Alma Mater Studiorum – Università di Bologna

DOTTORATO DI RICERCA IN

CHIMICA

Ciclo XXXII

Settore Concorsuale: 03/C2

Settore Scientifico Disciplinare: CHIM/04

Novel bio-based amine curing agents for epoxy resins: the way towards fully bio-based composite materials

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Esame finale anno 2020

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Chapter 1 - Introduction

1.1 Composite materials

Composite materials are products consisting of two or more phases, separated by a well-defined interface, which possess intrinsic properties, especially mechanical, better than those of the individual constituent materials [1]. The use of composite materials has very ancient origins: the first historical findings date back to Ancient Egypt, when mud and straw were mixed in order to obtain bricks stronger and less brittle [2]. However, the first modern industrial applications of composite materials occurred only during the Second World War in the military field. Subsequently, the development of production process technologies and prices reduction increased the fields of application of composite materials in many other industrial sectors, including the naval, aeronautical, aerospace, automotive, sports and building.

Generally, composite materials are composed by a continuous matrix and a discontinuous phase, represented by the reinforcing agent; a third phase is identified at the interface between the reinforcement and the matrix (Figure 1.1).

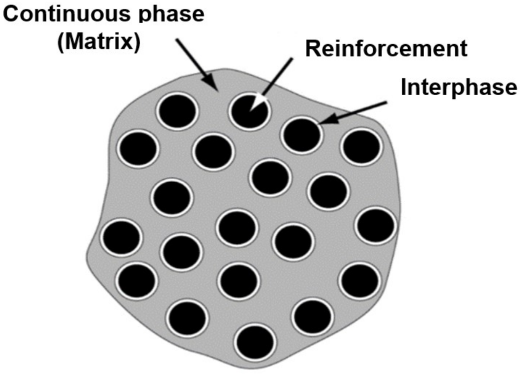


***Figure 1.1:** Different phases of a composite material*

- The **matrix** is the continuous phase where the reinforcing agent is contained, in this way it is protected from degradation, wear phenomena and allows a uniform transmission of stress [3]. The matrix is also fundamental to determine the final shape of the product, in addition to the operating conditions for the material application and for its subsequent processing.
- The **reinforcement** agent absorbs the stress applied to the artefact, avoiding the formation and propagation of cracks within the matrix [3].
- The **interphase**, despite being the smallest part of the composite, plays an important role in the final properties of product. In order to have an effective reinforcement it is necessary for the matrix and reinforcement to have an excellent adhesion, in order to avoid possible detachments at the interphase, leading to the failure of the composite.

Generally, composite materials can be classified according to the nature of the continuous phase and specifically they can be distinguished in metallic, ceramic and polymeric composites. A further distinction can be made on the reinforcement morphology: particle composites, continuous composites (long fibers reinforcement), discontinuous composites (short fiber reinforcement), nanocomposites, etc. Finally, a further classification can be made according to the chemical nature of the reinforcement: glass fiber, carbon fiber, etc.

Polymeric materials are undoubtedly the most developed and widespread materials, in virtue of their properties, such as high elastic modulus combined with their relative low density [1, 3]. Polymeric matrices can be subdivided into thermoplastics and thermosets polymers. Clearly, the choice of the matrix is made because of the required mechanical properties and the production parameters. **Thermoplastic matrices** typically consist of macromolecules interacting through secondary intermolecular bonds such as Van der Waals forces or hydrogen bonds [3, 4]. Depending on their degree of crystallinity, they can exhibit a glass transition temperature (T_g) and / or a fusion. For this reason they are recyclable and workable, but unsuitable at high temperatures. On the other hand, the phase transition, from molten to solid, of the thermoplastic matrix composite occurs by simple cooling below the glass transition temperature T_g, and this represents a huge advantage. For this reason, thermoplastic materials can be processed through very rapid injection processes, have high shelf life and do not require special precautions in storage [5]. Unfortunately, the high viscosity of polymer melts represent a problem during the impregnation process of fibers and the low operating temperature is one of the major obstacles for the application of thermoplastic matrices in composites materials [3]. However, thanks to low production cost and high productivity, the sectors of employment of these type of materials are growing [6]. The most commonly used thermoplastic polymers are polyamides (PA), polypropylene (PP), polycarbonates (PC), polyethylene terephthalate (PET), polyetherimide (PEI), polyether ether ketone (PEEK) and polyphenylene sulphide (PPS) [7].

The **thermoset polymers** are very different from thermoplastics. Thermoset matrices need to undergo through a curing processes, essential in order to obtain a three-dimensional network, that consist in the crosslinking reaction of the polymeric precursors with hardeners. The final products obtained after the curing process are infusible and insoluble and present high stiffness, remarkable high temperature and chemical resistance [4]. For these reasons, thermosetting polymers cannot be reprocessed or recycled, but are suitable for use at higher temperatures than thermoplastic matrices. In general before the crosslinking reaction, thermosetting resins are low viscosity liquids composed by low molecular weight molecules; this makes the reinforcing agents impregnation process easier [4]. Among the disadvantages in the use of these materials, there are undoubtedly the long times necessary to obtain complete crosslinking of the system (in particular for large pieces), the low shelf life at room temperature of the polymer precursors and the reduced breaking deformation. The most commonly used thermosetting matrices are epoxy, polyester, vinyl ester, polyurethane, phenolic, cyanate and ester.

1.2 Epoxy resins

The most commonly used thermosetting matrices for polymeric composites production are epoxy resins. They are extremely versatile, offer a wide range of properties and allow the use of multiple processing techniques. In addition, epoxy resins present remarkable mechanical characteristics and hardness, high resistance to chemical agents, moisture and corrosion, a low residual stress and shrinkage value, all combined with good thermal stability [8]. Currently, a large number of epoxy resin formulations can be found on the market. Generally, the resin crosslinking is obtained by reaction of prepolymers, possessing epoxy functionalities, with a curing agent [4, 9]. The hardener may already be mixed with the prepolymer, or added at a later time, right before use (two-component mixtures) [10]. In the formulations can also be present: accelerants, which speed up the crosslinking process, diluents, to specifically modify the viscosity, plasticizers and other additives depending on the final use of the material. The stiffness of the system is determined by the density and structure of the crosslinking points, which represent a very important parameter. Normally, the elastic modulus, the T_g, the thermal stability and the chemical resistance increase when a high density of crosslinking points is achieved, on the other hand the breaking strength and the deformation decrease [4]. Consequently, by modifying the structure and the functionality of prepolymers and hardeners and optimizing the crosslinking process, it is possible to modulate the properties of the final product according to specific requirements. The amount of epoxy groups present in a specific epoxy resin formulation can be expressed through the epoxy molar mass (EMM, Epoxy Molar Mass), which indicates the equivalent weight of resin containing an epoxy ring, expressed in grams. Otherwise, it can be expressed as a number of epoxy groups per kilogram of resin.

One of the most used bifunctional epoxy resins is based on diglycidylethers of bisphenol A (DGEBA), obtained through the reaction between bisphenol A and epichlorydrin [11]. The reaction is a polycondensation that releases HCl, in particular a nucleophilic substitution that takes place in a basic environment. The oligomers formed have a repeating number of monomer units typically between 0 and 12, which corresponds to a molecular weight ranging from 340 to 4000 g/mol. DGEBA is the simplest epoxy resin based on bisphenol A, with repetitive unit number n equal to zero [5]. (Figure 1.2).

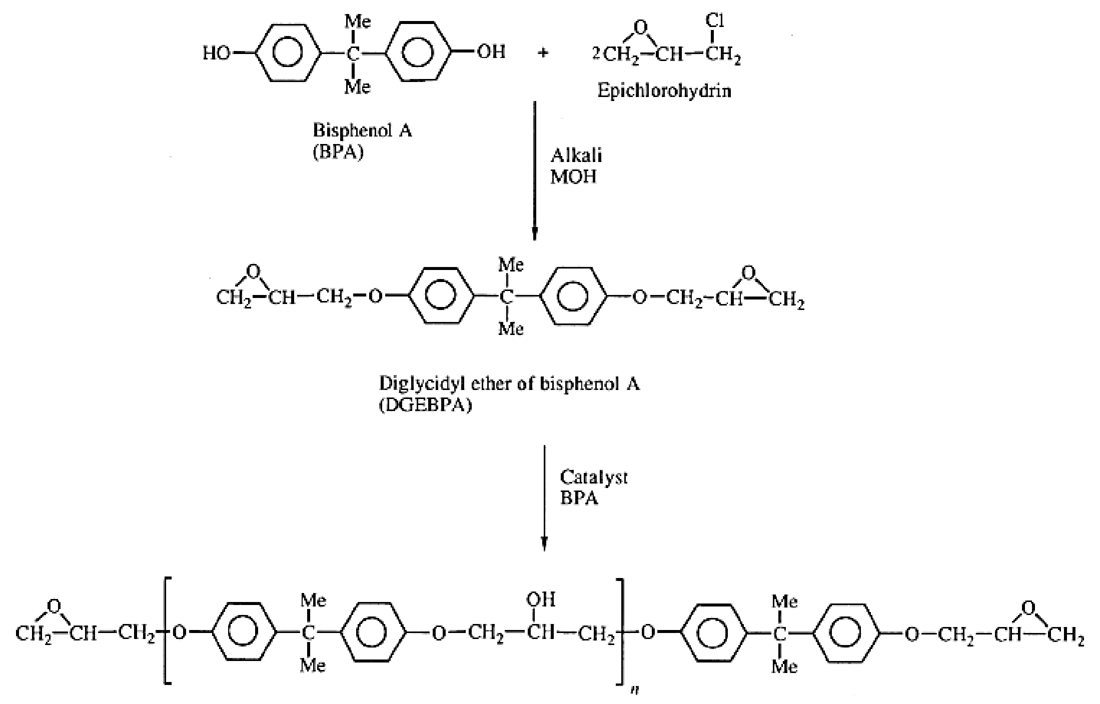


Figure 1.2: *Bisphenol A and epichlorydrin based epoxy prepolimers*

The maximum number of crosslinks obtainable is directly proportional to the number of epoxy groups contained in the resin. As the molecular weight of the oligomers increases, the number of epoxy functions in the resin decreases, and consequently a decrease of the mechanical properties and higher T_g can be achieved [12]. Table 1.1 shows the properties of some commercial epoxy resin formulations.

Table 1.1 *Properties of commercial epoxy resins based on bisphenol A and epichlorydrin*

Resin (Shell)	***Physical state***	***Viscosity at 25°C***	***Density [g cm^{-3}]***	M_w	***Epoxy groups content [mmol kg^{-1}]***
828	Liquid	12-14 Pa s	1.16	380	5260-5420
834	Semi-solid	2.1-2.3* mPa s	1.18	470	3800-4250
1001	Solid	6.3-7.79* mPa s	1.19	900	2000-2220
1010	solid	200-300* mPa s	1.20	-	210-330

* Viscosity of a solution in 40% of MEK

1.3 Crosslinking agents

The crosslinking of epoxy resins is promoted by hardeners, which react by opening the epoxy rings present in the polymeric precursors, and are the most important part of the three-dimensional network. The operating conditions of the curing process and the final properties of the composite are strongly influenced by the chemical nature of the hardener, its structure, its concentration, as well as by the number of functional groups it possesses. The more functionalities are present, the greater the number of crosslinking points generated for each hardener molecule, allowing a more rigid system to be obtained. Generally the most used hardeners for epoxy resins are amines, anhydrides, phenols, carboxylic acids, alcohols [13] and other compounds with mobile hydrogens [14]. In addition to hardeners, crosslinking systems may contain accelerating agents, used to lower the activation energy of the crosslinking process, thus reducing the necessary manufacturing time and temperature. Industrially, the most used class of hardeners are diamines. They may be aliphatic such as DETA (diethylenetriamine) or aromatic such as DDS (diaminodiphenylenesulfone) or MPDA (methaphenylenediamine) [15]. By varying the type and structure of hardeners it is possible to modulate the mechanical properties of the final composite [16]. The crosslinking reaction is a nucleophilic substitution of the diamine on the carbon of the epoxide, as shown in Figure 1.3 [5, 16].

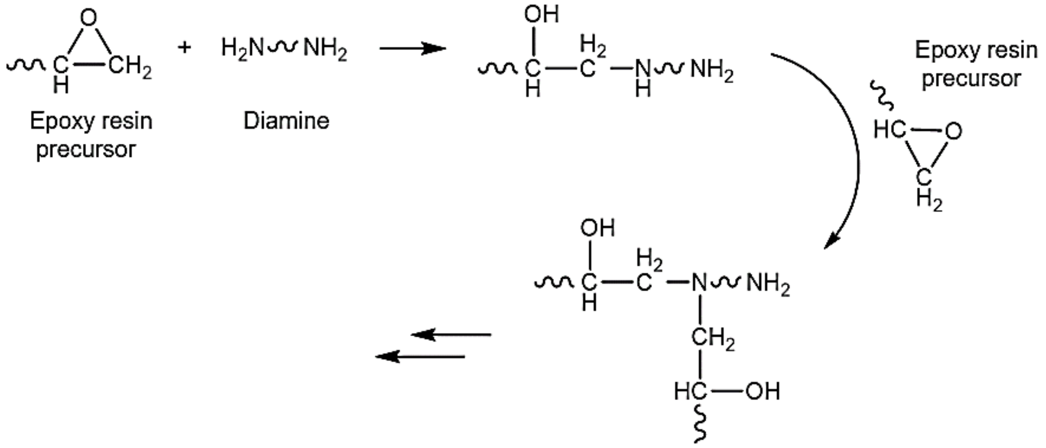


Figure 1.3: *Crosslinking reaction of epoxy prepolimers with a diamine*

Another widely used class of hardeners are latent curing agents. These resin-hardener systems are stable at room temperature and their crosslinking can be rapidly triggered by factors such as heat, light, pressure, etc.[15]. For this reason they are widely used in the production of prepregs [5, 17], since allow to avoid crosslinking at low temperatures and ensure a high shelf life of prepregs [18]. Industrially, amine complexes with boron trifluoride, DICY (diacyanimide) and hydrazides of organic acids are widely used [15].

The crosslinking reaction of an epoxy resin is an exothermic process, and the heat generated can also trigger the autocatalytic epoxy ring opening. In particular, if significantly thick material are produced, since the low thermal conductivity of the matrix, the occurrence of hot spots in the material may happen. This can lead to a localized degradation of the resin, with a consequent decrease properties of the final product [6]. The best solution to overcome this drawback is to optimize time and temperature of the curing process and to use polymeric solution homogeneously mixed.

1.3.1 Epoxy resin crosslinking reaction

The crosslinking process of a thermosetting resin is a complex phenomenon and includes several steps, as shown in Figure 1.4.

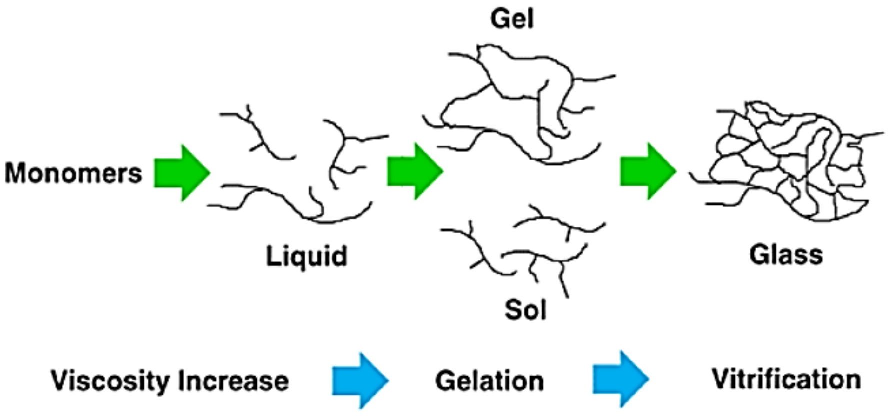


Figure 1.4: *Representation of the crosslinking phenomenon of thermosetting resins*

During the crosslinking, the epoxy groups react with the functional groups of the hardener forming oligomers. As the reaction progresses, the size of the molecules increases to form progressively high molecular weight structures. The critical point of this process is the gelation, where an instantaneous and dramatic increase of the viscosity of the system is achieved. This phenomenon is due to the formation of covalent bonds between linear macromolecular chains that form crosslinked regions, obtaining a system no longer able to flow. At the gel point the system is composed by two different phases: a *sol*, insoluble fractions of crosslinked material, and *gel*, fractions of non-crosslinked and therefore soluble material (Figure 1.5) [19].

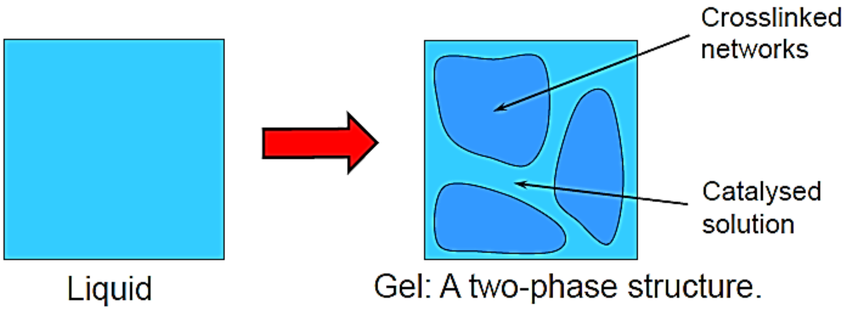


Figure 1.5: *Gelation of thermosetting polymers*

The phenomenon of gelation is the first real manifestation of a three-dimensional network. It is an irreversible phenomenon, which does not determine, however, the end of the curing process of the resin, since the reaction kinetics are not modified, and therefore in the presence of appropriate conditions, the crosslinking reaction can still achieve completion [20, 21]. After gelation, T_g continues to increase. When it exceeds the curing temperature process, vitrification takes place, producing a "freezing" of the conformation of the macromolecules. In these conditions, the crosslinking speed is significantly reduced, since a diffusion regime has been established within the system, due to the impossibility of the macromolecular chains to move without freely and to react by coming into contact with each other. Vitrification, however, is a reversible phenomenon. It is sufficient to increase the temperature of the system above T_g, to bring the material back to the "rubbery" state, thus eliminating the diffusion constraints. In order to obtain a complete crosslinking of the system, it is essential for the curing process temperature to be higher than the maximum T_g achievable by the resin. The events that come with the curing reaction of a thermosetting resin are shown in TTT (Time-Temperature-Transformation) diagrams (Figure 1.6).

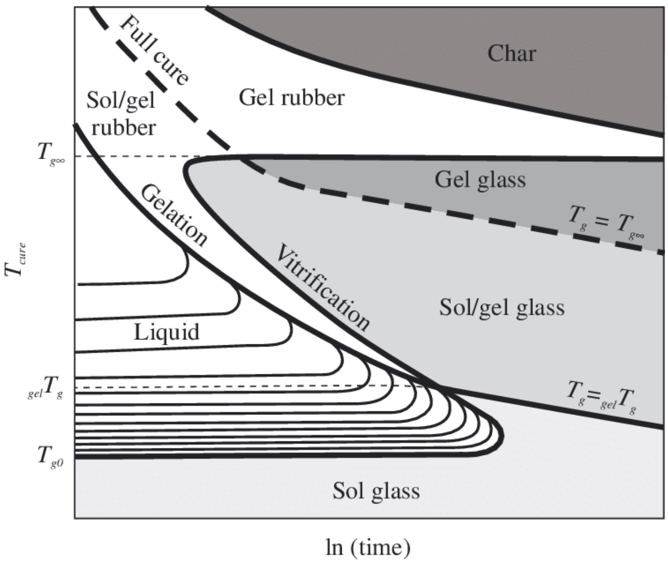


Figure 1.6: *Time-temperature transformation diagram of a thermosetting material*

In the crosslinking process, three critical temperatures can be distinguished:

- **T_{g0}:** Below this temperature there is no reaction between resin and hardener and it can be considered as the maximum storage temperature.
- **$T_{g\ gel}$:** At this temperature gelation and vitrification can take place, in some cases also simultaneously.
- **$T_{g\infty}$:** Is the glass transition temperature of the completely crosslinked thermosetting system.

Between T_{g0} and $T_{g\ gel}$, the resin precursors react with the hardener up to gelation. After gelation, the system will continue to react by establishing a more rigid network until the crosslinking is completed or the glass transition temperature corresponds to the curing temperature. After this point it is possible to observe the phenomenon of vitrification, the reaction speed is considerably reduced as it is no longer controlled by a chemical regime, but by the diffusive processes of the reacting species. When vitrification is achieved, the resin will not necessarily be completely crosslinked and a fraction of unreacted functional groups may therefore still be present and, depending on the experimental parameters or post-treatment, these groups may continue to react. In the temperature range between $T_{g\ gel}$ and $T_{g\infty}$, the viscous and partially reticulated liquid becomes a viscoelastic fluid, then a rubber and finally a glass. If the cure temperature exceeds the glass transition temperature of the completely cured material ($T_{g\infty}$), the material is not able to vitrify and remains in a rubbery state after gelation [8].

1.3.2 Crosslinking kinetics of an epoxy resin system

In order to define the ideal process parameters and conditions to crosslink a resin, kinetic studies are essential. The most widely used method to study crosslinking kinetics is Differential Scanning Calorimetry (DSC). Regarding the epoxy ring opening, the heat released by the exothermal reaction is considered directly proportional to the degree of crosslinking of the resin (α). It is also assumed that the heat released during the reaction depends exclusively on the exothermic opening of the epoxy ring [22, 23]. Thanks to this supposition, a simplified approach of crosslinking kinetics can be used and it considers all the reactions that occur as a single event; in this way the degree of crosslinking can be studied through the heat released [24]. To determine the degree of resin crosslinking at a defined time (α_t), it is possible to perform DSC analyses in isothermal heating conditions.

The ratio of the reaction heat released at a specific time (ΔH_t) and the total heat released at complete crosslinking (ΔH_{tot}) represents the instantaneous crosslinking degree. (Equation 1.1):

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{tot}} \qquad \textit{Equation 1.1}$$

The crosslinking reaction speed (*dα/dt)* depends on both the conversion and the temperature T, as described in Equation 1.2:

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \qquad \textit{Equation 1.2}$$

In Equation 1.2 the term k(T) is the kinetic constant, which can be described by the Arrhenius equation (Equation 1.3):

$$k(T) = Ae^{-\frac{E_a}{RT}} \qquad \textit{Equation 1.3}$$

The term A is the pre-exponential factor, E_a is the crosslinking reaction activation energy, R represents the gas constant and T is the absolute temperature. Working in isotherm mode the temperature factor becomes constant and the equation is further simplified [25].

1.4 Reinforcement agents for composite materials

As previously explained, a composite material is composed by a continuous phase, the matrix, and a discontinuous phase, the reinforcing agent. The function of reinforcing agents is to increase rigidity and hinder the propagation of cracks in the final product by absorbing the stresses applied, giving to the composite greater mechanical properties. They can be classified by shape, size, orientation, spatial distribution, chemical composition and for their ability to interact with the matrix. The reinforcing materials are divided into particles, flakes and fibers (Figure 1.7). These components must have at least the size of 1μm [3].

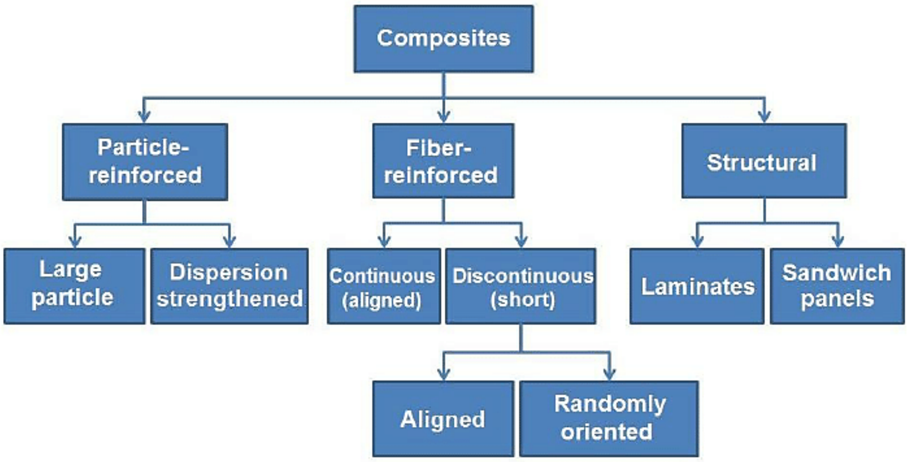


Figure 1.7: *Composite materials classification*

The effectiveness of the reinforcement is directly proportional to the surface / volume ratio of the reinforcing agent. Fibrous type reinforcement are the most effective, because they allow to modulate the fiber length in order to tune the final properties of the product. Also the shape and size of the reinforcing agents influence the isotropy or anisotropy of the mechanical properties of the final material. The properties of the fibro-reinforced composites, therefore, depend not only on the type and length of fibers, but also on their content and orientation. If fibers are all oriented in the same direction, they will be defined as unidirectional (UD). The product obtained will show an increase in the mechanical properties only along fibers direction, while orthogonally lower properties will be observed. In order to hamper this effect, known as anisotropy, several layers of unidirectional fibers, or even of fabrics, can be overlapped during the composite lamination. In this way a crossings between fibers can be obtained leading to more uniform properties in the final product (Figure 1.8). The cross-ply, where fibers are oriented in alternating layers perpendicular to each other, is the simplest type of laminate of this kind; if necessary, in order to obtain a material as much isotropic as possible, further layers with different orientations may be added [26].

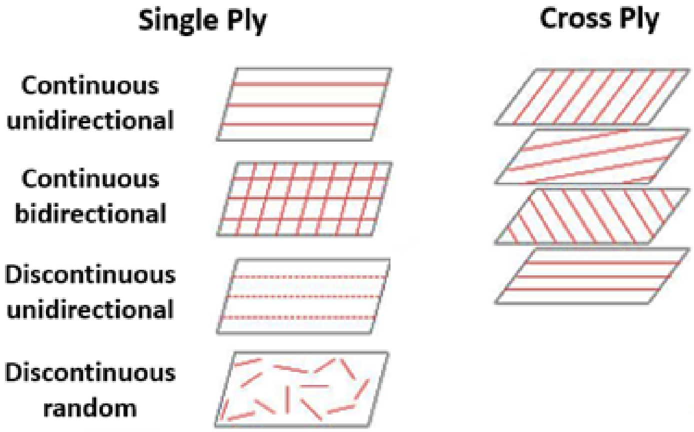


Figure 1.8: *Different single ply and cross ply fibers orientation*

Fibers can be divided into **short fibers** [4], long one millimeter or less, are mainly used for injection molding with thermoplastic matrices and **long or continuous fibers**, which have a length equal to final manufactured product. Continuous fibers are more complex to use but allow the optimization of the structure of the composite, the volumetric fraction added to the matrix and the possibility to establish its orientation. Fibers can also be divided according to the material that composes them. The most important fibrous reinforcements are glass fibers, carbon fibers and aramid fibers. Following, stress / deformation curves, for some types of fibrous reinforcements (Figure 1.9), and the relative properties are compared (Table 1.2) [4].

Table 1.2: *Main reinforcing agents mechanical properties*

Fiber/material	*Density*	*Elastic modulus E (GPa)*	*Tensile strength σ_t (Mpa)*	*Elongation at break ε (%)*
Carbon fiber	1.7-1.9	200-600	2000-3000	≤1
Glass fiber	2.5	70-85	3000-4500	0.4
Aramid fiber	1.45	60-130	2700-3000	0.2
Steel	7.8	200-210	500-2000	0.2
Aluminium	2.8	75	500	10
Titanium	4.5	110	1200	14

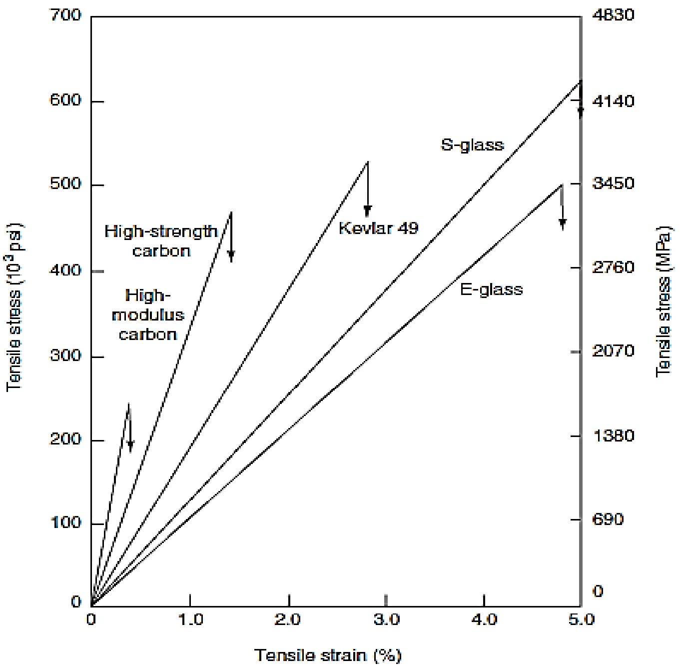


Figure 1.9: *Stress-Strain curves of fibrous reinforcing agents*

1.4.1 Glass fibers

Glass fibers are the most used reinforcing agent as they have a lower cost compared to other products. This type of fibers display high rigidity, comparable to aluminum, but a significantly higher resistance, furthermore the glass fibers are electrically insulating and the diameter of a single filament ranges between 12 and 17 μm. They are obtained by spinning of molten glass through platinum crucibles. Different types of glass fibers can be distinguished: **Type E**, which are the most commonly used, **Type S**, fibers for high mechanical performances and **Type C**, fibers able to resist chemical agents. The typical color of this fiber is white, but they become transparent after the resin impregnation process [26].

1.4.2 Carbon fibers

Carbon fibers were introduced as composite materials reinforcement agent in the late sixties to meet the needs of the aerospace industry, which required fibers with similar properties but a higher modulus than glass fibers. Only after ten years of research, sufficiently high resistance and modulus values were achieved for aerospace uses. From this point the modern generation of composite materials have rose, characterized by resistance and elastic modulus so high, that they became the first polymeric materials able to compete with metals in structural applications [6].

Generally, carbon fibers have the following advantages [5]:

- High modulus (especially pitch fibers);

- Good resistance (especially the PAN fibers);
- Low density;
- Available in different length and geometries, with a great variety of properties;
- Good thermal stability in an inert atmosphere;
- Good thermal conductivity along the fiber axis;
- Low coefficient of thermal expansion;
- High resistance to break;
- Good chemical inertia;
- Low electrical resistivity;

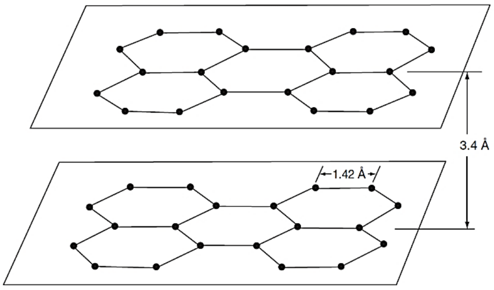


Figure 1.10: *Carbon atoms disposition in graphite lattice*

Carbon fibers are composed of longitudinally oriented graphite planes (considering the fiber axis), and amorphous carbon residues. Graphitic carbon atoms are arranged at the corners of an interconnected regular hexagons structure (Figure 1.10). The distance between different planes (3.4 Å) is greater than the distance between adjacent carbons on the same plane (1.42 Å) [5]. In fact, within the same ply, strong C-C covalent bonds are in force, while only weak Van der Waals interactions are present between different levels. Hence, carbon fibers display a strong anisotropy matched with high physical and mechanical properties [4].

Fibers can follow different geometries in the transverse direction of the alignment axis (Figure 1.11), with consequent modifications of the properties.

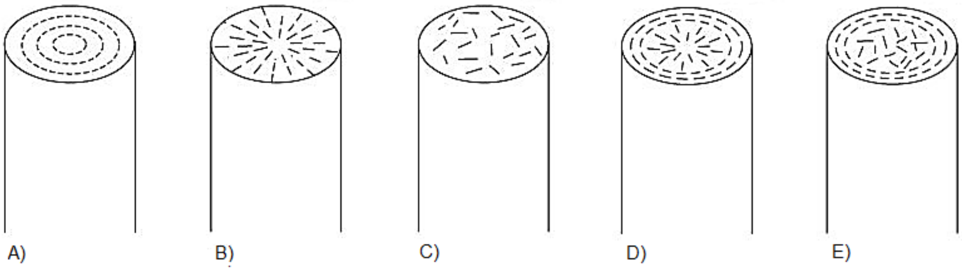


Figure 1.11: *Possible transversal orientations of C graphite surfaces respect to the fiber axis: A) circumferential; B) radial; C) random; D) radial-circumferential; E) random-circumferential [4]*

All commercially available types of carbon fibers are obtained by pyrolysis in inert atmosphere of fibers polymeric precursor. The main precursors used are rayon, polyacrylonitrile (PAN) and tar / pitch [4]. According to the fibers precursor used, the manufacturing process can differ, however, in general, it is always divided into the following phases [6]:

- **Spinning:** the precursor is spun; the rayon does not require spinning since it is already in fibrous form.
- **Oxidation or stabilization:** oxidation at 220-300°C - the thermoplastic strand of the precursor is converted into an infusible filament, capable of being heated in the subsequent stages without undergoing shrinkage and changes in shape;
- **Carbonization:** heating in inert atmosphere up to 1500°C - from the filament are removed volatile products (CO, CH_4, NH_3, N_2) and the first graphite domains begin to form.
- **Graphitization:** heating in inert atmosphere up to 2800-3000°C - if the precursor is rayon or PAN tensile force (stretching) is applied to the fibers.

The strength and elastic modulus of carbon fibers obtained depend on the chemical composition of the precursor, the final heating temperature and the degree of axial orientation of the crystalline planes internal to the fiber [3, 5, 6]. The presence of non-graphitized amorphous carbon decreases the elastic modulus of the fibers [4, 5]. In particular, pitch fibers tend to have higher elastic modules, index of better graphitization of the precursors, while PAN fibers exhibit higher values of tensile strength and elongation at break [3, 4]. In order to improve the fiber-matrix adhesion, most of the carbon fibers on the market are subjected to surface oxidation treatments and sizing agents addition. Single carbon fibers display diameters equal to 7-12 μm and therefore it is very difficult to process them in order to obtain a finished products. Consequently fibers are assembled in individual filament bundles and wrapped up spools or fabrics.

