (HCP 400 proved provided by diabgroup [36] with a density equal to 0.4 g/cm^3) are used for this purpose.

Therefore, three different types of sandwich structures were investigated, they differed in the core materials but had the same type of hemp skin. To assess the mechanical performances both of the core and of the sandwich composites, bending, compression, and tensile tests were performed

according to related ASTM standard. For each type of test five specimens were tested and the mean values and the standard deviations were calculated.

3.4.1.2 Part 2: Conventional and Un-conventional Processes

In addition to the materials described in the previous part (Part 1) in this case was also used a polyurethane foam as matrix and the same considerations regarding the fabric treatment and its enlargement were done.

The impregnation of the reinforcement, constituted by 4 fabric layers (Figure 3.4-1 b), was obtained through three different processes: (i) the unconventional infusion process showed in Part 1 using the epoxy resin, (ii) a conventional hand lay-up process with the use of the epoxy resin and (iii) an hand lay-up with the epoxy resin followed by injection moulding process using the polyurethane foam.

The (i) process was already presented in the previous part and through this method laminates thick 4.0 mm with a density of 0.6 g/cm^3 and a hemp content of around 32 wt.% were obtained. Despite the air inlet, the process is not able to obtain a complete porous structure and an excess of resin in some zones was detected, as showed in Figure 3.4-3.

The (ii) process, the hand lay-up, is well note in the composite manufacturing field and it was used in order to avoid the above-mentioned excess of resin. For each hemp fabric layer the ratio between its impregnated and un-impregnated weight was keep constant to 2.3 and the resin was applied by brushing. Then all the layers were stacked through the use of vacuum in a close mould constituted by a glass plane and a polymeric bag. Also in this case, a peel-ply layer was placed on the top laminate surface.

By using this technique, laminates thick 4.0 mm with a density of 0.42 g/cm^3 and an hemp content of around 43 wt.% were obtained (Figure 3.4-3).

Finally, in order to decrease further the density value the (iii) process was used. In this process, each hemp layer was impregnated by the epoxy resin as in the (ii) process and separately placed on a glass mould until the complete polymerization occurred. Also in this case, for each layer the ratio between its impregnated and un-impregnated weight was equal to 2.3. After this step, the hemp-epoxy layers (Figure 3.4-4 a) was placed into a steel mould (Figure 3.4-4 b) together with the polyurethane foam. By using this technique, laminates thick 4.6 mm with a density of 0.28 g/cm^3 and an hemp content of around 41 wt.% were produced (Figure 3.4-3).
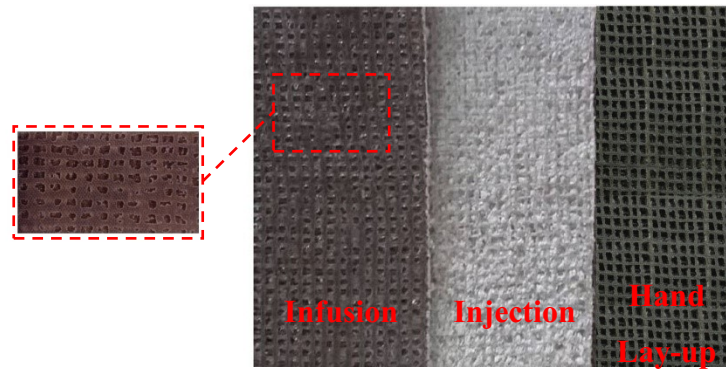
**Figure 3.4-3** Composite laminate surfaces.
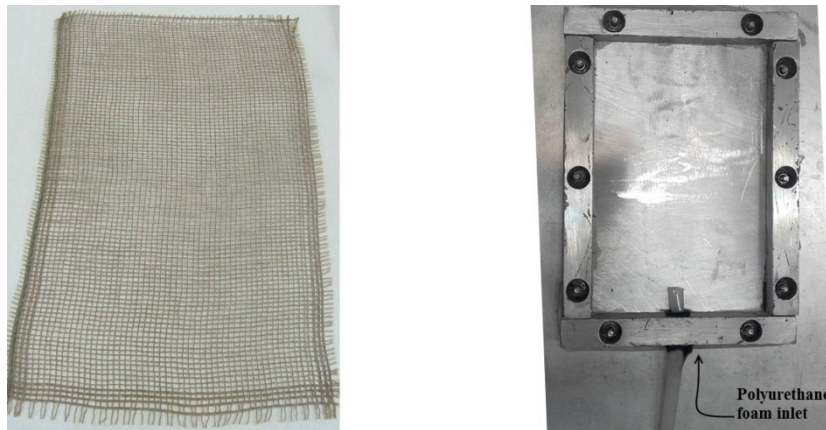
Figure 3.4-4 Single impregnated layer used for the injection process (a) and steel molud (b).

To assess the mechanical performances of the composites, bending, tensile and Charpy tests were performed according to their related standards. For each type of test, five specimens were tested.

3.4.1.3 Part 3: Continuous Impregnation Process

In this part, the same materials already presented were used. In particular both the fabrics show in Figure 3.4-1 and the SX10 epoxy resin were used and the same considerations on the fibre treatment was done.

The manufacturing of the composite laminates were made according to the idealized process proposed in Figure 3.4-5.
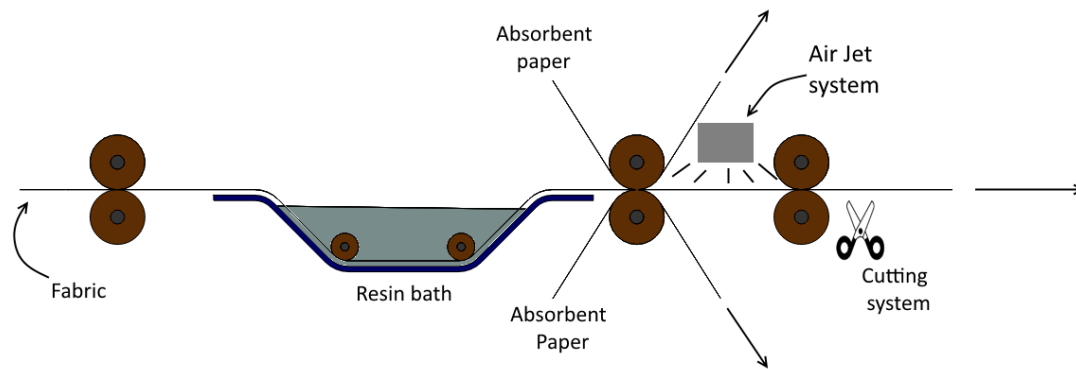
Figure 3.4-5 Schematization of the idealized system to produce impregnated hemp fabric in a continuous manner.

The process is divided in four steps:

1) Impregnation: the fabric wrapped on reels was pulled, and through the passing in the resin bath it was opportunely impregnated.

2) Resin absorption: the impregnated fabric was squeezed through the passing in the space between two rolls having on their surfaces renewable absorbent paper layers.

3) Resin content reduction: to reduce resin excess and obtain the desired fibre content, the fabric passes under an air jet system. Thanks to the large mesh of the fabric, the air jet is able to remove the resin between its spaces.

4) Cutting: the fabric was cut by using a cutting system.

However, the system is not automated yet and then all steps were manually conducted.

This technique was used to obtain impregnated hemp fabric layers by using both the standard (defined as A typology) and the enlarged mesh fabric (defined as B typology). In this way, laminates with different density values were obtained. Each hemp layer was impregnated with the epoxy resin keeping constant the ratio between the weight of the impregnated fabric and the weight of the un-impregnated one. This ratio was around 2.77 and then the hemp content was around 36 wt.% for each layer. After the cutting step, each single layer were stacked one on the other through the use of vacuum in a close mould constituted by a glass plane and a polymeric bag.

To produce laminates with different thicknesses, samples with 4, 8 and 10 layers of reinforcement using both the A and the B fabric types were produced. Table 3.4-1 summarized the typologies of the samples and their main characteristics. Concerning the volume content of the fibre, V_f, was evaluated

according to equation (1) using as fibres density, ρ_f, the value of 1.5 g/cm^3 (see Chapter 2) and as weight fibres content, W_f, and composite density, ρ_c, the values reported in Table 3.4-1.

$$V_f = \frac{\rho_c}{\rho_f} W_f \qquad\qquad (1)$$

Sample Typology	Fabric Mesh	Number of Layers	Mean Thickness [mm]	W_f [%]	ρ_c [g/cm^3]	V_f [%]
A4	No-Enlarged	4	5.3	38	0.74	19
B4	Enlarged	4	4.3	38	0.47	12
A8	No-Enlarged	8	10.0	38	0.79	20
B8	Enlarged	8	7.3	38	0.53	13
A10	No-Enlarged	10	12.3	38	0.80	20
B10	Enlarged	10	8.9	38	0.55	14

Table 3.4-1 Produced laminates and their properties.

To assess the mechanical performances of the composites, tensile, bending, shear, compression and Charpy tests were performed according to their related standards. For each type of test, five specimens were tested.

In addition, in order to study if the mechanical properties are in agreement with theoretical considerations, tensile tests on un-impregnated yarns were carried out.

3.4.2 Flame Resistance Improvement

The epoxy resin SX10 and the unidirectional hemp fabric of 340 g/m^2 with densities of 1.15 g/cm^3 and 1.5 g/cm^3 respectively, were used to produce composite laminates by resin infusion process, according to other works [22,23]. The technical datasheet both of the resin and of the hemp fabric is reported above.

Figure 3.4-6 shows, respectively, the fabric (Figure 3.4-6a), a magnification of a single hemp yarn that composes it (Figure 3.4-6b e c) and the infusion process for the realization of a laminate (Figure 3.4-6d).
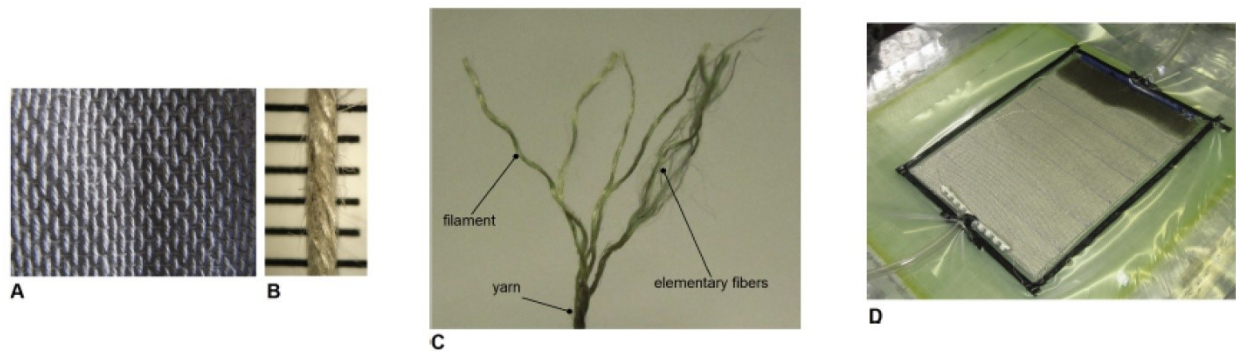
Figure 3.4-6 Unidirectional hemp fabric used in the experimental campaign (A), magnification of 1 cm of hemp yarn that composes the fabric (B), hierarchical yarn structure (C) and infusion process of a biocomposite laminate (D).

From Figure 3.4-6c, it is possible to observe that each yarn is formed by the winding of five filaments, with a twist angle equal to about 20°; in turn, each filament consists of several elementary fibres. Moreover, only 300 g/m^2 of hemp fibres are available in the fabric direction, since about 10% of the content is related to the filaments that hold together the yarns of the fabric.

For each produced laminate, the ratio of fibre to resin was kept constant and equal to 35% in weight. For the treated samples, the resin and APP particles (by Tecnosintesi Spa) were mixed on the ratio 100:5, 100:15 and 100:30.

Table 3.4-2 summarizes some of the characteristics of the flame retardant, extracted from the product data sheet, used in this work.

Monomer brute formula	P (wt.%)	N (wt.%)	PH*	Degradation temperature (°C)	Density (g/cm^3)	Particle dimension (μm)	Water solubility* (g/100ml)
-[NH$_4$PO$_3$]$_n$-	31.5	14.4	6	286	1.9	38	0.5

* Data at 25° C.

Table 3.4-2 Chemical composition and physical properties of APP.

Table 3.4-3 reports the denomination of the different samples and their composition (the data start from a reference untreated sample of 100 g).

Sample Denomination	Fibre (g)	Resin (g)	APP (g)	APP (%)
APP0	35	65	0	0
APP1	35	65	3.25	3.15
APP2	35	65	9.75	8.88
APP3	35	65	19.5	16.32

Table 3.4-3 Denomination of the different samples and their composition.

Before impregnation, the fabric was treated as previously reported.

The impregnation of the reinforcement, constituted by four fabric layers, with epoxy resin, along the fibres direction, was obtained by use of vacuum, generating also the reinforcement compaction, and by a close mould constituted by a glass plane and a flexible tool, a polymeric bag; no polymeric net (placed generally on the reinforcement layers) was employed as resin distributor because of the high values of permeability characterizing the fabric.

Indeed, the wide mesh of this unidirectional fabric allows the resin to flow freely without filter action with respect to APP during the infusion process. The dimensions of the laminates were 550 mm x 350 mm, 2.5 mm thick; the time measured for different distances of impregnating flow is reported in Figure 3.4-7.From the data, it is clear that the presence of the additive in the epoxy increases the impregnation time compared to the untreated case; however, the feasibility of the technological process is not affected.
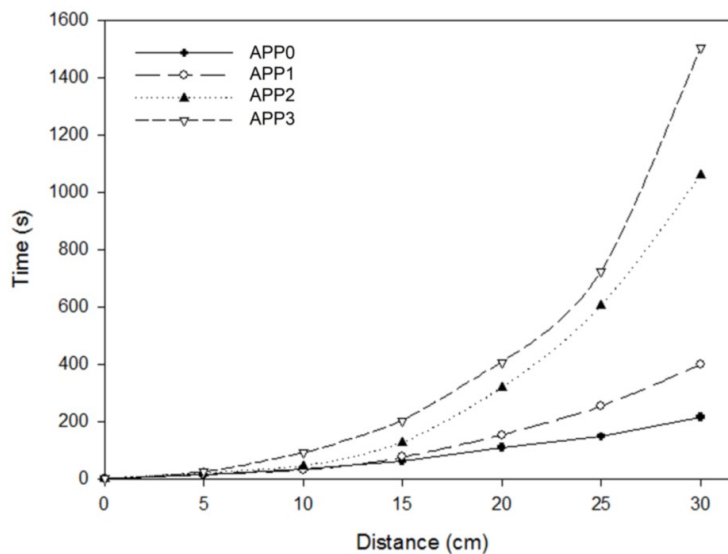
Figure 3.4-7 Impregnation time versus distance of impregnating flow for untreated and treated samples.

Therefore, cone calorimeter, vertical burning, dynamic mechanical analysis and bending tests were performed in order to study the fire and the mechanical behaviour of the produced biocomposites with different percentage of ammonium polyphosphate.

A single laminate for each typology of biocomposites proved to be sufficient to extract all the specimens to conduct the experiments. From each laminate, five specimens were cut for every test type.

References

[1]   C. Hill and M. Hughes, "Natural fibre reinforced composites: opportunities and challenges," *J Bio Bioenergy,* vol. 4, no. 2, pp. 148-152, 2010.

[2]   D. Lachenmeier, L. Kroener, M. F and B. Madea, "Determination of cannabinoids in hemp food products by use of headspace solid-phase microextraction and gas chromatography-mass spectrometry," *Anal Bioanal Chem,* vol. 378, no. 1, pp. 183-189, 2004.

[3]   I. De Rosa, H. Dhakal, C. Santulli, F. Sarasini and Z. Zhang, "Post-impact static and cyclic flexural chara hemp fibre reinforced laminates," *Composites: Part B,* vol. 43, no. 3, pp. 1382-1393, 2012.

[4]   M. Karus and D. Vogt, "European hemp industry:Cultivation, processing and product lines.," *Euphytica, vo* 12, 2004.