1.4.3 Aramid fibers

Another important of reinforcing fibers are the aramid fibers and among these, the most known is the KEVLAR® (developed by DuPont in the 50s) [27]. Aramid fibers are characterized by high strength and rigidity, considerable toughness and low density and an outstanding thermal resistance. For these reasons, they are used as ballistic protection material or for anti-cut fabrics. Cables in aramid fibers are used as ropes since they provide a much higher resistance than steel or other polymeric fibers (polyamides and polyester), but are characterized by a lower density and weight.

1.4.4 Natural fibers

In the current market, the role of products from renewable and biodegradable sources is increasingly important. Also in the world of composite materials there is a tendency towards this kind of attitude. While the development of polymeric matrices (such as those derived from lignin) is progressing slowly, reinforcements agents from renewable sources are currently being studied. These kind of fibers are very interesting and promising since their low environmental impact combined with good mechanical properties and low weight. Natural fibers can be divided into plant, animal or mineral fibers. All vegetable fibers are composed of three main polymers: cellulose, lignin and polysaccharide-based resins, pectin and hemicellulose. Fibers can be considered as composites consisting of millions of fibrous units called microfibrils. Microfibrils have a structure similar to a composite reinforced with Kevlar fibers: the reinforcement is composed of cellulose crystals while the matrix is made of lignin, hemicellulose and other polysaccharides. The microfibrils are arranged in lamellar form within the cell wall. The central part of the cell wall, also known as the secondary cell wall, is subdivided into further three layers, S1, S2 and S3 (Figure 1.12), with the layer S2 constituting most of the wall. Microfibrils in the secondary cell wall are arranged helically. Fibers with a high cellulose content and high degree of polymerization have higher values of tensile strength and Young's modulus (rigidity) [28] and can be chemically or enzymatically functionalized to improve their affinity with the polymer matrix [26].

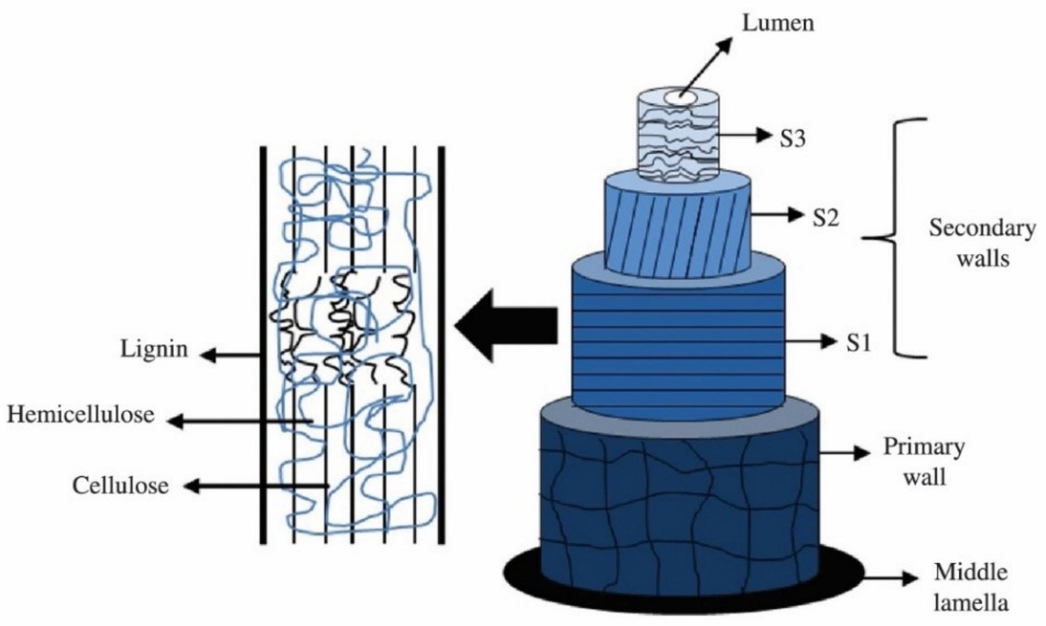


Figure 1.12: Layers of the fiber cell wall showing the primary orientation of the fibril (right) and the conformations of the constituents in the S1 layer (left)

- Flax fibers

Flax fibers have a long history in the textile industry. Flax was one of the most important sources of fiber in Europe between 1200 and 1700 and the first uses of it date back to 8000 BC in ancient Egypt [29]. The bundles of fibers obtained from the processing of the plant consist of several elementary fibers held together by lignin, hemicellulose and pectin. The fibers consist of highly oriented microfibrils with a high degree of polymerization (65-85%). The cellulose that makes up the fibers has numerous hydroxyl groups capable of creating hydrogen bonds with the epoxy matrix while the hemicellulose (amorphous) forms a matrix that supports microfibrils and is strongly hydrophobic like lignin. Various studies have been carried out to determine the chemical composition of flax fibers but the values vary considerably depending on whether the fibers are elementary or technical. In Table 1.3 the percentages of the components and the mechanical properties of linen fibers are presented [30–33]:

Table 1.3: *Composition and mechanical properties of Flax fibers*

Flax Fiber	
Dimensions L (mm) / D (μm)	750–900/50–150
Cellulose (%)	62–72
Lignin (%)	2–5
Young's modulus (GPa)	60–80
Ultimate tensile strength (MPa)	780–1500
Elongation at break (%)	1.2–2.4

- Jute fibers

Jute fibers, like other natural fibers, are totally biodegradable and recyclable. They have good thermal and acoustic insulation, moderate moisture absorption and are not irritating to the skin. World production is around 3.2 million tons per year. They have many applications but the most important consumer is the textile industry. Jute bags are a valid alternative to non-biodegradable polymers and paper ones, which require petrol or wood consumption. This material can be recovered and used as a reinforcing agent in composite materials since the fibers display excellent mechanical properties [30]. Jute fibers are composed by a complex mixture of components deriving from the natural processes that occur during the growth of the fiber in the stem of the plant. The composition of these fibers, as in all natural fibers, is not uniform: the soil conditions, the climate and the maturation of the plants can generate considerable variations in the characteristics of the fiber. The average composition and mechanical properties of a jute fiber are reported in Table 1.4 [30]:

Table 1.4: *Composition and mechanical properties of Jute fibers*

	Jute Fiber
Dimensions L (mm) / D (µm)	120/25–30
Cellulose (%)	59–71
Lignin (%)	11.8–12.9
Young's modulus (GPa)	10–30
Ultimate tensile strength (MPa)	400–800
Elongation at break (%)	1.5–1.8

1.5 Technique for composite materials production

Composite materials can be produced using various technologies, such as resin transfer molding, poltrusion, filament winding, lamination of prepregs, etc. The choice of the production process depends on many factors, such as the type of materials (reinforcing agent and matrix), the complexity and the dimensions of the piece and the productivity required [3].

1.5.1 Resin transfer molding (RTM)

In RTM (Resin Transfer Molding) process the thermosetting resin, not crosslinked, is poured in a mold where the dry reinforcement has been previously disposed (Figure 1.13). [34].

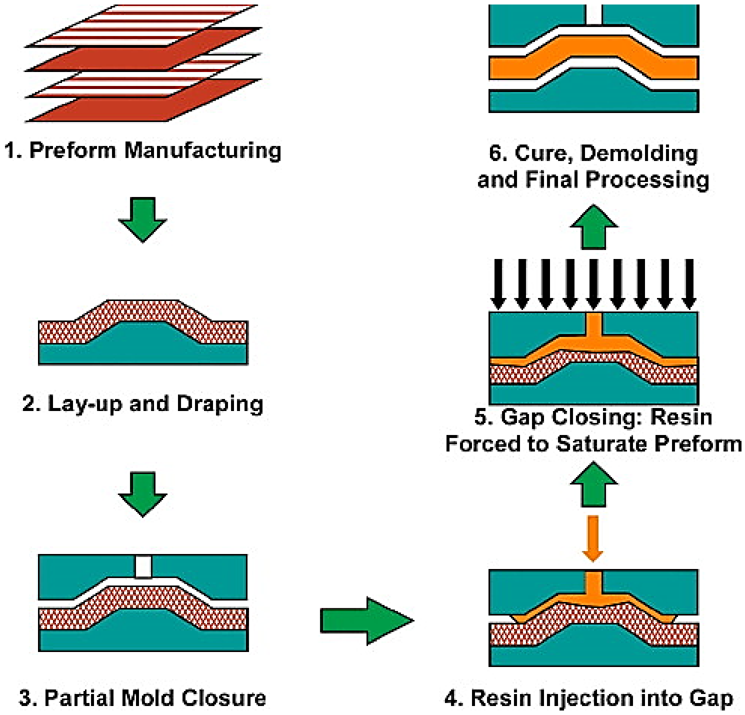


Figure 1.13: *Resin Transfer Molding process*

The treatment takes place directly inside the heated mold and the reinforcement is constituted by the superimposition of layers of glass, aramid or carbon fibers, unidirectional or woven [3]. The RTM process is undoubtedly one of the most efficient and attractive technologies for the production of high performance composite materials with low manufacturing costs. The fundamental prerogative of the RTM technology is the remarkable versatility, both in the characteristics of the products (complexity, performance and quality), and in the curing times required. The possibility to inject the resin allows this technology to produce pieces of complex geometry; however, only of limited size pieces can be manufactured [10]. Often, in order to simplify the correct positioning of the reinforcement it is pre-assembled and then shaped according to the geometry of the mold. The result of this operation is the so-called "preform" [6]. On the other hand, laminating directly into the mold is a long and laborious operation, since it is required to cut and display each layer in the mold, paying attention to fibers orientation and position [6].

1.5.2 Poltrusion

Poltrusion is a very common technology to produce, in continuous, bars with a constant section. The process requires a continuous fibrous reinforcement, and a low viscosity resin [5]. Fibers are pulled through a bath containing the polymeric precursors and the hardener, then the bundle of impregnated fibers is passed through a heated mold, where the curing process takes place. After the completion of curing process, a dragging force is applied to the solid section and it is moved by a drawing device [35]. The section bars can be cut to the desired lengths using a circular saw. A representation of a typical poltrusion plant is shown in Figure 1.14. In addition to the unidirectional fibers, it is possible to add, before entering the mold, some layers of fabric, to decrease the material anisotropy [6]. Poltrusion represents a highly automated composite material forming technology characterized by high productivity; however, it only allows the production of articles with a constant section, which limits their fields of application.

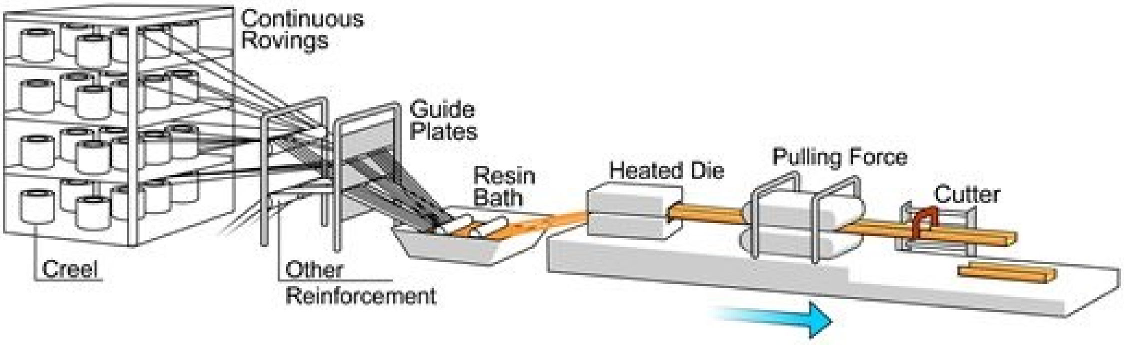


Figure 1.14: *Poltrusion plant representation*

1.5.3 Filament winding

Filament winding, or wire winding, is the traditional and preferred forming technique for the production of cylindrical items, such as pipes, rods and tanks [3]. Filament winding consists in the impregnation and coiling of long fibers along a rotating mandrel (Figure 1.15).

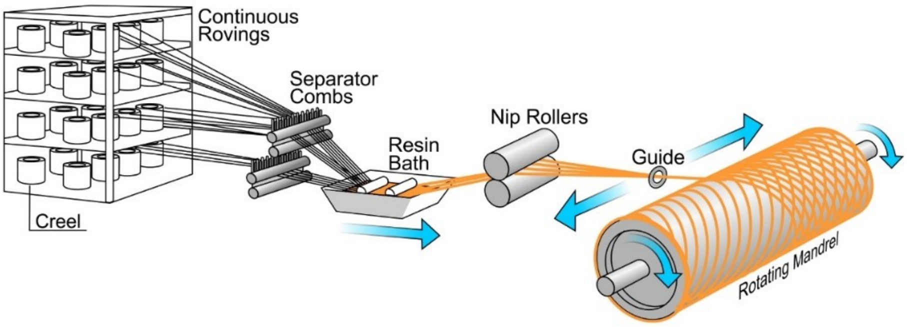


Figure 1.15: *Filament winding plant representation*

Different winding geometries such as circumferential, helical or polar [6] are possible depending on the final product desired characteristics. After the wrapping phase, the resin can be crosslinked through an autoclave process or, more commonly, under pressure at room temperature. Filament winding is a very simple and economical technique, but characterized by a low productivity, linked to the long winding times of the fibers. Furthermore, the possibility of obtaining only cylindrical geometries strongly limits the application fields.

1.5.4 Autoclave treatment cycle

Autoclave is the most used technology for the production of composite materials requiring high processing temperatures. It is a large pressurized furnace, composed of a cylindrical body, horizontally disposed and terminating on one side or both with a door, for the introduction and extraction of the pieces (Figure 1.16).

Figure 1.16: *Autoclave used to produce wings of Boeing 787*

The evolution of the materials used changed the processing parameters increasing the temperature from 120°C up to more than 200°C and the pressure from 3 atm up to dozens of atmospheres [36]. Different heating systems for autoclave are available. The most common, used for large autoclaves, uses diathermic oils which circulate in the special exchange circuit [37]. Smaller autoclaves are generally heated by electric resistors and generally the maximum heating speed are 1-4°C/min [13]. The pressurization of the system is obtained by using a service fluid, generally N_2 or CO_2; the external pressure is applied in order to expel the air and the volatiles dissolved in the resin, reduce the size of the voids and level the distribution of the fibers.

In order to obtain the best final characteristics of a composite, the following requirements must be met during the curing cycle [37]:

- Complete or advanced and uniform crosslinking degree in all the material, obtained in the shortest possible time;
- Elimination of voids inside the material;
- Solvent removal;
- Consolidation of the piece in the mold;
- Removal of any resin excess.

For the crosslinking to take place uniformly, the selection of the curing cycles depends on different factors such as the type of resin and hardener used, the complexity and the nature of the chemical reactions involved, the thickness and dimensions of the final product and the heating and cooling speeds. Changes in viscosity of the resin are also particularly important during the curing process. When a laminate is cured, the viscosity of the resin initially decreases due to the increase in temperature; then rapidly increases as soon as the crosslinking begins [4, 38] (Figure 1.17). The best moment to apply vacuum is when the viscosity of the resin is minimal [3, 38], in this way air and the gaseous molecules still contained in the resin can be completely eliminated [39]. Generally during a standard autoclave cycle the increasing temperature trend is not continuous, but occurs in steps with different stops at predetermined temperatures, to facilitate the flow of resin towards the outside of the piece and avoid the formation of voids. Moreover, the stops make it easier to obtain a uniform temperature distribution inside the laminate, in order to achieve the same degree of crosslinking almost simultaneously throughout the piece. However if the heating rate is too slow the crosslinking may occur at low temperatures increasing the viscosity of the resin. In these conditions, it is possible that gases remain trapped in the resin, and the possibility of voids and bubbles to occur increases.

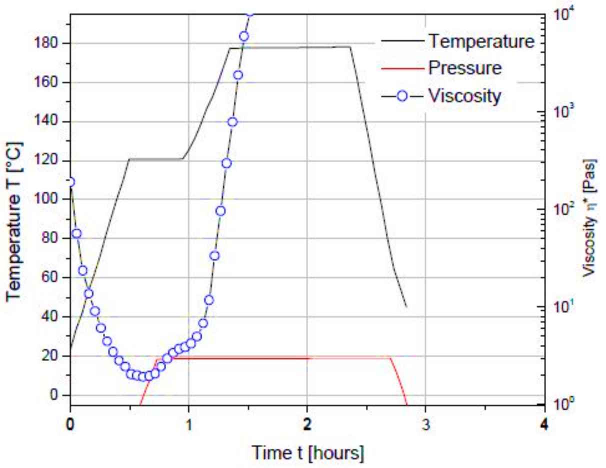


Figure 1.17: *Example of an autoclave curing cycle optimized considering viscosity modifications.*

An optimized autoclave cycle allows to obtain composites with properties close to the maximum potential achievable also for pieces of considerable dimensions, hard to produce with other methods. However, one of the great limits of autoclave is related to their thermal inertia and the long times required to reach the cure temperature, which inevitably lengthens the treatment process [6]. A further disadvantage is represented by the low productivity, only a limited number of pieces are produced every cycle, combined with the impossibility of customizing the curing treatment of pieces of different dimensions and shape loaded in the same autoclave. These limits promote the continuous research of alternative techniques to the autoclave, in order to reduce method times and allow more flexibility regarding the process parameter of the treatment [37].

1.6 Production of composite materials form prepregs lamination

Lamination of prepregs is one of the most flexible techniques for the production of polymer composite materials [4]. Prepregs are semi-finished materials and are composed by long fibers plays already impregnated with the exact quantity of resin precursors required. This characteristic is optimal to guarantee the preservation of fiber and matrix ratio and allows high quality and reproducibility of the final products [11]. Prepregs can be produce with different kind of fibers such as carbon, glass and aramid fibers [6], are available with both unidirectional oriented and woven fibers and different percentages of matrix volume can be chosen. Prepregs can be based on thermoplastic matrices but are mainly produced using thermosetting resins precursors. In particular, the resins used for prepregs production are mainly of epoxy type, which guarantee the best quality of the finished product. Important features for thermosetting prepregs are [10]:

- Adhesion of the prepreg at room temperature (tack); It is essential to simplify the rolling process and reduce the risk of delamination. It depends essentially on the matrix used [4];
- Ability of the prepreg to take complex forms without deforming or forming wrinkles (drapability). This characteristic is strictly dependent on the fiber and the viscosity of the matrix [4].

Before the curing process, thermosetting matrix prepregs are typically stored at -18°C, below T_g, in order to have vitrification of the oligomeric precursors and block a further undesired crosslinking. Generally, prepregs shelf life, stored in such conditions, ranges from six months to a year [3].

1.6.1 Thermosetting resins based prepregs production processes

The physical state of a thermosetting resin during the crosslinking process can be described by the following steps [4, 5]:

- **A-stage:** the resin components are mixed and the crosslinking reaction has not started yet.
- **B-stage:** crosslinking degree has occurred between 15-25%, the viscosity of the system has increased, although the gelation point has not yet been reached. The crosslinking progress can be stopped by vitrifying the system bringing the temperature lower than T_g.
- **C-stage:** the crosslinking of the resin is complete.

The main prepregs production techniques use hot-melt or solvent type impregnation processes. The two technologies use different approach to lower the viscosity of the resin in the impregnation process, as well as increase the viscosity once the impregnation of the fibers is finished.

In **solvent impregnation process**, a solvent (acetone or methylethylketone MEK) is added to the precursors of the resins, it allows to decrease the viscosity of the system, improving the impregnation and wettability of the fibers (A-stage). Once the resin has been added to the fibers, the system is sent to an oven where the solvent is evaporated (Figure 1.18 C) and a partial crosslinking until reaching the B-stage occurs [40]. The heating step is essential to obtain the total evaporation of the solvent, otherwise voids or bubbles could develop in the material, with consequent decrease of the mechanical properties.

In **hot-melt impregnation process**, the lowering of resin viscosity, necessary for the correct impregnation of the fibers, is obtained by rapidly heating the system, without any solvent addition. The consolidation of the resin on the fiber after impregnation is obtained both by lowering of temperature (Figure 1.18 B), and possibly by partially crosslinking of the resin (B-stage) [40] (Figure 1.18 A). One of the advantages of hot-melt processes is the lack of release of volatile solvents into the environment.

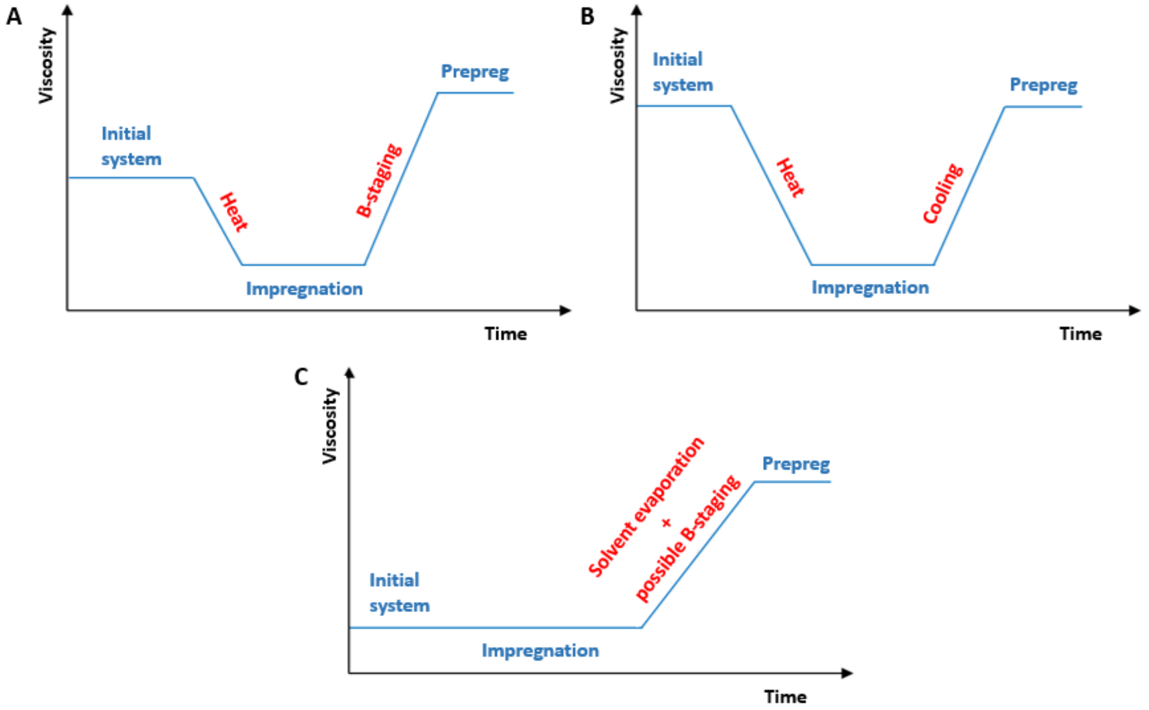


Figure 1.18: *Prepreg production viscosity over time diagram; A) hot-melt with B-stage; B) hot-melt without B-stage; C) solvent impregnation without B-stage.*

Although a partial crosslinking may be desired to help the consolidation of the prepreg (B-stage), in order avoid damages to the impregnation equipment, it is essential that polymeric precursor does not present excessive reticulation. This makes conventional fast curing resins, characterized by high reactivity, unsuitable for the production of prepregs [38]. The degree of crosslinking obtained during the production of prepregs has effects on their fundamental characteristics, in particular as the degree of the B-stage increases a decrease in the adhesiveness of the prepregs occurs and a decrease in drapability is observed. Figure 1.19 shows a generic impregnation plant that can be used by both solvent technology and hot-melt processes. The impregnation of fibers starting from thermosetting matrices, generally characterized by relatively low molecular weight precursors, is normally easier than using much more viscous thermoplastic polymers [13].

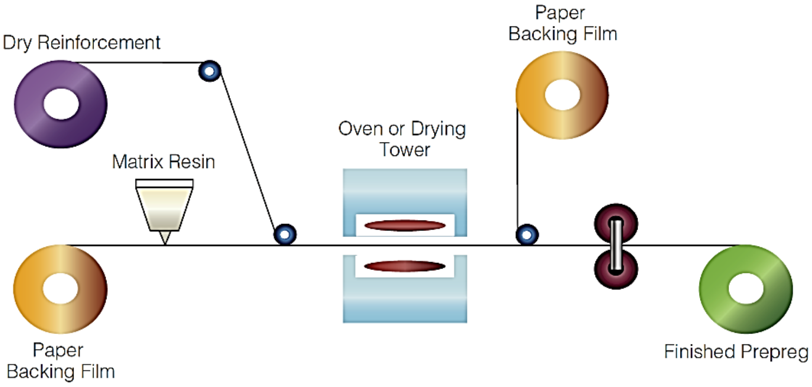


Figure 1.19: *Scheme of an impregnation plant*

1.6.2 Lamination sequence importance

The lamination sequence describes the type and the orientation of the different prepreg layers. Given the strong anisotropy due to the use of long fibers as reinforcing agents, it is essential to design the stacking sequence considering future stresses that the material will withstand. The different laminae can be made of different materials and have different thicknesses. In general, in order to facilitate the adhesion between the different plies and hinder delamination phenomena [6], is desirable the use of prepregs based on the same type of matrix. To describe the orientation of the different plies of a laminate, a Cartesian system (axes x, y, z) should be used [41]. Some examples of plying sequences are reported in Figure 1.20.

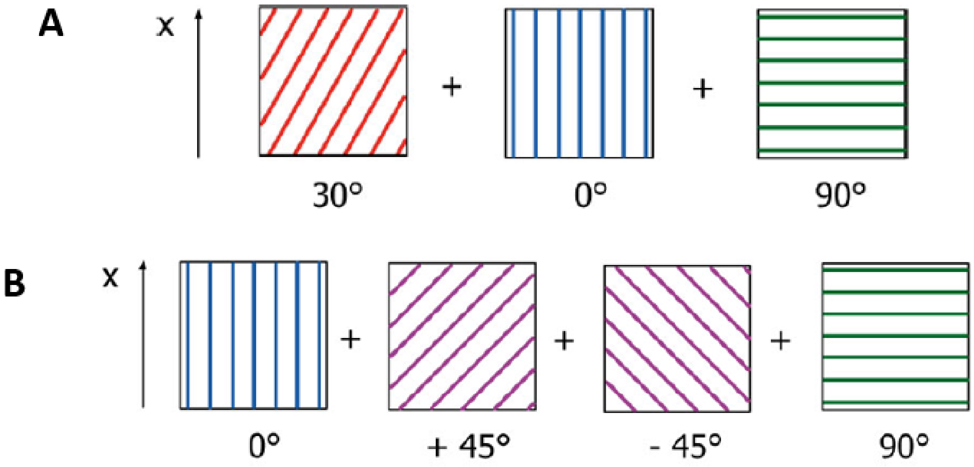


Figure 1.20: *A) Lamination sequence [30/0/90]; B) Lamination sequence [0/+45/-45/90].*

In order to limit the distortion of the components due to both the thermal contraction following the curing cycle and the application of external loads, the use of symmetrical rolling sequences with respect to the laminate center plane is frequent [41].

1.6.3 Vacuum bag molding

The vacuum bag molding process involves cutting the prepreg into the desired shape, and arranging it on a mold [42]. Once the stacking is complete, the piece is covered by a vacuum bag, layers of transpiring material are inserted, necessary to allow the air, solvents or dissolved volatile substances to be removed before the curing cycle [6] and a flexible film, typically of nylon. Furthermore, it is necessary to use releasing agents to ease the piece extraction once the crosslinking is complete. With the function of absorbing, if necessary, any excess resin of the prepregs, layers of absorbent materials (bleeder), in contact with the pre-impregnated sheets, can be introduced. The combination of the vacuum inside the bag and the external pressure applied during the autoclave cycle, promote the resin excess to flow from the laminate to the absorbent layer, ensuring the desired content of resin in the final composite. The internal vacuum also has the purpose of simplifying the extraction of air and other volatiles dissolved and allow migration and expulsion of bubbles [43]. External pressure, on the other hand, is required for the consolidation and compacting of the laminate [44]. A diagram of the layers used in the vacuum bag is shown in Figure 1.21.

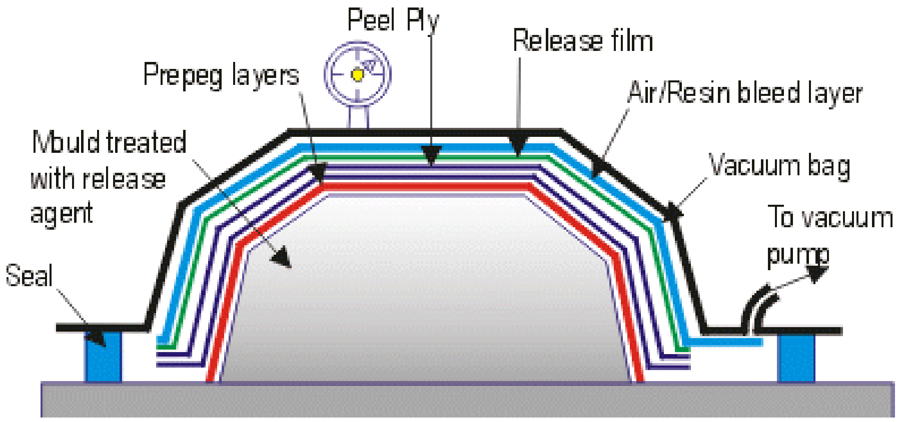


***Figure 1.21:** Vacuum bag molding diagram*

1.6.4 Wrapping molding

Wrapping molding technique allows to produce small pipes of low diameters and thickness with great manufacturing precision. Prepregs, already cut appropriately, are wrapped on a mandrel following an appropriate rolling sequence. The wrapping machine (Figure 1.22) is constituted by two mobile planes that moving close one to the other produce the wrapping of the prepreg ply on the mandrel [6]. At the end of the lamination, the piece is wrapped into a film of heat-shrink material, so that during the subsequent curing process, a suitable pressure can be applied on the material due to the shrinkage of the film. This pressure exercised by the heat shrink film on the laminate performs the following functions [45]:

- Contribute, together with the pressure exerted by the autoclave, to consolidate the product.
- Preventing the resin from leaking during the initial phase of the treatment process.
- Prevent the formation of bubbles due to the release of air and volatile substances eventually dissolved in the resin.

The design of the geometry greatly influences the quality and cost of the finished product [6]. In fact, a bad design or construction can result in damage to the fibers, dimensional errors and excessive residual stresses [5].

Figure 1.22: *Wrapping machine*

1.7 Recycling of CFRPs

In the last years, CFRP industry has been experiencing a steady growth, in particular towards new mass-oriented market segments, instead of being limited to high value-added market sectors. According to the latest projections, the global demand is estimated to reach 194.000 tons per year by 2022 [46]. Such an increase in CFRPs is now imposing significant and critical studies regarding their end-of-life (EoL); furthermore, an increase of wastes deriving from the production processes (offcuts of prepregs; offcuts and scraps of cured composites) was generated by the intensification in the production of CFRPs. The investigations have led to the development of new procedures and technologies to process CFRPs in order efficiently recycle and re-use them. The recycle of CFRPs is one method for reducing environmental impact and resource depletion [47]. This can help to preserve natural resources, since CFRPs are currently prepared from non-renewable petroleum derivatives, and to reduce the quantity of residues in landfills and the quantities of waste requiring a costly disposal. In addition, recycling a CFRP implicates recovering a high cost and energy-intensive materials, the carbon fibers. CFRPs, as well as all the others Fiber-reinforced polymers (FRPs), due to their heterogeneous composition, are intrinsically difficult to separate in the single components. In addition, the crosslinked nature of thermoset resins (which are not recyclable), and the combination with other materials (additives, fillers, fixings, honeycombs, metals, hybrid composites, etc.) make even more problematic the CFRPs recycling. For many years CFRP waste has not been controlled, therefore in order to protect the environment and encourage recycling to take place, new legislations were introduced [48]. New economic and environmentally friendly technologies are studied in order to provide new potential and sustainable methods to obtain renewable carbon fibers. However, one of the major obstacles against the recycling of CFRPs is the uncertainty about the cost-effectively process: carbon fibers retrieved from high-performance materials cannot be reincorporated in the same kind of products with the same application. For this reason, in order to reclaim carbon fibers, new suitable uses were developed; in particular new recycled carbon fiber polymer (Re-CFRP) can be produced through a re-impregnation of fibers with a new polymer matrix. Therefore, the existing manufacturing processes, developed for virgin materials, must be adapted to the unique recycled-fiber form. The mechanical properties of recycled fibers are also strictly dependent on the recycling process adopted: the recycled carbon fibers in fact are usually fragmented into short lengths due to the breakage and chopping during the recovery. In addition, all recycling processes remove the sizing from the fibers and the final products are in a filamented, random, low-density-packed form [49]. In the last two decades, many different recycling techniques have been proposed and developed for thermoset composite materials such as mechanical processes (mainly grinding), pyrolysis and other thermal processes such as oxidation in fluidized bed, microwave, and solvolysis. A general description of the most relevant recycling CFRPs techniques is reported in the next paragraphs.

1.7.1 Mechanical recycling

The mechanical recycling consists in breaking-down CFRP waste more finely by shredding, crushing, milling, or other similar mechanical process. First, the material is shredded into pieces of 50-100 mm size and then is grounded into a finer product ranging from typically 10 mm down to particles less than 50 μm in size. In the mechanical recycling process, all the constituents of the original composite are reduced in size and the final product is composed by a mixture of polymer, fibers and additives. These powders can find application as a filler or reinforcement in new composite manufacturing or in construction industry such as artificial woods, asphalt or as mineral-sources for cement. However, this technology does not recover carbon fibers but only a low-value product. Mechanical recycling is mostly used for glass fiber reinforced polymers (GFRPs) or thermoplastic CFRPs.

1.7.2 Pyrolysis

Pyrolysis process involves the thermal decomposition of organic molecules in inert atmosphere (N_2 or Ar) and in absence of oxygen. When pyrolysis is applied to CFRPs, it allows volatilizing the polymeric matrix into lower-weight molecules, while the carbon fibers remain inert and can be eventually recovered. The thermal decomposition of polymer chains generally occurs, when the material is heated up to 450°C to 700°C and it leads to the formation of oil, gases and solid products (carbon fibers, fillers and char). After pyrolysis treatment, char can contaminate the recycled carbon fibers and a post-treatment in an oxidative atmosphere at 450-600°C is required to burn it before reusing them. The best advantages of pyrolysis processes are the high retention of carbon fiber mechanical properties and the possibility to recover chemical feedstock from the polymer matrix. Among the CFRP recycling processes, pyrolysis have reached an industrial scale and some CFRP pyrolysis industrial plant are already running [48–50].