[5]   M. Karus, S. Ortmann, C. Gahle and C. Pendarovski, Use of natural fibers in composites for the Germa production from 1999 till 2005, Nova Institute GmbH, 2006.

[6]   A. Shahzad, "Hemp fiber and its composites – a review," *Journal of Composite Materials,* vol. 8, pp. 973-9

[7]   "Hemp Industry on Global Course of Expansion," [Online]. Available: www.jeccomposites.com.

[8]   L. Pil, F. Bensadoun, J. Pariset and I. Verpoest, "Why are designers fascinated by flax and hemp fibre comp 83, pp. 193-205, 2016.

[9]   "Mobitecture," [Online]. Available: http://www.mobitecture.com/portfolio/hemp-bike/.

[10]   ".collective-evolution," [Online]. Available: http://www.collective-evolution.com/2013/11/01/the-wor friendly-car-its-made-entirely-from-hemp/.

[11]   "nocohempexpo," [Online]. Available: http://nocohempexpo.com/2016/03/driving-hemp-futu biodegradable/.

[12]   FOCAL, "Flax Cone," [Online]. Available: http://www.Focal.Com/En/209-Flax-Cone-2-3-Way.

[13]   "Blackbird El Capitan Guitar," [Online]. Available: https://Blackbirdguitar.Com/Content/Blackbird.

[14]   "Aisslinger Studio. Hemp Chair & Hemp House," 2011. [Online]. http://www.Aisslinger.De/Index.Php%3Foption%3Dcom_Project%26view%3Ddetail%26pid%3D121%26

[15]   B. Glasner and S. Ott, "Wonder wood: a favorite material for design,," 2012. [Online].

[16]   D. J. Macintosh, the 5 minute guide to Industrial Hemp in New Zealand, New Zealand Hemp Industries Ass 1998.

[17]   J. L. Deferne and D. W. Pate, "Hemp seed oil: A source of valuable essential fatty acids," *Journal of the Hemp Association,* vol. 3, no. 1, pp. 4-7, 1993.

[18] P. Cappelletto, M. Brizzi, F. Mongardini, B. Barberi, M. Sannibale, G. Nenci, M. Poli, G. Corsi, G. Grassi "Italy-grown hemp: yield, composition and cannabinoid content," *Industrial Crops and Products,* vol. 13, 113, 2001.

[19] "www.ndsu.edu," [Online].
https://www.ndsu.edu/pubweb/chiwonlee/plsc211/student%20papers/articles02/cthielen/hemp.htm.

[20] S. Amziane and L. Arnauld, Bio-aggregate-based Building Materials - Applications to Hemp Concretes, W

[21] H. L. Bos, M. J. Oever and O. C. Peters, "Tensile and compressive properties of flax fibres for natural fib composites," *Journal of Materials Science,* vol. 37, pp. 1638-1692, 2002.

[22] "TPP Industrial Hemp Guide, in Health Canada," p. 4, 1998.

[23] M. Liu, D. Fernando, G. Daniel, B. Madsen, A. S. Meyer, M. T. Ale and A. Thygesen, "Effect of harvest t retting duration on the chemical composition, morphology and mechanical properties of hemp fibers," *Ind and Products,* vol. 69, pp. 29-39, 2015.

[24] P. Pereira and et al, "Vegetal fibers in polymeric composites: a review," *Polímeros,* vol. 25, no. 1, pp. 9-22

[25] A. Thygesen, A. B. Thomsen, G. Daniel and H. Lilholt, "Comparison of composites made from fungal def with composites of traditional hemp yarn," *Industrial Crops and Products,* vol. 25, pp. 147-159, 2007.

[26] [Online]. Available: http://www.jrs.eu/jrs_en/innovative-funktionen/uebersicht-funktionen-jrsprodukte/.

[27] M. Liu, A. S. Meyer, D. Fernando, D. A. S. Silva, G. Daniel and A. Thygesen, "Effect of pectin and hemicellu from hemp fibres on the mechanical properties of unidirectional hemp/epoxy composites," *Composites: P* pp. 724-735, 2016.

[28] A. Sakakibara and N. Shiraishi, Wood and Cellulose Chemistry, New York: Marcel Dekker, 1991.

[29] R. M. Rowell, "A new generation of composite materials from agro-based fibre," in *The Third Internationa on Frontiers of Polymers and Advanced Materials*, Kuala Lumpur, Malaysia, 1995.

[30] "Fidiaglobalservice," [Online]. Available: http://www.fidiaglobalservice.com/ita/tessuti_lino_canapa.html.

[31] M. Singla and V. Chawla, "Mechanical Properties of Epoxy Resin – Fly Ash Composite," *Journal of Materials Characterization & Engineering,* vol. 9, no. 3, pp. 199-210, 2010.

[32] K. P. Unnikrishnan, *Studies on toughening of epoxy resin,* kochi, India, 2006.

[33] M. S. Islam, *The Influence of Fibre Processing and Treatments on Hemp Fibre/Epoxy and Hemp Fibre/PLA* Hamilton, New Zealand, 2008.

[34] "mikecompositi," [Online]. Available: http://www.mikecompositi.it/manufacturer/3-m srl.aspx?pageindex=8.

[35] "eckagranules- Metal-Power-Technologies," [Online]. Available: https://www.ecka-granules.com/de/produ

[36] "Diab," [Online]. Available: http://www.diabgroup.com/.

Chapter 4: Results and Discussions on the Manufacturing of Lightweight Hemp Structure

4.1   Part 1: Use of an Innovative Infusion Process

Tests on core material

On hemp core material, compression, bending and tensile tests were performed using a universal testing machine (MTS Alliance RT/50).

Flatwise compression tests on sandwich core material were performed according to ASTM 365/365M. Specimens were in form of tetragonal prism with 30 x 30 mm square base and a thickness of 10 mm. All tests were performed at constant crosshead displacement of 0.5 mm/min and the results are shown in Figure 4.1-1.
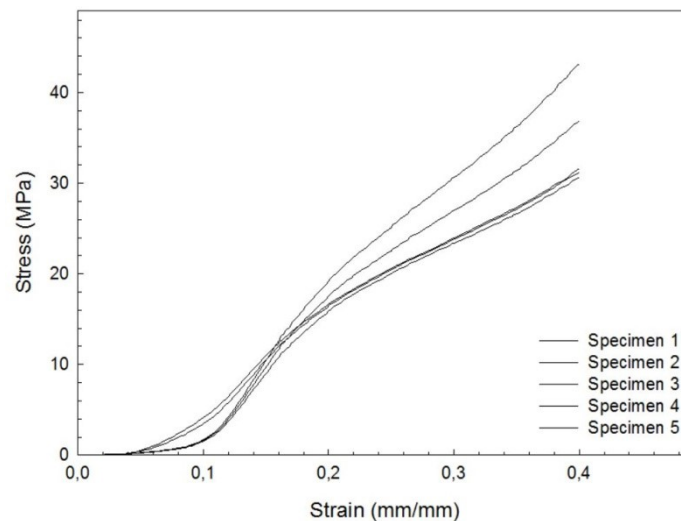
Figure 4.1-1 Stress-strain curves of the hemp core composites in the flatwise compression.

Three points bending tests were performed to determine flexural performance on the sandwich core composites. The dimensions of the specimens were selected according to ASTM D790-10. Then, the span length, the total length and the width were 160 mm, 200 mm and 35 mm, respectively. The thickness of the specimens was always 10 mm. All tests were performed at constant crosshead displacement of 0.5 mm/min and the resulted curves are shown in Figure 4.1-2.
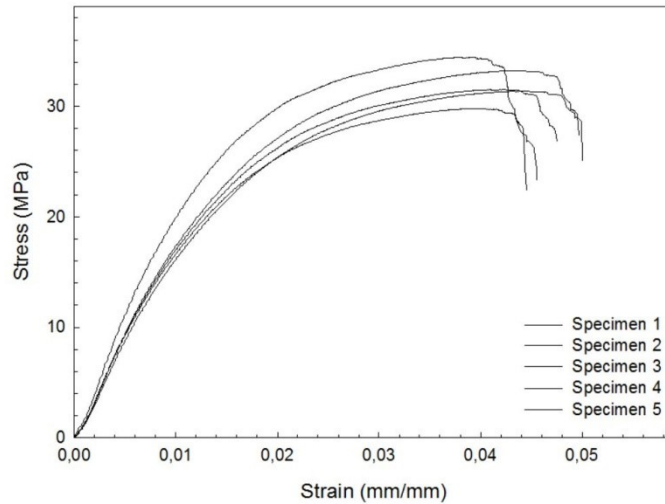
Figure 4.1-2 Stress-strain curves of the hemp core composites in the3-point bending conditions.

Finally, tensile tests were also performed according to ASTM D3039/D3039M-14. Specimens with a width of 25 mm, an overall length equal to 250 mm and a tab length of 50 mm were tested under a crosshead displacement of 2 mm/min.

The results of this test are reported in Figure 4.1-3, whilst in Table 4.1-1 the mechanical properties of the hemp core are compared with those of the aluminum and divinycell core.
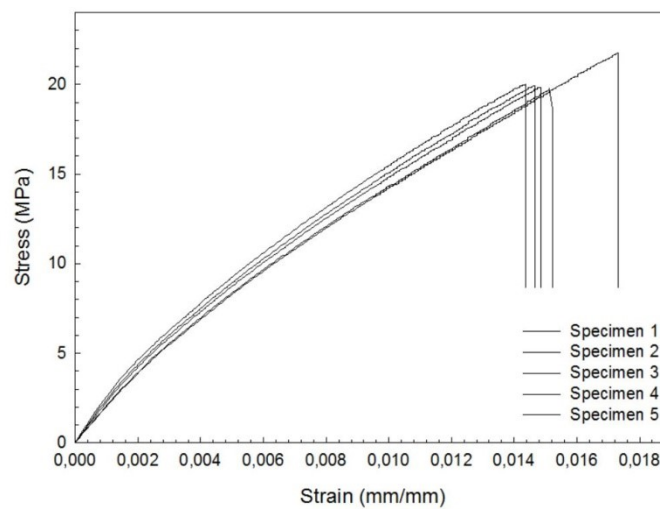
Figure 4.1-3 Stress-strain curves of the hemp core composites in the tensile conditions.

		Hemp core		Aluminium core		Divynycell core	
		mean	St.dev	Mean	St.dev	mean	St.dev
Compression	σ_c (Mpa)	17,4	1,3	3,3	1,2	10,8	10
	E_c (Mpa)	174,5	21,5	11,0	0,8	595,0	55
Flexural	σ_f (Mpa)	32,0	1,6	9,4	0,3	-	-
	E_f (Mpa)	2188,5	191,8	275,9	11,13	-	-
Tensile	σ_t (Mpa)	20,2	0,7	5	0.8	12,8	0,6
	E_t (Mpa)	1767,0	43,91	39,6	1,2	-	-

Table 4.1-1 Comparison among the mechanical properties of the hemp, aluminum and divinycell core.

From Table 4.1-1, it is possible to observe that the hemp core under investigation showed the highest mechanical properties, considering that its density is comparable with that of the others core materials. In particular, due to its high value of the compression strength, this core can be used to produce sandwich structures in which the indentation failure will not occur and then to make sandwich structures in which the skins can be applied by compression moulding technique without compression failure of the core. However, despite the air inlet during the infusion process, the process was not able to produce a complete porous structure and an excess of resin in some zones was detected, as showed in Figure 3.4-3; then the density of 0.6 g/cm^3 is not the minimum allowed value. This means that the process could be optimized and/or others manufacturing techniques could be proposed and investigated.

Tests on sandwich structures

On sandwich structures, bending tests were performed using a universal testing machine (MTS Alliance RT/50).

Three points bending tests were conducted according to ASTM C393/393M-11 standard in order to evaluate the core shear properties of sandwiches. Then, the span length, the total length and the width were 150 mm, 200 mm and 40 mm, respectively. The thickness of the specimens was always 13.2 mm and the force deflection curves of the specimens are given in Figure 4.1-4.
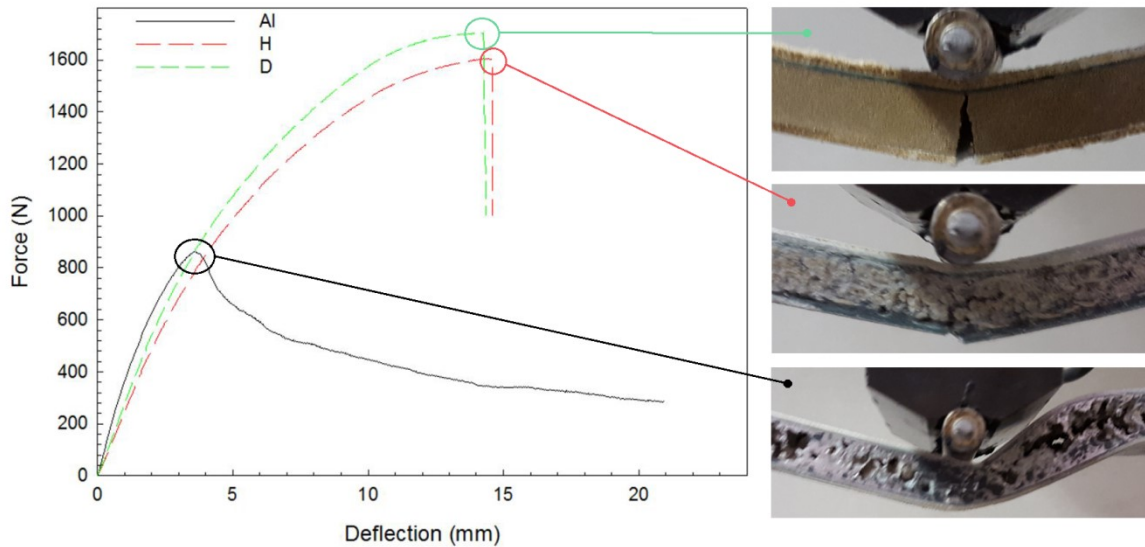
Figure 4.1-4 Force deflection curves of the sandwich composites under bending.

As shown Figure 4.1-4, the shear failure occurred only for the sandwich with aluminium foam, whilst in the others cases the failure was always for tension. This occurred for all types of specimens. The values of the flexural stress (σ_f) and of the shear stress (τ) are evaluated by the following equations:

$$\sigma_f = \frac{F_{max}S}{2(t+c)\mathrm{b}}$$

$$\tau = \frac{F_{max}}{(d+c)b}$$

in which F_{max} is the maximum force prior to failure, S is the span length, b is the sandwich width, t is the nominal facing thickness, d is the sandwich thickness and c is the core thickness. The value of σ_f, for the sandwich with hemp and divinycell core, in term of mean and standard deviation is equal to 102.3 (2.8) MPa. Instead, the value of the aluminium core shear strength is equal to 1.01 (0.4) MPa. In order to detect the shear strength both of the hemp and of the divinycell core, tests with lower span length equal to 100 and 50 mm were carried out. In the case with span length equal to 100 mm, the failure occurred also on the tensile facing both for hemp and for divinycell core, then in this case only the value of σ_f can be evaluated. Obviously, it was very similar to the one obtained previously then equal to 105.1 (1.7).

As shown in Figure 4.1-5, also in the case with a span length equal to 50 mm the failure on the tensile facing occurred.

Figure 4.1-5 Indentation phenomenon during the three-point bending test of the divinycell sandwich (A). Failure of the divinycell (B) and hemp sandwich(C).

However, only for the sandwich with the divinycell core the phenomenom of the indentation occurred. This involved that the σ_f, equal to 84.07 (1.3) MPa, obtained in this case was lower than the one of the sandwiches with hemp core. As expected, since σ_f is an intrinsic characteristic of the skin, also in this case its value for the sandwich with hemp core was equal to 100 (1.2) MPa.

Therefore, it is possible to conclude that:

- By using the proposed process hemp/epoxy composites with a density of 0.6 g/cm^3 can be produced; this value is close to the density of others materials conventionally used as core, such as aluminium and divinycell foams.

- The mechanical characterization of the core showed that the mechanical properties in term of compression, tensile and bending strength of the hemp core was higher than the ones of the others investigated materials. In order to compare the shear strength, sandwich with skins in hemp/epoxy composites were made. From the comparison, it was highlited that in the sandwich with the hemp core the failure was always for tensile. Unlike of the other case, no shear and indentation phenomena was observed. In particular, due to its high value of the compression strength and the absence of indentation failure, the proposed hemp core could be used to produce sandwich structures in which the skins can be applied by compression moulding technique without compression failure of the core.

- However, the process was not able to produce a complete porous structure and an excess of resin in some zones was detected; then the density of 0.6 g/cm^3 is not the minimum allowed value. This means that the process could be optimized and/or others manufacturing techniques could be proposed and investigated. This disadvantage lays the groundwork for the Part 2 of this section, where others processes are proposed.

4.2 Part 2: Conventional and Un-conventional Processes

Bending and tensile tests were performed using a universal testing machine (MTS Alliance RT/50) and the Charpy test were performed by using a CEAST Resil Impactor.

Tensile tests were performed according to ASTM D 3039/D3039 M-14. Specimens with a width of 25 mm, an overall length equal to 250 mm and a tab length of 50 mm were tested under a crosshead displacement of 1 mm/min. Figure 4.2-1 shows both the stress-strain and the specific stress-strain curves for each specimen while the tensile test results are summarized in Table 4.2-1. First of all, it is possible to observe that the processes have different level of repeatability, directly connected with the specific standard deviation value. In fact, its highest values are reached in the case of the specimens produced through the hand lay-up process and the lowest when the infusion is used, while the specimens manufactured by means of the injection process showed an intermediate behaviour between the previous ones. This is particularly true considering the specific standard deviation (the ratio between the standard deviation and the mean value) of the strain at braking values. Its highest value, reached for the hand lay-up process, is due to the slip between the fibres that is allowed when the fibres are impregnated through this process.

a   b
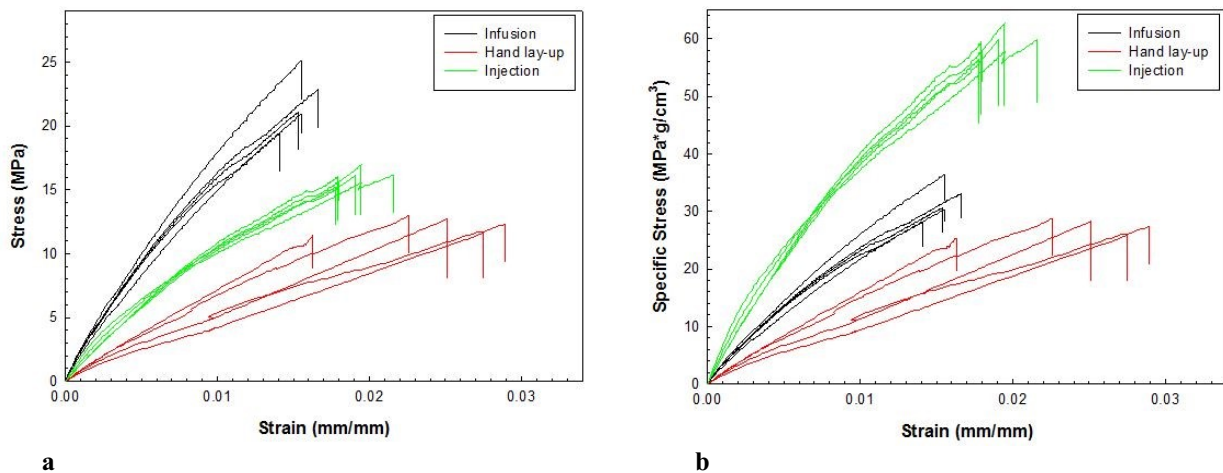
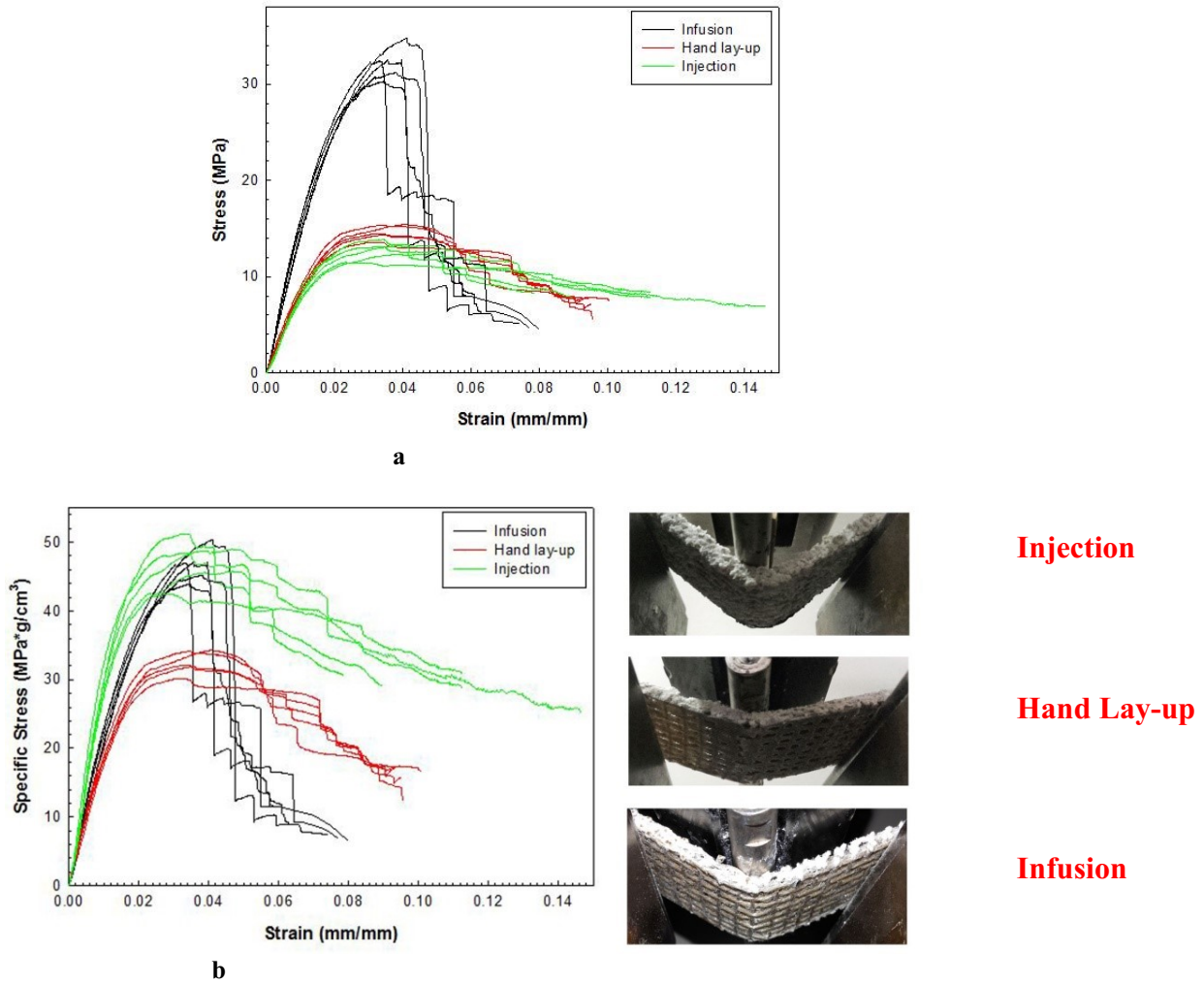**Figure 4.2-1** Tensile stress-strain (a) and specific stress-strain curves (b).

Tensile Properties

		Infusion	Hand Lay-up	Injection
σ (MPa)	Mean	21.88	12.20	16.11
	St. dev.	1.94	0.60	0.55
	Specific St. dev.(%)	8.88	4.94	3.43
ε (mm/mm)	Mean	1.54E-02	2.41E-02	1.92E-02
	St. dev.	7.93E-04	4.44E-03	1.38E-03
	Specific St. dev.(%)	5.15	18.45	7.19
E (MPa)	Mean	2677.11	862.28	1685.07
	St. dev.	184.66	90.50	150.21
	Specific St. dev.(%)	6.90	10.49	8.91

Flexural Properties

		Infusion	Hand Lay-up	Injection
σ (MPa)	Mean	32.23	14.62	12.80
	St. dev.	1.50	0.69	0.80
	Specific St. dev.(%)	4.67	4.74	6.26
ε (mm/mm)	Mean	4.22E-02	-	-
	St. dev.	4.33E-03	-	-
	Specific St. dev.(%)	10.25	-	-
E (MPa)	Mean	1782.49	1018.43	1038.06
	St. dev.	166.58	60.07	99.13
	Specific St. dev.(%)	9.35	5.90	9.55

Table 4.2-1 Tensile and flexural properties.

Only observing the curves of Figure 4.2-1a and the respective properties in Table 4.2-1, the infusion process appears to be the best in terms of repeatability and absolute properties. However, the investigation on the specific properties emphasizes the interest in the use of a foam as matrix, considering the advantages concerning the density reduction.

Three points bending tests were performed according to ASTM D790-10. Then, the span length was 64 mm, 68 mm and 74 mm respectively for the infusion, the hand lay-up and the injection specimens typology. Their width was always 35 mm and all tests were performed at constant crosshead displacement of 0.5 mm/min. Figure 4.2-2 shows both the bending stress-strain and the specific bending stress-strain curves for each specimen while the results are summarized in Table 4.2-1.

Figure 4.2-2 Bending stress-strain (a) and specific bending stress-strain curves with example of specimens at the end of the test (b).

In this test, the influence of the process repeatability is less evident respect to the tensile test. However, by these tests it possible to observe that the process influenced the failure mode, as showed in Figure 4.2-2b, and the elongation at breaking. It reached the minimum value for the specimens manufactured by means of the infusion process due to their brittle failure mode. Also in this case the specific properties values highlighted the interest in the use of a foam as matrix.

Finally, Charpy impact tests in three-point bending conditions, were performed in order to evaluate the energy absorption capability of the proposed lightweight hemp composites, according to ISO 179 - 1:2010 standard. In the experiment, un-notched beam specimens were used. The experimental setup consists of the specimen, the anvils where the specimen is freely supported and a pendulum with a defined mass attached to a rotating arm pinned at the machine body. The pendulum falls following a circular trajectory and hits the test specimen at the middle span length transferring kinetic energy to it. Also in this case, rather than the process repeatability, the manufacturing technique influenced the

failure mode and the impact resistance, indeed its lowest value was detected for the specimens produced by means of the infusion process that showed a brittle failure mode (see Figure 4.2-3). From the results of Figure 4.2-3 it is possible to note that in this case the advantages in the use of a foam as matrix was also highlighted by observing the absolute impact resistance values and not only their specific values as for the previous cases.
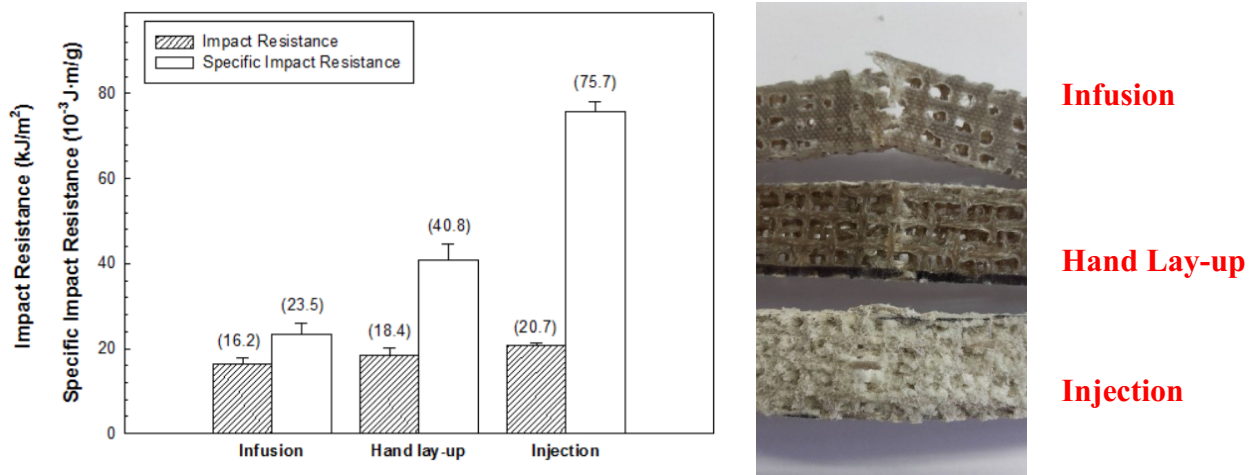
Figure 4.2-3 Impact and specific impact resistance of the hemp composites and example of specimens at the end of the test.

Therefore, in this section part lightweight bio-composite laminates by using four woven hemp fabrics were manufactured by means of the infusion, the hand lay-up and the injection processes. These processes allowed to obtain laminates with three different density values: 0.60, 0.42 and 0.27 g/cm^3 and the lowest one was reached for the specimens produced through the injection moulding process, by using both the polyurethane foam and the epoxy resin as matrix. In addition to this advantage, the specimens manufactured by means of this technique showed the best properties in terms of specific tensile strength, flexural elongation at breaking and specific impact resistance.

Therefore, considering the conclusions of the Part 1, the main results of this part are:

- Using others processes respect to the infusion technique, it was possible to reduce the density of the final products reaching interesting mechanical properties.

- The lowest density value was reached by using both the polyurethane foam and the epoxy resin as matrix as well as the higher specific dynamic properties. If on one hand this seem to be interesting, on the other hand the use of both these polymers involves in the loss of the concept of eco-friendly composites materials. A possible solution, could be the use of both resins and foam with lower environmental impact; however, this is not the aim of this thesis.

- The brushing hand lay-up technique could be interesting as good compromise between mechanical properties and the epoxy content and so the density value. However, the process needs to be improvement in order to increase and to more control the epoxy content and to reduce the mechanical properties variability that show the composites produced through this technique.

The considerations reported in the last bullet point lay the groundwork for the Part 3 of this section, where a way to overcome these limitations is proposed.

4.3   Part 3: Continuous Impregnation Process

Tensile tests on un-impregnated hemp yarns were carried in order to evaluate the tensile strength and the tensile modulus of the used hemp yarns. For this purpose, ten yarns under a crosshead displcament of 1 mm/min were tested. Figure 4.3-1a shows the set-up of the test and the results are listed in Table 4.3-1.

About the composites, tensile tests were carried out according to ASTM 3039 standard, then specimens with a width of 25 mm, an overall length equal to 250 mm and a tab length of 50 mm were tested under a crosshead displacement of 1 mm/min as reported in Figure 4.3-1b.

a   b
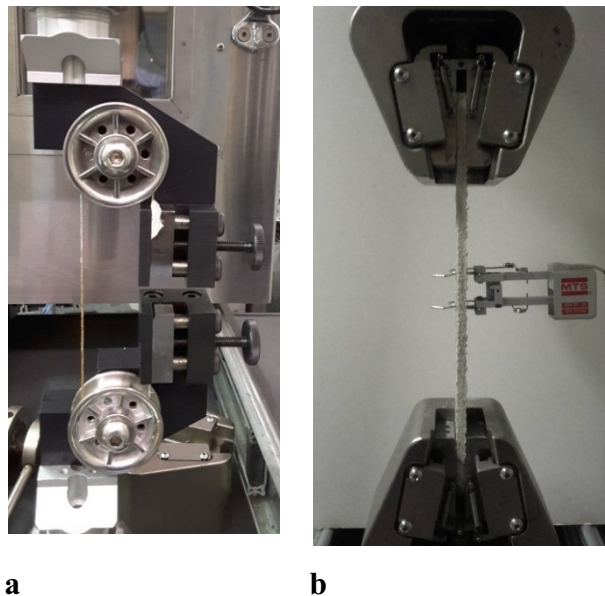
Figure 4.3-1 Tensile test set-up.