1.7.3 Fluidised bed

Fluidised-bed process has been applied to the recycling of CFRPs [48]. This process consists in degradation the polymeric matrix in a hot and oxygen-rich flow using a fluidised bed plant. CFRPs are initially reduced in size and fed into the plant, previously filled with a silica sand with a particle size of about 0.85 mm. When the sand is fluidised with a stream of hot air at temperatures in the range of 450–550°C the resin decomposes; both the oxidised molecules and the carbon fiber filaments are carried up within the air stream, while heavier metallic components sink in the bed. Then fibers are separated from the gas stream in a cyclone, and the resin is fully oxidised into a high temperature secondary combustion chamber. The fluidised bed process does not allow recovery of chemicals from the polymer matrix but energy can be recovered from the combustion of products in the secondary chamber. This technology generates clean carbon fibers with typically 20% lower strength than pristine fibers with retention of the original stiffness when processed at 550°C [48]. With this technology is possible to treated also mixed and contaminated materials, with painted surfaces, foam cores or metal insert; for this reason, fluidised bed-process is particularly suitable for end-of life waste, however it has not largely been applied to recover carbon fibers.

1.7.4 Solvolysis

Solvolysis consists of a chemical treatment to degrade the resin using a solvent. When the solvent is in vapour phase or has a gas-like density in the supercritical fluid state, the process is more a thermal process than a solvolysis [51]. This process offers a large number of possibilities thanks to a wide range of solvents, temperature, pressure and catalysts usable. This chemical method for CFRP recycling is based on a reactive medium such as a catalytic solutions, benzyl alcohol and supercritical water, under low temperature (typically <350°C) [48, 51]. The reactive solvents, sometimes in mixture with a co-solvent or with a co-reactive solvent, diffuses into the composite and breaks specific bonds. It is therefore possible to recover monomers from the resin and to avoid the formation of char residues. Polyester resins are generally easier to process than epoxy resins and require lower temperatures to be degraded. During the last decade, as the recovery of carbon fibers has become economically interesting, this method has been more intensively used to recycle composites, in particular CFRP [50, 51]. Among all the tested solvents, water appears as the most used, sometimes alone, and sometimes with a co-solvent (alcoholic, phenolic, amine) [48, 51]. A few other solvents have also been used, mainly alcohols like methanol, ethanol, propanol, acetone or even glycols, with or without additives/catalysts. Numerous lab-scale experiments have been carried out, but only a few studies have reached semi-industrial or industrial scale; in addition, some environmental issues might arise when aggressive and toxic solvents are used [48, 51].

1.8 Epoxy resin: health, safety and environmental impact

Most epoxy resins are obtained from the reaction between an epoxy precursor (pre-polymer) and a hardener. Almost 75% of the epoxy resins produced in the world are based on diglycidyl ether of bisphenol A (DGEBA), produced from the reaction of bisphenol A and epichlorohydrin in the presence of sodium hydroxide. The structure of bisphenol A, containing aromatic rings, allows to achieve good thermal and mechanical resistance to the final product [52]. Unfortunately, bisphenol A is classified as a reprotoxic R2 substance [33] and, as endocrine disruptor, can mimic the hormones of the body leading to several adverse health effects [54], including alterations of both the immune system and the reproductive system along with changes in the neurological system [54].

Concerning epichlorohydrin, it was classified by IARC (International Agency for Research on Cancer) in group 2A (probable carcinogenic to humans) [55]. This substance may contaminate drinking water supplies, through flocculants based on epichlorohydrin or epoxy coated tubing, since it is slowly hydrolyzed in aquatic environments [56]. Epichlorohydrin is easily absorbed through oral, respiratory or skin exposure and it is able to reach various organs such as kidney, liver, pancreas spleen and adrenal glands [57]. No embryotoxic, fetotoxic or teratogenic effects were observed. In in vitro and in vivo tests, epichlorohydrin has been shown to be mutagenic and to induce chromosomal aberrations [58]. Carcinogenicity studies have pointed out that this substance induces the onset of squamous cell carcinomas in the nasal cavity after inhalation, and gastric tumors following oral exposure. In humans, acute exposure to epichlorohydrin causes severe local irritation and damage to the central nervous system [59]. Chronic exposure in the workplace seems to be among the factors responsible for an increase in tumors and heart disease [60].

The crosslinking reaction of epoxy resins requires the use of hardening agents, such as anhydrides or amines. Anhydride hardeners, such as trimellitic anhydride, are strongly irritating to skin, eyes and respiratory tract and can cause burns [61]. Instead, amine hardeners can be either aliphatic or aromatic. Aliphatic amine, such as diethylenetriamine (DETA) or triethylenediamine (TETA), are strong bases with low molecular weight. They are moderately toxic by ingestion, inhalation or by contact with skin, and are also irritating agents for eyes or skin and corrosive in undiluted form. The risk of exposure to the highly irritating vapors of these substances increases with the volatility of the amines and if high temperatures are required in the treatment process [62]. Aromatic amines such as methylenedianiline (MDA) are less corrosive, irritant and sensitizing than aliphatic amines. However, in this group of compounds there are substances identified as carcinogens for animals and humans. If swallowed, these can cause severe damage to internal organs, especially to the liver and kidneys, as well as reducing the ability of the blood to transport oxygen, due to the formation of methemoglobin. It is important to strictly avoid exposure to this class of hardeners by inhalation and in particular by the dermal route [63]. In terms of environmental impact, it should be noted that liquid epoxy resins and some reactive diluents are not easily biodegradable. Although epoxy functions are hydrolyzed in contact with water, they have a potential for bioaccumulation and are moderately toxic to organisms. These products are generally classified as harmful to the environment in accordance with the classification criteria of the European Union [64]. Waste obtained from the production of epoxy resins must be treated as hazardous waste in accordance with national regulations [65]. Finished articles made of fully polymerized epoxy resins are hard and infusible solids that pose no risk to the environment [66].

1.8.1 B*io-based* thermosetting resins: present and future

Thermosetting materials account for less than 20% of plastic production and globally, epoxy resins make up at least 70% of the market for thermosetting resins [67, 68]. The global production of epoxy thermosetting polymers has been estimated at 2 million tonnes in 2010 and is expected to reach 3 million tons by 2018. Their global market was estimated around 18 billion $ in 2012 and reached 21.5 billion $ in 2015 [69, 70]. The control of the final properties of the product and the whole process are generally based on the selection of appropriate epoxy precursors or combination of monomers, on the selection of the hardening agents and on the addition of organic or inorganic fillers and other components. Concerning the price and availability of oil, in addition to global policies and institutional trends towards green and ecological chemistry, it is necessary to lead the chemical industry towards a sustainable chemical. In order to produce chemical products from bio sources, renewable materials, derived from plant, animal or fungal, were deeply investigated [67]. Epoxy resins partially or totally derived from bio sources are nowadays an essential goal and a challenge from both an academic and an industrial point of view and, to date, several studies have already been conducted [9].

1.8.2 Bio-Epichlorohydrin based epoxy monomers

Epichlorohydrin is conventionally used to obtain epoxy monomers following reaction with hydroxyl compounds [71], however, epichlorohydrin is classified as a carcinogen agent. Usually, it was obtained from the hydrochloration of allyl chloride, which was synthesized by the reaction between chlorine and propylene. Today, epichlorohydrin is industrially produced from bio-based glycerol (Figure 1.23) [67, 72].

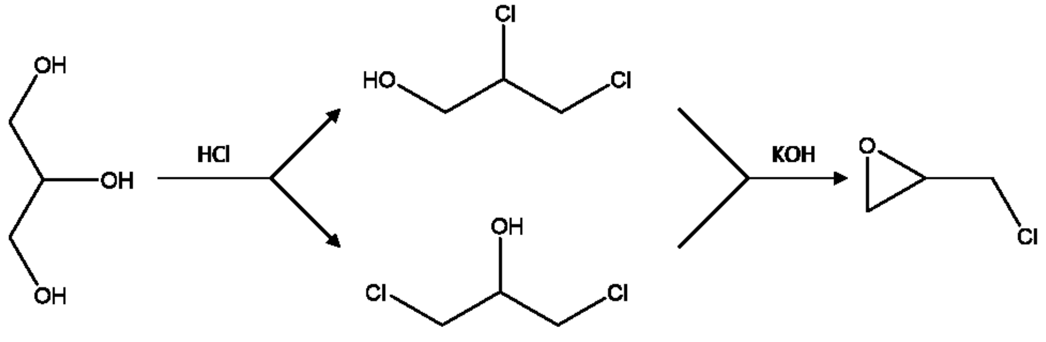


Figure 1.23: *Synthesis of Epichlorohydrin from bio source*

This process provides about 100 kt per year of product [73], moreover the conversion of glycerol into epichlorohydrin is economically convenient. The weight content of DGEBA from bio source is about 25% if the synthesis is made from this bio-based reagent [74].

1.8.3 Epoxy monomers obtained from polyphenol derivatives

As previously mentioned, epoxy monomers can easily be obtained, without the use of epichlorohydrin, from the oxidation of a carbon-carbon double bond. Two different strategies are used, depending on the type of double bond in natural products:

- When natural reagents already contain double bonds in the aliphatic chain, such as vegetable oils, the epoxidation reaction is carried out in the presence of H_2O_2 [74], since hydrogen peroxide is probably the best oxidizing agent containing O_2 both from an economic and environmental point of view.
- Whether allyl type double bonds are present, stronger oxidizing agents than hydrogen peroxide must be used to obtain the epoxy groups [75].

1.8.4 Epoxy monomers obtained from tannins

One of the new renewable resources used to produce epoxy resin are tannins. Tannins are non-hazardous products with antiallergenic and antimicrobial properties. These positive effects on human health can be associated with the antioxidant properties of these compounds [76]. Tannins are natural poly-phenolic molecules and can be found as hydrolysed tannins, condensed tannins, complex tannins and florotannins. Both hydrolysed and condensed tannins are used for the preparation of epoxy monomers. In particular, catechin and gallic acid are the most investigated tannin derivatives. Catechin can be epoxidized by reaction with epichlorohydrin or by alkylation with a halogenated unsaturated compound followed by its oxidation [77]. The characterization of the obtained compounds shows the presence of by-products, which decrease the average epoxy functionality. These by-products result from an internal cyclization reaction between phenolic alcohol and epichlorohydrin after its addition through a SN_2 mechanism (Figure 1.24) [67, 78].

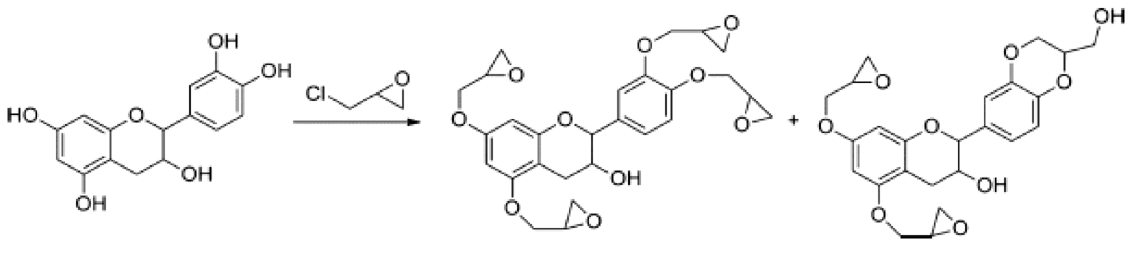


Figure 1.24: *Epoxy monomer and by-product of catechin epoxidation reaction*

Gallic acid can be easily found mostly in vegetables, especially in Gallic walnuts, and can be combined with a tannic structure. The epoxidation of Gallic acid with epichlorohydrin or with other halohydrins, occurs through the addition of this on both the carboxylic acid group and on at least one phenolic group (Figure 1.25) [67, 79].

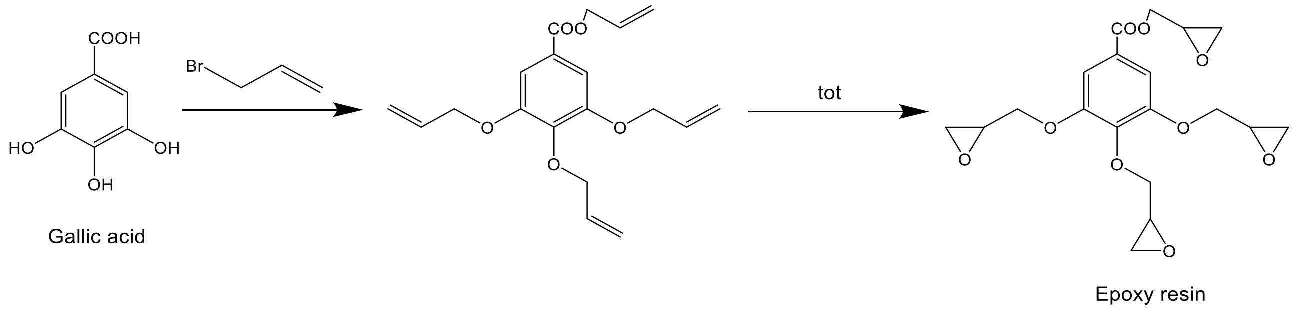


Figure 1.25: *Epoxy monomer obtained from Gallic acid*

1.8.5 Epoxy monomers obtained from cardanol

Another rich source in polyphenols, is represented by the liquid contained within cashew nuts (Western Anacardium), a renewable natural resource obtained as a by-product during the process of removing the walnut kernel from a nut [80]. The total production of Cashew liquid is approaching 1 million tons every year, and is one of the most important and economic sources of natural phenols. Cashew nut liquid can be considered as a versatile and precious raw material for the production of polymers and represents a good natural alternative to petrochemical phenolic derivatives. It constitutes almost 25% of the total mass of the nut and is composed primarily of anacardic acid with the long saturated aliphatic side chain, with an average value of two double bonds per molecule [81]. The partial decarboxylation of the anacardic acid, contained in the cashew nuts, is induced by heat treatment. The result is industrial cardanol, in the form of a yellow oil, containing mainly cardanol (about 90%), with lower percentages of cardol and methylcardol [67, 82] (Figure 1.26). Thanks to its aromatic and aliphatic structures, cardanol seems to be a promising candidate for the substitution of petrol-based phenol derivatives. Moreover, cardanol improves mechanical and chemical resistance, flexibility and the anti-corrosion [83].

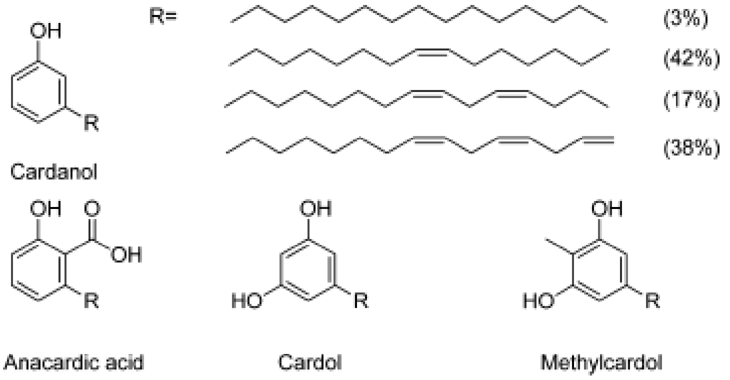


Figure 1.26: *Cardanol structures and other compounds extracted from cashew nut liquid*

The epoxy monomers are synthesized from cardanol mainly by two methods: the first is the epoxidation of the double bond in the presence of enzymes (lipase) and acetic acid in toluene, with the addition of H_2O_2 during the reaction; then the epoxidized compound is polymerized with H_2O_2 in the presence of 2-propanol at room temperature (Figure 1.27) [67].

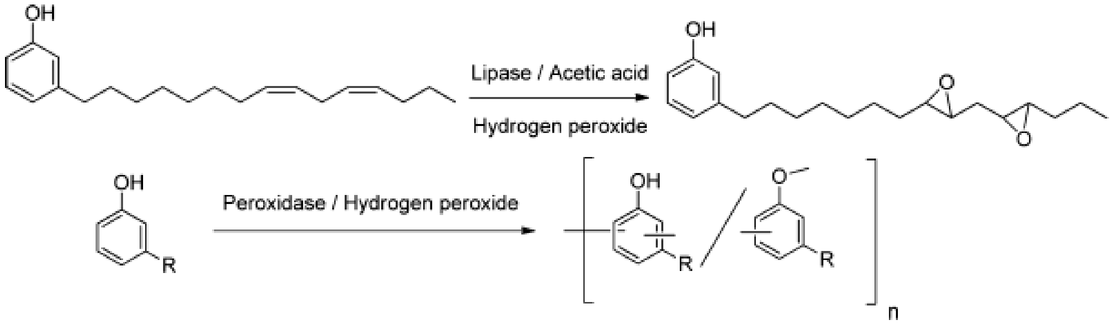


Figure 1.27: *Cardanol e poxydation and polymerization*

The second method is a phenolization of cardanol followed by a reaction with epichlorohydrin of the obtained diphenol (Figure 1.28).

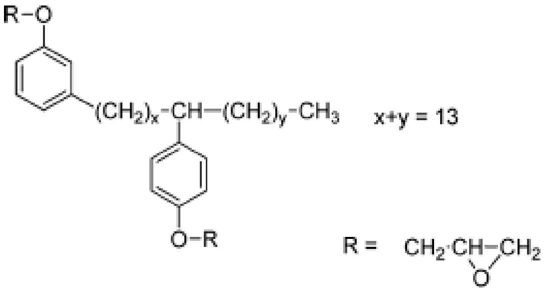


Figure 1.28: *Diepoxy-cardanol structure*

1.8.6 Epoxy monomers obtained from lignin

Natural polymers, including cellulose, hemicellulose, polysaccharides, lignin, chitin and chitosan, are considered as abundant and low-cost raw materials. Lignocellulose includes lignin, cellulose and hemicellulose, which are covalently linked [84]. The first step to obtaining molecules usable as new epoxy resins sources, consists in the deconstruction of the wood. The decomposition can be carried out through physical or chemical processes, such as high temperature steam, acids, bases, phenols or ozone, followed by an extraction in water or methanol. At the end of the purification processes it is possible to isolate the lignin (Figure 1.29), a highly crosslinked complex polymer composed by substituted phenols. The main functional groups of lignin are hydroxyl, methoxyl and phenylpropane units, which allow copolymer grafting. The individual units are connected by aryl-alkyl-ether bonds to form a three-dimensional network [67]. The presence of an aromatic and crosslinked structure gives relatively good thermal resistance and good mechanical properties [85].

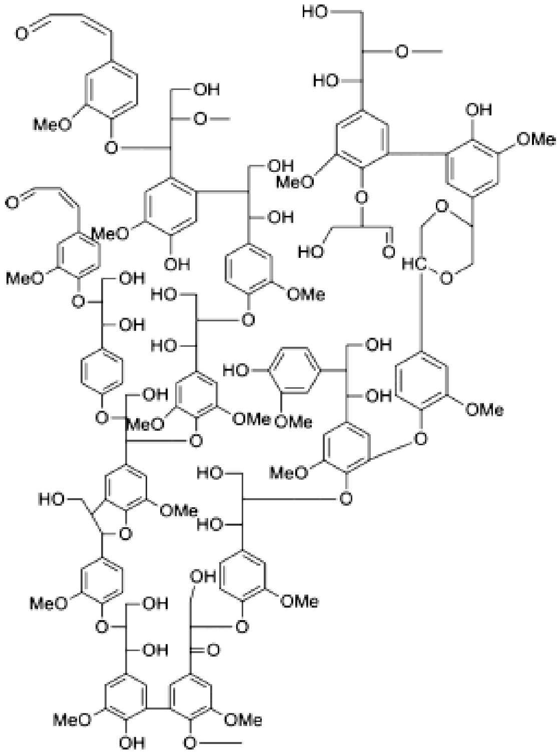


***Figure 1.29:** Lignin structure obtained from wood*

Lignin can be extracted from biomasses and reduced to oligomers by different processes:

- The **sulfite process** with SO_2, sulphites and sulfuric acid, allows the hydrolysis of ether and ester bonds in acidic environment. This technique, performed at high temperatures and under high pressure, leads to lignin fragmentation, which after degradation, becomes lignosulphate.
- The **Kraft process**, used to produce lignin containing aliphatic thiols, consists in the hydrolysis in basic environment in presence of Na_2S. A further process is based on the use of anthraquinone as a catalyst in the presence of NaOH. Both processes allows to obtain lignin from modified structures [86].

- **The solvolysis process** allows the extraction of lignin through the addition of organic solvents. It leads to an organolysis and a lignin with a high degree of purity is obtainable.
- The **CIMV process** (Compagnie Industrielle de la Matière Végétale), allows the production of white lignin from vegetable sources at atmospheric pressure using a catalyst-solvent system based on formic acid / acetic acid / water [87].

Other chemical and physical processes (such as solvent extraction) have been developed, but rarely applied on an industrial scale [88]. Lignin, after extraction and purification, can be epoxidized through three processes. The former, mainly aims to increase the content of the phenolic groups in the lignin [89]; acetone is used to create in situ, inter-sulfur bridges. Phenolated lignin reacts with epichlorohydrin, leading to epoxidized lignin [90]. The ideal molar mass for lignin is in a range of 300 to 10000 g/mol and the glass transition temperature, T_g, of the resulting epoxy resin based on lignin, is higher than 180°C [84]. In the second process, the lignin reacts with an aliphatic dioxide compound in DMF at 80°C in order to obtain a lignin functionalized with epoxy groups. The third process is based on oxipropylation of lignin in order to obtain a functionalization of lignin with hydroxyl groups. These hydroxy groups are then converted into epoxy groups upon reaction with epichlorohydrin.

1.8.7 Epoxy monomers derived from vanillin e levulinic acid

An additional way to obtain epoxy precursors from renewable sources involves chemical degradation and transformation of natural polymers. Lignocellulosic biomasses represent an abundant and sustainable raw material and source of multiple aromatic compounds. Lignocellulose consists of lignin, cellulose and hemicellulose. In particular, cellulose consists mainly of C6 and C5 sugars (glucose polymerization), while hemicellulose is a glucose and xylose polymer. Several bio-refinery processes lead to the production of primary synthons such as vanillin, 2-pyrone, 4,6-dicarboxylic acid, p-coumaryl acid, coniferous acid, synaptic and muconic acid [91]. Several research groups have already used vanillin to synthesize bio-based epoxy monomers by a chemo-enzyme process with Antarctic Candida lipase (Figure 1.30) [67]; the obtained epoxy resins showed interesting thermal properties.

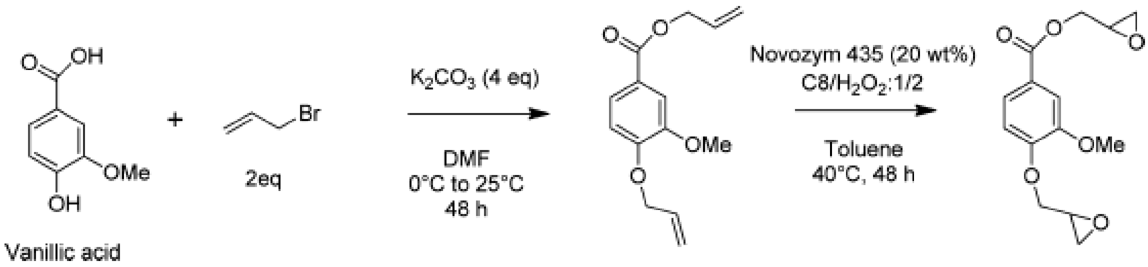


Figure 1.30: *Epoxidation of vanillic acid via chemoenzymatic process*

A further process has been reported regarding the synthesis of epoxy monomers starting from vanillin (Figure 1.31) [67]. Interactions between methoxy and hydroxyl groups have been shown to improve impact strength and tensile and elongation strength [92]. In several studies, the conversion in the same reactor and in a single step of the intermediate lignocellulosic raw materials has been proposed. For example, the Biofine Process [93] has developed a process of high-temperature diluted acid hydrolysis that converts cellulose biomass into soluble sugars which are then transformed into a mixture, composed at 50% of levulinic acid, which can react as both a carboxylic acid and a ketone [94].

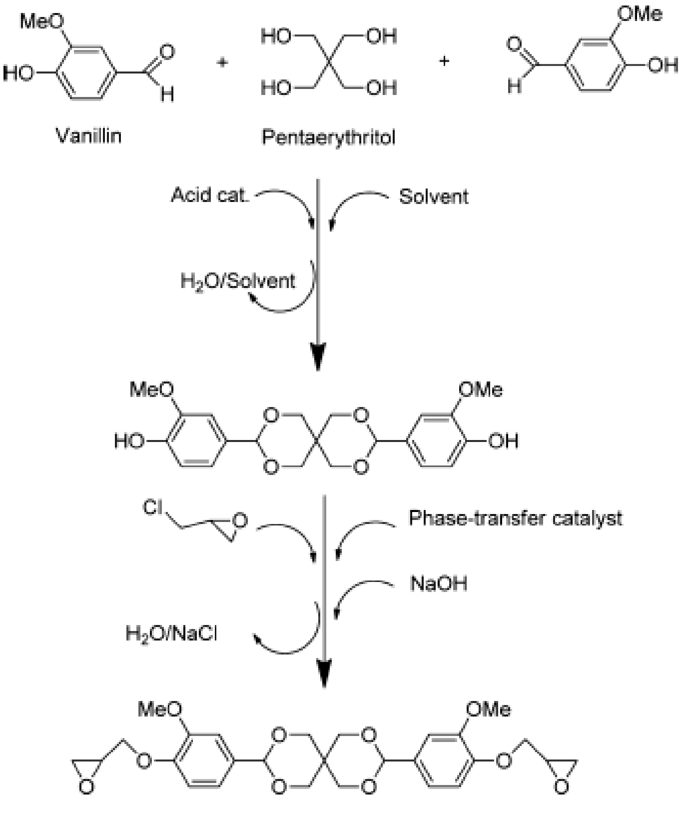


Figure 1.31: *Synthesis of a difunctional epoxy monomer from vanillin*

The catalyzed hydroxyalkylation of this compound leads to the formation of a bio-diphenol (Figure 1.32) [67], which was once commercially used in various epoxy formulations, before it was replaced by the petrochemical derivative bisphenol A which is supplied at a lower price. However, a reduction in the cost of producing levulinic acid could allow the diphenolic acid to recollect part of the market share.

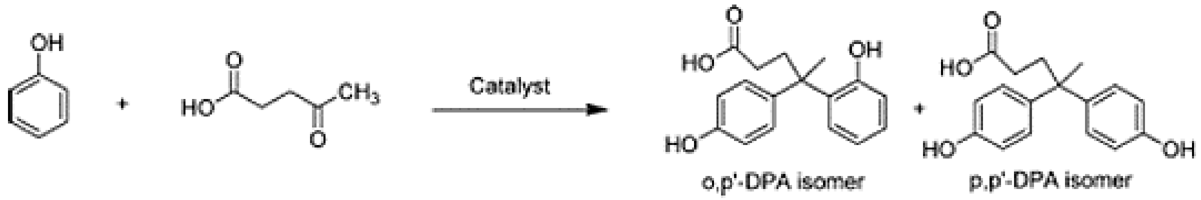


Figure 1.32: *Synthesis of the diphenolic acid*

1.8.8 Epoxy monomers derived from carbohydrates

The carbohydrates deriving from biomass are the most abundant renewable resources, since glucose is produced from starch, but also from cellulose or woody biomass by chemical transformation. Many poly-(epoxy) prepolymers, obtained from bio-source polyols, such as glycerol and sorbitol, are commercially available and are commonly of aliphatic glycidyl ether type [95]. Some studies report the synthesis of poly-(epoxy) prepolymers from glycerol (Figure 1.33) [67].

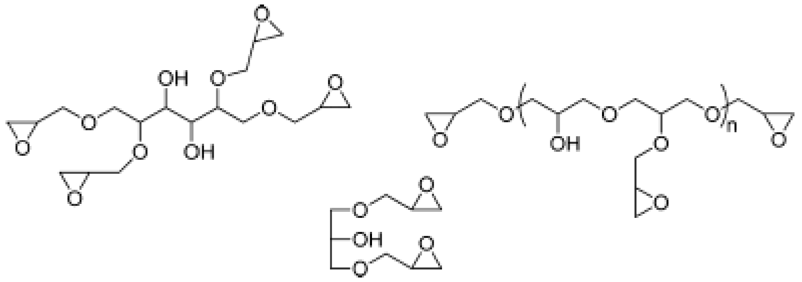


Figure 1.33: *epoxy based monomers based on glycerol and sorbitol*

The reaction of the epichlorohydrin with natural aliphatic polyols, can generate new alcoholic groups, which show reactivity quite similar to the starting polyols. There is a strong interest towards 1,4:3,6-dianhydrohexitols, in order to find new synthetic ways to produce polymers from renewable sources, mainly due to potential industrial applications that these may have. Regarding this class of compounds, isosorbide, obtained by the dehydration of sorbitol, has met considerable success. This chiral and non-toxic molecule also gives stiffness to polymer chains such as polyesters, polycarbonates and polyurethanes. Several processes allow the synthesis of diglycidyl ethers of isosorbide as well as the oligoglycidyl ethers of isosorbide. Furthermore, two methods lead to the monomer or oligomers of epoxidized isosorbide by reaction with epichlorohydrin. The first, quite similar to the synthesis of DGEBA, is based on the reaction between a diol, epichlorohydrin and a strong base in an aqueous environment (Figure 1.34) [67]. This method often also generates isosorbide epoxy oligomers.

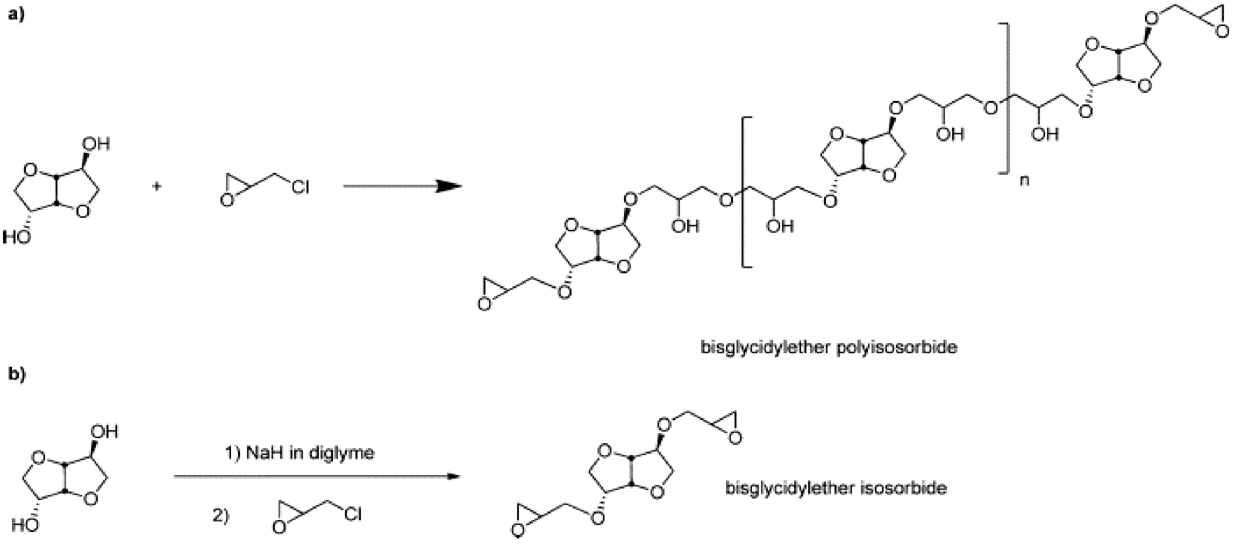


Figure 1.34: *Synthesis of diglycidyl ether of isosorbide and diisosorbide structure*

The second method is a two-step reaction, in anhydrous environment, between epichlorohydrin and isosorbide. The first step consists in generating the isosorbide alcoholate in the presence of NaH, which leads to the opening of the epichlorohydrin ring. The second step corresponds to the formation of the oxirane in the presence of a strong base. This method is selective because it only leads to diglycidyl ether disosorbide [96]. However, epoxidized isosorbide can also be obtained through the reaction with allyl bromide as shown in Figure 1.35 [55].

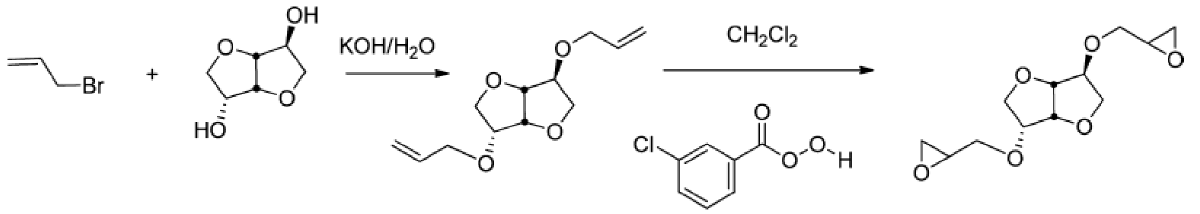


Figure 1.35: *Synthesis of diglycidyl ether of isosorbide by oxidation reaction*

A further way to obtain epoxy prepolymers uses starch and sugar as a basis, in particular from lactic acid, succinic acid, itaconic acid, etc. Lactic acid, used as a lactide and glycidol, can give both linear and hyper-branched epoxy prepolymers, depending on the process conditions used [67]. Epoxy monomers produced from sugars are usually obtained by oxidation of the double bond, using a strong oxidizing agents such as MCPBA in large excess. In the literature it is reported the oxidation of sucrose which has both allylic and crotonic groups; the use of aqueous peracetic acid allows to perform an efficient epoxidation reaction [97]. From what has been said so far, we can deduce that versatility is one of the strengths of epoxy polymers and that different methods to obtain epoxy prepolymers starting from waste materials or in general from renewable sources already exists.