Tensile strength [MPa]	E modulus [Mpa]	Strain at failure [mm/mm]
400 (30)	31750 (200)	0.03 (0.009)

Table 4.3-1 Main mechanical properties of the hemp tow.

The tensile curves of the specimens for each typology are reported in Figure 4.3-2 and summarized in Figure 4.3-3 and Figure 4.3-4.

The main result was that the tensile properties are not affected from the thickness value but only from the sample typology (A and B). The results in terms of modulus and maximum stress are in agreement with the theoretical ones considering the sample volume contents reported in the previous section. According to the mixtures low the elastic modulus of the composite, E_c, and the tensile strength, σ_c, can be expressed as:

$$E_c = W_f E_f + W_m E_m \tag{2}$$
$$\sigma_c = W_f \sigma_f + W_m \sigma_m \tag{3}$$

Where, E_f and σ_f are respectively the elastic modulus and the tensile strength of the hemp yarn, W_f, is the fibre volume fraction in the direction of interest, E_m and σ_m are the elastic modulus and the tensile strength of the matrix respectively and W_m the volume fraction of the matrix.

Considering that the contribute of the matrix is almost zero, we have:

$$E_c \approx W_f E_f \tag{4}$$
$$\sigma_c \approx W_f \sigma_f \tag{5}$$

By using the equations (4) and (5) the theoretical values of both the tensile strength and the E modulus can be evaluated and the results are summarized in Figure 4.3-5.

A4

B4

A8

B8

A10

B10
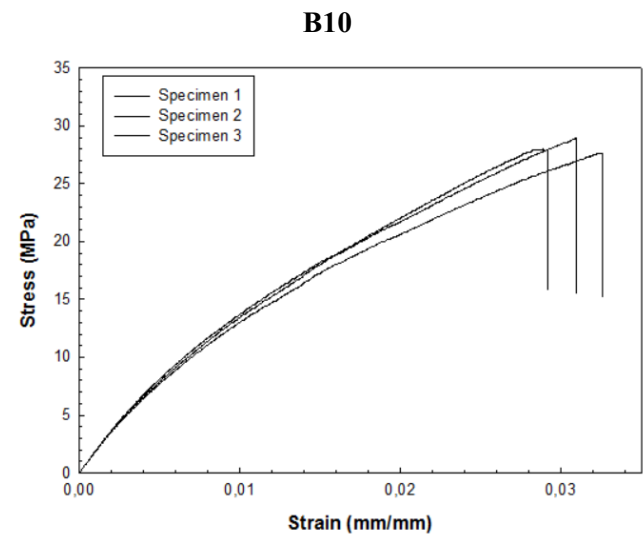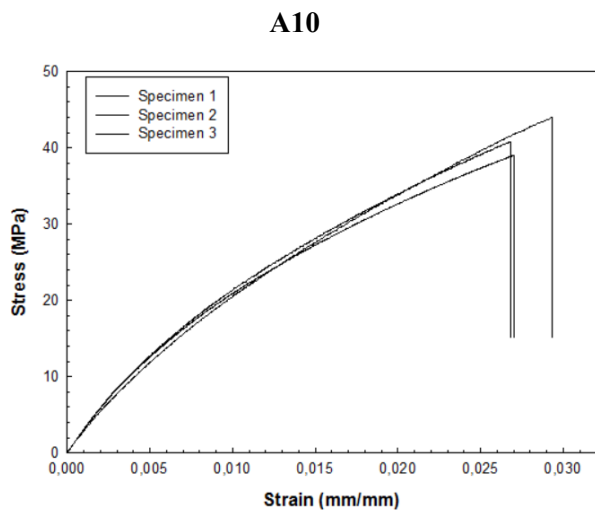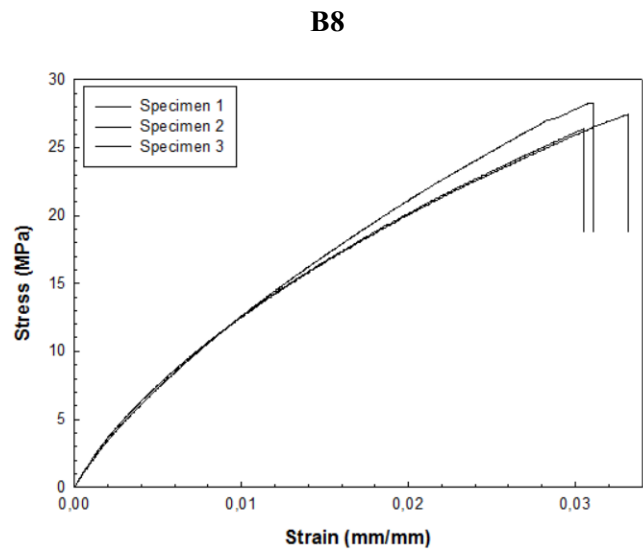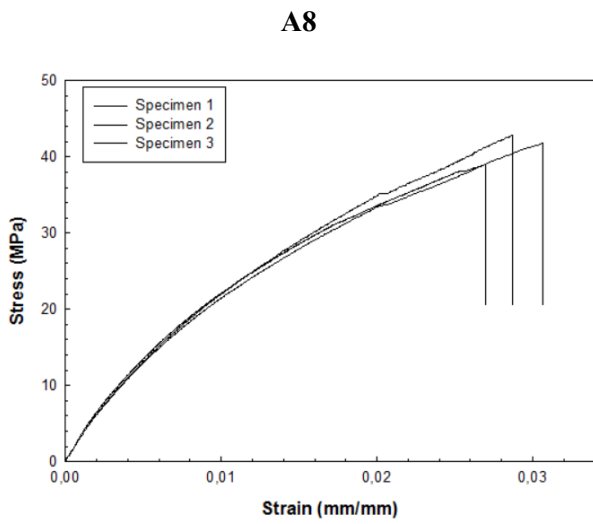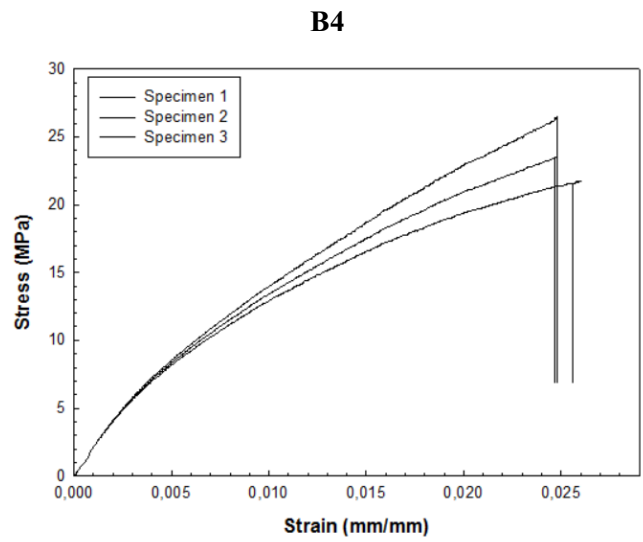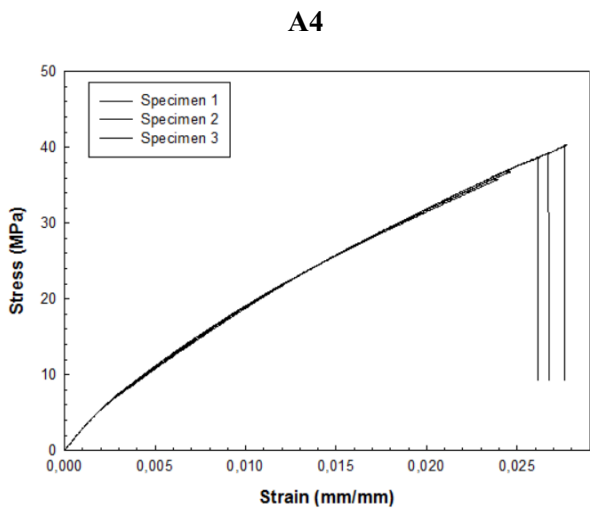
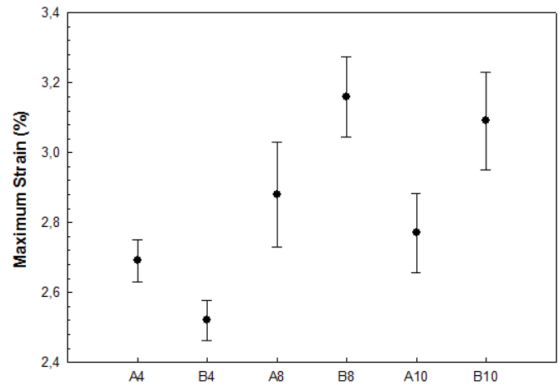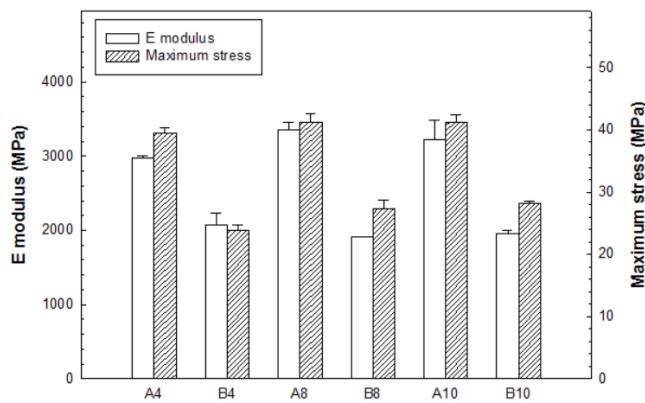**Figure 4.3-2** Tensile test results for each sample typology.
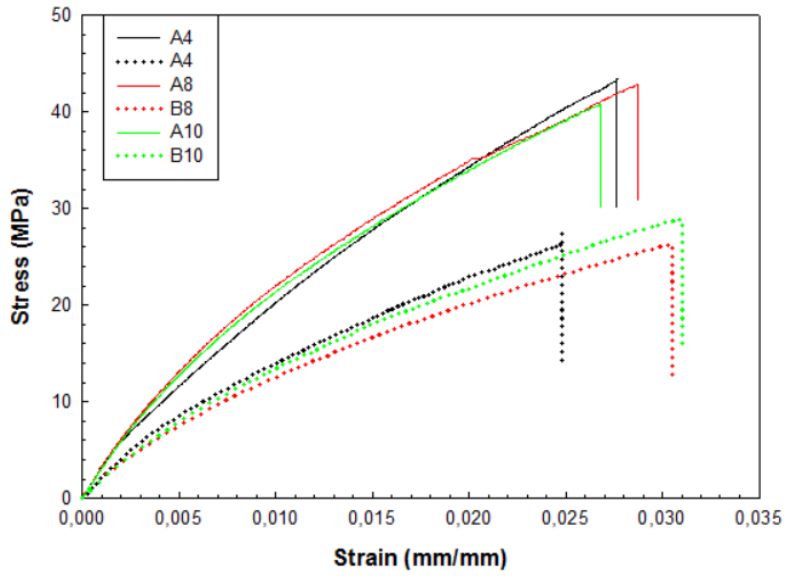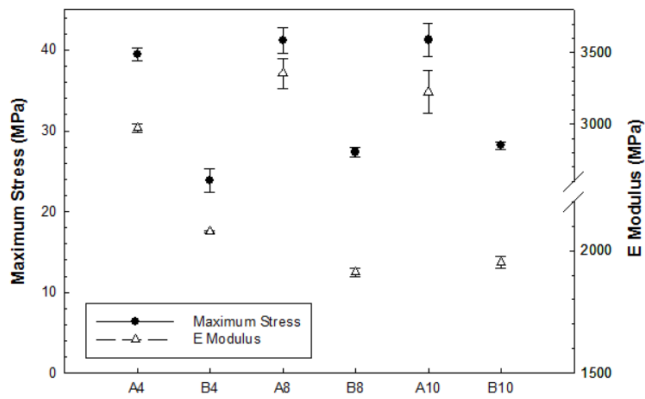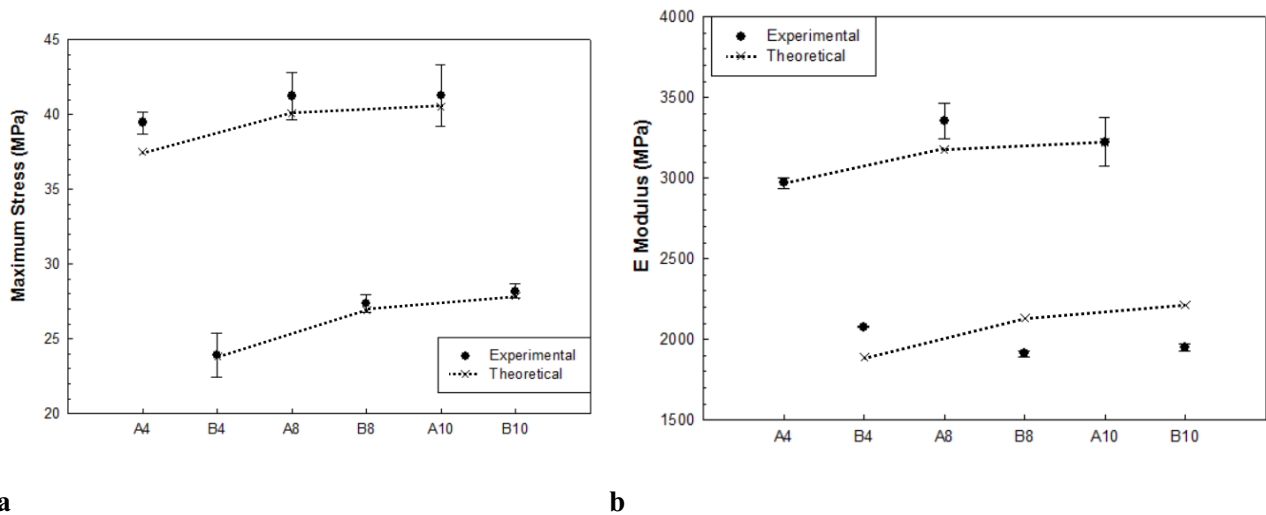
Figure 4.3-3 Typical tensile stress-strain curves for each typology.

a

b

Figure 4.3-4 Summarized results for each typology: maximum tensile stress and modulus (a) and maximum strain (b).

a   **b**

Figure 4.3-5 Experimental and theoretical comparison for the tensile strength (a) and E modulus (b).

Three points bending tests were performed according to ASTM D790-10 in order to study the bending properties and the failure modes of the samples. Then, the span length was 84 mm, 68 mm, 160 mm, 116 mm, 196 mm and 142 mm respectively for the A4, B4, A8, B8, A10 and B10 specimens typology. Their width was always 35 mm and all tests were performed at constant crosshead displacement of 0.5 mm/min.

Figure 4.3-6 shows the bending stress-strain curves for each specimen while the results are summarized in Figure 4.3-7 and Figure 4.3-8.

It is possible to observe that the trend of the maximum stress (see Figure 4.3-8) is very similar to the maximum tensile stress and almost the same values are reached, instead of the trend of the E modulus for the B typology. In this last case, the bending modulus increases as the layers number increases due to the thickness effect.