1.9 Amine-based curing agents from renewable sources

Hardeners also play an essential role in the improvement of mechanical and thermal properties of epoxy resins. The main epoxy hardeners are mercaptans, carboxylic acids, anhydrides, amines and phenols. Amines are the most widely used hardeners [98], and can be applied for different purposes depending on their structures and the final properties of the desired product. Aliphatic amines are very reactive and can be used even at room temperature [99] and cycloaliphatic amines are very versatile: they show a good balance between reactivity and final properties. By the other hand, aromatic amines are the least reactive but provide better mechanical properties (high T_g), in addition to a higher resistance to heat and chemicals. Since the structure and functionality of hardeners strongly influence the final properties of the material, having a wide range of curing agents with different structures, functionality and reactivity, to modulate the properties of epoxy thermosets, is of fundamental importance. In literature, information regarding bio-based amine hardeners, such as amino acids (tryptophan, lysine) [100, 101], plant oils, isosorbide or chitosan, are scarce. To date, there are only a few commercial solutions based on renewable sources. To be accepted as valid solutions, bio-based formulations must offer the same versatility as conventional products. In order to modulate the final properties of epoxy thermosets as much as today is done with fossil hardeners, it is necessary to increase the number of amine-based hardeners from bio-available sources, to choose from. Furthermore, it is also of utmost importance to compare the properties that these new hardeners provide with existing systems. Nowadays, two types of amines from renewable sources can be highlighted; the former are synthesized from modified compounds such as fatty acids, sugar derivatives, and others, while the latter are made up of bio-resources having amino groups, such as chitosan, or containing amines such as amino acids.

1.9.1 Bio-based amine from vegetable oils and sugar products

Amine-based hardeners can be produced from renewable sources through derivatization reactions, which are carried out with nitrogen-containing reagents. If nitrogen is not present in the starting materials, the addition of an amino function can be performed on all the molecules containing ester/acid functions and double bonds in the structures [102].

Two of the most common methods are reported in the literature to synthesize ω-amino acids from vegetable oils [103]. The first involves the use of purified linoleic acid which is transformed into poly-amino acid by reaction with liquid ammonia, while in the second method the double bond of the fatty acids reacts with tetranitromethane followed by a subsequent reduction reaction [104–106]. There are also other types of production processes, which lead to the formation of mono or di-functional amines, such as the catalytic reduction of nitriles, direct amination or amidification with diamines starting from dimers of fatty acids. Diamines such as 1,4 butandiamine can be obtained from succinic acid. Renewable succinic acid is obtained through different types of fermentation processes of carbohydrates, mainly from glucose [107]. For example 1,6-hexamethylenediamine, is produced by adipodinitrile, obtained from adipic acid, which can be converted into 1,6-hexanediol and adipodinitrile through amidation and dehydration. Adipic acid can also be produced through a green process of carbohydrates by fermentation [108]. There are also other ways that involve the use of other fatty acids such as azelaic acid, extracted from rapeseed oil, to synthesize for example the 1,9-nonan-diamine, usually produced with butadiene from fossil sources [96] . In literature are also reported some processes of catalytic amination of alcohols from renewable sources using ruthenium or iridium catalysts. Recently it has been proposed a catalytic system able to selectively convert various bio-alcohols and diols into primary amines using ammonia at high temperatures. Evonik, has patented a process to produce aminated isosorbide by simple amination of this, with ammonia [109]. The aminomethyl-hydroxymethylfuran derivatives, well known for their pharmacological properties, should also be mentioned. Such structures are generally produced both by furfuryl alcohol and by furfural. However, the procedures for converting pentosans or pentoses into furfurylamine require difficult reaction conditions, with low selectivity, in a two-step process, which involves acid-induced dehydration to obtain furfural followed by a reductive amination. Similar reactions are also performed between furfurylamine and formaldehyde (Figure 1.36), including aldehydes and ketones, to obtain amines in dimer form [99].

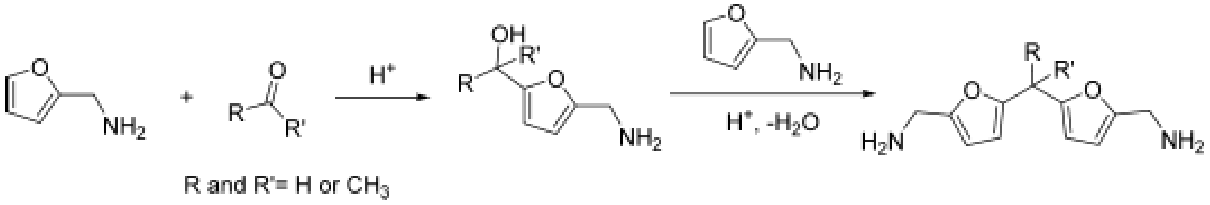


Figure 1.36: *Reaction between furfurylamine and an aldehyde*

1.9.2 Bio-based amine from chitosan

Chitosan is obtained from chitin deacetylation (Figure 1.37), which is the most abundant natural polymer in the world after cellulose, it is present in shells of crustaceans, insects and fungal walls and its global availability is estimated at 10^9 tons.

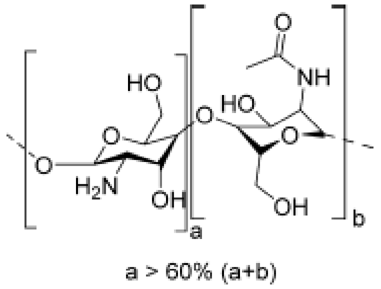


Figure 1.37: *Chitosan structure*

This bio-polymer is cheap and has interesting properties: it is bio-compatible, bio-degradable, non-toxic and antibacterial. It is a weak acid and has different functions along its chain: primary alcohol, secondary alcohol, amine and amide, if the deacetylation process is not complete. Because of its high molecular mass, it is difficult to use chitosan directly as a reactive amine. Therefore, chemical, physical or enzymatic modifications are necessary to increase the solubility of this polymer. Various modification methods are reported in the literature, for example chitosan can be depolymerised to reduce its molecular weight and thus improve its solubility. Another method consists in a reaction with hydroxybenzotriazole (HOBt) in order to solubilize it in water. HOBt forms a complex with the amino groups of chitosan, then an organic salt soluble in water is obtained (Figure 1.38).

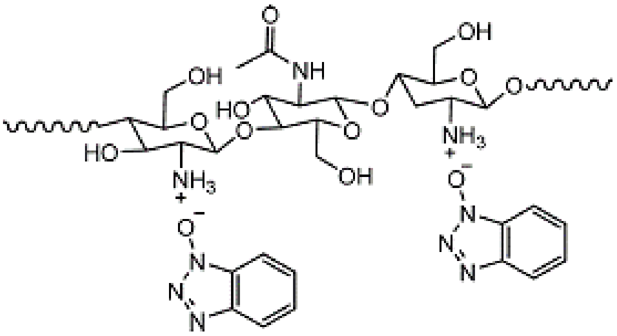


Figure 1.38: *HOBt – Chitosan complex*

1.9.3 Bio-based amine from amino acids

Peptides and amino acids are perhaps among the most important bio-molecules possessing amino groups. It is possible to distinguish amino acids already containing amine groups and modified amino acids (products containing mono or diamine) obtained through decarboxylation reaction [110], or by deamination (Figure 1.39) [111]; this reaction is used for example for lysine or for diacids such as glutamic acid.

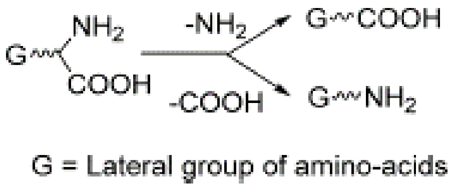


Figure 1.39: *Possible deamination or decarboxylation of an amino acid*

In literature, amino acids are one of the more studied class of compound able to be used as amine hardeners, since they are one of the few available source examples of natural renewable amines. Enzymes and bacteria allows the transformation of biomass into different basic amino acids in a specific and targeted way and through the biochemical processes of decarboxylation, a large variety of amines can be obtained [112]. However, the ideal hardener for material applications should have at least two amine functions or an amine function and another reactive function to participate in the epoxide opening process. The most studied amino acids for this purpose are lysine, glutamic acid and tryptophan (Figure 1.40) [113], known to be ecofriendly curing agents for epoxy resins, in which both the amine and carboxyl groups are capable of opening an epoxy group.

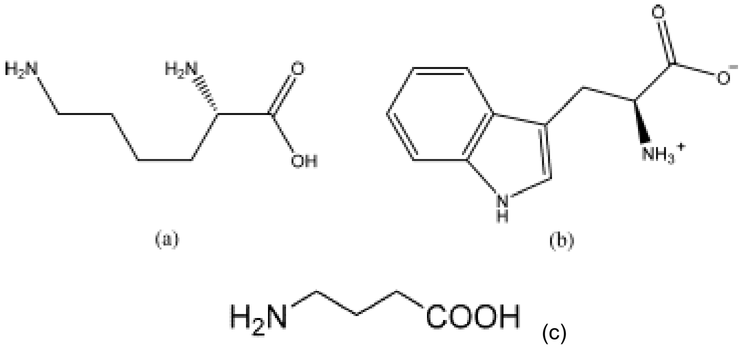


Figure 1.40: *Chemical structure of (a) Lysine, (b) Tryptophan and (c) Glutamic acid*

Glutamic acid has a higher production compared to lysine and tryptophan, and is also the main component of bio-fuel production waste such as bio-ethanol. Glutamic acid is a good starting point for the creation of different amines and other useful products, such as N-vinyl-2-pyrrolidone (NVP) or acrylonitrile, which is an interesting molecule for the synthesis of amines from alcohols [111]. From the data reported in the literature, however, it can be seen that epoxy resins obtained from DGEBA and crosslinked with lysine or glutamic acid exhibit T_g and thermal degradation temperatures reasonably lower than those reticulated with tryptophan [114]. This phenomenon can be explained considering that tryptophan is composed of a partially heterocyclic system that makes the final product more rigid and thermally stable. Polymers consisting almost entirely of aromatic systems, have received much attention in recent times because of their unique properties such as thermal stability, mechanical properties and superior chemical resistance [115]. Although great progress has been made, the combination of good thermal and chemical properties and unique features for high-performance polymers is still a major challenge.

1.9.4 Use of Purine as crosslinking agent for epoxy resins

In order to obtain the desired properties in a composite material, fully heterocyclic molecules, having amine functional groups, could be the used as hardeners [116]. Starting from tryptophan, similar and even more satisfactory results could be achieved, taking into account other nitrogen containing heterocyclic systems without lateral aliphatic chains, such as purines, in particular nitrogenous bases such as Adenine (Figure 1.41).

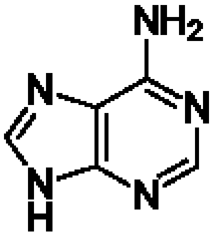


Figure 1.41: *Chemical structure of Adenine*

Adenine is an amino-substituted purine known to be an important part of DNA. This molecule has gained a lot of attention due to its marked bio-activity and unique bio-compatibility [117]. Several studies have also shown that Adenine can easily be obtained on an industrial scale even by fermentation processes [118]. In the last years, the studies carried out on this molecule have been predominantly in the medical field [119] but recently, due to its particular heterocyclic aromatic structure, Adenine has attracted many researchers to study its applications in composite materials. In fact, thanks to its stable heterocyclic structure, in the presence of both proton donors (-NH-, =CH-), and of proton acceptors (=N-, C=O) and to hydrogen bonds, Adenine represents a potential from renewable sources for the design of high-performance polymers [104].

Adenine can be produced from DNA degradation and specifically obtained by fermentation through the production of adenosine (Figure 1.42). Fermentation occurs mainly on an industrial scale through microbial fermentation (Figures 1.43), with yields up to 16.4 g/l [113].

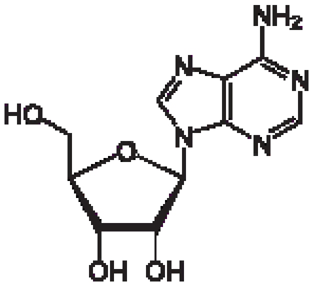


Figure 1.42: *Chemical structure of Adenosine*

Figure1.43: *Batch and continuous industrial bio-reactor*

The microbial production of this molecule has attracted a lot of attention because of its inexpensiveness and because of the environmentally friendly production process, compared to the chemical production processes of this substance (Figure 1.44).

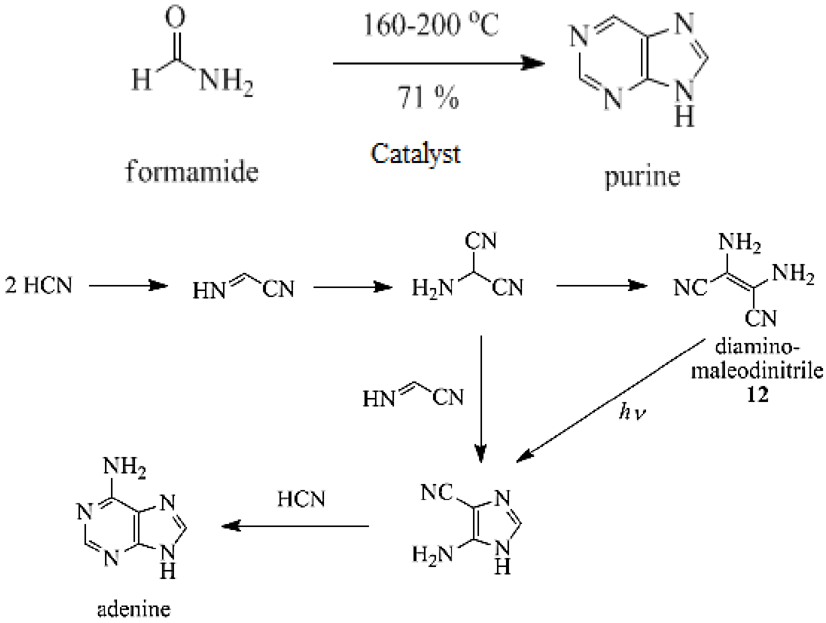


Figure 1.44: *Some chemical production processes of Adenine*

Bacillus subtilis is one of the candidates for the industrial production of adenosine; it is also known to be a safe and stable producer of inosine, guanosine and other valuable enzymes involved in commercial processes [120]. Nowadays adenosine strains used in the biotechnology industry were mainly obtained by random mutagenesis, induced by ultraviolet radiation, treatment with diethyl sulfate, or with low-energy ions. However, these conventional methods rely on the chance to find the desired mutants among the resulting colonies, which however inevitably accumulate numerous unidentifiable and unwanted changes. Furthermore, unwanted changes in physiology and growth delays can occur. Therefore, in order to increase the production of adenosine, it must be adopted appropriate strategies based, for example, on the transcriptional analysis of key genes involved in the synthesis of adenosine or on the analysis of the metabolite pool, in order to identify the main metabolic obstacles to production of adenosine [121]. The concentration of adenosine produced through these processes is generally measured by High Performance Liquid Chromatography (HPLC), which is able to accurately quantify traces of adenosine but requires pretreatment to remove proteins and other molecules before analysis. Therefore, expensive and voluminous instruments are needed and the samples should be measured one after the other. An accurate and rapid screening method after cellular mutagenesis would seem to be that based on enzymatic analysis [108], because it can analyze multiple samples simultaneously without any specialized or expensive tool. In this regard, in literature are reported several works based on the enzyme dosage with adenosine deaminase, to determine the adenosine in the production broth of Bacillus subtilis and improve the efficiency of the screening of high yielding strains producing this substance. Adenine can be produced from adenosine as well as chemically by reduction or through bacterias (Figure 1.45), with yields up to 2.88 g/l [113]. This activity was detected, for example, in a large number of Mycoplasmatales, grown in broths or in cell cultures.

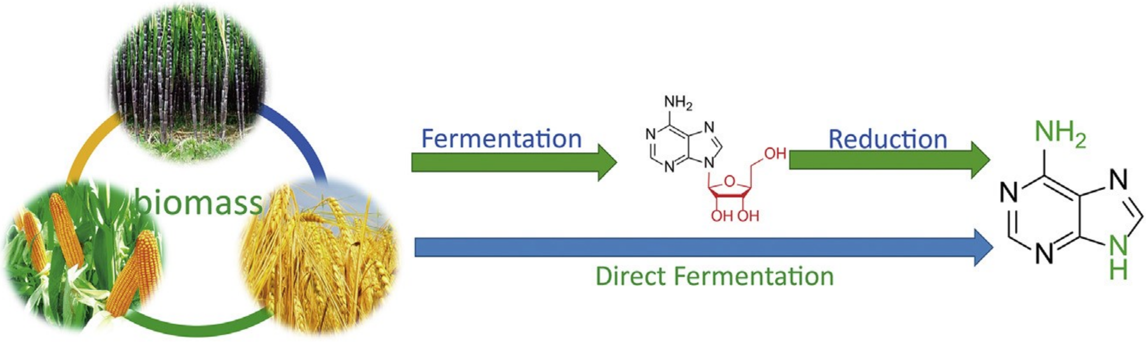


***Figure 1.45:** Direct and indirect fermentation process of Adenine*

The enzyme responsible for this transformation is adenosine phosphorylase. This enzyme is able to catalyze both the formation of adenosine from Adenine and ribose 1-phosphate.

Adenosine phosphorylase is apparently common to Mycoplasmatales but is not universal, therefore, organisms belonging to that order can be classified into three groups (Table 1.5) [109], based on their use of adenosine as a substrate.

Table 1.5: Reaction of Mycoplasmatales with adenosine.

Mycoplasmatales (species)	***Adenosine converted to***
Acholeplasma laidlawii	*Adenine*
Spiroplasma citri	
Mycoplasma arginini	
M. hominis	
M. salivarum	
M. orale	
M. buccale	
M. faucium	
M. fermentans	
M. hyorhinis	
M. gallisepticcum	
M. agalatcie var. bovis	
M. sp	
M. liophilium	*Inosine*
M. pneumoniae	*None*
M. sp.	

From the data reported, it can be observed that only thirteen types of Mycoplasma including *Acholeplasma* and *Spiroplasma*, exhibit the activity of adenosine phosphorylase. *M. lipophilium* differs from other mycoplasmas and possesses the ability to convert adenosine into Adenine by deamination, and finally *M. pneumoniae* and *M. sp* show no reaction with adenosine. The activity of these bacteria is of fundamental importance because the mammalian cells have the enzymes to convert adenosine into inosine by deamination and inosine to hypoxanthine by phosphololysis, but they do not possess the enzymes necessary to form the free base, Adenine, from adenosine.

1.10 Bio-based composite materials

Thermosetting materials represent less than 20% of the production of plastics. Globally, epoxy resins make up 70% of the thermosetting resin market [122]. The production of global epoxy thermosetting polymers was estimated 2 million tons in 2010 and is expected to reach 3 million tons by 2018. Their global market was estimated at around 18 billion dollars in 2012 and reached $ 21.5 billions in 2015 [69]. More than 60% of global production is used in the coatings industry [123]. Excellent mechanical and thermal properties are usually displayed by composite materials made from glass or carbon fibers and epoxy resins, making them widely applicable in various industrial fields. The control of the final properties of the product and the entire process are generally based on the selection of appropriate epoxy precursors, hardeners and the addition of organic or inorganic fillers and others components. However, these materials have serious end-of-life disposal, cost and health issues. As a result, in the last years, a renewed interest in renewable composite materials, that are environmentally safe, has grown. Bio-based composite materials derived from a new category of products including one or more components such as reinforcing agents and resins, obtained from a sustainable resource [124]. In the new sub-category defined as “Green composites”, both resins and fibers are most commonly derived from plants, making them fully sustainable [124]. In the last years, interest in bio composites or green composites has been growing rapidly in terms of their industrial applications such as automotive, transport, sports goods, military, structural and packaging application [125]. The greener composites combine degradable fibers with non-degradable resins and the idea of bio composites made from cellulose-based reinforcement agents and bio-based resins appears to be the best route to achieve ‘green’ composites [126].

The use of renewable resources for the synthesis of epoxy monomers, which make up most of the current resin market for advanced composites results, are now a commercially available. Even considering the high cost of the manufacturing process used to convert renewable sources into the monomers, various methods to obtain epoxy resin precursors have been developed and proved to decrease the environmental impact, such as the consumption of non-renewable resources and the risks involved in chemicals [127, 128].

Concerning the reinforcement agents, Fibers extracted from the bast layer of plant have shown considerable potential to be sustainable, environment-friendly alternatives to traditional synthetic fibers as reinforcement in composite materials [31, 33, 129–131]. Natural fibers can be subdivided into three broad categories: vegetable (plant-based), animal, and mineral fibers. Plant-based fibers can themselves be classified as either wood or non-wood fibers. Non-wood fibers may be further subdivided into bast, leaf or seed hair fibers, depending on their origin [132–134] in the plant, and wood fibers can be further subdivided into softwood and hardwood fibers. All plant-based fibers, whether from wood or non-wood origin, are composed of three main cell wall polymers: cellulose, lignin and polysaccharide resins constituted of pectins and hemicelluloses [135]. In addition to these, several nonstructural components, such as waxes, inorganic salts and nitrogenous substances, broadly referred to as extractives, are also present in plants [132].

The major interest in natural cellulosic fibers depends on their eco-friendly advantages, low production cost, worldwide availability and higher specific strength/stiffness compared to their traditional synthetic counterparts [136–138]. Plant-based natural fiber composites (NFCs) offer good specific mechanical properties [32, 130, 139] good thermal and acoustic insulation, greater energy absorption at large strain rates [140], are low-cost, lightweight, and require less energy to manufacture, are CO_2-neutral, are easier to tool and less toxic during processing, and result in simpler, non-toxic recycling [30, 131, 141].

Moreover, the manufacturing process of bio-based composites is health-friendly and provides better working conditions [142–144]. Fibers may be converted to various suitable textile forms/ structures and may be used separately or can be combined to tailor the properties of the composites. Fibers may also be chopped to the desired length and added to the resin to fabricate composites. In order to design a structural material, an experimental investigation is required to understand the mechanical parameters of the chosen materials to be used in the manufacture of the composite (matrix and reinforcement). Although the great number of advantages offered by natural fibers over synthetic products, they display some not negligible disadvantages [145] such as possible water/moisture absorption, low thermal stability and unavailability of fibers in continuous form, unless spun into yarns [146–149]. However, considering the overall properties the advantages of natural cellulosic fibers outweigh their disadvantages [150].

Given the high importance developed in the production of completely bio-based composite materials, it could be of great interest testing different kinds of fibers, some obtained from renewable sources, with a fully bio-based resin system in order to produce a “Green Composite”.

Chapter 2- Evaluation of novel bio-based amino curing agent systems for epoxy resins

2.1 Introduction

Epoxy resins are widely used in many applications, such as paints, adhesives and matrices for composites materials, since they present the possibility to be easily and conveniently tailored in order to display a unique combination of characteristics such as excellent adhesion, chemical and heat resistance, good mechanical properties, and very good electrical insulating properties [8]. In order to obtain the desired product properties, besides the resin, the nature and the structure of the curing agents (also known as hardeners, accelerants, late curing agents and catalysts) are crucial. Hardeners are actually responsible for the opening of the epoxy rings present in the polymeric precursors, hence governing the effective kinetics of the overall curing process, to finally generate hard, infusible, thermosetting networks. It is thus essential to define important parameters in the hardener choice, which are crucial for the curing process as well as for the final resin structure, such as the initial viscosity of the hardener system, the crosslinking reaction pathway, the curing temperature range in which the system is reactive. Moreover it is of paramount importance to define an optimized stoichiometry for all the reactants. For all the above-mentioned characteristics, the chemical nature of the hardener, its structure and the number of functional groups it possesses are crucial properties. Indeed, as an example, the higher is the number of functionalities, which are present on the hardener, the greater is the potential number of crosslinking points achievable for each molecule, thus leading to a more rigid system attainable. The most commonly used curing agents for epoxies are synthetic amines, anhydrides, phenols, carboxylic acids, alcohols [151] and other compounds with mobile hydrogens [14]. Industrially, the most widely used crosslinking agent classes are the amines, either aliphatic or aromatic [98], and they can be very versatile. These hardeners show a good balance between reactivity and specific characteristics and find application for various purposes depending on their structures and the final properties of the desired product. Hence, it is of utmost importance to have access to the widest possible range of curing agents with various structures, functionality and reactivity in order to modulate the properties of epoxy thermosets and possibly deriving from alternative feedstocks with respect to the presently extensively used fossil based raw materials. With the increasing interest into developing sustainable alternatives in all industrial fields, in the latest years the next generation feedstocks from nonfood competitive resources, such as waste or low added-value supply, have been deeply investigated. Given their widespread use, thermosetting epoxy resins represent a great opportunity to develop environmentally sustainable products. Although many bio-based feedstocks for the production of the epoxy precursors might already be available, such as vegetable oils and dicarboxylic acids, it is essential, in the future, for all components of the formulation to be obtained from renewable resources, since this thermosets are hardly degradable, and alternative routes have to be developed to guarantee their recycling [50, 152, 153]. In literature, various examples of bio-based epoxy resin obtained from a wide range of sources such as catechin [77, 122, 154], cardanol [83] and lignin [84, 155] can be found. Concerning the curing agents, their toxicity and safety have not been deeply investigated and it was observed that all of them still present some environmental problems. In particular almost all the epoxy resin hardeners are low molecular weight toxic compounds [8, 69, 156]. Anhydride hardeners, such as trimellitic anhydride, are strongly irritating to skin, eyes and respiratory tract and can cause burns [61]. Instead, amine hardeners can be either aliphatic or aromatic. Aliphatic amine, such as diethylenetriamine (DETA) or triethylenediamine (TETA), are strong bases with low molecular weight. They are moderately toxic by ingestion, inhalation or by contact with skin, and are also irritating agents for eyes or skin and corrosive in undiluted form. The risk of exposure to the highly irritating vapors of these substances increases with the volatility of the amines and if high temperatures are required in the treatment process [62]. Aromatic amines, such as methylenedianiline (MDA), are less corrosive, irritant and sensitizing than the aliphatic ones. However, in this group of compounds there are substances identified as carcinogens for animals and humans. If swallowed, these can cause severe damage to internal organs, especially to the liver and kidneys, as well as reducing the ability of the blood to transport oxygen, due to the formation of methemoglobin. It is important to strictly avoid exposure to this class of hardeners by inhalation and in particular by the dermal route [63]. In terms of environmental impact, it should be noted that liquid epoxy resins and some reactive diluents are not easily biodegradable. Although epoxy functions are hydrolyzed in contact with water, they have a potential for bioaccumulation and are moderately toxic to organisms. These products are generally classified as harmful to the environment in accordance with the classification criteria of the European Union [64]. Waste obtained from the production of epoxy resins must be treated as hazardous waste in accordance with national regulations [65]. Finished articles composed of fully crosslinked epoxy resins are hard and infusible solids that pose no risk to the environment [66].

Therefore, the development of new environmentally friendly fully bio-based epoxy systems is of great importance for designing green, non-toxic and sustainable materials [157], [158]. Furthermore, information regarding bio-based amine hardeners are scarce [113]. To be accepted as valid solutions, bio-based formulations must offer the same versatility and performance reliability as conventional products. In order to modulate the final properties of epoxy thermosets as much as done with fossil hardeners, it is necessary to increase the number of amine based hardeners from bio-available sources. In particular aliphatic amines are very reactive and can be used even at room temperature [99] while cycloaliphatic amines are very versatile and show a good balance between reactivity and final properties. By the other hand, aromatic amines are the least reactive but provide better mechanical properties (high T_g), in addition to a higher resistance to heat and chemicals. Moreover, it is also of utmost importance to compare the properties provided by these new hardeners with those obtained upon the use of existing systems. To date, there are only a few commercial solutions based on renewable sources, and some of these are only partially bio-based [52, 113]. Until now, two types of amines from renewable resources have been deeply investigated. The first class of hardeners is synthesized from modified compounds such as fatty acids [105], sugar derivatives [159], and others [100, 113], while the second one is made up of bio-resources having amino groups, such as chitosan, or containing amines such as amino acids [100, 101, 110, 111, 160] (see Chapter 1.9). In recent studies, Lysine and L-Tryptophan were proposed as novel green and biocompatible amine curing agent for epoxy resins [100, 121]. It was observed that epoxy resins crosslinked with Lysine exhibit T_g and degradation temperature significantly lower than those crosslinked with L-Tryptophan, possibly due to the fact that the latter one displays an aromatic heterocyclic structure, and therefore is intrinsically more rigid. L-Tryptophan amino acid was able to react with Diglycidyl Ether of Bisphenol A (DGEBA) but the mixture displayed too high reaction temperature (216°C), low reaction heat and T_g (80°C) suggesting a low reactivity of the system and confirming the impossibility to be applied at industrial level [100].

In this context the present investigation aims at further exploring the possibility of using L-Tryptophan (Trp) together with other bio-based compounds as curing agents for epoxy resin precursors. Initially, L-Tryptophan, mixed with two commercial Late Curing Agents (LCA), 2-Undecyl-1H-imidazole (I) and 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dimethylurea) (U) (Figure 2.1), which have the purpose of lowering the activation energy of the process, was used for the crosslinking of diglycidyl ether of bisphenol A (DGEBA). The use of this epoxy precursor, thanks to its well defined chemical structure, allows the evaluation of the effect of the stoichiometry on the crosslinking reaction. Hence, different bio-based curing systems were preliminarily assessed to evaluate their potential in the production of valuable high performing epoxy resins. In particular, starting from the data obtained from the hardener systems with commercial LCA, various bio-based and nontoxic amine compounds (Figure 2.1 Urea (A), Theobromine (B), Theophylline (C), Melamine (D)) were added to DGEBA-Tryptophan mixture in order to study their effect on the whole reaction and on the resin final properties. Finally, the possibility to crosslink DGEBA was studied in presence of Guanine (G, Figure 2.1), which possesses an hetero-aromatic structure and display amine functional groups. Guanine, bearing both a secondary aromatic amine and a primary amine functionality, could trigger a fast reaction with the epoxy groups of the resin behaving as hardener, replacing alone the multicomponent curing systems studied before.

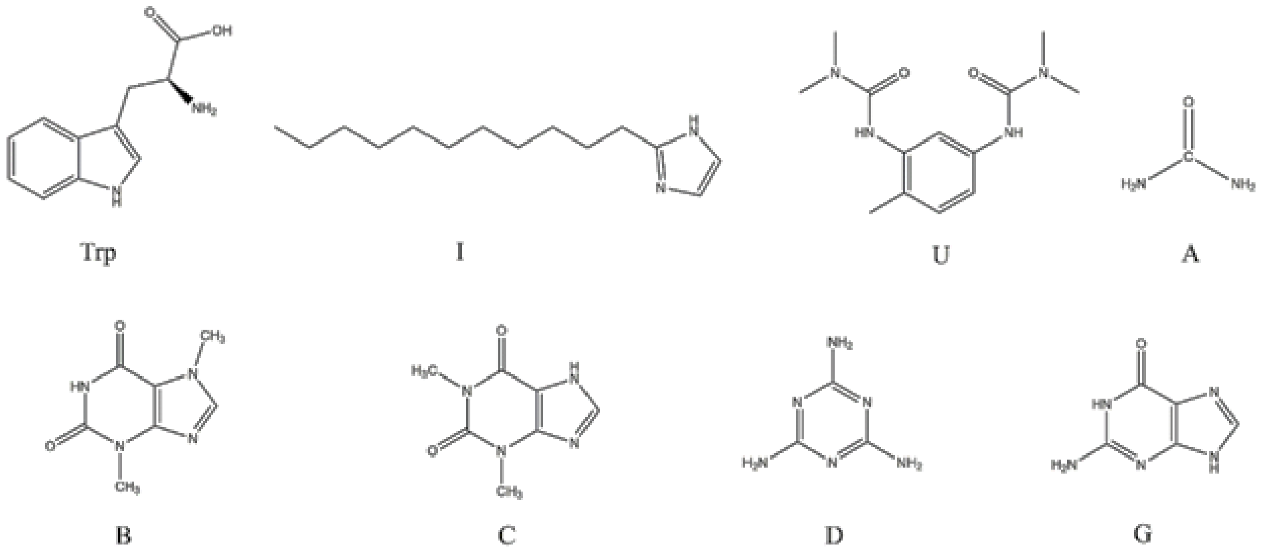


Figure 2.1: *Molecular structure of Tryptophan (Trp), Undecyl-1H-imidazole (I), 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dimethylurea) (U), Urea (A), Theobromine (B),Theophylline (C), Melamine (D) and Guanine (G).*

The crosslinking reactions of the different systems were studied by Differential Scanning Calorimetry (DSC) and the thermal performance in terms of T_g of the obtained thermosets was also explored and compared.

2.2 Experimental

2.2.1 Materials

Bisphenol A Diglycidyl Ether (DGEBA) with an epoxy equivalent weight of 170 g/equivalent, Undecyl-1H-imidazole, 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dimethylurea), Theobromine, Theophylline and Urea were purchased from Sigma Aldrich. L-Tryptophan and Guanine were purchased from Alfa Aesar. Melamine was purchased from Fluka.

2.2.2 Formulation preparation

- DGEBA – L-Tryptophan – bio-based hardener systems

Different amounts (1, 2.5 and 5 phr) of the investigated hardener [Undecyl-1H-imidazole (I), 3,3'-(4- Methyl-1,3-phenylene)bis(1,1-dimethylurea) (U), Urea (A), Theobromine (B), Theophylline (C), Melamine (D)] were added to a mixture of 0.5 g (1.47 mmol) of DGEBA and 0.167 mg (0.82 mmol) of Tryptophan. The obtained formulations were magnetically stirred with a speed of 300 rpm at 60°C until complete homogenization. When the mixture appeared completely homogenous, the vial was cooled and used for the preparation of the DSC samples. Different mixtures were produced and labelled according to the list reported in Table 2.1. For the sake of comparison, a mixture of 0.5g (1.47 mmol) DGEBA and 0.167 mg (0.82 mmol) of Tryptophan was also produced as reference, which is labelled as DT.

Table 2.1: *Compositions of the different investigated thermosets formulations of DGEBA and LTryptophan (Trp) (DT) with Undecyl-1H-imidazole (DTI), 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dimethylurea) (DTU), Urea (DTA), Theobromine (DTB), Theophylline (DTC) or Melamine (DTD).*

Sample	DGEBA (w%)	Trp (w%)	I (phr)[a]	U (phr)[a]	A (phr)[a]	B (phr)[a]	C (phr)[a]	D (phr)[a]
DT	75	25	/	/	/	/	/	/
DTI-1	75	25	1	/	/	/	/	/
DTI -2.5	75	25	2.5	/	/	/	/	/
DTI -5	75	25	5	/	/	/	/	/
DTU-1	75	25	/	1	/	/	/	/
DTU-2.5	75	25	/	2.5	/	/	/	/
DTU-5	75	25	/	5	/	/	/	/
DTA-1	75	25	/	/	1	/	/	/
DTA -2.5	75	25	/	/	2.5	/	/	/
DTA -5	75	25	/	/	5	/	/	/
DTB-1	75	25	/	/	/	1	/	/
DTB-2.5	75	25	/	/	/	2.5	/	/
DTB -5	75	25	/	/	/	5	/	/
DTC-1	75	25	/	/	/	/	1	/
DTC-2.5	75	25	/	/	/	/	2.5	/
DTC -5	75	25	/	/	/	/	5	/
DTD-1	75	25	/	/	/	/	/	1
DTD-2.5	75	25	/	/	/	/	/	2.5
DTD-5	75	25	/	/	/	/	/	5

[a] amount in phr of additional Late Curing Agents with respect to 100 phr of DGEBA/Trp

- DGEBA – Guanine systems

For the formulations DG, containing DGEBA and Guanine, the amount of hardener selected in the range 0.037-0.123 mg (0.29-0.82 mmol) was added to 1g of DGEBA (2.94 mmol), then magnetically stirred with a speed of 300 rpm at 75°C until complete homogenization. When the mixture appeared completely homogenous the vial was cooled and used for the preparation of the DSC samples. Different mixtures were produced and labelled according to the list reported in Table 2.2.

Table 2.2: *Compositions of the different investigated DGEBA/Guanine formulations (DG).*

Sample	***DGEBA (w%)***	***Guanine (w%)***	***DGEBA (mmol)***	***Guanine (mmol)***	***Molar ratio [DGEBA]/[Guanine]***
DG1	96	4	2.94	0.29	10
DG2	94	6	2.94	0.42	7
DG3	92	8	2.94	0.59	5
DG4	91	9	2.94	0.65	4.5
DG5	90	10	2.94	0.73	4
DG6	89	11	2.94	0.82	3.5

2.2.3 Characterization

The thermal behavior of the reacting mixtures was evaluated by Differential Scanning Calorimetry (TA Instruments Q2000 DSC Modulated apparatus equipped with RCS cooling system) and the measurements were carried out in dynamic and isothermal mode. Dynamic DSC analysis were performed, under nitrogen flow, heating the samples at a heating rate of 5°C/min from −50 up to 260°C for formulations containing Tryptophan while the one containing Guanine were heated up to a maximum temperature of 300°C. After the first heating, the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation. Isothermal DSC analysis were performed at 180 and 240°C introducing the sample in the pre-heated furnace. After the isothermal step the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation.

2.3 Results and discussion

The DSC analysis of DT formulations (Figure 2.2) shows, in the first scan, a stepwise transition centered around −18°C, which can be ascribed to the glass transition of the non-cured epoxy-hardening precursor system and an exothermic peak at 207°C, which can be associated to the crosslinking reaction of DGEBA with L-Tryptophan, (Figure 2.1-Trp) are observed. In particular, a reaction heat of 236 J/g and a T_g, obtained from the second heating, of 71°C were observed. All the obtained data suggest the feasibility of using L-Tryptophan as a novel curing agent for DGEBA. Unfortunately, the system shows a low reaction heat and a low glass transition temperature of the cured material (Table 2.3). Such a behavior can be due to the electrostatic interactions between zwitterions [$^{+}H_3N$–CH(–R)–COO^{-}] in L-Tryptophan, which have a much lower reactivity than the free primary amine and carboxylate anions.

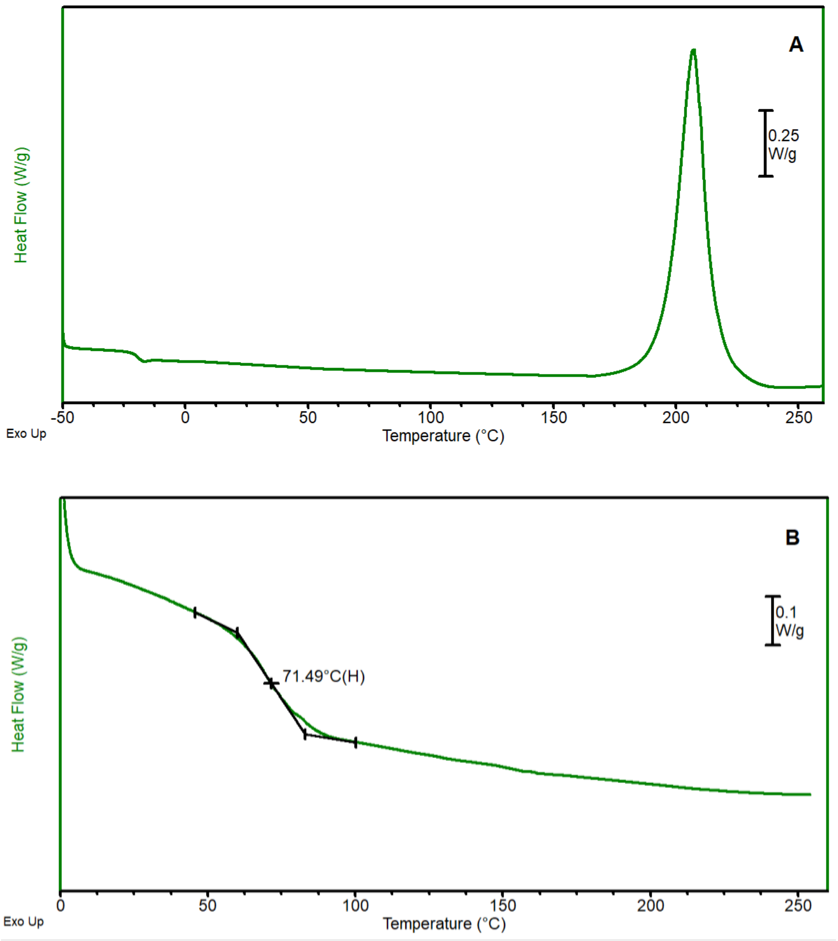


Figure 2.2: *DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) of DT formulation.*

Moreover the possible vitrification of the system, achieved once the reaction begins, sets in quickly the three-dimensional structure hampering further reactivity of the residual moieties. Thus, the properties of the studied system result not consistent with industrial applications [100].

Table 2.3: *Relevant DSC data of DT and oil-based DTI and DTU.*

Sample	***ΔH (J/g)*** ^{a}	***T*** $_{r\,max}$ ***(°C)*** ^{b}	***T*** $_{g}$ ***(°C)***
DT	236	207	71
DTI-1	341	163	100
DTI -2,5	408	152	102
DTI -5	416	143	104
DTU-1	313	156	95
DTU-2,5	319	157	99
DTU-5	354	148	101

[a] ΔH is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] T $_{r\,max}$ is the temperature corresponding to the fastest kinetic of the crosslinking reaction

2.3.1 DGEBA – L-Tryptophan – Commercial hardeners systems characterization

In order to decrease the reaction temperature and increase the ΔH and T_g of the DGEBA – L-Tryptophan system, the crosslinking of DGEBA with Trp in presence of different bio-based amine hardeners was investigated. To confirm the reliability of such hardener systems, DGEBA was selected as epoxy precursor since it represent the simplest epoxy reagent possible.

Initially, with the aim to promote the crosslinking of DT, attaining higher T_g, the reaction of DGEBA was thus studied in the presence of Trp together with commercial fossil-based late curing agents (LCA) Undecyl-1H-imidazole (I) and 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dimethylurea) (U) (Figure 2.1-I,U) [161]. In particular, various mixtures containing DGEBA/Tryptophan (DT) and LCA in different ratios were prepared and their reactivity was evaluated by Dynamic DSC analysis (Figure 2.3 and Table 2.3). Due to the low molecular weight of both the DGEBA, as epoxy precursor, and of the hardening systems components, a highly crosslinked structure was expected.

Dynamic DSC scans have been performed with a controlled heating step (usually carried out at 5°C/min) followed by a quench cooling and a further heating segment at a faster rate (usually carried out at 20°C/min). The latter scan allows for the evaluation of the attained glass transition temperature and potential residual reaction enthalpy, stemming from the inability to reach full conversion of the reacting moieties during the first heating step. Such dynamic scans represent a simple tool to quickly compare the reactivity of different systems. As shown in Figure 2.3-A all the investigated mixtures show, in the first scan, an exothermal transition which can be ascribed to the epoxy moiety reaction, thus accounting for the crosslink of the system to occur. It is worth noting that the exothermal transitions of DTI and DTU (Table 2.3) mixtures (ranging from 143-163°C and 148-157°C respectively) are centered at temperatures lower than the reference DT (207°C). Such a behavior suggests that the addition of both late curing agents allows the crosslinking reaction to take place at significant lower temperatures than the plain DGEBA/L-Tryptophan mix. Additionally, in both cases, an increment in the reaction heat is recorded with a consequent increase of the final T_g of resins (Table 2.3). Comparing DTI and DTU, it is possible to notice that the two late curing agents act similarly and lead to resins with comparable T_g around 100°C (Table 2.3).

These data are encouraging in order to use L-Tryptophan based systems as a novel more environmentally friendly curing agent for DGEBA, but it also emphasizes the need for a coadjutant for Trp to perform in an acceptable way.

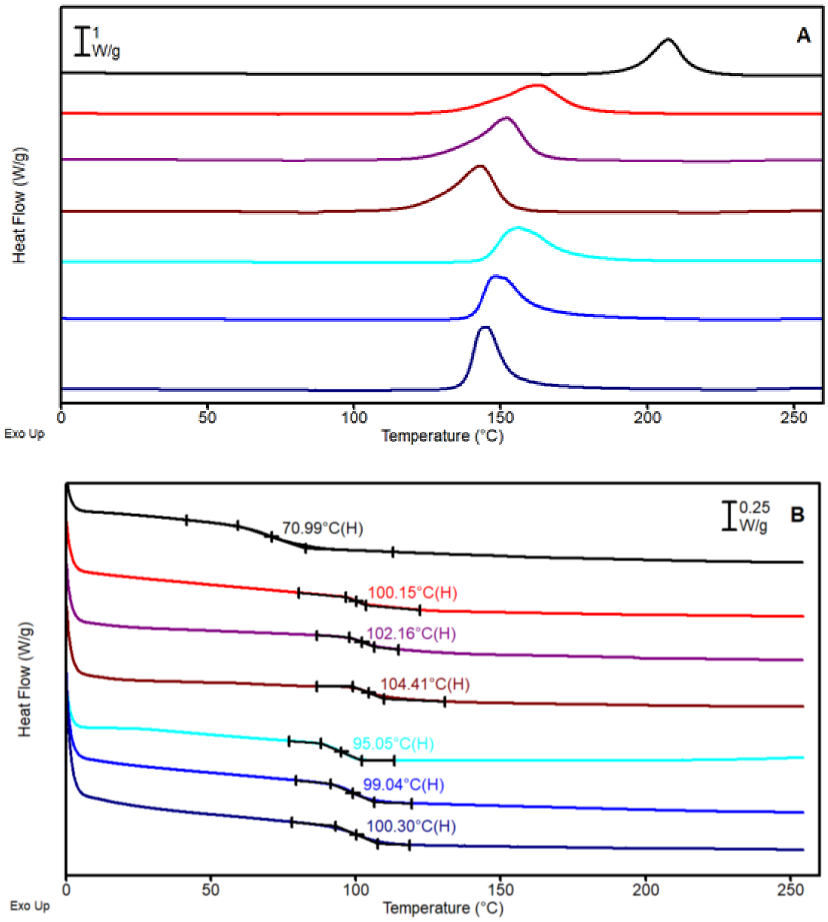


Figure 2.3: *DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) of DT(**---**), DTI-1 (**---**), DTI-2.5 (**---**), DTI-5 (**---**), DTU-1 (**---**), DTU-2.5 (**---**) and DTU-5 (**---**).*

2.3.2 DGEBA – L-Tryptophan – Urea systems characterization

Given the promising results obtained with the tested commercial LCAs, four bio-based late curing agents have been investigated for the first time with L-Tryptophan. The first tested compound is Urea (A), a linear molecule with four amine functionalities, able to open the epoxy groups [162–164] (Figure 2.1-A). The reactivity of DGEBA and Tryptophan in presence of different amounts of Urea (1, 2.5 and 5 phr with respect to 100 phr of DT resin; DTA-1, DTA-2.5 and DTA-5 respectively) was evaluated by Dynamic DSC in the same condition used for the samples containing the commercial LCAs and the obtained results are reported in Table 2.4 and Figure 2.4. The maximum temperature set in these tests was 260°C in order to avoid the degradation of the resin-hardener systems. Analyzing the first DSC heating scan (Figure 2.4-A) all three samples (DTA-1, DTA-2.5 and DTA-5) display a stepwise transition centered around –18°C, which can be ascribed to the glass transition of the non-cured epoxy-hardening precursor system.

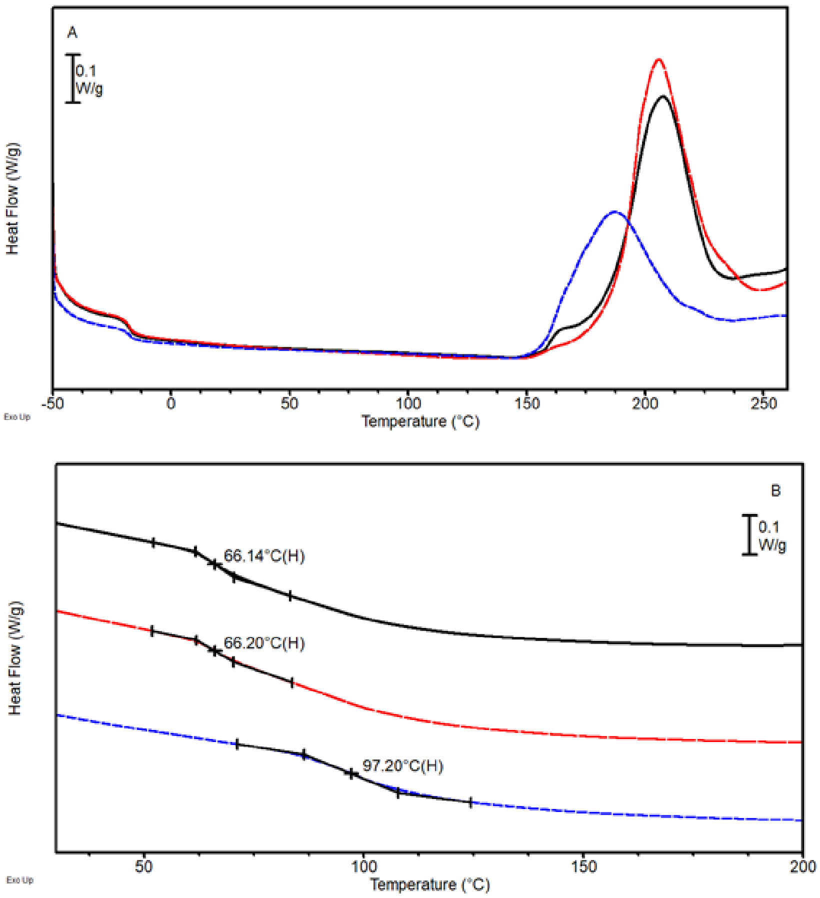


Figure 2.4: *DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) of DTA-1(**---**), DTA-2.5(**---**) and DTA-5 (**---**).*

In all formulations, an exothermic transition, associated to the occurrence of the crosslinking reaction between the components of the mixture, is observed. This event is characterized, in all formulations, by the presence of a single peak, around 160°C, with different intensity, depending on the amount of Urea added, and it is possible to observe a shift towards lower temperature values, the greater is the fraction of added hardener.

Table 2.4: *Relevant DSC data of bio-based DTA samples*

Sample	***T_g first scan (°C)***	***ΔH (J/g) [a]***	***$T_{r\,max}$ (°C) [b]***	***T_g (°C)***
DTA-1	–18	158	207	66
DTA-2.5	–18	157	206	66
DTA-5	–18	189	187	97

[a] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$, is the temperature corresponding to the fastest kinetic of the crosslinking reaction

The values of ΔH related to the total crosslink enthalpy for formulations DTA-1, DTA-2.5 and DTA-5 (Table 2.4), show an increasing trend with the increasing amount of Urea and, accordingly, a similar trend is observed in the T_g values of the cured materials which have been evaluated in the second scan (Figure 2.4-B).

The increase in T_g and reaction enthalpy is thus ascribed to the amount of Urea in the system, since a greater quantity of such hardener brings in the reaction environment a higher number of reactive groups able to react with the epoxy rings of DGEBA. However, Tryptophan-Urea systems do not show remarkable results compared to the previously investigated DT, DTI and DTU formulations.

Comparing DTA samples performance with that of the batch containing L-Tryptophan only (DT), no significant increase in the final T_g of the cured resin is registered. The crosslinking happens at almost the same temperature (apart from the sample containing 5 phr of Urea) and the crosslinking enthalpy is even lower, a sign that the reaction is not pushed to completion with respect to the plain DT system. Compared to commercial LCA-containing systems, DTI and DTU, Tryptophan-Urea hardeners are less performing in all the principal parameters analyzed.

2.3.3 DGEBA – L-Tryptophan – Theobromine systems characterization

In order to increase the rigidity of the final system, other aromatic coadjutants were investigated and mixed with Trp, starting with Theobromine (B). Theobromine is a bio-based molecule with a heterocyclic structure and amine functionalities [165, 166] (Figure 2.1-B). For the DGEBA-Trp-Theobromine formulation (DTB), different amounts of Theobromine (1, 2.5 and 5 phr) were tested and the samples prepared are listed in Table 2.1. Once again, the reactivity of DTB systems was evaluated via Dynamic DSC in the same condition used for the previous samples and the obtained results are reported in Table 2.5 and Figure 2.5.

Analyzing the first heating scan it is possible to notice, for all three samples, a stepwise transition around −18°C, associated to the T_g of the non-crosslinked resin. All the analyzed formulations show a clear exothermal transition, ascribed to the epoxy resin precursor reacting to provide the three dimensional thermoset network.

DTB-1 and DTB-2.5 samples show only one exothermal peak, while DTB-5 formulation displays a shoulder at higher temperature than the main peak, suggesting the presence of some different processes (with different kinetics) occurring when Theobromine is present in a significant amount. Such hypothesis is confirmed by the values related to the determined crosslinking enthalpy (Table 2.5): ΔH shows a slight increase passing from DTB-1 to DTB-2.5, while DTB-5 displays a significant increase in the reaction enthalpy, that support the idea of additional reactive processes setting in with the higher Theobromine fraction. The tendency of the T_g value obtained with this dynamic curing process is instead more linearly growing, reaching with DTB-5 specimen, a value close to 100°C, 24°C higher than plain DT.

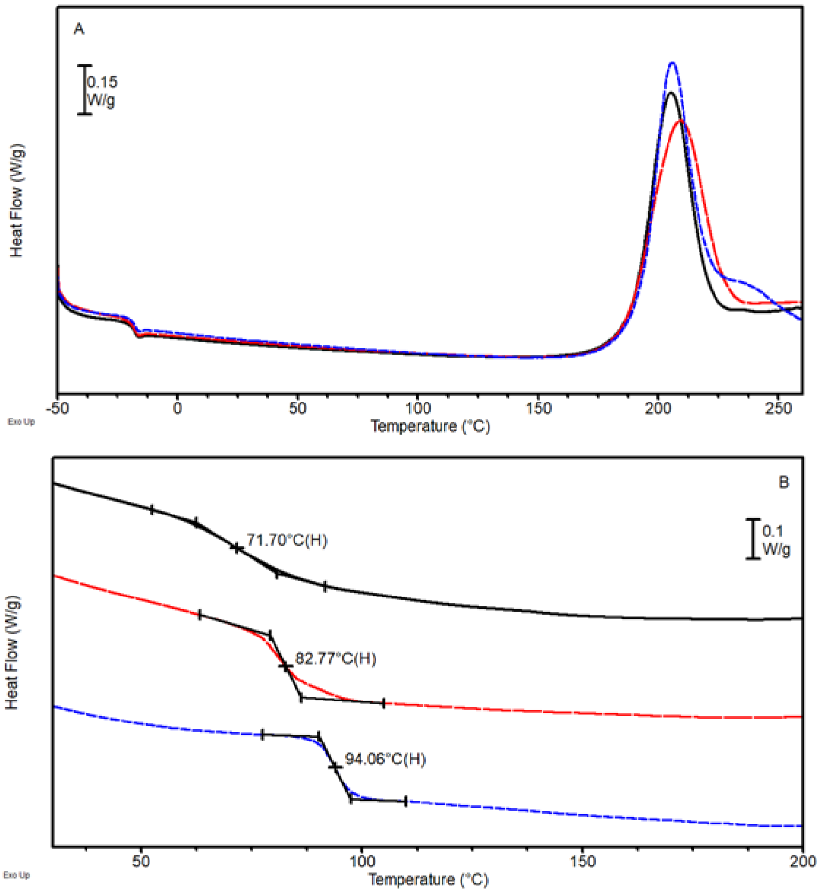


Figure 2.5: *DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) of DTB-1(---), DTB-2.5(---) and DTB-5 (---).*

The higher is the amount of hardener added, the more amine groups are present and capable of reacting with the DGEBA. However, Theobromine has just one secondary amine group that is prone to react with DGEBA; on the other side, the extreme rigidity of the heterocyclic aromatic compound is definitely contributing in increasing the glass transition temperature of mixture, once Theobromine is actively included in the network.

Table 2.5: *Relevant DSC data of bio-based DTB samples*

Sample	**T_g first scan (°C)**	**ΔH (J/g) [a]**	**$T_{r\,max}$ (°C) [b]**	**T_g (°C)**
DTB-1	-18	191	206	72
DTB-2,5	-18	198	209	83
DTB-5	-18	247	206	94

[a] ΔH is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$ is the temperature corresponding to the fastest kinetic of the crosslinking reaction

While the crosslinking reaction temperature seems unaffected by the presence of Theobromine, the concentration of B looks a critical parameter to instill the reactivity of additional functional groups that result in the appearance of the exothermal peak shoulder and increased glass transition of DTB-5. With the addition of Theobromine, an aromatic compound, some overall better results have been achieved in comparison to DT and DTA samples. Unfortunately, Theobromine-based formulations do not show results as good as the ones obtained with fossil-based late curing agents, which display even higher T_g, ΔH and lower reaction temperature.

2.3.4 DGEBA – L-Tryptophan – Theophylline systems characterization

As second aromatic hardener, Theophylline (C) was thus investigated [167]. Theophylline is a heterocyclic bio-based molecule, very similar to Theobromine, but it bears, among the others, an aromatic amine functionality (Figure 2.1-C). Analogously to the previously investigated formulations, also for this hardener system three different compositions of DGEBA-Tryptophan-Theophylline (DTC-1, DTC-2.5 and DTC-5) have been prepared and tested (Table 2.1). The results of the Dynamic DSC analysis are reported in Table 2.6 and Figure 2.6.

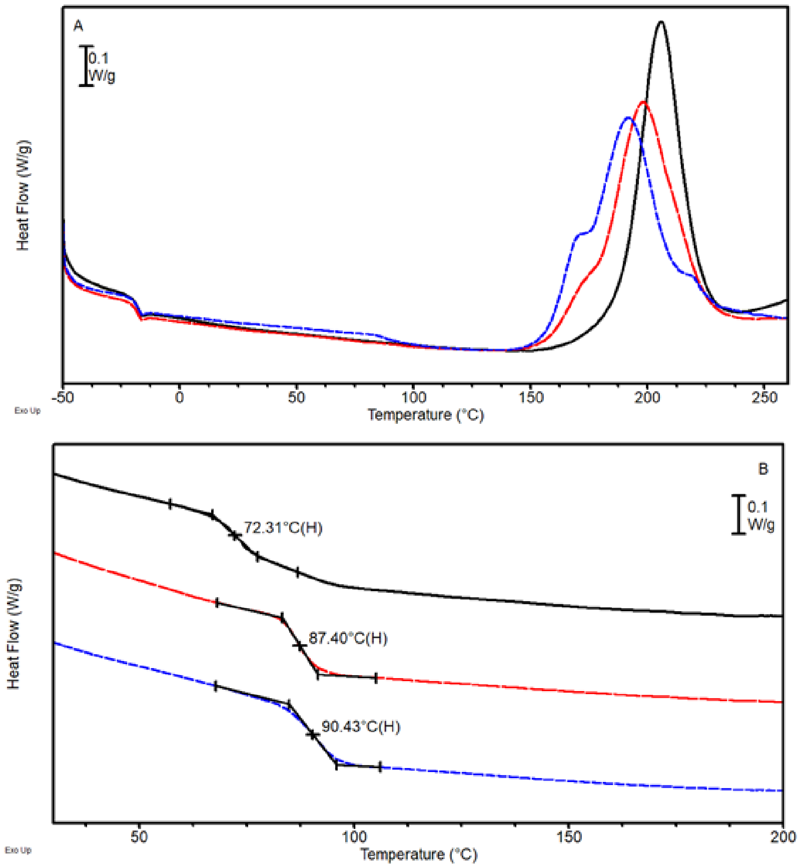


***Figure 2.6:** DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) for the systems DTC-1(**---**), DTC-2.5(**---**) and DTC-5 (**---**).*

The first heating scans (Figure 2.6-A) once again clearly display, for all three samples, the typical stepwise feature around –18°C belonging to the T_g of the non-crosslinked resin.

The crosslinking of the epoxy resin precursor is confirmed by the clear exothermal transitions present in each sample's thermogram.

In the presence of Theophylline, however, the exothermal transition of DTC-1 sample is characterized by only one peak, while for formulation DTC-2.5 and DTC-5 shoulders appear and peaks maxima move to lower temperature (Figure 2.6-A) when increasing the Theophylline fraction in the starting mixture. A concomitant increase in the reaction enthalpy (Table 2.6) is observed at increasing Theophylline content, that leads, in turn, at a higher T_g as measured in the second heating scan (Figure 2.6-B). Such a behavior, when compared with Theobromine (B), suggests that Theophylline acts prevalently as catalyst coadjutant within the hardener system, with a lower T reaction peak and a concomitant increase in the associated enthalpy.

Table 2.6: *Relevant DSC data of bio-based DTC samples*

Sample	***T_g first scan (°C)***	***ΔH (J/g)*** ^{a}	***$T_{r\,max}$ (°C)*** ^{b}	***T_g (°C)***
DTC-1	-18	205	206	72
DTC-2.5	-18	231	198	87
DTC-5	-18	245	191	91

^{a} ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, ^{b} $T_{r\,max}$, is the temperature corresponding to the fastest kinetic of the crosslinking reaction

However, comparing the results obtained with those for Theobromine-based systems (DTB), they are very similar: the attained ΔH and T_g are comparable and only a slight decrease in the crosslinking temperature is displayed, probably due to the catalytic activity of Theophylline. Again Theophylline based formulations display lower crosslinking enthalpy, T_g and higher reaction temperature when compared with fossil-based late curing agents (DTI and DTU).

2.3.4 DGEBA – L-Tryptophan – Melamine systems characterization

In order to increase the reactivity of the hardener system, Melamine (D) was used with L-Tryptophan. Melamine is a heterocyclic aromatic compound with three primary amine groups (obtainable from Urea) [168], with a total number of six functionalities able to open epoxy rings (Figure 2.1-D). The reason underlying the choice of Melamine as L-Tryptophan coadjutant stands in the possibility of such a high amount of primary amine groups of reacting with the epoxy moieties, thus promoting the crosslinking, together with the extreme stiffness of the aromatic central ring that should also help promoting the increase of the T_g. For DGEBA-Trp-Melamine formulations (DTD), the same mixture compositions have been produced, with increasing Melamine content (1, 2.5 and 5 phr), as listed in Table 2.1. The reactivity of DTD systems was evaluated by Dynamic DSC analysis and the obtained results are reported in Table 2.7 and Figure 2.7.

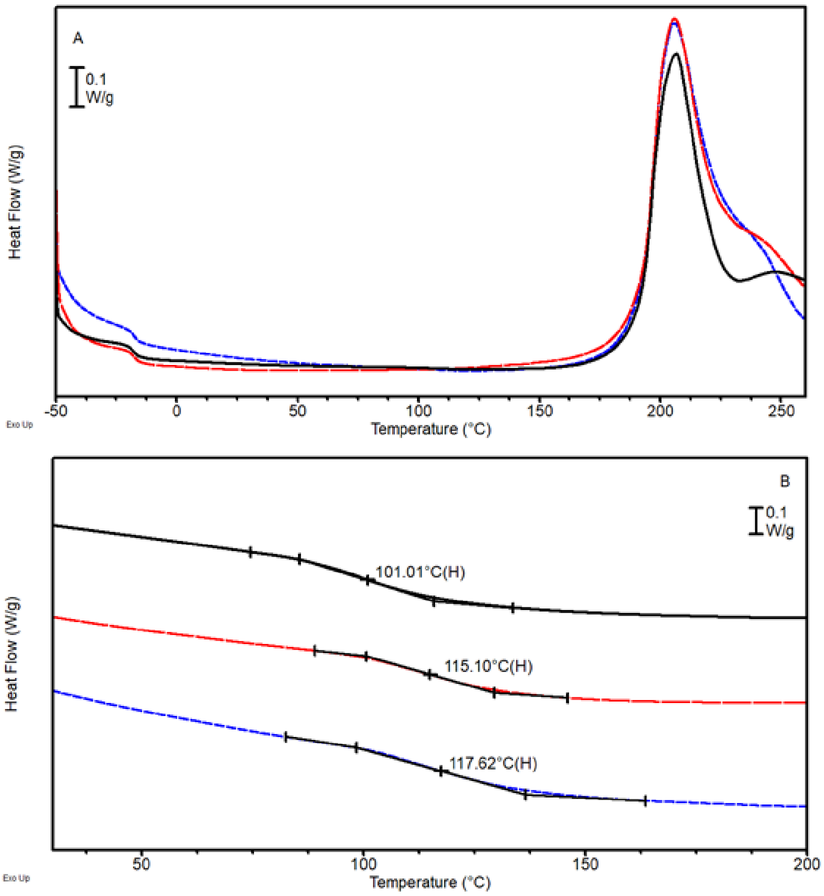


***Figure 2.7:** DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) of DTD-1(---), DTD-2.5(---) and DTD-5 (---).*

The presence of a stepwise transition around –18°C in the first heating scan, ascribed to the glass transition of the non-crosslinked resin DTD, confirms once again that all the hardeners coadjutants used in the present work do not seem to affect the behavior of the unreacted mixture and are not starting crosslinking reaction (at least to a significant extent) prior to the actual desired curing process.

***Table 2.7:** Relevant DSC data of bio-based DTD samples*

Sample	**T_g first scan (°C)**	**ΔH (J/g) [a]**	**$T_{r\,max}$ (°C) [b]**	**T_g (°C)**
DTD-1	–18	199	206	101
DTD-2,5	–18	274	206	115
DTD-5	–18	315	206	118

[a] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$, is the temperature corresponding to the fastest kinetic of the crosslinking reaction

The crosslinking of the epoxy resin precursor triggered by the presence of the hardener system is confirmed by the exothermal transitions detected in each thermogram (Figure 2.7-A). In the DSC thermograms of DTD samples, the exothermal peaks are characterized by a peculiar pattern, with the main signal displaying a shoulder at high temperature for every tested sample (DTD-1, DTD-2.5 and DTD-5).

The crosslinking enthalpy keeps increasing with the increase of the Melamine fraction in the formulations, and in turn this behaviour results in an increase of the glass transition of the mixture in the cured samples. Conversely, the position of the reaction peak is not altered, temperature-wise, by the addition of the new hardener coadjutant. This event is probably due to the small dimensions of Melamine molecule, which requires a high crosslinking temperature in order to accomplish the complete reaction of all the amine groups crowded onto the hardener.

Comparing the obtained results with all the previously tested formulations, DTD samples display higher ΔH and T_g, even in comparison with fossil-based DTI and DTU formulations. The addition of a multifunctional amine molecule with an aromatic structure, like Melamine, appears thus able to increase the overall rigidity of the system. This is probably due to the intrinsic stiffness of Melamine and the high number of epoxy groups that can react with a single molecule of hardener, increasing the rigidity of the 3D crosslinked structure.

2.3.5 DGEBA – Guanine systems characterization

Given the interesting results obtained for hetero aromatic compounds such as Melamine, an attempt to obtain such combined properties in a single product was performed introducing a totally heterocyclic molecules displaying amine functional groups. Taking as a basis the above mentioned products and amino acids, the investigation of N-containing heterocyclic systems free of any lateral aliphatic chain, such as Guanine (nitrogenous base, known to be an important component of DNA), was reputed highly interesting in order to obtain even more satisfactory results. Guanine (Figure 2.1-G), thanks to its particular heterocyclic aromatic structure, represents a potential starting point for the design of high performance polymers, from renewable sources, since it is produced mainly by direct fermentation [169, 170]. Guanine bears both a secondary aromatic amine and a primary amine functionality and the presence of both functionalities in the same molecule could trigger a fast reaction between the epoxy group of the resin precursor and the hardener. On preliminary basis, different ratios of DGEBA-Guanine (DG samples) have been tested and six different formulation have been prepared, in particular molar ratio ranging from 3,5 to 10 were used (DG1-DG6). The formulation prepared are reported in Table 2.2.

In order to study the crosslinking reaction of DGEBA with Guanine it was decided to perform DSC tests using a maximum temperature of 300°C. The formulations were characterized using DSC analysis in dynamic mode, applying a heating ramp of 5°C/min for the first heating and a 20°C/min ramp for the second; DSC thermograms and the relevant data are reported in Figure 2.8 and Table 2.8.