Up to the failure all curves show the same behaviour, but when the maximum stress value was reached and then the specimens started to fail, the behaviour changes. This is observed by comparing the curves of A and B typologies of Figure 4.3-6 and also the type of failure in Figure 4.3-7. The curves of the A typology showed a significant drop in the stress and then a brittle failure of the specimens was observed, instead the curves of the B typology showed a smoother decrease in the stress connected to a sliding failure.
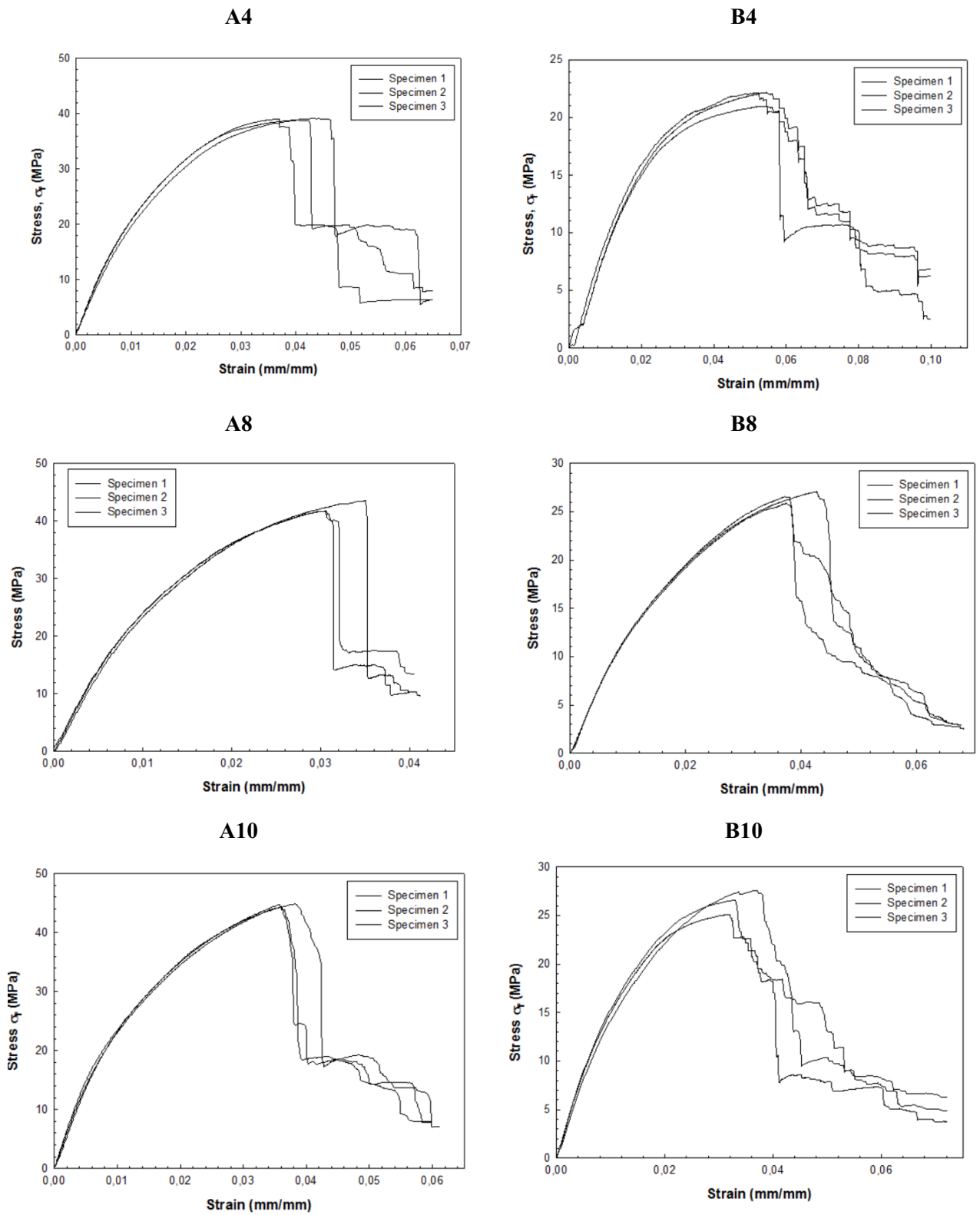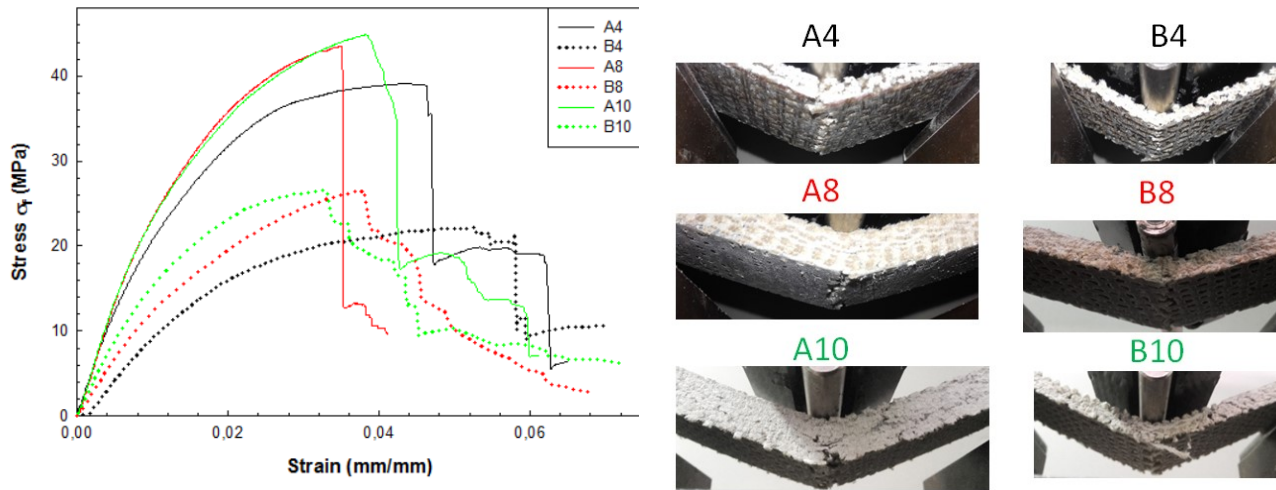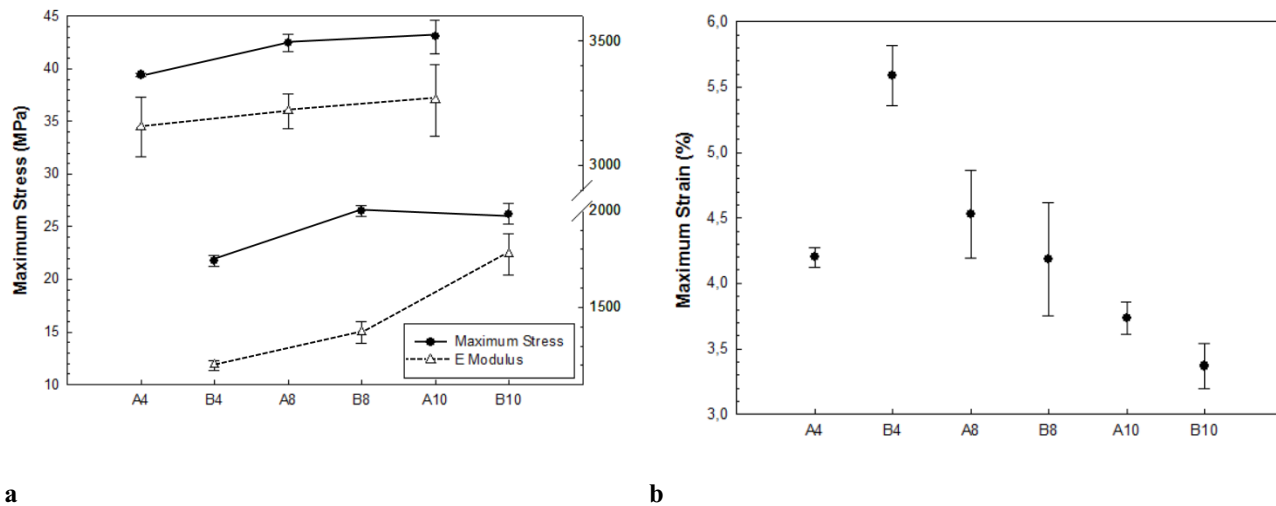
Figure 4.3-6 Three-point bending test results for each sample typology.

Figure 4.3-7 Typical bending stress-strain curves for each sample typology with image examples of the specimens during the test.

a   b

Figure 4.3-8 Summarized results for each typology: maximum bending stress and modulus (a) and strain at first failure (b).

The maximum shear stresses, τ_{xz}, according to the equation (6) are also evaluated for each case:

$$\tau_{xz} = \frac{3F}{4bt} \tag{6}$$

where F is the maximum load, b is the width and t is the thickness of the specimen; mean values of 1.42 and 0.65 MPa were detected for the A and B typology respectively. Considering the images showed in Figure 4.3-7, shear failure was not detected, it means that the evaluated shear stress values are lower than the shear strength of the specimens. Therefore, in order to detect the shear strength at

bending, three points bending tests on short beam specimens were conducted according to ASTM D2344 standard. Then, the span length to thickness ratio, was set equal to six and the width of the specimens was always two times the thickness. All tests were performed at constant crosshead displacement of 0.5 mm/min.

Figure 4.3-9 shows the bending stress-strain curves for each specimen while the results are summarized in Figure 4.3-10.

From these results, it is possible to observe that mixed tensile-shear failures were detected. This is highlighted both from the images of the specimens at the end of the tests (Figure 4.3-10) and from the maximum stress values. The maximum values of σ_f are very close to the ones detected in the previous tests, this means that despite the short span length all the specimens were able to reach their maximum strength showing a tensile failure. However, immediately after the tensile failure, the thickness starts to decrease and then the shear effects begin to be non-negligible involving shear cracks in the cross section of the specimens. This was observed for all the specimens except for the B4 typology due to its small thickness.

The maximum τ_{xz} values depend on the sample typology and its mean value is equal to 3.7 and 2.3 MPa for the A and B typology respectively, showing a slight increase with the sample type thickness.
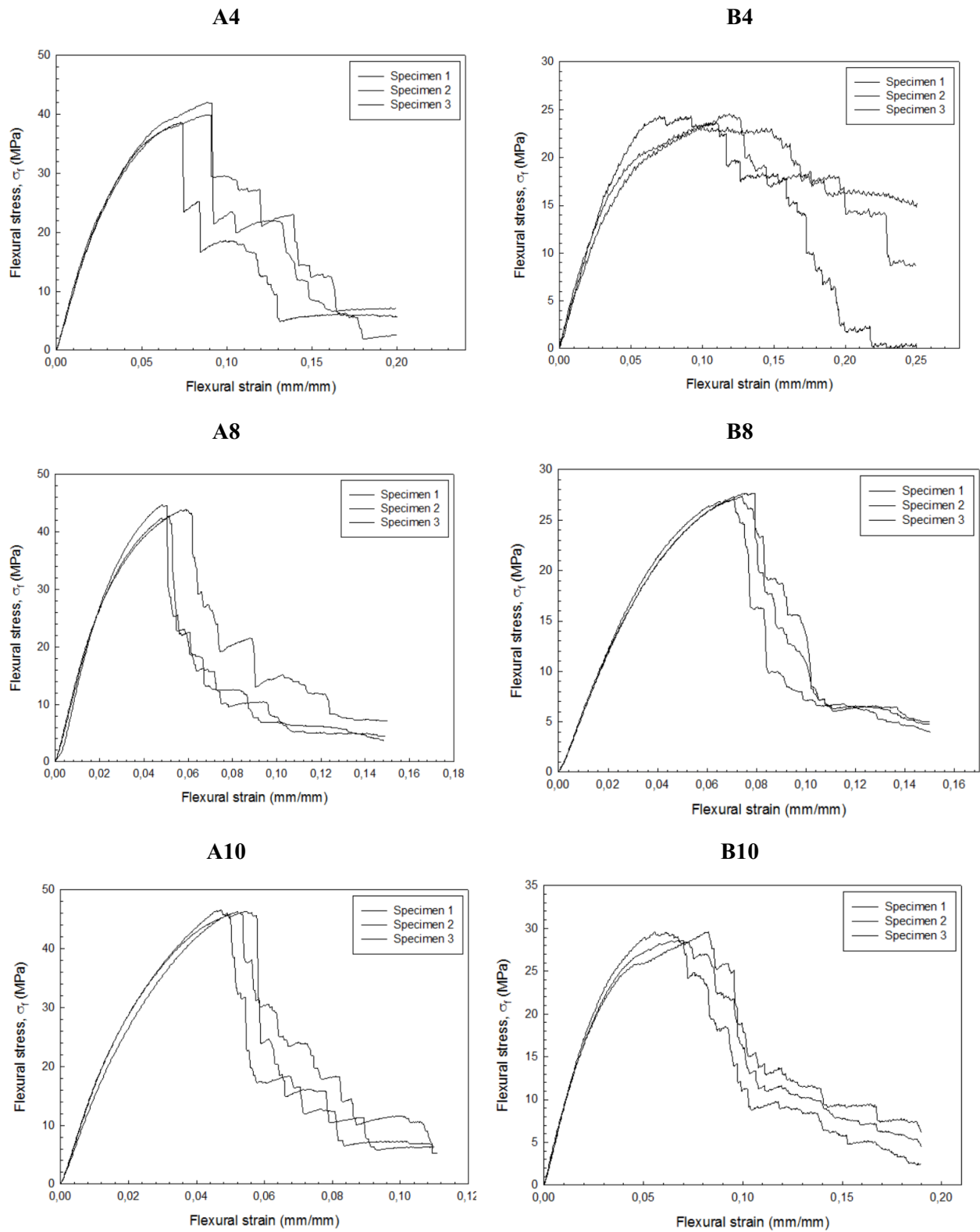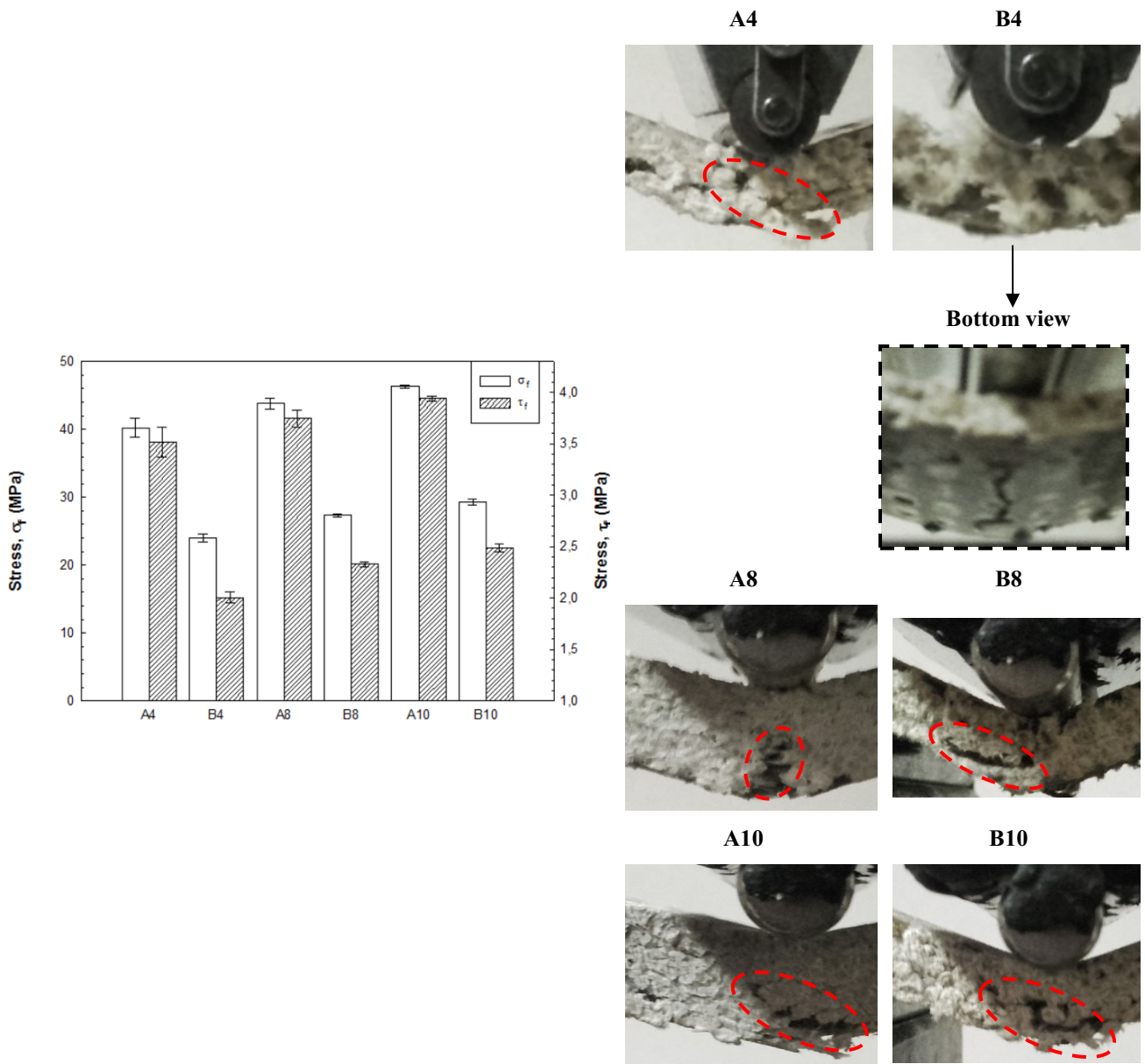
A4

B4

A8

B8

A10

B10

Figure 4.3-9 Results of three-point bending test conducted on short beam for each sample typology.