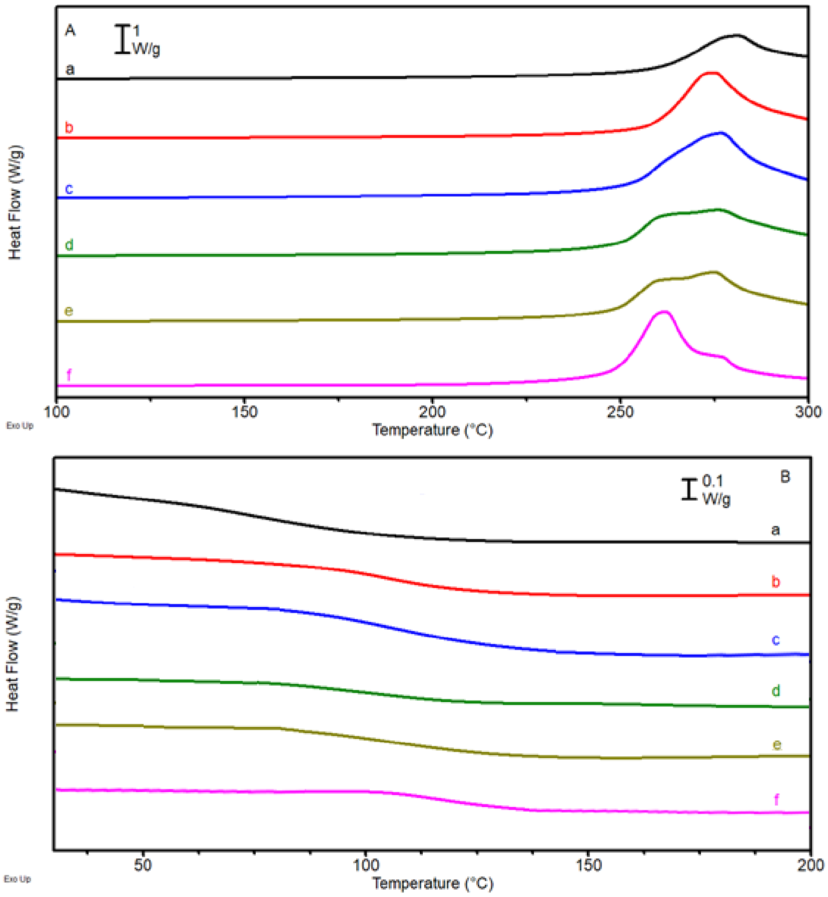


Figure 2.8: *DSC thermograms of the first heating scan (heating rate 5°C/min) (A) and second heating scan (heating rate 20°C/min) (B) of DG-1 (a), DG-2 (b), DG-3 (c), DG-4 (d), DG-5 (e) and DG-6 (f).*

The first heating scans (Figure 2.8-A) once again clearly display, for all six samples, the typical stepwise feature around –18°C belonging to the T_g of the non-crosslinked resin.

All the analyzed formulations show a clear exothermal transition, ascribed to the epoxy resin precursor reacting to provide the three-dimensional thermoset network. For DG1, DG2 and DG3 samples, only one peak is present in the exothermal transition, while for DG4, DG5 and DG6 formulations, a shoulder appears at higher temperature than the main peak, suggesting the presence of some different processes (with different kinetics) occurring when higher amount of Guanine is present. It is possible to observe a shift towards lower temperature values upon increasing the Guanine fraction in the starting mixture. The crosslinking enthalpy keeps increasing with the increase of the Guanine fraction in the formulations, resulting also in an increase of the glass transition in the cured samples.

The higher is the amount of Guanine added the more amine groups are present and capable of reacting with the DGEBA. Guanine, displaying both primary and secondary amine groups, is prone to react with DGEBA and the great rigidity of the heterocyclic aromatic compound is definitely contributing in increasing the glass transition temperature of mixture, once a 3D crosslinked network sets in.

Table 2.8: *Relevant DSC data of DEGBA/Guanine (DG) samples*

Sample	***T_g first scan (°C)***	***ΔH (J/g)[a]***	***$T_{r\,max}$ (°C)[b]***	***T_g (°C)***
DG1	-18	325	280	82
DG2	-18	648	275	105
DG3	-18	664	277	108
DG4	-18	669	275	109
DG5	-18	708	275	109
DG6	-18	790	262	118

[a] ΔH is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$ is the temperature corresponding to the fastest kinetic of the crosslinking reaction

The crosslinking peak temperature (262-280°C), when compared to the formulations containing L-Tryptophan, is sensibly higher (about 60-75°C more). This event is probably due to the small dimensions of Guanine molecule, which requires a high temperature in order to accomplish the complete reaction of the amine groups, and the absence of a less hindered hardener molecule (like L-Tryptophan) which allows the activation of the crosslinking reaction of the resin at lower temperature.

Based on the data obtained via dynamic DSC tests, isothermal DSC analyses were also performed, working at 240°C, 20°C lower than the crosslinking peak temperature (262°C). Isothermal analyses are fundamental in order to identify the reaction enthalpy, the time required to obtain the maximum reaction rate and to attain complete resin crosslinking, all essential parameters for the simulation of the industrial cure process. In particular, as an example, only three formulations (DG2, DG4 and DG6) have been tested in DSC isothermal mode. For the sake of comparison also the DT formulation, containing DGEBA and L-Tryptophan, was tested in isothermal mode at 180°C, still about 30°C lower than the relative crosslinking peak temperature (207°C). The obtained results are shown in Table 2.9 and, in Figure 2.9, the trends of DG2, DG4 and DG6 under isothermal conditions at 240°C and DT under isothermal conditions at 180°C are reported.

In isothermal mode, as observed for dynamic DSC analysis, a dependence of reaction heat, T_g, maximum reaction rate and total reaction time with the amount of Guanine present in the formulation is observed. At 240°C, a complete crosslinking is observed for all formulations both in terms of reaction enthalpies and T_g (all over 135°C) and residual crosslinking heat is not present for any of the samples during the second heating scan, a proof of a complete curing process.

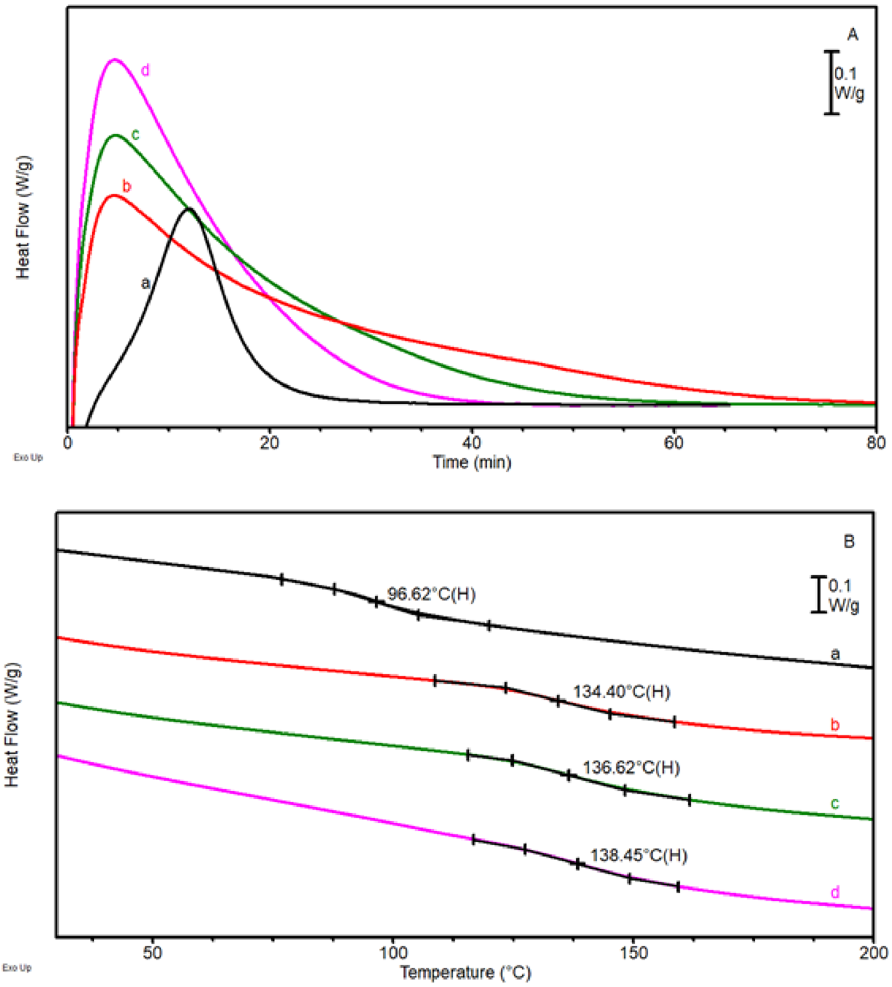


Figure 2.9: *DSC thermograms of the isothermal step at 240°C (A) and the second heating scan (heating rate 20°C/min) (B) of DT (a), DG-2 (b), DG-4 (c) and DG-6 (d).*

Comparing the results obtained for the DG formulations with DT sample, the former all display higher ΔH, T_g and lower maximum reaction rate time confirming that the addition of a multifunctional amine molecule with an aromatic structure, like Guanine, increases the overall rigidity of the system.

Table 2.9: *Relevant isothermal DSC data of DT at 180°C and DG-2, DG-4 and DG-6 at 240°C.*

Sample	***T iso (°C)*** [a]	***Time peak (min)*** [b]	***Time tot (min)*** [c]	***ΔH (J/g)*** [d]	***T_g(°C)***
DT	180	12,1	59	181	96
DG2	240	4,78	98	509	135
DG4	240	4,63	87	523	137
DG6	240	4,59	64	532	140

[a] T iso is the temperature chosen for the curing process, [b] t peak is the time corresponding to the maximum speed of the crosslinking reaction, [c] t tot is the time needed to achieve a complete crosslink of the resin system, [d] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener.

Concerning the time necessary to obtain complete resin crosslinking, DT formulation is able to fully react in an overall shorter time, probably due to the less hindered structure of L-Tryptophan, which allows the activation of the crosslinking reaction of the resin at lower temperature (180°C). Finally, all the analysis carried out on Guanine-based systems demonstrated the possibility to use it as novel bio-based amine hardener for epoxy resins, obtaining final products displaying interesting thermal properties.

2.4 Conclusions

New curing systems fully based on renewable resources were studied as coadjutants of L-Tryptophan in the crosslinking of the DGEBA epoxy resin precursor. Such a preliminary screening demonstrated that bio-based hardening systems are able to provide high-T_g epoxy resins. The most relevant results were obtained with aromatic compounds. In particular the use of Melamine, a heterocyclic molecule with six amine functionalities, allows to achieve a final T_g around 118°C, 50°C higher than plain L-Tryptophan. Unfortunately the crosslink reaction occurs at high temperature (206°C), not consistent with industrial application. Anyway, the aromatic heterocycles seem to be promising as catalytic helping promoters within the hardened system. The promising results obtained with this preliminary screening approach, pave the way to the combination of the different actions envisaged with the different actors proposed, such as, for example, Melamine and Theophylline, in order to exploit the catalytic activity of the latter together with the multifunctional primary amine structure of the Melamine in addition to its rigidity. Taking as a basis the above-mentioned amino acids, Guanine, being a nitrogen-heterocyclic systems without lateral aliphatic chains, was tested alone as epoxy resin hardener. The use of Guanine allows a crosslinking reaction with the epoxy groups at high temperature (260-280°C), higher than the plain L-Tryptophan, but higher crosslinking reaction heat and final T_g were achieved. This new system is very promising since Guanine is a biocompatible, non-toxic and environmentally friendly molecule and, already in low amounts (9% in weight with respect to 25% in weight of L-Tryptophan), it allows to achieve satisfactory results in terms of final T_g. Moreover, the isothermal DSC analysis performed on the samples, even if with high curing temperature, demonstrated the feasibility of Guanine, and Purine in general, as a new bio-based epoxy resin hardener.

Chapter 3- Preliminary study of crosslinking reaction of Adenine with epoxy resin precursors

3.1 Introduction

Epoxy resins are a product that find widespread use in various application fields such as coating, adhesives and matrices for composites materials. This thermosetting polymer present the possibility to easily combine specific characteristics such as excellent adhesion, chemical and heat resistance, good mechanical and electrical insulating properties [8] in order to obtain the desired final product. The two main component of an epoxy system are the resin itself and the curing agents. The nature and the structure of hardeners are essential to produce a hard, infusible, thermosetting network after the curing process of the material. The most common curing agents for epoxies are anhydrides, phenols, carboxylic acids, alcohols [14, 151] and industrially, the most widely used crosslinking agent classes are the amines, either aliphatic or aromatic [98]. One of the main issues of curing agents is their toxicity, safety and environmental harm [8, 61–63, 69,156].

In the latest years, a growing interest in the development of sustainable, ecofriendly and safe materials in various application fields was observed. Given their widespread use, thermosetting epoxy resins represent a great opportunity to develop environmentally sustainable products. Various bio-based feedstocks for the production of the epoxy precursors, such as vegetable oils, dicarboxylic acids [50, 152, 153], catechin [77, 122, 154], cardanol [83] and lignin [84, 155] are already used and are commercially available. Concerning, instead, bio-based amine hardeners information and researches regarding their development are scarce [113]. In order to be a competitive solution, able to withstand the comparison with oil-based products, bio-based formulations must achieve good properties modulation, performance reliability and acceptable mechanical and thermal characteristics. For this reason, it is essential to increase and develop the highest possible variety of curing agents with different structures, functionality and reactivity, obtained from renewable and safe sources, in order to modulate the final properties of epoxy systems as much as possible.

In a previous work, different bio-based curing agents coadjutants (Urea, Theobromine, Theophylline and Melamine), mixed with L-Tryptophan to produce fully bio-based a curing system [100, 161], were tested as epoxy resin hardeners. This screening investigation offered interesting hints concerning the crosslinking reaction and the best properties achievable for each hardener-resin system in terms of heat of reaction and final T_g. It was observed that the most remarkable results have been obtained when aromatic hardeners were added. Polymers composed by a high fraction of aromatic chains, have in fact recently received great attention, since their unique properties such as thermal stability, mechanical properties and superior chemical resistance [52]. In order to obtain products characterized by high mechanical and thermal properties using a single reagent as crosslinking agent, Guanine was tested as novel hardener for epoxy resin systems. Guanine, thanks to its particular heterocyclic aromatic structure, represents a potential starting point for the design of high performance thermosetting polymers, derived from renewable sources, since it is produced mainly by direct fermentation [169, 170]. Guanine displays both a secondary aromatic amine and a primary amine group. The presence of both functionalities in the same molecule was confirmed to trigger a fast crosslinking reaction between the epoxy group of the resin precursor and the hardener. The results obtained demonstrated the feasibility of Guanine, and Purine in general, as new biocompatible, non-toxic and environmentally friendly epoxy resin hardener.

Therefore, in order to find a more performing fully heterocyclic product with amine functional groups and having characteristic similar to Guanine, Adenine was investigated (Figure 3.1).

Regarding Adenine (nitrogenous bases, known to be an important piece of DNA), this molecule has gained a lot of attention for its unique bio-activity and bio-compatibility. Thanks to its stable heterocyclic structure, in the presence of proton donors (-NH-, =CH-) and proton acceptors (=N-) (Figure 3.1), Adenine represents a potential epoxy curing agent. Moreover, it does not display any carbonyl group and, even if it possess only one secondary amine, it may be more active since the hydrogens of amine groups are more active and the epoxy ring opening reaction might be promoted.

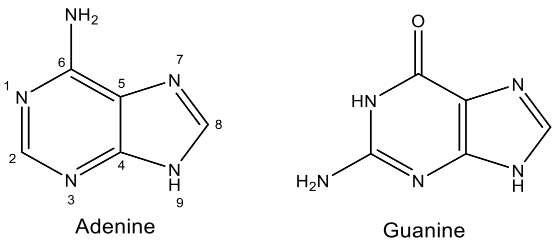


Figure 3.1: *Chemical structure of Adenine and Guanine*

In particular this molecule represents a potential starting point for the design of high performance polymers, from renewable sources, since it is produced mainly by direct fermentation or through chemical reduction of adenosine [116–118, 120, 121]. Specifically, Adenine can be produced from DNA degradation and obtained by fermentation through the production of adenosine and the process already occurs mainly on an industrial scale through microbial fermentation, with yields up to 16.4 g/l [113, 120].With the final purpose of finding an aromatic amide bio-based epoxy hardener, able to achieve high T_g in the crosslinked product, the aim of the present work is to verify the possibility of using Adenine as epoxy resin hardener. Initially Adenine will be used with DGEBA in order to understand the best hardener/resin stoichiometric ratio, the kinetics and conversion of the reaction and the final mechanical properties of the systems obtained. The tests on the resin formulations will be performed through Thermogravimetric Analysis (TGA), Dynamic Scanning Calorimetry (DSC). Then, in order to have a better understanding of the crosslinking of epoxy resins, the reaction pathway of Adenine, reacting with epoxy groups, will be studied through ^{1}HNMR technique. In particular as epoxy component, Glycidyl 2-Methylphenyl Ether will be used since it possess a structure very similar to DGEBA and displays only one epoxy functionality allowing the production, after the reaction, of a not crosslinked solution analyzable through NMR technique.

3.2 Experimental

3.2.1 Materials

Bisphenol A Diglycidyl Ether (DGEBA) with an epoxy equivalent weight of 170 g/equivalent and Glycidyl 2-Methylphenyl Ether (G2MPE) 90% pure where purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO) 99.5% was purchased from Carlo Erba. Adenine (99% pure) was purchased from Alfa Aesar. All the reagents were used as received without further purification.

3.2.2 Formulation preparation

DGEBA - Adenine systems: different amount of Adenine (ranging from 3.5 to 7 w%) were added to DGEBA. The obtained formulations were mechanically stirred with a speed of 300 rpm at 80°C until complete homogenization of the hardener within the resin. When the mixture appeared completely homogenous, the flask was cooled and used for the preparation of the TGA and DSC samples. Different mixtures were produced and labelled according to the list reported Table 3.1.

Table 3.1: *Compositions of the investigated thermosets formulations of DGEBA with Adenine.*

Sample	*DGEBA (w%)*	*Adenine (w%)*	*DGEBA (mol)*	*Adenine (mol)*	*Molar ratio*
DA1	96.5	3.5	0.0147	0.0014	10.80
DA2	95.3	4.7	0.0147	0.0018	8.11
DA3	93.2	6.8	0.0147	0.0027	5.42

G2MPE - Adenine systems: all reactions were carried out in glass vials (15 ml) equipped with a sealed cap and magnetic stirrer and 0.05 g (3.70×10^{-4} mol) of Adenine were placed with 1 ml of DMSO and a predefined amount of G2MPE. Initially the molar ratio of Adenine to G2MPE was investigated in the range of 1:0.5 up to 1:8 (Table 3.2). The content of the vial was heated to 90°C and kept at this temperature for 24 hours.

Table 3.2: *Compositions of the investigated Adenine/G2MPE solutions.*

Sample	***G2MPE (mol)***	***Adenine (mol)***	***Molar ratio***
GA1	3.70×10^{-4}	3.70×10^{-4}	1
GA4	1.48×10^{-3}	3.70×10^{-4}	4
GA8	2.96×10^{-3}	3.70×10^{-4}	8

The formulation with Adenine/G2MPE molar ratio of 1:4 was selected in order to assess the reaction mechanism. All reactions were carried out in glass vials (15 ml) equipped with a sealed cap and magnetic stirrer and 0.35 g (2.59×10^{-3} mol) of Adenine were placed with 7 ml of DMSO and a predefined amount of G2MPE (1.89 g). The reaction mixture was heated at different temperatures (90 and 95°C) and the reaction was stopped after different times (1-3-5-7-9 hours) quenching the vials into cold water. After the cooling of the solution a sample for ^{1}H-NMR analysis was prepared with the aim to estimate the Adenine substitution vs reaction time.

3.2.3 Characterization

- Thermogravimetric analyses (TGA) were carried out on a TA Instruments SDT Q600, in nitrogen atmosphere (flow rate: 100 ml/min) heating from RT°C to 600°C at 10°C/min, followed by a switch to oxidizing atmosphere (air) and an isothermal step of 20 min.
- The thermal behavior of the reacting mixtures was evaluated by Differential Scanning Calorimetry (DSC, Q2000 TA Instruments) and the measurements have been carried out in dynamic and isothermal mode. Dynamic DSC analysis were performed, under nitrogen flow, heating the samples at a heating rate of 1°C/min from –50 to 280°C. After the first heating, the samples were cooled to 0°C and then heated again with a heating rate of 20 °C/min from 0 to 260°C for T_g evaluation. Isothermal DSC analysis were performed at 160-180-200°C and the sample was introduced in the furnace already heated to the experimental temperature. After the isothermal step the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation.

- ^{1}H-NMR analysis was performed on DMSO-d^6 solutions with Varian Mercury Plus VX400 (^{1}H, 399,9 MHz) model. All chemical shift values have been reported in ppm (δ scale).

3.2.4 ^{1}H-NMR attributions

- *GA4 0h:* ^{1}H-NMR (DMSO-*d*^{6}): δ= 12.75 (s, 1H, -N(9)**H**-), 8.08 (s, 1H, C(8)**H** aromatic Adenine) 8.05 (s, 1H, C(2)**H** aromatic Adenine), 7.15 (m, 2H, C**H** aromatic G2MPE), 7.03 (s, 2H, -N**H**$_2$), 6.88 (d, 1H, C**H** aromatic G2MPE), 6.81 (m, 1H, C**H** aromatic G2MPE), 4.26 e 3.80 (2 m, 2H, (CH-C**H**$_2$-O-Ar G2MPE), 3.30 (m, 1H, -C**H**-O epoxy group), 2.80 e 2.52 (2dd, 2H, C**H**$_2$-O epoxy group), 2.13 (s, 3H, -C**H**$_3$) ppm.
- *GA4 24h:* ^{1}H-NMR (DMSO-*d*^{6}): δ = 8.12 (s, 1H, C(8)**H** aromatic Adenine) 8.03 (s, 1H, C(2)**H** aromatic Adenine), 7.30-6.75 (m, 4H, C**H** aromatic G2MPE reacted and not-reacted), 4.50 e 3.50 (m, 8H, (C**H**$_2$-O-Ar, C**H**$_2$-N, C**H**-OH, CH-O unreacted epoxy group), 2.80 e 2.52 (2dd, 2H, C**H**$_2$-O unreacted epoxy group) 2.13 (s, 3H, -C**H**$_3$) ppm.

3.3 Results and discussion

In order to assess the feasibility of Adenine as epoxy hardener, its reaction with DGEBA, that is the simplest polymeric precursor possible, has been studied. On preliminary basis different ratios of DGEBA-Adenine have been tested and different formulations have been prepared; in particular molar ratios ranging from 5 to 11 led to the best results, specifically DA1 (10.80 mol / mol), DA2 (8.11 mol / mol) and DA3 (5.42 mol / mol) have been selected for further investigation. The formulation prepared are reported in Table 3.1.

3.3.1 TGA analysis of DGEBA - Adenine system

The thermal stability of the epoxy precursor DGEBA and the systems DA1, DA2 and DA3 was carried out through Thermogravimetric Analysis (TGA). The thermograms for the three formulations and DGEBA are reported in Figure 3.2 and Table 3.3. As reported in Figure 3.2, DGEBA displays a single weight loss of 99% with onset at 305°C. Concerning samples DA1, DA2 and DA3, they all present a single weight loss in the heating step with similar final residue around the 16%, which is completely degraded in the isothermal step in air (oxidizing atmosphere) at 600°C; furthermore, an increase in the degradation temperature of 45-50°C, compared to the polymeric precursor, is displayed.

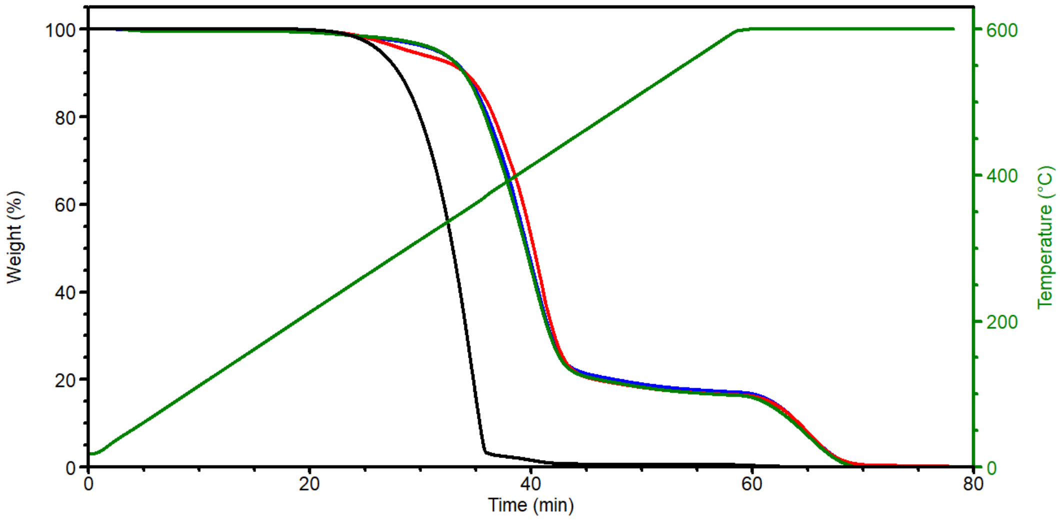


Figure 3.2: *TGA curves in nitrogen and air of DGEBA (---), DA1(---), DA2 (---), and DA3(---) formulations*

This increase in thermal properties of D1, D2 and D3 can be ascribed to the reaction of DGEBA with Adenine during the heating phase, and the consequent formation, of a crosslinked system.

Table 3.3: *Results of TGA analysis of samples DGEBA, DA1, DA2 and DA3*

Sample	***Weight loss N_2 atmosphere (w%)***	***Onset (°C)***	***Residue N_2 atmosphere (w%)***
DGEBA	99	305	1
DA1	84	357	16
DA2	83	356	17
DA3	84	351	16

3.3.2 DSC analysis of DGEBA - Adenine system

In order to study the crosslinking reaction of DGEBA with Adenine, it was decided to perform dynamic and isothermal Differential Scanning Calorimetry (DSC) tests, using a maximum temperature of 280°C in order to avoid degradation of the system.

Initially the three formulations DA1, DA2 and DA3 were thermally characterized with DSC in dynamic mode, applying a heating ramp of 1°C/min for the first heating and a 20°C/min ramp for the second heating; DSC thermograms and data are reported in Figure 3.3 and Table 3.4.

The first heating scans (Figure 3.3A) clearly display, for all samples, the typical stepwise feature around –18°C belonging to the T_g of the non-crosslinked resin. All the analyzed formulations show a clear exothermal transition, ascribed to the epoxy resin precursor reacting to provide the three-dimensional thermoset network, with a reaction heat between 360-425 J/g.

Exothermal transitions of DA1, DA2 and DA3 samples, are characterized by the presence of multiple peaks of different shape and intensity dependent on the amount of Adenine in the systems, suggesting the presence of some different reaction process (with different kinetics). The more the hardener, the more amine groups are capable of reacting with DGEBA, leading to a higher reaction heat due to the opening of more epoxy rings, and a greater number of crosslinking points in system can be formed, leading to an increase in the intrinsic rigidity of material and higher T_g values.

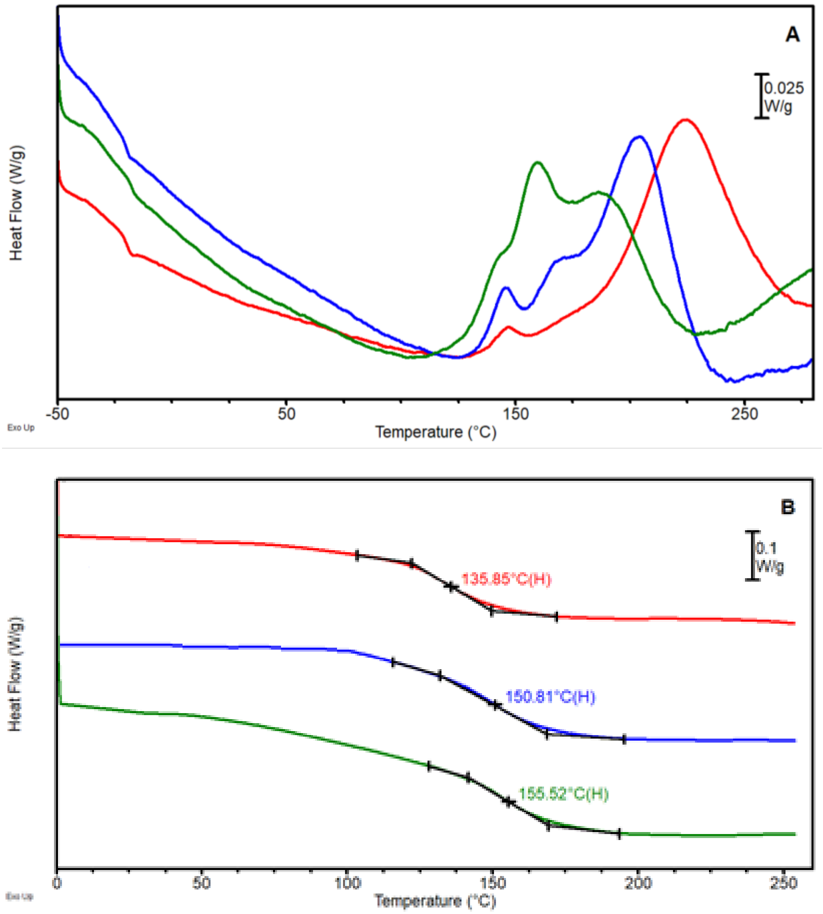


Figure 3.3: *DSC thermograms of the first heating scan (heating rate 1°C/min) (A) and second heating scan (heating rate 20°C/min) (B) for DA1(**---**), DA2 (**---**) and DA3 (**---**).*

The ΔH values related to the crosslinking enthalpy for the formulations DA1, DA2 and DA3 show a growing trend dependent on the increase of Adenine added and in the same way, a shift towards higher values of the T_g is observed.

Table 3.4: *Relevant DSC data of DEGBA/Adenine (DA) samples*

Sample	***ΔH (J/g)*** [a]	***$T_{r\,max}$ (°C)*** [b]	***T_g (°C)***
DA1	362	225	136
DA2	402	204	151
DA3	422	159	156

[a] ΔH is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$ is the temperature corresponding to maximum rate of the crosslinking reaction

Thus, DSC analysis suggested the feasibility of using Adenine as a novel curing agent for DGEBA.

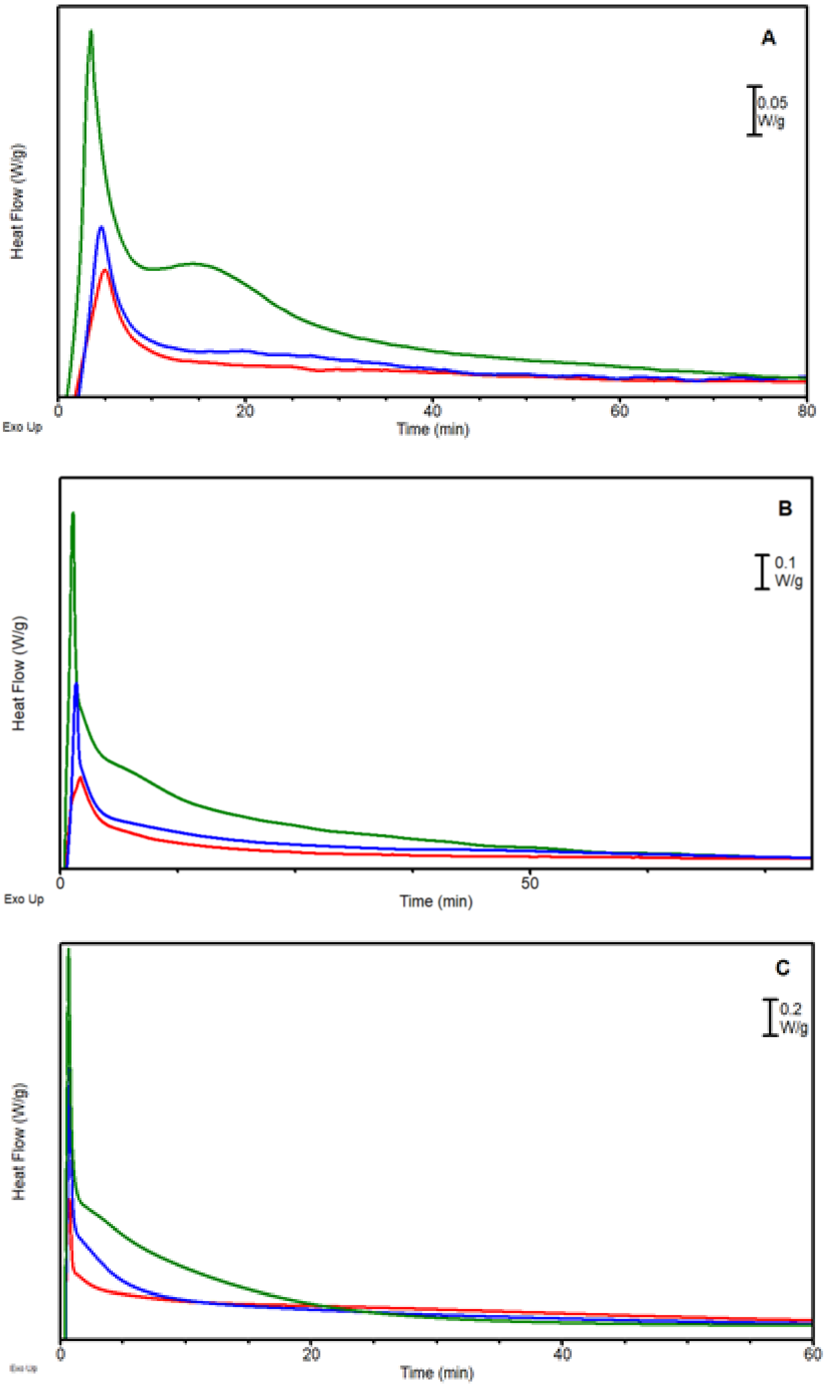


Figure 3.4: *DSC thermograms of the isothermal step of the systems at 160°C (A), 180°C (B) and 200°C (C) of the systems DA1(---), DA2 (---) and DA3(---).*

Based on the data obtained through dynamic DSC tests, isothermal DSC analyses were performed at 160, 180 and 200°C, since at these temperatures it is possible to observe the development of the crosslinking reaction without any degradation of the system. Isothermal analyses are fundamental in order to identify the reaction enthalpy, the time required to obtain the maximum reaction rate and the time necessary to obtain complete resin crosslinking, essential parameters for the simulation of the industrial cure process.

The results obtained are shown in Table 3.5 and, in Figure 3.4, the trends of DA1, DA2 and DA3 under isothermal conditions at 200°C are reported as example.

It is possible to point out, as the isotherm temperature increases, a clear shift towards shorter times of both the crosslinking peak and the time necessary to complete the reaction. Both these events are dependent on the different temperatures at which the isothermal processes have been conducted; in fact, more the temperature increases, more the hardener reacts faster with DGEBA. Furthermore it is worth noting the increasing of ΔH by enhancing the quantity of hardener in the mixture by keeping constant the curing temperature. Such a behavior can be ascribed to the dependence of the crosslinking reaction rate on the number of amine groups which are prone to react with the epoxy precursor.

At 160°C, a complete crosslinking is observed only for the formulation DA3 and a final T_g of 182°C was achieved. DA 1 and DA2 display low reaction heat and T_g and the presence of residual crosslinking in the second scan suggesting they are not yet completely cured.

At 180°C a complete crosslinking is observed for DA2 and DA3 formulations while the DA1 sample is still not completely cured in the analysis conditions.

Lastly, at 200°C, the all three formulations show, both in terms of reaction enthalpies and T_g (all over 150°C), a complete crosslinking (Table 3.5).

Table 3.5: Relevant isothermal DSC data of DA1, DA2 and DA3 samples at 160-180-200°C

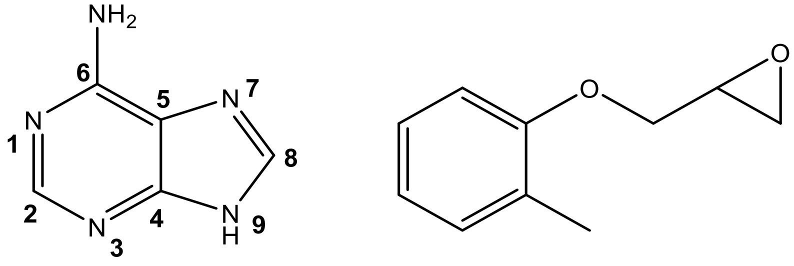
Sample	***T iso (°C)*** [a]	***Time peak (min)*** [b]	***Time tot (min)*** [c]	***ΔH (J/g)*** [d]	***T_g(°C)***
DA1	160	4,99	84	65	11
DA2	160	4,61	68	90	51
DA3	160	3,53	159	375	182
DA1	180	2,16	180	199	117
DA2	180	1,55	137	357	173
DA3	180	1,39	128	495	198
DA1	200	0,70	151	442	152
DA2	200	0,70	117	474	164
DA3	200	0,68	120	562	168

[a] T iso, is the temperature chosen for the curing process, [b] t peak, is the time corresponding to the maximum speed of the crosslinking reaction, [c] t tot, is the time needed to achieve a complete crosslink of the resin system, [d] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener.

Observing the trend of T_g for the formulations of resin DA2 and DA3, it can be noted a decrease changing the isothermal temperature from 180 to 200°C. Such a phenomenon could be ascribed to the occurrence of secondary reactions which are promoted by the high temperatures used and the high quantity of Adenine present.

3.3.3 Definition of G2MPE - Adenine reaction mechanism

Given the excellent results obtained for the Adenine-DGEBA formulation, it could be of great interest to define the reaction mechanism of Adenine with epoxy resins, allowing a better understanding of the reaction steps and the overall process. In order to define the reaction mechanism of Adenine with epoxy resin precursors, the crosslinking reaction was investigated through ^{1}H NMR technique. Generally, the product of the crosslinking reaction between thermosetting resins and hardeners is an infusible and insoluble material with highly branched crosslinked structure. For this reason, instead of a multifunctional epoxy resin precursor, Glycidyl 2-Methylphenyl Ether (G2MPE) was selected as epoxy component for the investigation of the reaction pathway of Adenine. G2MPE possesses a structure very similar to DGEBA (Figure 3.5) but bearing only one epoxy functionality allowing the obtainment, after the reaction, of a not crosslinked soluble material analyzable through NMR technique.

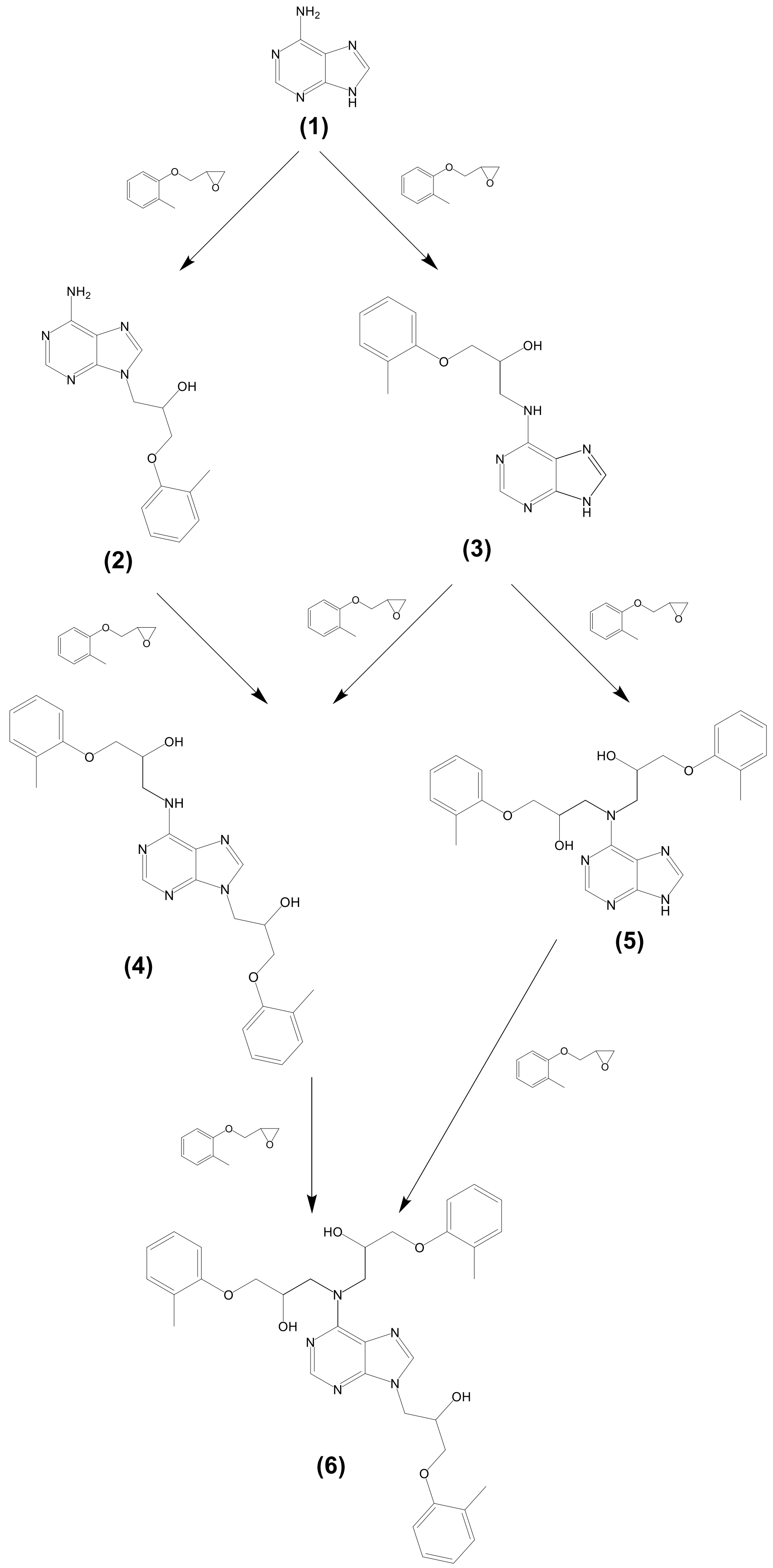


Adenine

Glycidyl 2 Methyl Phenyl Ether

Figure 3.5: *Chemical structure of Glycidyl 2-Methylphenyl Ether (G2MPE))*

Adenine is not soluble in the majority of solvents. For this reason, the reaction was conducted in DMSO, varying the molar ratio between the two reagents. In particular, conditions with equimolar amounts (Adenine / G2MPE 1: 1) and excess of epoxy compound (Adenine / G2MPE 1: 4 and 1: 8) were investigated. The mixtures obtained after 24 hours of reaction were named, respectively, GA1, GA4 and GA8. All reactions were performed in DMSO at 90°C for 24 hours. Scheme 3.1 shows the possible reaction products.



Scheme 3.1: *Possible reaction products between Adenine and G2MPE.*

In Figure 3.6 the ^{1}H-NMR spectra of the Adenine, of the Adenine / G2MPE mixture in molar ratio 1 to 4 before the reaction (GA4 blank) and of various molar ratios of the two reactants (GA1, GA4 and GA8) after 24 hours of reaction at 90°C, are reported.

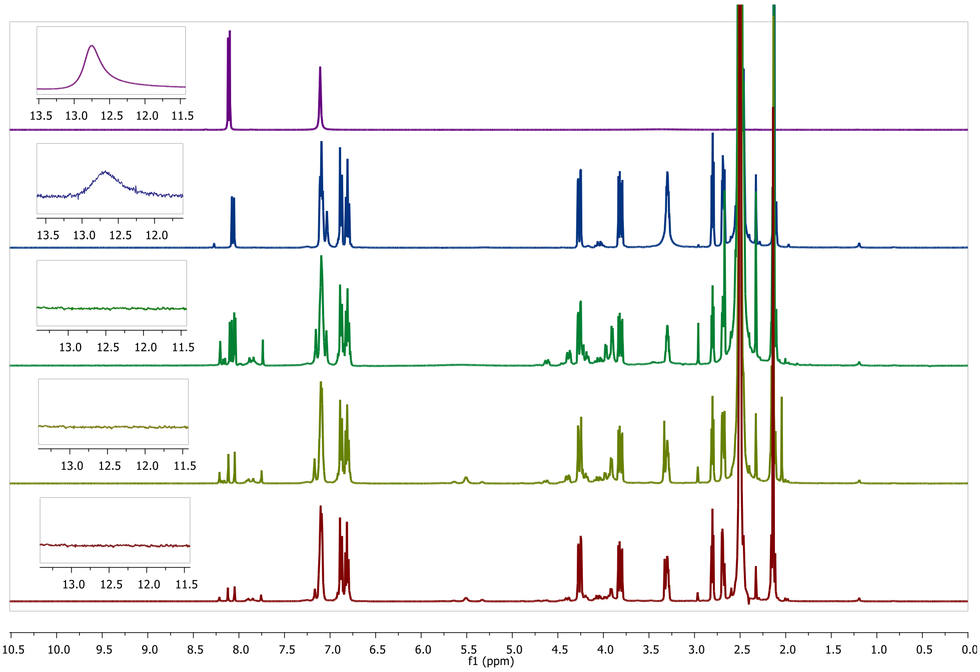


Figure 3.6: *^{1}H NMR spectra of Adenine (**---**), GA4 blank (**---**) and GA1 (**---**), GA4 (**---**), GA8 (**---**) after 24 hours of reaction at 90°C.*

In the ^{1}H-NMR spectrum of Adenine three characteristic signals are observed: the most acidic proton of the molecule, the one linked to the pyrrole nitrogen, resonates at low fields and displays a signal at 12.8 ppm. Furthermore it is possible to observe the signals corresponding to the two aromatic protons CH [C(2) and C(8) see Figure 3.1] around 8 ppm and the signal associated to the amino group at 7.0 ppm. The mixture before the reaction (GA4 blank) shows, in addition to the Adenine peaks, the signals belonging to G2MPE; in particular the signals of the aromatic protons falling around 7 ppm and the characteristic signals of the aliphatic CH of the epoxy ring between 3.5 and 2.5 ppm are observed. After 24 hours of reaction GA1 spectrum shows the formations of the signals between 4.2 and 3.7 ppm associated to the presence of CH-OH and CH_2-N groups, respectively. This event confirms the occurrence of the reaction between Adenine and the epoxy group. The reaction is also confirmed by the variations displayed by the signals in the aromatic zone (Figure 3.6): it is possible to observe a decreased intensity of the two singlets corresponding to the two aromatic Adenine protons, clearly visible before the reaction around 8 ppm (GA4 blank), and the formation of two other signals in the same area.

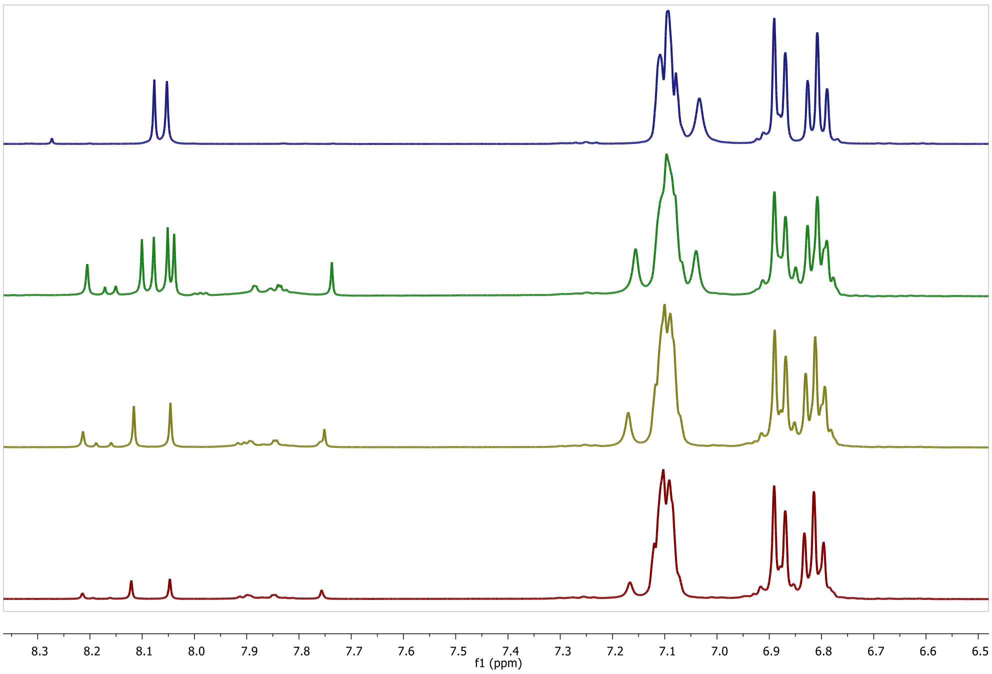


Figure 3.7: *^{1}H NMR spectra of GA4 blank (**---**), GA1 (**---**), GA4 (**---**) and GA8 (**---**) after 24 hours of reaction at 90°C.*

After a reaction time of 24 hours, the signal at 12.8 ppm completely disappears while the signal at 7.1 ppm is still present (Figure 3.7). This event suggests that the imidazole nitrogen atom is primarily involved in the nucleophilic substitution reaction (Product 2 in Scheme 3.1); the attack on the primary amine starts later, although it is less sterically hindered. This is due to the higher predisposition to nucleophilic attack of the nitrogen of the pyridine residue, which is more basic than the primary amine of Adenine, having the electronic doublet more delocalized on the aromatic cycle. Another possible reason explaining why pyridine nitrogen is more reactive could be due to the greater capacity of the aromatic heterocyclic system to stabilize, in the two aromatic rings, the positive charge that is formed in the intermediate of reaction. This is in agreement with what has already been reported in the literature for the reaction between Adenine and ethylene oxide [177]. It is also possible to notice, in the presence of equimolar amounts of the two reagents (GA1), a decrease in intensity of the signal corresponding to the primary amine on the pyrimidine ring of Adenine (7.1 ppm), and then its complete disappearance when in excess of epoxy compound (G4 and G8). At the same time, a new signal at 7.2 ppm is formed: this could be due to the reaction of the amino group in C(6) (Figure 3.5) with an epoxy group with consequent formation of a secondary amine (Product 4 in Scheme 3.1). These evidences suggest the competition between pyridine nitrogen and the primary amine in the nucleophilic reaction attack of Adenine on the epoxy ring.

In order to study the mechanism in detail, the reaction between Adenine and G2MPE, in a 1:4 molar ratio (GA4), was monitored over time by ^{1}H-NMR analysis. In particular, the reaction was carried out at 90 and 95°C recording the NMR spectra at different reaction times: after 1, 3, 5, 7 and 9 hours. Figure 3.8 shows the obtained ^{1}H-NMR spectra in the range of the aromatics.

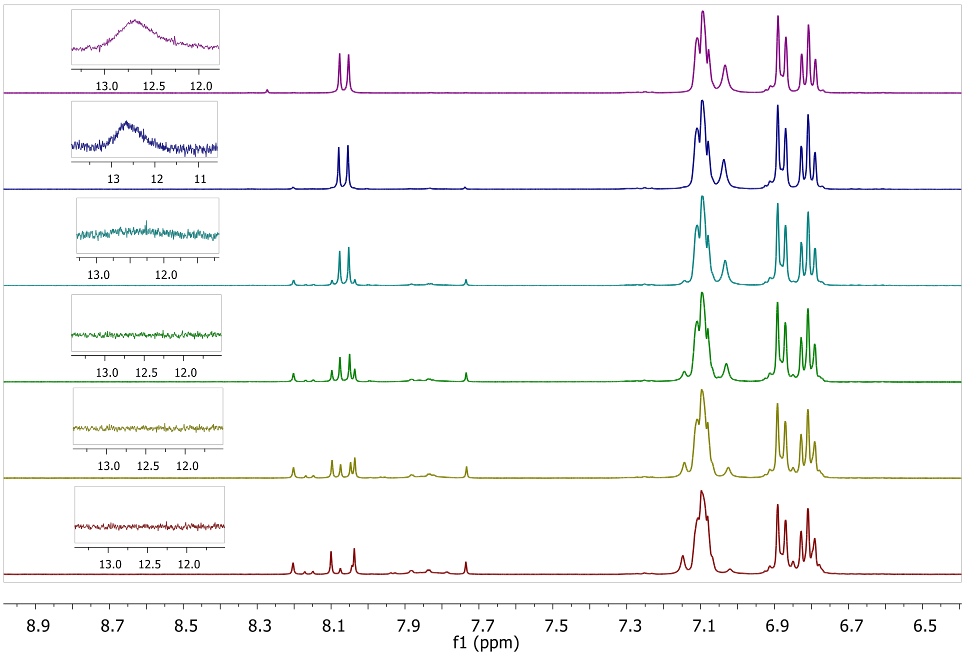


Figure 3.8: *^{1}H-NMR of GA4 at 0 (---), 1 (---), 3 (---), 5 (---), 7 (---), and 9 (---) hours of reaction at 90°C.*

Between the first and the third hour of reaction, the characteristic band of the pyrrole nitrogen, around 12.5 ppm, decreases in intensity up to disappeared. Such a behavior suggests that G2MPE reacts with the secondary amine on the imidazole ring; the signal at 7 ppm, corresponding to the NH_2 protons, remains almost unchanged. Thus, the substitution of pyridine nitrogen is completed already after three hours of reaction, leading to the formation of product (2) (Scheme 3.1). Between 3 and 9 hours of reaction, the decrease in the intensity of signal of the primary amine, at 7.0 ppm, and the appearance of a new band at slightly lower fields (7.2 ppm) is observed. This suggests that the primary amine of Adenine reacts with the epoxy molecule resulting in the formation of the secondary pyrimidine amine (Product 4, Scheme 3.1). Concerning the signal associated with aromatic Adenine CH groups (8.1 ppm), the formation of a multiplet is already observed at 3 hours due to the change of the chemical surrounding of the molecule, which resolves again in two singlet, at slightly different fields, after 9 hours of reaction. NMR analysis highlights the complete substitution of the pyrrole nitrogen (C9, Figure 3.5). The primary amino group, instead, seems to react just in part, probably because it is too hindered to be able to react again with an epoxy ring to form the three-substituted product

(Product 6, Scheme 3.1). Presumably, therefore, only the formation of a bi-substituted reaction product (Product 4) can be achieved as confirmed by the comparison of the CH_2-O integrals of the unreacted epoxy ring and the CH-CH_2-O of the reacted epoxy residue.
In order to increase the reaction speed and push it until the possible formation of the three-substituted product (6), the reaction was carried out at higher the temperature (95°C). The NMR spectra obtained with the Adenine / G2MPE 1: 4 mixture are shown in Figure 3.9.

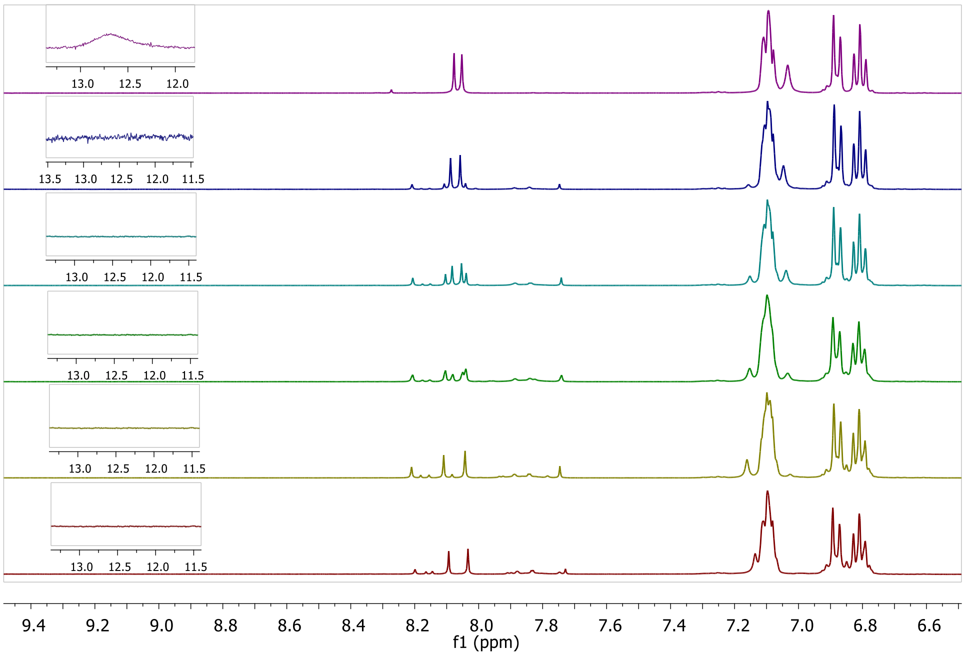
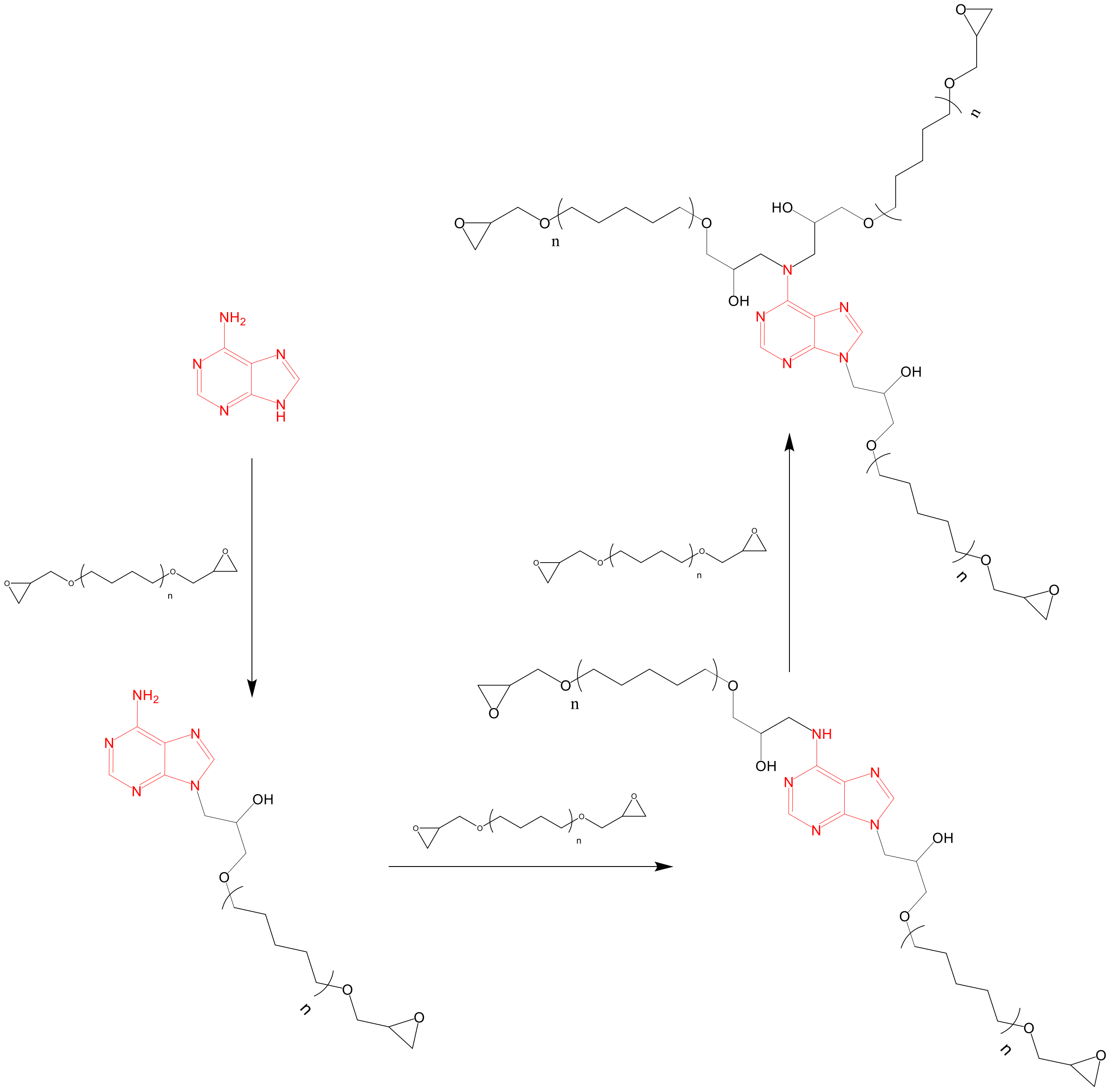


Figure 3.9: *^{1}H-NMR of GA4 system at 0 (---), 1 (---), 3 (---), 5 (---), 7 (---) and 9 (---) hours of reaction at 95°C.*

At 95°C, after one hour of reaction, the disappearance of the signal at 12.8 ppm, corresponding to the complete replacement of the secondary amino group, is observed. At the same time the signal corresponding to the primary amine decreases. Furthermore a chemical shift variation of the signal associated to the aromatic CHs (8.1 ppm) is observed and already after one hour of reaction the formation of a multiplet is noted. As the reaction time increases, an evident decrease in intensity of the signal at 7.1 ppm, until its total disappearance, and the formation of a new band at 7.2 ppm in observed. These events are again associated with the partial substitution of NH_2, which forms a secondary pyrimidine amine. After nine hours of reaction, a different chemical shift of the signals related to the aromatic Adenine CHs is observed and it is possible to hypothesize the formation of the bi-substituted product (Product 4, Scheme 3.1). Even in these conditions, the NMR analysis does not show the formation of the three-substituted product (Product 6, Scheme 3.1), probably due to the steric hindrance present on the molecule.

In the studied mild conditions (temperature below 100°C) it was not possible to push the reaction to the formation of the three-substituted compound. Anyway, increasing the temperature up to the real conditions used in industrial curing processes of epoxy resins (120 and 180°C), the subsequent reaction of the secondary amine with formation of the desired product (6) could be possible. However, the mild synthetic conditions used allowed to determine, for the first time, the sequence of consecutive reactions that leads to the formation of the three-dimensional lattice of a generic epoxy resin in the presence of Adenine (Scheme 3.2).



Scheme 3.2: *general synthetic reaction mechanism of Adenine with epoxy derivatives.*

3.4 Conclusions

In order to find a novel bio-based aromatic curing agent for epoxy resins, Adenine was tested with DGEBA polymeric precursor. The crosslinking reaction was studied by TGA and DSC analysis, confirming to the feasibility of using Adenine as novel bio-based hardener and produce high performance epoxy resin systems. In particular DSC allowed to estimate the total heat reaction rate and how different amounts of hardener affect the reaction kinetics, the resin crosslinking speed, the time taken to complete the crosslinking reaction at different temperature conditions and the final T_g achievable after the curing process. DA systems displayed interesting heat of reaction (400 J/g) and T_g values, ranging between 136-156°C, suggesting the feasibility of using Adenine as a novel curing agent for epoxy resins.

The crosslinking mechanism of epoxy resins with Adenine was studied by ^{1}H-NMR analysis of reaction mixtures containing Adenine and the mono-epoxy compound Glycidyl 2-methylphenyl ether (G2MPE) in different molar ratio. The obtained results show that the epoxy ring initially reacts selectively with the imidazole nitrogen; the attack on the primary amine starts later, although it is less sterically hindered. This is due to the higher predisposition to nucleophilic attack of the nitrogen of the pyridine residue, which is therefore more basic than the primary amine of Adenine, having the electronic doublet more delocalized on the aromatic cycle. Another possible reason explaining why pyridine nitrogen is more reactive could be due to the greater capacity of the aromatic heterocyclic system to stabilize, in the two aromatic rings, the positive charge that is formed in the intermediate of reaction.

Chapter 4 - Study of Adenine as hardener for commercial epoxy resin and production of carbon and natural fibers composite materials

4.1 Introduction

Nowadays carbon fiber reinforced polymers (CFRPs) are one of the more used structural materials since their outstanding mechanical and physical properties like lightweight, low coefficient of thermal expansion (CTE), high stiffness and high strength [173]. These multifunctional materials are widely used, not only in the aerospace or military industries, but also in large and increasing number of commercial mechanical engineering applications, such automotive, sports goods, medical equipment, pressure vessels, wind power and transport [173, 174]. Carbon fibers possess exceptional specific tensile strength and modulus ranging from 20-1000 GPa and 1-7 GPa, respectively, which represent the highest values for any commercial reinforcing fibers [174–176]. Currently, carbon fibers are produced from PAN-fibers (more than 90%); consequently, their cost is strongly influenced by the price and availability of fossil fuels and energy required for their manufacturing (see 1.4.2 in Chapter 1). According to the latest estimations, the worldwide demand for carbon fibers will continue to grow reaching the 117.000 tons by 2022 [46]. This growing demand can be directly associated with the unique advantages of CFRPs and their new industrial applications. Renewable alternative to PAN for carbon fiber precursors are under investigation since the first commercialization of carbon fibers [175–179]. However, due to expensiveness or non-comparable mechanical properties, carbon fibers obtained from renewable sources are still not completely developed. By contrast, in the last decades, a number of recycling technologies have been proposed and developed to recover high-quality recycled carbon fibers from scraps or end of life (EoL) CFRPs [48, 180–182]. Among these, pyrolysis process allows a cost-effective recovery of carbon fibers, still preserving high mechanical properties, and it is currently the only process which has reached early stages of commercialization [180, 183–185].

Recycled carbon fibers are usually found as short fibers [48, 185–187] since they are recycled from shredded CFRPs waste, crushed or cut into small pieces before the pyrolysis treatment. Furthermore, recycled carbon fibers cannot be reused in same applications but they can only be randomly incorporated into products such as short carbon fiber-reinforced polymers (SCFRPs). Despite the lower performance, SCFRPs show some advantages in comparison with continuous fiber-reinforced composites, like lower cost, isotropic mechanical properties and easier and cheaper manufacturing processing [188]. A LCA study [189] highlighted a considerable reduction on the environmental impact of CFRPs when recycled carbon fibers are used. Hence, depending on the products final purpose, the use of recycled carbon fibers, might be an environment sustainable and ecofriendly choice when the use of SCFRPs is required.

Another way to decrease the environmental impact of composite materials could be the inclusion of one or more bio-based components such as reinforcing agents and resins, obtained from a sustainable resource. Natural fibers can be subdivided into three broad categories: vegetable (plant based), animal, and mineral fibers. Plant based fibers can themselves be classified as either wood or non-wood fibers. Non-wood fibers may be further subdivided into bast, leaf or seed hair fibers, depending on their origin [132, 190, 191] in the plant, and wood fibers can be further subdivided into softwood and hardwood fibers. All plant based fibers, whether from wood or non-wood origin, are composed of three main cell wall polymers: cellulose, lignin and polysaccharide resins constituted of pectins and hemicelluloses [135]. The production of high quality natural fibers is a very complicate process. Fibers can be extracted from plants by chemical, mechanical and/or biochemical methods [192]. However, the total processing includes extraction, treatments for specific use and getting them into desirable textile forms, e.g., yarns, fabrics, nonwovens, etc., depending on the final purpose of the composite product. Natural fibers with high aspect ratio obtained from plants and animals can be spun into yarns and further twisted together to produce ropes or cords [132]. The yarns can also be woven or knitted to form fabrics. Fibers can also be matted or bonded to form nonwovens for use in many day-to-day applications. These fiber forms are also suitable for combining with resins to form composites. The more performing natural reinforcement agents, they can be obtained from long plant fibers (flax, ramie, hemp, jute, sisal, etc.), short fibers, obtained from recycled wood or waste paper, or byproducts derived from food crops [191].

With the aim of producing ecofriendly composite materials, it could be of interest to test different kinds of fibers, some obtained from renewable sources, with a bio-based resin system. In a previous work the possibility to use Adenine as epoxy resin hardener was validated (see chapter 2). Initially Adenine was tested with DGEBA in order to understand the crosslinking process with the simplest polymeric precursor system possible. Formulations containing DGEBA have been found difficult to thermally control in case of a scale up; moreover, the final product is very rigid and fragile and, therefore, not applicable in industrial fields. For these reasons, for a further implementation of the final products, it was decided to test Adenine as crosslinking agent of a commercial infusion epoxy resin (Elan-tron® EC 157, Elantas) and a commercial impregnation epoxy resin (Epikote 828 Hexion), both already used at industrial level. The main aim of this work was initially to verify the feasibility of Adenine as crosslinking agent for commercial infusion and impregnation resins, achieving high T_g crosslinked products. Hence the more promising formulations were coupled with carbon (virgin and recycled), flax and jute fibers in order to produce short fiber reinforced composite materials. The use of recycled carbon fibers and natural fibers was performed in order to study the possibility to produce composite materials reinforced with fibers obtained from more ecofriendly resources. The resin formulations and the obtained composite materials have been characterized through Thermogravimetric Analysis (TGA), Dynamic Scanning Calorimetry (DSC) and Dynamic Mechanical analysis (DMA).