Figure 4.3-10 Maximum σ_f and τ_f for each sample typology and image examples of the specimens at the end of the test.

Therefore, also using a short beam length according to ASTM D2344, the specimens showed a mixed tensile-shear failure, although shear phenomena occurred (to see the previous images). To emphasize shear phenomena during the bending test a smaller span length should to be used in order to make the shear the prevalent effect.

Considering that:

$$\sigma_x = \frac{3FL}{2bt^2}$$

(7)

and

$$\tau_{xz} = \frac{3F}{4bt} \tag{8}$$

Their ratio is equal to:

$$\frac{\sigma_x}{\tau_{xz}} = \frac{2L}{t} \tag{9}$$

Where L is the span length (mm), b the width (mm), t the thickness (mm) and F the load (N). Defining σ_m as the flexural strength detected in the previous three-point bending tests and τ_m as the hypothesized shear strength, in order to have theatrically a shear failure the following condition have to be satisfy:

$$\sigma_x < \sigma_m$$

$$\tau_{xz} = \tau_m$$

And then

$$\frac{t}{2L} > \frac{\tau_m}{\sigma_m} \tag{10}$$

Knowing the thickness, t, the flexural strength, σ_m and imposing the shear strength, τ_m, the desired span length, L, can be evaluated as follows:

$$L < \frac{\sigma_m}{\tau_m} \cdot \frac{t}{2} \tag{11}$$

By using this last equation and imposing τ_m equal to 13 and 6 MPa for the A and B typology, the maximum allowable span length is reported in Table 4.3-2.

Sample Typology	Specimen mean thickness [mm]	Flexural strength σ_m [MPa]	Imposed τ_m [MPa]	L_{max} [mm]
A4	5.3	39.4	13	8.0
B4	4.3	23.9	6	8.5
A8	10.0	41.2	13	15.8
B8	7.3	27.3	6	16.6
A10	12.3	41.2	13	19.5
B10	8.9	28.2	6	20.9

Table 4.3-2 Span length evaluated for each typology.

Therefore, in order to emphasize the shear effect during the bending test, other three-point bending tests were performed. However, considering the values evaluated and reported in Table 4.3-2, there are span length values too small for the test feasibility. Then, only the tests on the A10 and B10 typology using a span length of 18 mm were conducted and the results in terms of stress-strain curves are summarized in Figure 4.3-11. Since the previous tests showed that the mechanical properties were only affected from the sample typology (A or B), the conduction of these tests only on the type A10 and B10 was enough.

The results showed that the failure of the specimens was always for shear, indeed for both the cases the maximum value of σ_x was lower than their flexural strength, σ_m, and a mean shear stress, τ_{xz}, equal to 14.1 and 6.9 MPa respectively for A10 and B10 typology was detected.
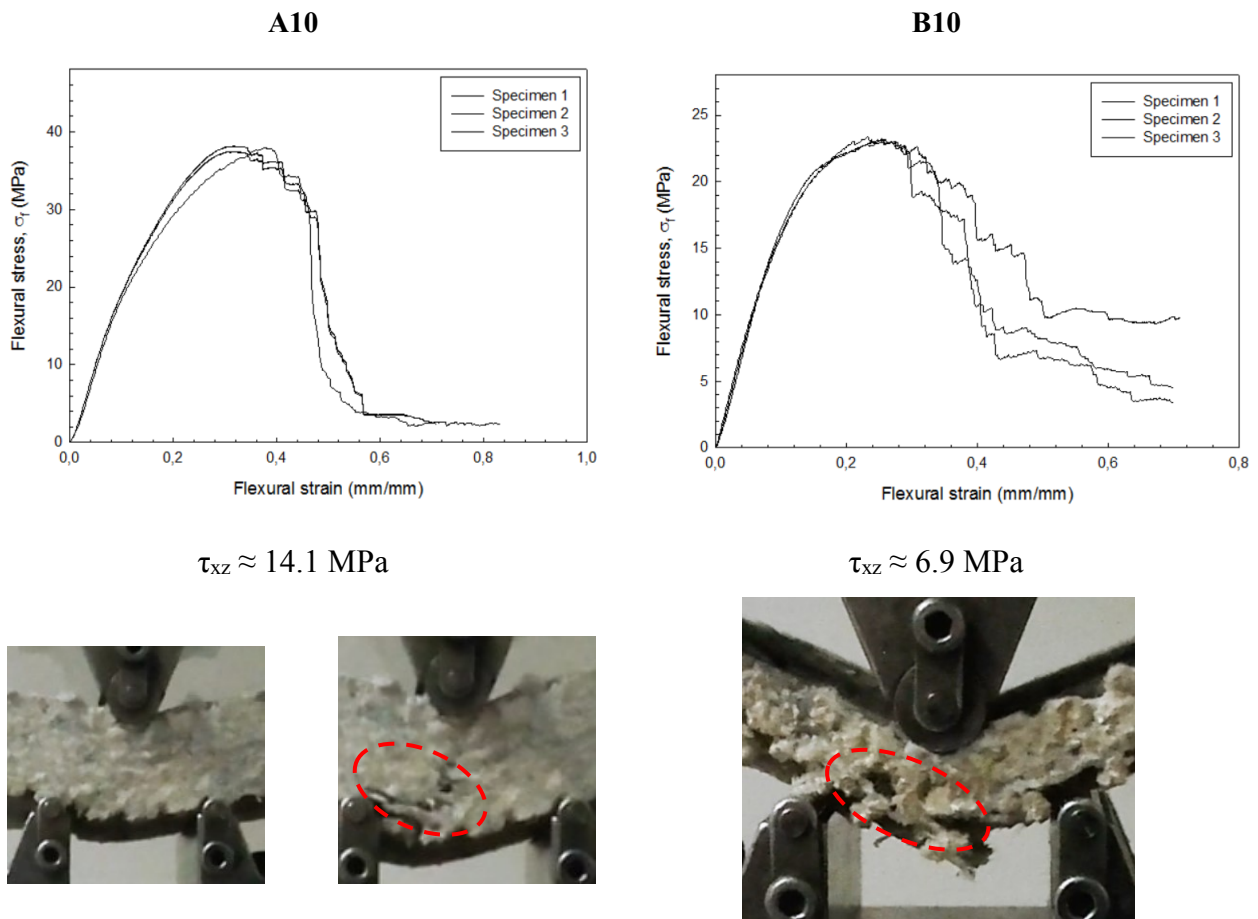

Figure 4.3-11 Results of three-point bending test conducted on short beam on A10 and B10 sample typology.

On the base of the previous tests results, it was highlighted that apart from flexural modulus carried out according to ASTM D790, the main difference in the properties does not lie on the thickness but

only on the typology (A or B). For this reason, the compression tests were carried out on the thicker specimens for typology, i.e. on A10 and B10 samples.

Flatwise compression tests were performed according to ASTM 365/365M. Specimens were in form of tetragonal prism with 30 x 30 mm square base. All tests were performed at constant crosshead displacement of 0.5 mm/min and the results in terms of typical stress-strain curves are shown in Figure 4.3-12.
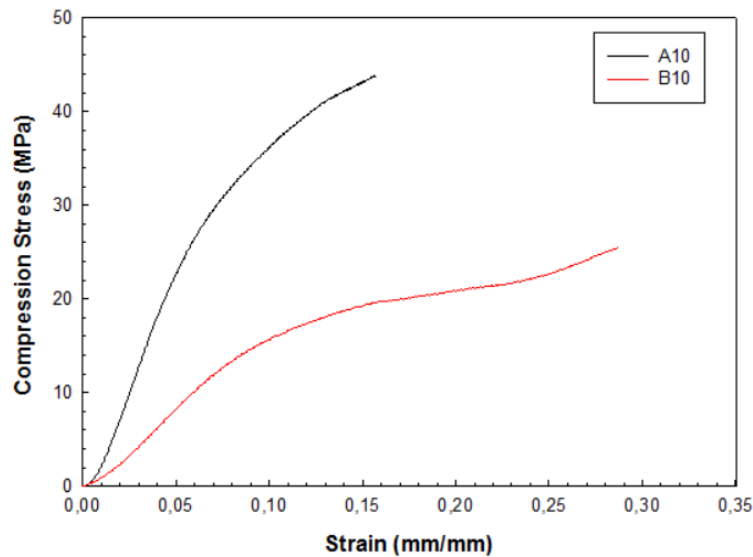
Figure 4.3-12 Typical compression stress-strain curves for A10 and B10 typology.

Because of the 2 % of deflection is achieved prior to stopping the test, the compression strength can be evaluated as the flatwise compressive stress at 2 % deflection and the compression modulus as the slope of the linear region according to ASTM 365/365M standard.

The results in terms of mean value and standard deviation values are summarized in Table 4.3-3.

| Sample Typology	Compression Strength, σ_c [MPa]	Compression Modulus, E_c [MPa]
A10	7.86 (0.5)	538.5 (20)
B10	2.40 (0.3)	190.8 (10)

Table 4.3-3 Compression test results.

In this case, the compression strength and the compression modulus of the B typology is almost the 30-35 % of the ones of the A typology, whilst for the other properties (i.e. tensile and flexural strengths and modulus) the values detected for the B typology was almost the 55-60 % of the ones of

the A typology. This means that the compression properties are more sensitive to the fabric typology and in particular to the fabric mesh. As wider the fabric mesh is, as simpler the tows slip one on the others under a compression load.

Finally, Charpy impact tests in three-point bending conditions, were performed in order to evaluate the energy absorption capability of the proposed lightweight hemp composites, according to ISO 179 - 1:2010 standard. In the experiment, un-notched beam specimens were used. The experimental setup consists of the specimen, the anvils where the specimen is freely supported and a pendulum with a defined mass attached to a rotating arm pinned at the machine body. The pendulum falls following a circular trajectory and hits the test specimen at the middle span length transferring kinetic energy to it. The results are summarized in Figure 4.3-13. No specimen showed a complete brittle failure with its detachment in two parts.
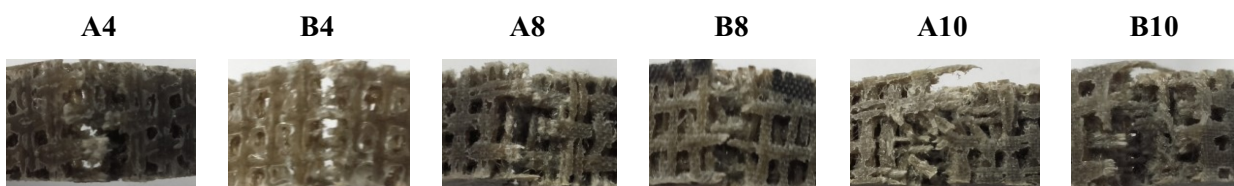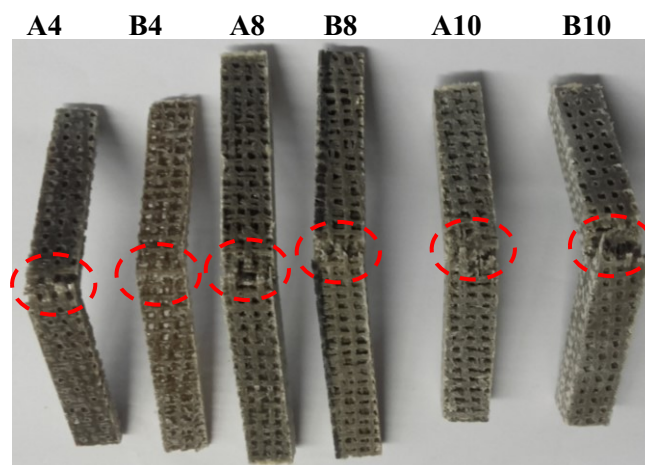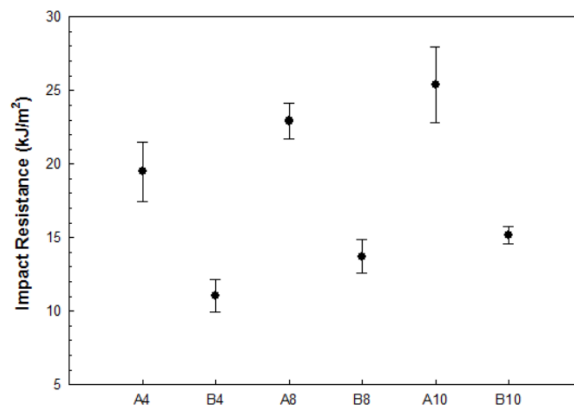

Figure 4.3-13 Impact resistance results and example of specimens at the end of the test.

For the impact properties, the same considerations wrote for the tensile and the bending properties can be done, in fact the trend of the impact resistance values versus the sample typology is very similar to the one of the tensile and bending strength. The impact energy resistance for the B typology is almost the 56 % of the A typology and for both the type this value increases as the number of layer, and then as the specimen thickness, increases.

Chapter 5: Results and Discussions on the Improvement of Fire Properties

5.3   Cone calorimeter analysis

The cone calorimeter tests were carried out following the procedures indicated in the ISO 5660 standard with a FTT cone calorimeter. Square specimens (100 mm x 100 mm), aluminium foil wrapped on the sides and at the bottom and placed in a holder, were irradiated with a heat flux of 50 kW/m2; under the holder, a load cell evaluated the mass loss during the experiment. The combustion gases that were produced passed through the cone and, after a filter system, reached the gas analysers [27]. The distance between the source and the specimens was kept constant and equal to 25 mm. Figure 5.3-1 shows the used equipment (Figure 5.3-1a) and the execution of a test (Figure 5.3-1b).
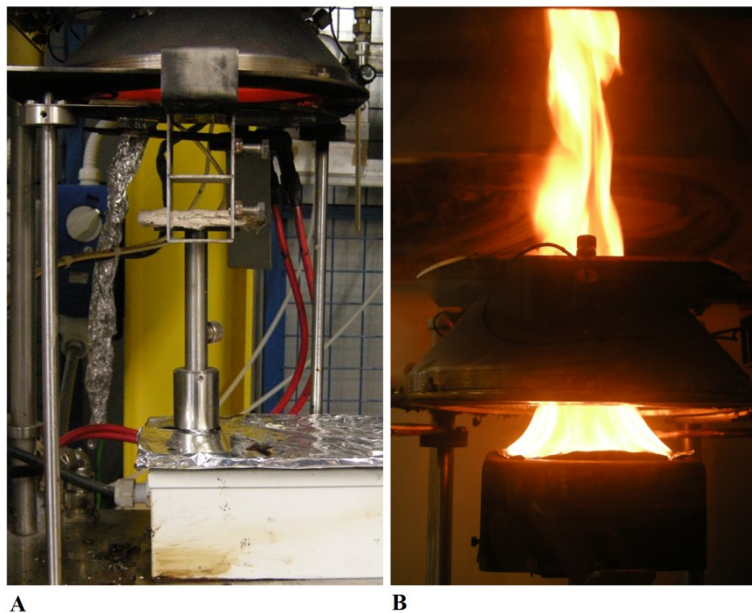
Figure 5.3-1 Cone calorimeter equipment used (A) and execution of a test (B).

Therefore, several combustion parameters were determined:

•   Heat release rate (*HRR*), its mean value (*HRR$_m$*), time to peak (*TTP*) and the total heat release (*THR*). *HRR* is determined by measurement of the oxygen consumption derived from the oxygen concentration and the flow rate in the combustion product stream;

•	Peak of heat rate release (*PHRR*), which is considered as the parameter that best expresses the maximum intensity of a fire indicating the rate and extent of fire spread;

•	Time to ignition (*TTI*) and fire performance index (FPI). This latter is defined as the ratio of *TTI* to *PHRR*, and it is a parameter related to the time available to escape in a real fire situation [1, 2];

•	Parameters related to the smoke evolution were also obtained, such as average of CO and CO_2 emission, the loss of mass and the total smoke released (*TSR*), calculated by integrating the rate of smoke released (*RSR*) curve.

From the cone calorimeter tests, comparative plots of *THR*, *HRR* and mass loss percentage versus time are shown in the figures from Figure 5.3-2 to Figure 5.3-4, it is possible to observe that increasing the percentage of APP, the *THR* decreases; moreover, the *HRR* curves go down and move to the left. This means a decrease of HRR_m, *PHRR* and *TTP*. A possible explication of this phenomenon is that the flame retardant additive, while performing properly its action of retardant, triggers the advance ignition of the laminates.

In addition, it is interesting to analyze, by determining the percentage of mass loss, the different degradation of the samples. From Figure 5.3-4, the degradation rate results to be inversely proportional to the content of APP.

Then, the targeted action of APP on the fibres inhibits mass transfer in the combustion zone and thus improves the fire behaviour of the composites.

The results from the cone calorimeter, in terms of average and standard deviation, are reported in Table 5.3-1 and Table 5.3-2. From Table 5.3-1, concerning to the heat release parameters, it can be deduced that:

•	time to ignition (*TTI*) is almost the same whilst time to peak (*TTP*) decreases with the percentage of APP;

•	the heat released (HRR_m and *THR*) and *FPI* are reduced with the increasing of additive, for the above-mentioned reasons. The values of PHRR remain in agreement with expectations.
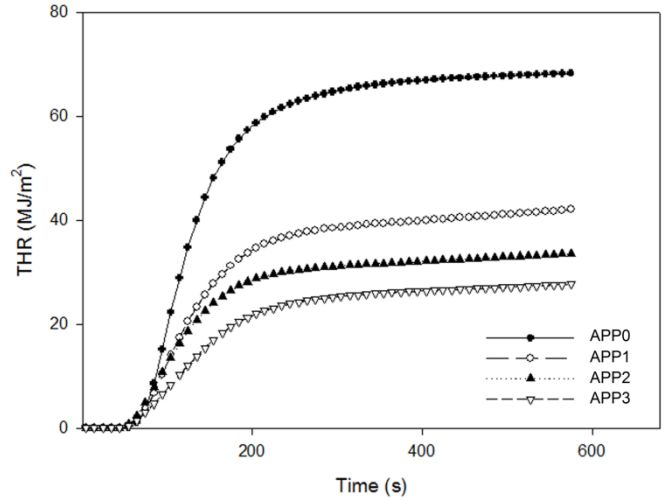
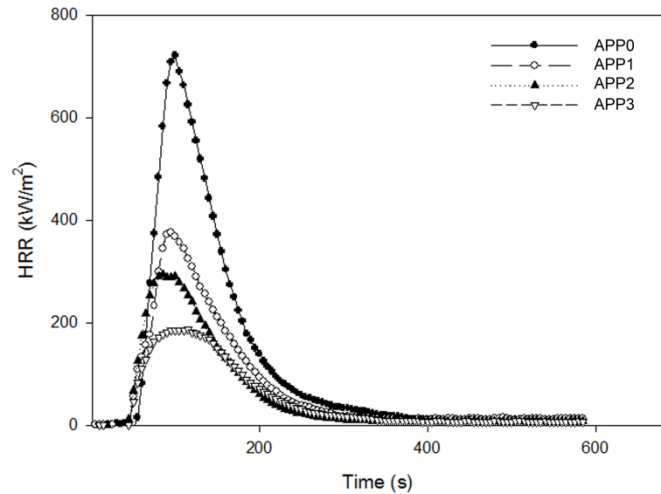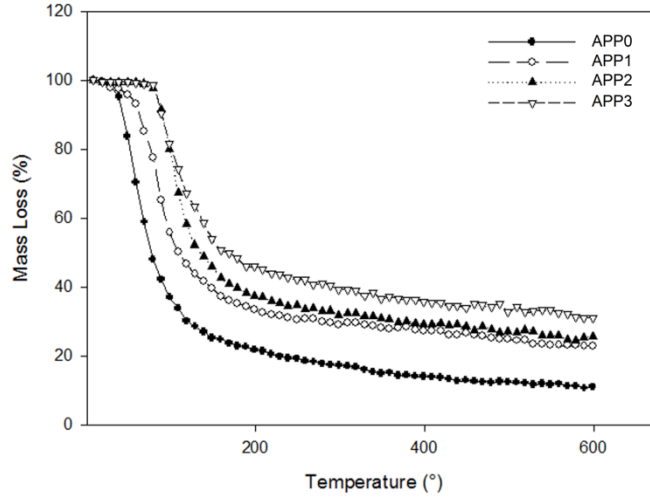**Figure 5.3-2** Total heat release versus time for untreated and treated samples.

Figure 5.3-3 Heat release rate versus time for untreated and treated samples.

Figure 5.3-4 Mass loss versus time for untreated and treated samples.

Sample	TTI (s)	HRR_m (kW/m^2)	TTP (s)	PHRR (kW/m^2)	FPI x 10^{-2} (m^{2}s/kW)	THR (MJ/m^2)
APP0	21.2 [1.3]	121.6 [2.3]	100.1 [2.8]	720.5 [6.3]	2.9	68 [5.1]
APP1	20.3 [2.2]	69.2 [1.9]	95.3 [1.6]	375.3 [5.8]	5.4	42 [3.3]
APP2	18.1 [1.1]	59.5 [3.5]	88.6 [1.4]	293.8 [4.5]	6.2	33 [4.8]
APP3	21.0 [0.9]	48.6 [1.8]	85.8 [2.2]	186.7 [3.4]	11.2	27 [2.7]

Table 5.3-1 Combustion parameters obtained from cone calorimeter tests (standard deviations between square brackets).

| Sample	Residual mass (wt.%)	TSR (m^2/m^2)	CO emission (g/Kg)	CO$_2$ emission (g/Kg)	CO$_2$/CO ratio
APP0	11.8 [1.2]	1612.2 [102.3]	65.5 [0.8]	1795.3 [15.3]	27.4
APP1	22.3 [1.9]	1233.3 [98.2]	131.3 [1.3]	1483.8 [13.3]	11.0
APP2	24.3 [2.1]	1104.5 [88.8]	153.2 [1.6]	1327.5 [10.5]	8.7
APP3	31.1 [2.4]	1006.7 [81.4]	164.1 [1.8]	1283.4 [11.2]	7.5

Table 5.3-2 Residual mass, TSR and average emission of CO and CO2 (standard deviations between square brackets).

A possible explanation of this behaviour is that, during the cone calorimeter test, the thermal degradation of APP leads to the formation of phosphoric acid, which combines with the hydroxyl function of hemp forming a phosphorus ester. This ester catalyzes the dehydration of the fibres and leads to the formation of a carbonaceous structure [3]. Hence, the vapour phase composition is changed and the released energy is lower.

The parameters related to the residual and the smoke evolution are presented in Table 5.3-2; it can be deduced that:

• the presence of the additive generates a protective carbonaceous layer on the surface of the laminate, opposing the degradation process of the composite. This behaviour increases with the content of APP;

• the presence of APP also affects the emission of fumes; indeed, the *TSR* and the CO_2/CO ratio decrease with increasing the content of APP. The analysis of carbon oxides (CO and CO_2) generated during burning is useful in order to obtain some information on the decomposition mechanism. Lower values of the CO_2/CO ratio suggest inefficiency of combustion inhibiting the conversion of CO to CO_2.

Finally, Figure 5.3-5 shows the residues of the analysed specimens, at the end of the test, in order to observe the structure of burnt laminate. It is immediately evident that, compared to the treated samples, the untreated one is completely burned (the residue is almost zero). This content underlines already the effectiveness of the flame retardant in question.
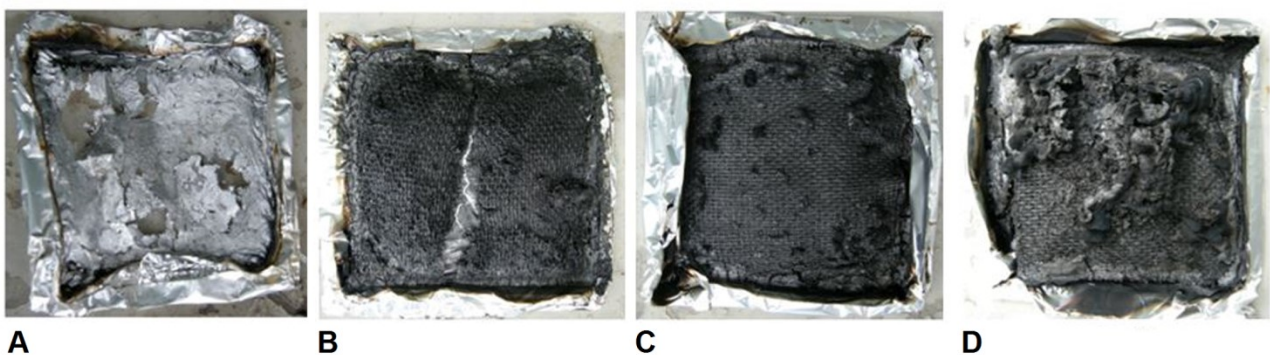
Figure 5.3-5 Residues at the end of the cone calorimeter test: APP0 (A), APP1 (B), APP2 (C) and APP3 (D).

It is possible to observe the phenomenon of intumescence, due to the presence of APP, that increases with the content of additive.

It is also possible to note that, despite what happens for the untreated sample, the treated ones show to resist into the flame without a complete consumption (for times longer than 600 s). In addition, starting from 8.88 wt.%, APP is a real barrier to the fibres, which maintain their integrity in shape. Figure 5.3-6 shows an unsound 3.15 wt.% sample (Figure 5.3-6 a), compared to a sound 8.88 wt.% sample (Figure 5.3-6 b).
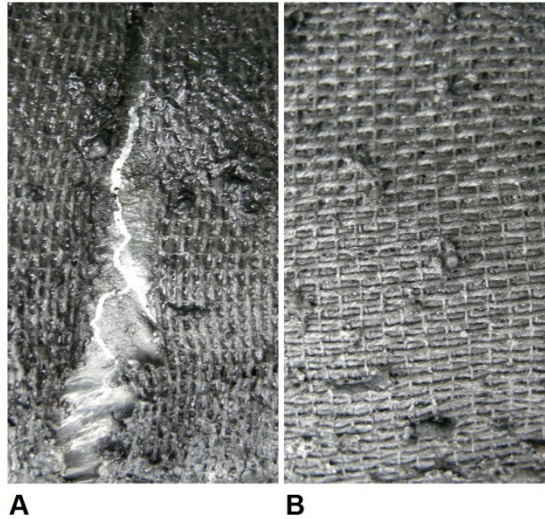
Figure 5.3-6 Top surface of the cone calorimeter specimens at the end of the test: APP1 (A) and APP2 (B).

5.4   Flammability test

Flammability of the samples was studied by a vertical burning test V12 according to FAR25.853A standard. The flame time (t_f), the drip time (t_d) and the burn length (L_b) were evaluated. Before the test, rectangular specimens, 310 mm x 75 mm, were conditioned for 24 h at 27°C and with a humidity of about 50%. Methane 99% pure was employed for this type of test. Figure 5.4-1 shows a specimen during the burning phase of the test.

**Figure 5.4-1** Example of a specimen during the test.

According to FAR25.853A standard, the t_f must be less than 15 s, the t_d has not to be more than 3 s and the maximum allowable L_b is equal to 152.4 mm.

In Table 5.4-1, the average and standard deviation values of the data are reported. The results obtained from these tests were excellent. All samples, except the untreated one and the one with 3.15 wt.% of APP, have successfully passed the test. Indeed, the t_f is almost instantaneous, there is not dripping and the L_b is between 2 and 7 mm. These results show a decisive improvement of the fire behaviour of the examined samples, that increases as APP content increases over the 3.15 wt.%.

Finally, the specimens at the end of the tests are shown in Figure 5.4-2.

Sample	L_b (mm)	t_f (s)	t_d (s)	Status of the test
APP0	260.2 [15.0]	250.4 [15.3]	1.0 [0.1]	Failed
APP1	72.6 [4.7]	60.7 [4.1]	0.0 [0.0]	Failed
APP2	6.4 [0.8]	2.1 [0.2]	0.0 [0.0]	Passed
APP3	5.0 [0.3]	1.3 [0.1]	0.0 [0.0]	Passed

Table 5.4-1 V-12 tests results (standard deviations between square brackets).
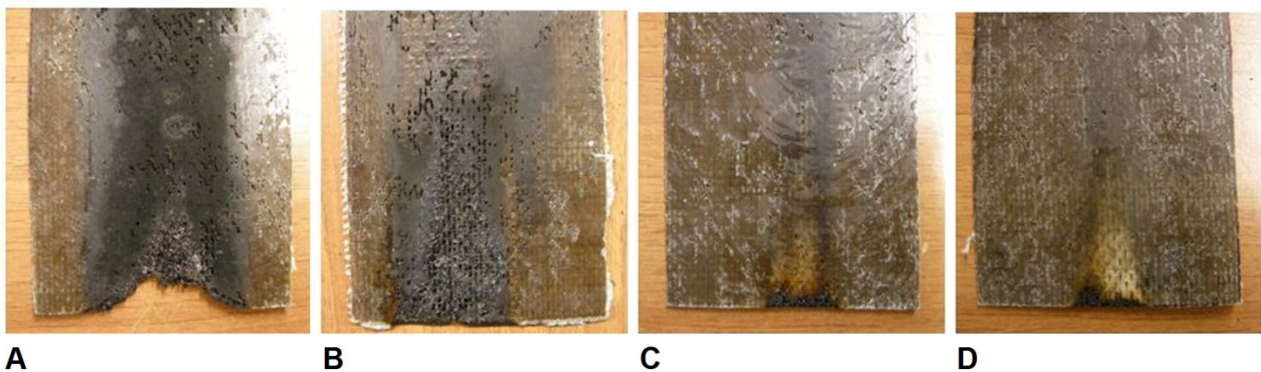
Figure 5.4-2 Specimens at the end of the V12 test: APP0 (A), APP1 (B), APP2 (C) and APP3 (D).
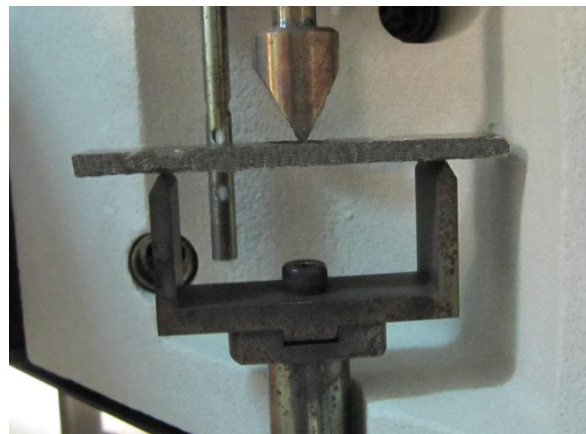
5.5 DMA test

The DMA (Dynamic Mechanical Analysis) tests were performed in order to evaluate the viscoelastic properties of the samples at different temperatures. The test involves the application at different temperatures of an oscillatory strain, at low frequencies, to a specimen. The resulting sinusoidal stress is measured and correlated against the input strain; then, the viscous and elastic properties of the specimen are simultaneously measured. The viscous and elastic stresses can be related to material

properties through the moduli, so the ratio of stresses to strain. Thus, the ratio of the elastic stress to strain is referred to as the elastic or storage modulus (E'), which represents the ability of a material to store energy elastically. The ratio of viscous stress to strain is referred to as the viscous or loss modulus (E'') and is the measure of a materials ability to dissipate energy. Finally, the ratio of the viscous modulus to the elastic one is the tangent of the phase angle δ shift between stress and strain ($tan\ \delta = E''/E'$).

The tests were performed in three-point bending mode using a TA Instruments RSA III (Figure 5.5-1). The tests were run at a frequency of 1 Hz and an amplitude of 30 μm, on rectangular specimens, 60 mm x 10 mm, with a span length equal to 40 mm. The temperature was ramped from 35°C to 200°C at a rate of 3°C/min.

The glass transition temperature (T_g) of the specimens was determined by evaluating the maximum of the *tan δ*–temperature curve.

Figure 5.5-1 DMA test in three-point bending mode.

DMA tests were performed in order to evaluate if the presence of additive affected the viscoelastic properties of the material.

Figure 5.5-2 emphasizes that the presence of APP does not affect significantly the mechanical properties of the considered composites, particularly after the glass transition temperature (T_g). In fact, the storage modulus curves are found to be very similar for all samples. Moreover, Figure 5.5-3 shows *tan δ* curves; from the maximum values of these ones, it is possible to obtain the values of T_g. Then, it is possible to observe that T_g remains practically the same; in fact, it is in the range 52-55 °C. Therefore, the results of this analysis show that the presence of APP does not involve variations in viscoelastic properties of the samples in the temperatures range 30-200 °C.
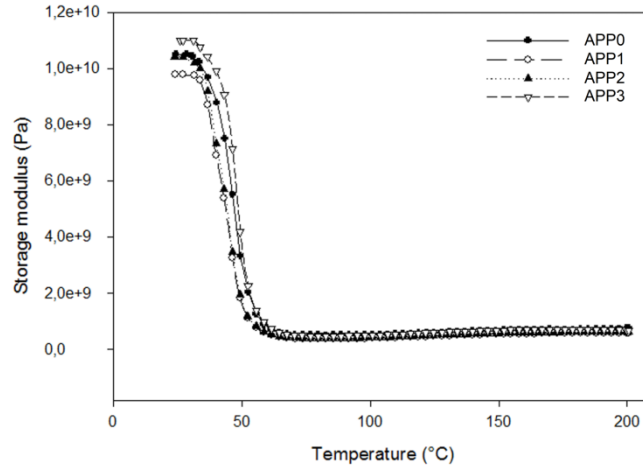
Figure 5.5-2 Storage modulus versus temperature for untreated and treated samples.
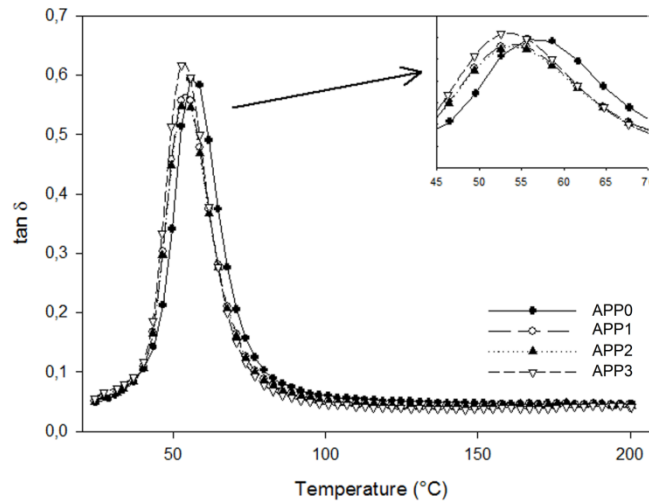

Figure 5.5-3 *tan δ* versus temperature for untreated and treated samples.

5.6   Mechanical Tests

Since the addition of flame retardant could disturb the adhesion between fibres and matrix, it is a big challenge to develop a fire resistant biocomposite that will maintain its level of mechanical performance. For this purpose the mechanical properties, in terms of bending modulus (E_b) and flexural strength (σ_f), were evaluated by bending tests. For each sample, the mechanical data were obtained from the average of three specimens. Three-point bending tests were performed (Figure 5.6-1), according to ASTM D790 standard, using a universal testing machine (RTS Alliance RT/50).

Rectangular specimens, 100 mm x 25 mm, were loaded with a recommended span length of 64 mm with a crosshead speed of 2 mm/min.
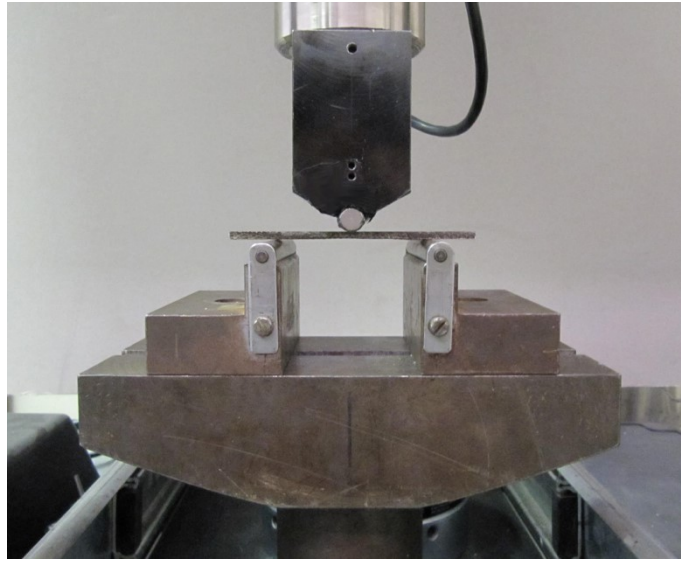
Figure 5.6-1 Three-point bending test.

Figure 5.6-2 shows flexural stress–strain characteristic diagrams for treated and untreated samples. The values of stress and strain were calculated according to equations (1) and (2), due to the rectangular cross section of the flexural specimens:

$$\sigma_f = \frac{3FL}{2bs^2} \tag{1}$$

$$\varepsilon_f = \frac{6fs}{L^2} \tag{2}$$

In these ones, F is the applied load, L is the support span, f is the deflection of the center of the specimen, and b and s are, respectively, the width and the thickness of the specimen.

The value of the flexural modulus, E_b was obtained from the ratio of stress to strain in the initial straight-line portion of the stress–strain curve.
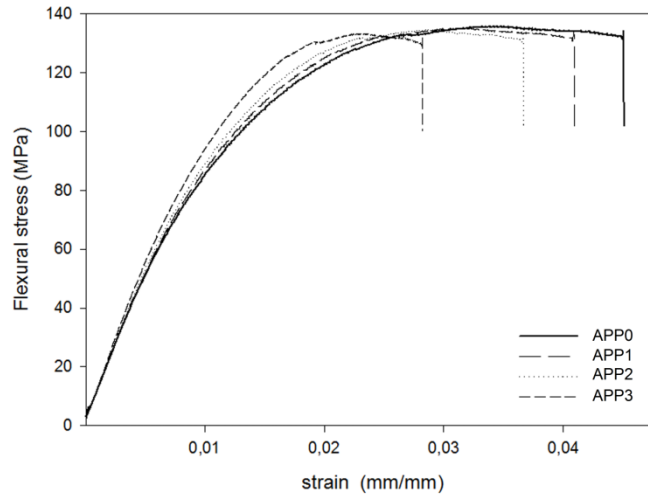
Figure 5.6-2 Typical flexural stress–strain diagrams for untreated and treated samples.

During the test, no specimens failed by delimitation and the failure mode shown little fibre pull-out. The crack always initiated on the tension side of the specimen and the fracture was observed in correspondence of the section in which the maximum stress value occurs.

Mechanical characteristics of fabric composites are lower than those calculated by rule of mixture due to the difficulty of the resin to flow within the single yarn, in addition to the twist angle of the individual filaments of the yarn that causes a loss of directionality, as specified in Chapter 3. Indeed, the bending properties are in agreement with [4], in which the same fabric was used. Nevertheless, the use of fabric allows a better technological feasibility.

By comparing the properties of the samples in Table 5.6-1, in which the average values and the standard deviations are reported, it can be concluded that the presence of the additive does not adversely affect the flexural modulus and stress. However, the value of the strain to failure (ε_r) decreases as APP content increases. Then, APP produces an embrittlement of the composite.

Sample	E_b (GPa)	σ_f (MPa)	ε_r (%)
APP0	10.4 [0.4]	128.3 [8.6]	4.5 [0.5]
APP1	9.8 [0.6]	127.1 [9.2]	4.0 [0.2]
APP2	10.4 [0.3]	131.3 [7.3]	3.7 [0.4]
APP3	11.0 [0.4]	127.3 [7.6]	2.8 [0.7]

Table 5.6-1 Flexure properties (standard deviations between square brackets).

References

[1] M. Fu and B. Qu, "Synergistic flame retardant mechanism of fumed silica in ethylene-vinyl acetate/magnesium hydroxide blends," *Polym Deg Stab,* vol. 85, no. 1, pp. 633-639, 2004.

[2] L. Haurie, A. Fernandez, J. Velasco, J. Chimenos, J. Lopez Cuesta and F. Espiell, "Synthetic hydromagnesite as flame retardant. Evaluation of the flame Synthetic hydromagnesite as flame retardant. Evaluation of the flame behaviour in a polyethylene matrix.," *Polym Deg Stab,* vol. 91, pp. 989-994, 2006.

[3] N. Suppakarn and K. Jarukumjorn, "Mechanical properties and flammability of sisal/PP composites: effect of flame retardant type and content," *Compos Part B,* vol. 40, pp. 613-618, 2009.

[4] R. Petrucci, C. Santulli, D. Puglia, F. Sarasini, L. Torre and J. Kenny, "Mechanical characterisation of hybrid composite laminates based on basalt fibres in combination with flax, hemp and glass fibres manufactured by vacuum infusion.," *Mater Des,* vol. 49, pp. 728-735, 2013.

Conclusions

In this thesis, different manufacturing techniques for the production of natural fibre composites (NFCs) using hemp fabrics and epoxy resin were studied, and then the properties of the produced composite materials were widely investigated.

In particular processes such as, vacuum infusion, brushing hand lay-up, injection moulding and continuous impregnation process were used both for the manufacturing of lightweight hemp structures and for the production of hemp/epoxy composites characterized by both high mechanical and fire resistance properties.

- Regarding the **production of lightweight structures**, by using a woven hemp fabric (GMS = 380 g/m^2) characterized by a wide mesh, it was possible to obtain final products with a density value in the range of 0.60 – 0.27 g/cm^3.

Specifically, using the un-conventional infusion process proposed in the **Part 1** of Chapter 3, hemp/epoxy composites with a density of 0.6 g/cm^3 were obtained. This value of density is close to the density of other materials conventionally used as cores for sandwich structures, such as aluminium and divinycell foams. Then this product was called as ''hemp core''.

Therefore, to compare these materials (hemp core, aluminium and divinycell foams), tensile, bending and compression tests were carried out and the results showed the superiority of the hemp core. Using another woven hemp fabric (GMS = 190 g/m^2), skins were produced and glued to the different cores in order to obtain three types of sandwich structures. These ones were tested under three-point bending tests with different values of span length. From the comparison, it was highlighted that in the sandwich with the hemp core the failure was always for tensile. Unlike of other cases, no shear and indentation phenomena were observed. In particular, due to its high value of the compression strength and the absence of indentation failure, the proposed hemp core could be used to produce sandwich structures in which the skins can be applied by compression moulding technique without compression failure of the core.

However, the process was not able to produce a complete porous structure and an excess of resin in some zones was detected; then the density of 0.6 g/cm^3 is not the minimum achievable value. This means that the process could be optimized and/or other manufacturing techniques could be proposed and investigated. This disadvantage lays the groundwork for the **Part 2** of

the work, where other processes are proposed. In particular in this part, lightweight biocomposite laminates by using four woven hemp fabrics were manufactured by means of the un-conventional infusion, the brushing hand lay-up and the injection processes. These processes allowed to obtain laminates with three different density values: 0.60, 0.42 and 0.27 g/cm^3 and the lowest was reached for the specimens produced through the injection moulding process, by using both the polyurethane foam and the epoxy resin as matrix. In addition to this advantage, the specimens manufactured by means of this technique showed the best properties in terms of specific tensile strength, flexural elongation at breaking and specific impact resistance.

Considering the conclusions of the Part 1, it is possible to highlighted the main results of Part 2 are:

- Using others processes respect to the un-conventional infusion technique, it was possible to reduce the density of the final products reaching interesting mechanical properties.

- The lowest density value as well as the highest specific dynamic properties were reached by using both the polyurethane foam and the epoxy resin as matrix. On one hand this seem to be interesting but on the others the use of both these polymers involves in the loss of the concept of eco-friendly composites materials. A possible solution, could be the use of both resins and foams with lower environmental impact; however, this was not the aim of this thesis.

- The brushing hand lay-up technique could be interesting as good compromise between mechanical properties and epoxy content and so the density value achieved. However, the process needs to be improvement in order to increase and to guaranty a more control of the epoxy content and to reduce the mechanical properties variability that affects the composites produced through this technique.

The considerations reported in the last bullet point lay the groundwork for the **Part 3** of the section, where a way to overcome these limitations was proposed. In this Part, the method proposed (continuous impregnation process) was used to produce hemp/epoxy composites with different thickness and density values, using two type of woven hemp fabric characterized by two different meshes. By using this method, composites with a density range of 0.47-0.80 g/cm^3 (it depends on the type of fabric used) and a fixed hemp fibre weight ratio

equal to 38% were produced with a high level of repeatability. This one represents the first advantage of this technique over others previously proposed, in addition this process lends itself good for an industrial scale-up. The good process repeatability was directed reflected on the mechanical properties repeatability, showing also a good relation between xperimental and theoretical properties.

Concluding, in terms of mean values, composites with density of around 0.77 g/cm^3 was characterized by tensile strength of 42 MPa, tensile modulus of 3300 MPa, bending strength of 43 MPa, bending modulus of 2000 MPa, bending shear strength 14.1 MPa, compression strength of 7.8 MPa and impact resistance equal to 22 kJ/m^2.

Instead, the composites with density of around 0.50 g/cm^3 was characterized by tensile strength of 26 MPa , tensile modulus of 1500 MPa , bending strength of 27 MPa, bending modulus of 1700 MPa, bending shear strength of 6.9 MPa, compression strength of 2.40 MPa and impact resistance equal to 13 kJ/m^2.

- Regarding the **improvement of flame retardant properties**, unidirectional hemp/epoxy composites were manufactured by using the infusion process and the effects of the APP content, into the resin, on the technological feasibility of the process, on mechanical and flame behaviour of composites were studied.

The results show that the epoxy resin added with APP particles, up to a maximum content of 16.32 wt.%, can be used in infusion processes of biocomposites because, although an increase of the processing time is observed, the technological feasibility of the process is not affected; this is also due to the large mesh of the used unidirectional fabric that ensures a good permeability.

The fire behaviour and smoke emission systems were evaluated using the cone calorimeter test. In the case of 16.32 wt.% APP content, the results compared to untreated sample have showed:

- a 60% reduction of HRR_m;
- a 74% reduction of PHRR;
- a 60% reduction of THR_m;
- a 38% reduction of TSR;
- an increase about three times of the residual mass.

Moreover, V12 test shows the real possibility to use these materials also in aircraft applications.

The results of the DMA analysis show that the APP presence does not involve variations of the elastic modulus and in the glass transition temperature. Finally, three-point bending tests highlighted that the presence of APP does not affect the mechanical properties of the samples. Therefore, these results show a decisive improvement of the flame properties of the examined materials, without affecting their mechanical properties. From the experiments carried out according to the stringent standards of the Aeronautics sector, it is clear that these materials can be used in aircraft applications such as interior components.