4.2 Experimental

4.2.1 Materials

Elan-tron® EC 157 resin, with an average molecular weight of 700 g/mol was kindly supplied from ELANTAS Europe S.r.l.. Epikote 828 (Hexion) resin, with an average molecular weight of 377 g/mol, was kindly supplied from Reglass S.r.l.. Both resins were used as received without further purification.

Adenine (99% pure) was purchased from Alfa Aesar and used as received.

Virgin chopped carbon (VC) fibers (25 mm) were obtained cutting down Unidirectional Fabric UC 301 based on Toray T700S 12K dry fabrics. The recycled chopped carbon fibers (labelled as RC) (25 mm) were obtained from pyrolysis of Toray T700S 12K based carbon fibers, post-treated at 500°C for 60 minutes under oxidizing atmosphere. Both virgin and recycled carbon fibers were used without any further treatment.

Flax and jute fibers, kindly supplied from Groningen University, Netherlands, were manually chopped at a length of 25 mm and used without any further treatment.

4.2.2 Formulation preparation

Elan-tron® EC 157 - Adenine systems (ELA): different amounts of Adenine (2.32 and 4.54 w%) were added to Elan-tron® EC 157 resin. The obtained formulations were mechanically stirred with a speed of 300 rpm at 75°C until complete homogenization of the hardener with the resin. When the mixture appeared completely homogenous, the flask was cooled and used for the preparation of the TGA and DSC samples. Different mixtures were produced and labelled according to the list reported Table 4.1.

Table 4.1: *Compositions of the different investigated thermosets formulations of Elan-tron® EC 157 with Adenine.*

Sample	Elan-tron (w%)	Adenine (w%)	Elan-tron (mol)	Adenine (mol)	Molar ratio
ELA1	97.68	2.3	0.0143	0.0018	8.11
ELA2	95.46	4.5	0.0143	0.0035	4.05

Epikote 828 - Adenine systems (EPA): different amounts of Adenine (2.3, 4.5, and 7.5 w%) were added to Epikote 828 resin. The obtained formulations were mechanically stirred with a speed of 300 rpm at 85°C until complete homogenization of the hardener with the resin. When the mixture appeared completely homogenous, the flask was cooled and used for the preparation of the TGA and DSC samples. Different mixtures were produced and labelled according to the list reported Table 4.2.

Table 4.2: *Compositions of the different investigated thermosets formulations of Epikote 828 with Adenine*

Sample	Epikote 828 (w%)	Adenine (w%)	Epikote 828 (mol)	Adenine (mol)	Molar ratio
EPA1	97.7	2.3	0.0265	0.0017	15.25
EPA2	95.5	4.5	0.0265	0.0035	7.61
EPA3	92.5	7.5	0.0265	0.0060	4.42

The technical data of these two resins are reported below, in Table 4.3.

Table 4.3: Properties of commercial epoxy resins

Resin	Density (kg/L)	Average molecular weight (g/mol)	Viscosity 25°C (Pa*s)
Epikote 828	1.16	374	13
Elan-tron® EC 157	1.16	700	0.6

4.2.3 Composite materials production

Chopped carbon fiber reinforced composite materials production:

Virgin (VC) and Recycled Carbon (RC) fibers of the average 2.5 cm length (15 g) were mixed with the pre-mixed Adenine-epoxy resin precursor (Elan-tron® EC 157 or Epikote 828) mixture (50g) at 75°C in order to obtain a uniform wetting of the fibers and avoid an increase of the resin viscosity during the mixing phase. In Table 4.4 are reported the fiber/resin weight ratio used for the production of chopped carbon fiber reinforced composites.

Table 4.4: *Fiber/resin weight ratio used for carbon fiber composite production.*

Sample	Fiber content (w%)	Resin content (w%)
ELA2-VC	55	45
ELA2-RC	55	45
EPA2-VC	62	38
EPA2-RC	62	38

The mixture was stirred until complete uptake of the resin by the CFs, then the resin/Carbon Fibers mixture (33 g for ELA2 and 40g for EPA2) was poured into a 60 x 60 x

10 mm cavity and hot-press (DAN12T4CPT model, produced by Monti Sistemi, equipped with water cooling plates) cured at according to the following procedure: the mold was inserted in the press with the plates already heated at 140°C, where it was kept in isotherm for 45 minutes with an applied pressure of 1 bar. After the isothermal step, the temperature was raised at 180°C and the applied pressure was increased up to 50 bar. The sample was kept in isothermal condition for 200 minutes Finally, before opening the hot-press plates, the mold was cooled at RT and then the pressure was decrease and the mold removed from the press. After cooling down to RT, a 60 x 60 x 4 mm composite panel was removed from the mold. Thus, it was possible to obtained composite materials containing carbon fibers (virgin and recycled), using infusion and impregnation resins crosslinked with Adenine. Then every composite panel was cut for the preparation of the different specimens in order to perform thermal and mechanical characterization.

Chopped natural fiber reinforced composite materials production:

The epoxy resin systems ELA2 and EPA2 were prepared in big amount (40g) by adding and stirring the selected amount of Adenine to Elan-tron® EC 157 and Epikote 828 resin respectively. Then flax (F) or jute (J) fibers (10g) were added and carefully hand-stirred with pre-mixed systems kept at 75°C in order to obtain a uniform wetting of the fibers and avoid an increase of the resin viscosity during the mixing phase. In Table 4.5 are reported the fiber/resin weight ratio used for the natural fiber reinforced composite products.

Table 4.5: *Fiber/resin weight ratio used for natural fiber composite production.*

Sample	*Fiber content (w%)*	*Resin content (w%)*
ELA2-F	50	50
ELA2-J	50	50
EPA2-F	57	43
EPA2-J	57	43

Each one of the randomly oriented resin/carbon fiber mixtures (20g for ELA2 and 23g for EPA2 products) was transferred into an iron mold with a 60 x 60 x 10 mm cavity, which was closed with a counter-mold designed to allow the come out of the resin excess from the edges. Hence, the system, closed in the mold, was placed in a hot-press and cured according to the following procedure: the mold was inserted in the press with the preheated plates and kept at 160°C for 45 minutes with an applied pressure of 1 bar. After the isothermal step, the temperature was raised at 190°C and the applied pressure was increased up to 50 bar. The sample was kept in isothermal condition for 200 minutes. Finally the mold was cooled at RT, the pressure was decrease and the mold removed from the press. After cooling down to RT, a 60 x 60 x 4 mm composite panel was removed from the mold and the samples obtained were post-cured at 180°C for 120 minute in order to complete the crosslinking reaction of the resin. Thus, it was possible to obtained composite materials containing flax and jute fibers using infusion and impregnation resins crosslinked with Adenine. Then every composite panel was cut for the preparation of the different specimens in order to perform thermal and mechanical characterization.

4.2.4 Characterization

- Thermogravimetric analysis (TGA) were carried out on a TA Instruments SDT Q600, in nitrogen atmosphere (flow rate: 100 ml/min) heating from RT to 600°C at 10°C/min, followed by a switch to oxidizing atmosphere (air) and an isothermal step of 20 min.
- The thermal behavior of the reacting mixtures was evaluated by Differential Scanning Calorimetry (DSC, Q2000 TA Instruments) and the measurements have been carried out in dynamic and isothermal mode. Dynamic DSC analysis were performed, under nitrogen flow, heating the samples at a heating rate of 1°C/min from -50 to 280°C. After the first heating, the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation. Isothermal DSC analysis were performed at 160, 180, or 200°C and the sample was introduced in the furnace already heated to the experimental temperature. After the isothermal step the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for $\mathrm{T_g}$ evaluation.
- Dynamic mechanical analysis (DMA) were performed with NETZSCH 242 E Artemis instrument, in Three Point Bending mode with 20 mm sample holder. The following conditions, in mixed control, were used during the analysis: heating ramp at 3°C/min from RT up to 250°C, frequency 1 Hz, maximum amplitude ± 10 μm, maximum dynamic force 10 N, additional static force 0.5 N and proportional factor (Fstat/Fdin) = 1.1.

4.3 Results and discussion

Short carbon fiber reinforced polymers (SCFRP) find various kind of applications, since they display isotropic properties and allow an easier manufacturing process when compared to long-fiber composites [13, 193–195]. SCFRPs final properties depends on various factors such as manufacturing processes, types of matrix and fibers used, fiber content, length, and orientation, and fiber-matrix adhesion [186, 187, 196, 197]. Natural fibers have been used since they represent a potential starting point for the design and production of high performance composite materials, obtained from renewable sources

[132]. With the aim of verifying the possibility to produce composite materials, reinforced with different kind of fibers (Carbon, Recycled carbon, Flax and Jute fibers), the feasibility of Adenine as crosslinking agent for commercially used epoxy resin was initially tested with an infusion resin and the impregnation resin.

4.3.1 Study of the Elan-tron® EC 157 - Adenine system

On preliminary basis different ratios of Elan-tron® EC 157-Adenine have been studied and different formulations have been prepared. In particular resin-hardener molar ratio ranging from 4 to 8 led to the best results, specifically ELA1 (2.3 w% - 8.11 mol/mol) and ELA2 (4.5 w% - 4.05 mol/mol) formulations have been selected for further investigations (see Experimental section 4.2).

4.3.1.1 TGA analysis of Elan-tron® EC 157 - Adenine system

Preliminary TGA analyses have been performed on the epoxy precursor Elan-tron® EC 157 and on ELA1 and ELA2 systems in order to evaluate their thermal stability and the possible release of volatile compounds. The thermogravimetric curves of the three formulations and Elan-tron® EC 157 are reported in Figure 4.1 and Table 4.6. The black curve inherent to the Elan-tron® EC 157 commercial resin shows two weight losses; the first one can be ascribed to the release of volatile substances with low molecular weight (such as additives or solvents), and the second one to the actual degradation of the resin.

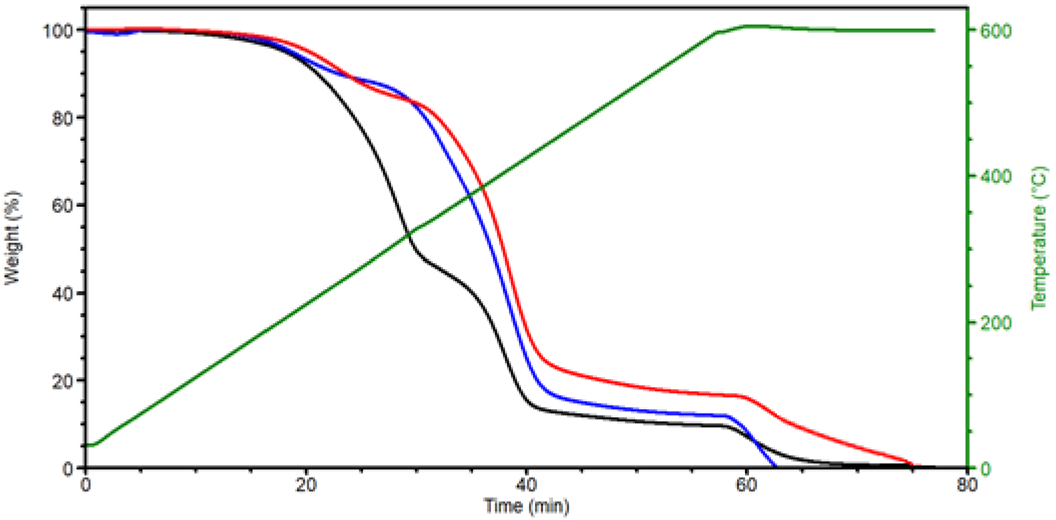


Figure 4.1: *TGA curves in nitrogen atmosphere then air of Elan-tron® EC 157 (**---**), ELA1 (**---**) and ELA2 (**---**) formulations*

The first onset is positioned at 247°C and correspond to a weight loss of 59% while the second is observed at 384°C. The commercial resin displays a final residue at 600°C lower than 10%, which is completely degraded in the isothermal step in air (oxidizing atmosphere). The ELA1 formulation shows three weight losses; the first, with onset positioned at 178°C, is probably referred to the release of lower molecular weight compounds, while the other two, associable to the degradation of the crosslinked resin fraction, present onsets at 329°C and 382°C respectively. ELA2 formulation also shows three losses, very similar to the ELA1 formulation; the first two have onsets at 189 and 321°C and the last one at 383°C. Both ELA1 and ELA2 show less than 20% of carbon residues after the heating in nitrogen atmosphere and are completely degraded in the isothermal step in air at 600°C.

Table 4.6: *TGA analysis of Elan-tron® EC 157, ELA1 and ELA2*

Sample	Weight Loss I (w%)	Weight Loss II (w%)	Onset I (°C)	Onset II (°C)	Onset III (°C)	Residue N_2 (w%)
Elan-tron® EC 157	*59*	*32*	247	384	-	9
ELA1	17	67	178	329	382	16
ELA2	13	75	189	321	383	12

It can be observed that thermograms related to the formulations ELA1 and ELA2 present higher degradation temperatures compared to the plain resin. This is due to the fact that the ELAN-tron® EC 157 resin, during the heating, has formed a crosslinked system reacting with Adenine, and therefore a more rigid material, with a consequent intrinsic increased thermal stability, was obtained.

4.3.1.2 DSC analysis of Elan-tron® EC 157 - Adenine system

With the aim to study the crosslinking reaction of Elan-tron® EC 157 with Adenine, it was decided to perform dynamic and isothermal Differential Scanning Calorimetry (DSC) tests, using a maximum temperature of 280°C in order to prevent degradation of the system. The selected infusion resin was Elan-tron® EC 157 which, having an average molecular weight about twice the DGEBA, for the same amount of resin, possesses about half of the epoxy functional groups compared to the latter. For this reason, less crosslinking points and more flexible chains will be present inside the material and, therefore, a lower crosslinking heat, a lower T_g, a slower and more controllable reaction and a lower intrinsic rigidity of the system will be theoretically achieved, compared to those based on DGEBA.

Initially the two formulations ELA1 and ELA2 were thermally characterized with DSC in dynamic mode, applying a heating ramp of 1°C/min for the first heating (to study the crosslinking reaction) and a 20°C/min ramp for the second one (to verify the complete crosslinking and asses the final T_g of the system). DSC thermograms and data are reported in Figure 4.2 and Table 4.7.

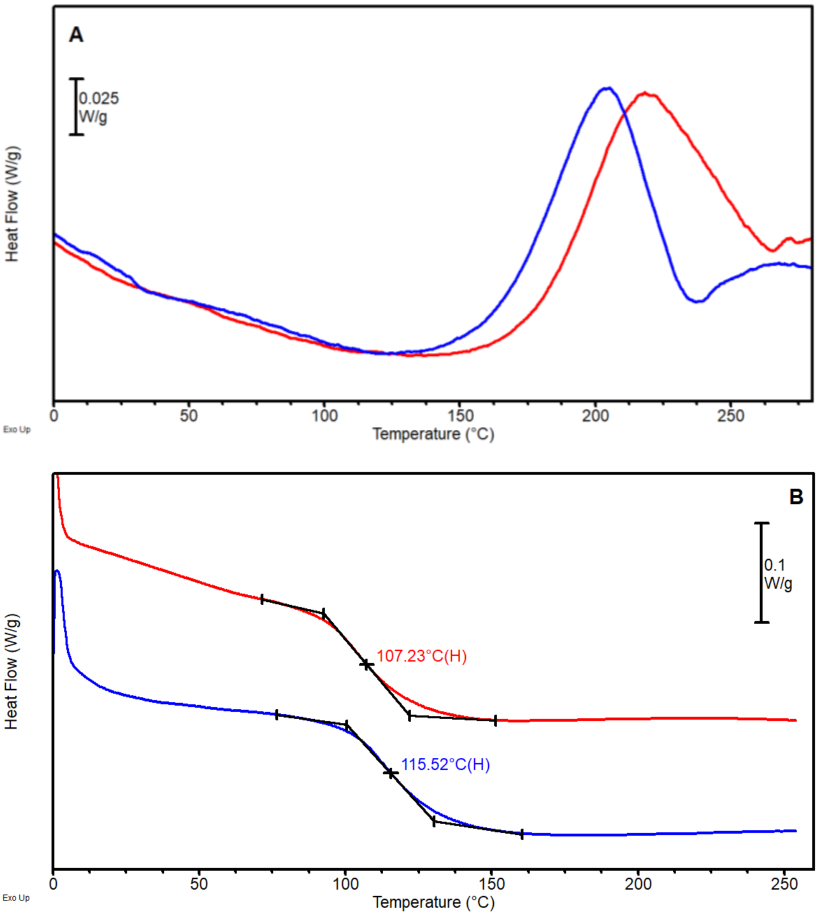


Figure 4.2: *DSC thermograms of the first heating scan (heating rate 1°C/min) (A) and second heating scan (heating rate 20°C/min) (B) for ELA1(---), ELA2 (---).*

All the analyzed formulations show, in the first heating scan, a clear exothermal transition, ascribed to the epoxy resin precursor reaction with the hardener to provide the three-dimensional thermoset network, with a reaction heat between 240-250 J/g (Table 4.7). Exothermic transitions of ELA1 and ELA2 samples are characterized by the presence a single peak, of different intensity dependent on the amount of Adenine in the systems, suggesting the presence of a single step kinetic.

Table 4.7: *Relevant DSC data of Elan-tron® EC 157/Adenine (EA) samples*

Sample	***ΔH (J/g)***	***$T_{r\,max}$ (°C)***	***T_g (°C)***
ELA1	*250*	*218*	*108*
ELA2	*246*	*203*	*116*

[a] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$, is the temperature corresponding to the fastest kinetic of the crosslinking reaction

Both samples ELA1 and ELA2 show a similar crosslinking enthalpy, and the T_g values present an increasing trend when more hardener is used. These events are due to the greater amount of hardener in sample ELA2, which leads to a greater number of crosslinks in the material and a consequent increase of T_g. Both the exothermic peaks and the corresponding T_g values, ranging between 108-116°C, suggest the feasibility of using Adenine as a novel curing agent for the commercial epoxy system Elan-tron® EC 157.

Based on the data obtained through dynamic DSC tests, isothermal DSC analyses were performed at 160, 180 and 200°C. Isothermal analysis are fundamental in order to identify the reaction enthalpy, the time required to obtain the maximum reaction rate and the time necessary to obtain complete resin crosslinking, essential parameters for the simulation of the industrial cure process. The results obtained in isothermal DSC mode are shown in Table 4.8 and Figure 4.3.

It is possible to highlight, as the isotherm temperature increases, a clear shift towards shorter times of both the peak crosslinking speed, which becomes always higher and narrower, and of the time necessary to complete the reaction.

At 160°C it is observed that the total reaction time of ELA2 formulation is greater than that relative to ELA1. This depends on the fact that at 160°C the temperature is not high enough to reach the complete crosslinking of the ELA1 formulation, which consequently requires shorter curing time. Both events are dependent on the different temperatures used in isothermal processes: by increasing the temperature, the hardener reacts faster with the resin. Furthermore, it can be observed an enhancing of the reaction ΔH (see Table 4.8) both when the isotherm temperature increases and when the concentration of hardener present in the system is higher.

At 160°C the crosslinking is very slow, ELA2 sample reacts about twice as fast compared to the ELA1 but the shape of the reaction peaks of both formulations appears to be broaden and low values T_g are observed. These two events can indicate that the curing reaction of both samples is not complete.

At 180°C, ELA2 displays a reaction speed 5 times higher than the ELA1 and, ΔH and T_g values in this conditions are higher than the ones at 160°C, hinting a more advanced, but still uncompleted, crosslinking of the resin.

Finally, at 200°C both formulations show high reaction enthalpies and T_g, suggesting a complete crosslinking process.

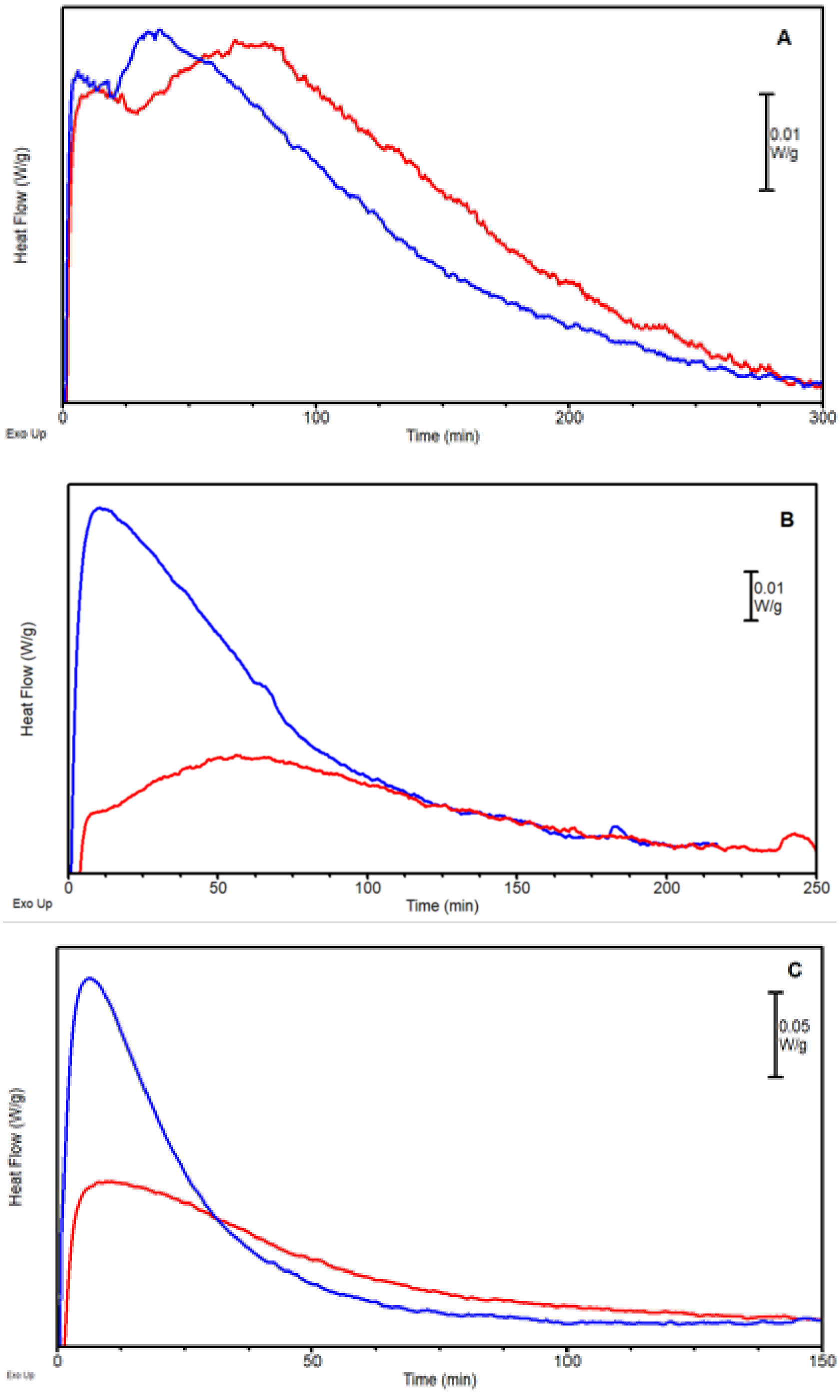


Fig. 3: *DSC thermograms of the isothermal step of the systems at 160°C (A), 180°C (B) and 200°C (C) for the systems ELA1(---) and ELA2 (---).*

In general, in this system enthalpy and T_g are considerably lower with respect to the DGEBA based systems (Chapter 3), because of the different amount of epoxy groups available for crosslinking per mass unit. In order to test the possibility to use the commercial infusion system crosslinked with Adenine, the formulation ELA was tested as matrix for composite materials production using different kinds of short fibers as reinforcing agent.

Table 4.8: *Relevant isothermal DSC data of ELA1 and ELA2 samples at 160-180-200°C*

Sample	***T iso (°C)*** [a]	***Time peak (min)*** [b]	***Time tot (min)*** [c]	***ΔH (J/g)*** [d]	***T_g (°C)***
ELA1	*160*	82	286	145	68
ELA2	*160*	38.18	293	280	103
ELA1	*180*	55.93	258	157	74
ELA2	*180*	10.42	203	282	114
ELA1	*200*	10.5	194	274	93
ELA2	*200*	6.31	122	324	122

[a] T iso, is the temperature chosen for the curing process, [b] t peak, is the time corresponding to the maximum speed of the crosslinking reaction, [c] t tot, is the time needed to achieve a complete crosslink of the resin system, [d] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener

4.3.1.3 Production and characterization of Elan-tron® EC 157 - Adenine chopped fibers reinforced composites

The previously discussed ELA2 system, which is the more promising, was reinforced with different kind of short fibers in order to produce composite materials. In particular carbon (both virgin VC and recycled VR), flax (F) and jute (J) fibers, chopped down to a suitable length (25mm) were combined with the ELA system in order to obtain new sustainable short fibers reinforced composites.

The composite materials have been produced using an iron mold, specially manufactured for this study, and the curing process was performed by hot compression molding technique. The curing cycle was optimized for Carbon and natural fibers reinforced materials (See Experimental section).

Composites were obtained as flat panels that were then cut in specimens suitable for further characterization. In order to determine the final composite weight to the real fiber/resin ratio, after the curing process, each composite panel was weighted, and knowing the amount of fibers added, the amount of resin present in each sample was assessed. For all the carbon reinforced composite panels, the average resin content was estimated to be around the 24 w%, while for the natural fiber reinforced products it was ranging between 26-34 w%, as reported in Table 4.9.

Each of the obtained samples was measured and weighed in order to obtain an index of the compactness of the sample, defined as Apparent Density (AD): the AD of each coupon has then been averaged in order to provide information about the overall homogeneity of the samples. As reported in Table 4.9, the produced carbon fiber composites possess Average Apparent Densities (AAD) ranging from 1.45 to 1.51 g/cm^3, in agreement with the expected density for a quasi-isotropic epoxy CFRP (1.55 g/cm^3) [193]. Both natural flax and jute fiber reinforced composites displayed lower density values, in the range 0.92-0.94 g/cm^3, if compared to Carbon fiber reinforced product since the density of natural fibers is lower than carbon fibers. The determined AAD suggest that a good compaction has been reached for all the composites produced, although a manual lab scale process was used, and in presence of a high fiber dosage (about 65-80%). It is also worth noting that, besides the untreated VC fibers, none of the other fibers has been subjected to a sizing treatment, thus lacking a surface coupling agent helping to promote adhesion toward the polymer matrix in the composite production.

Table 4.9: *Fiber content and Average Apparent Density (AAD) of the produced chopped fiber reinforced composites.*

Sample	***Fiber content (w%)***	***Resin content (w%)***	***AAD (g/cm^3)*** [a]
ELA2-VC	77	23	1.45
ELA2-RC	74	26	1.51
ELA2-F	74	26	0.92
ELA2-J	66	34	0.94

[a] Average Apparent Density (AAD) determined as the average of the ratio between measured weight and volume of the single bars as cut in the convenient dimension for mechanical tests.

In order to determine the final thermo-mechanical properties of the products, the produced composite materials have been characterized by Dynamic Mechanical Analysis (DMA). For each kind of sample, three specimens have been tested. The DMA results obtained for all the composite materials produced are reported in Figure 4.4 and Table 4.10. Concerning carbon fiber reinforced composite materials the E′ modulus at 30°C (E’$_{30}$) confirms the good reinforcing properties of fibers added to the resin. The good results obtained for recycled carbon fibers can be due to the partial oxidation of their surface, which can enhance the fiber-matrix adhesion even without the using of a sizing agent. In particular, the preservation of E’ moduli for samples containing recycled carbon fibers, confirms their feasibility as reinforcing agent and assess the recycling process as the non-destructive. Natural fiber reinforced materials display promising E’ modulus, even if, as expected, lower than carbon fibers. The best results have been obtained with flax fibers, which display a modulus twice the one obtained with jute fibers.

Table 4.10: *Results of DMA analysis of the composite material produced with ELA2 resin system.*

Sample	***E’$_{30}$ (MPa)***	***E’ onset (°C)***	***tan δ peak (°C)***
ELA2-VC	34500±10100	90	113
ELA2-RC	34600±4800	94	120
ELA2-F	16100±300	85	101
ELA2-J	8900±1500	83	100

Analyzing E’ onset temperatures of the composites (E’ onset), virgin and recycled carbon fibers composites display the same values and in the same way the results obtained with flax fibers are similar to the one obtained with jute fibers. The highest E’ onset temperatures have been obtained with carbon fiber products since these materials, probably, display a partial heat conductivity and therefore present a better distribution of heat to the resin during the curing process, if compared to natural fibers. The tan δ curves are plotted as a function of temperature in Figure 4.4 B. All the analyzed composites show a main relaxation process (T_α) associated to the T_g achieved after the curing process, whose position depends on the type of fiber-resin system. Again the best results have been obtained when carbon fibers have been used and all the products displayed tan δ peak over 100°C.

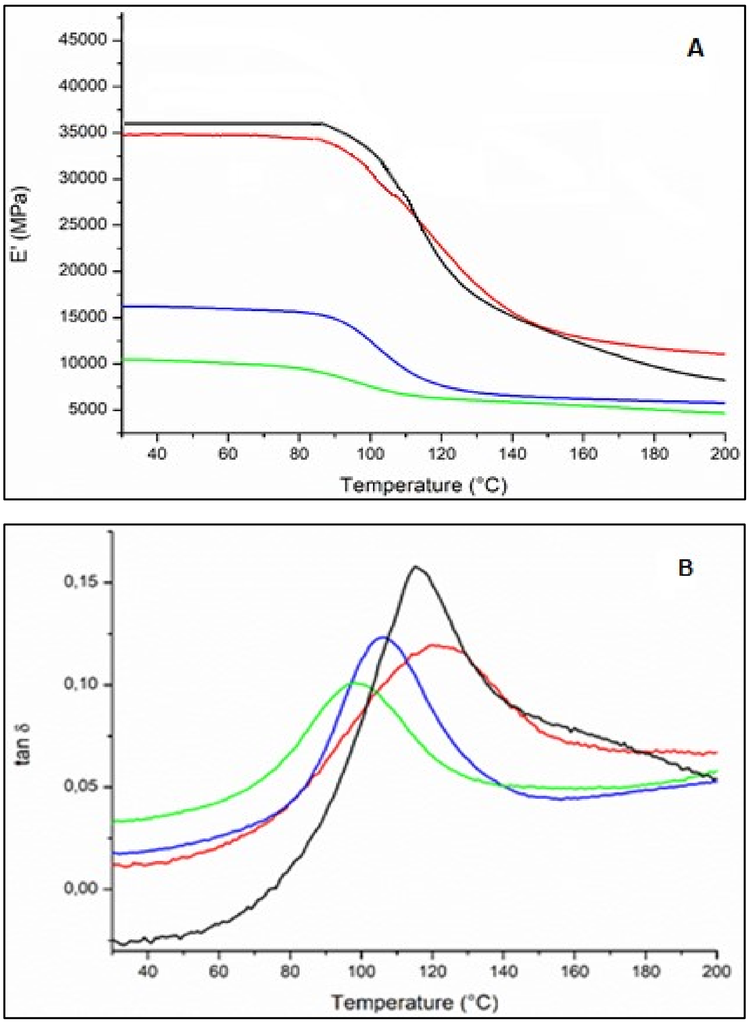


Figure 4.4: *DMA analysis of ELA2-VC (**---**), ELA2-RC (**---**), ELA2-F (**---**) and ELA2-J (**---**) samples.*

In general, all the results obtained confirm a good adhesion and interactions between all fiber types and the ELA2 resin system, proving the possibility to produce composite materials with good T_g and high mechanical properties.

The TGA thermograms of composite materials and the data obtained are shown in Figure 4.5 and in Table 4.11.

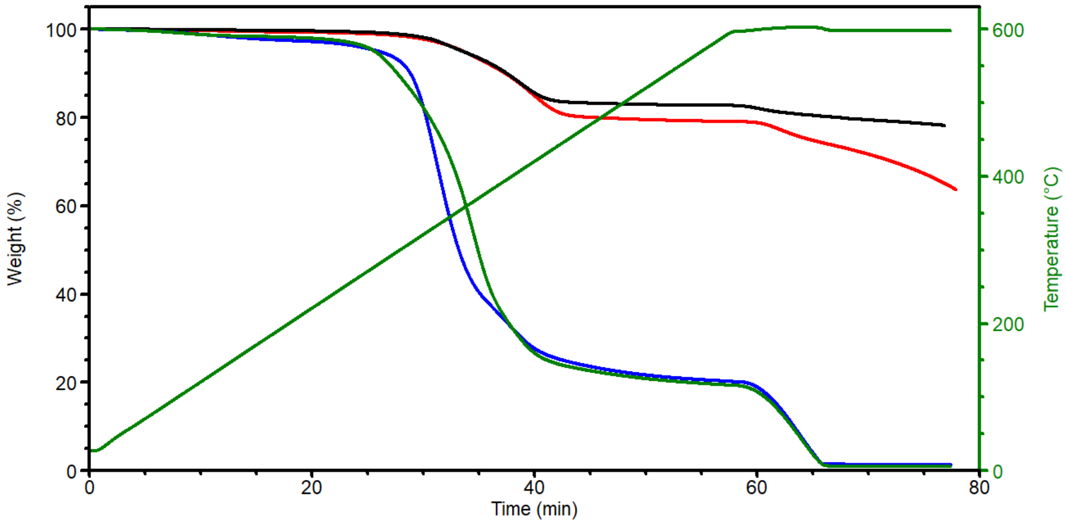


Figure 4.5: *TGA thermograms of ELA2-VC (---), ELA2-RC (---), ELA2-F (---) and ELA2-J (---) samples.*

The thermograms show different weight losses at different temperatures depending on the type of reinforcement used (natural or carbon). The samples reinforced with flax and jute fibers show a weight loss (about 2-3%) around 160°C that is not present on the thermograms of carbon fibers reinforced composites.

Table 4.11: *TGA results of ELA2 fiber reinforced composite materials.*

Sample	H_2O loss at 100°C (w%)	T onset (°C)	I weight loss (w%)	II weight loss (600°C) (w%)	Residue (w%)
ELA2-VC	/	339	17	5	78
ELA2-RC	/	336	21	15	64
ELA2-F	3	309	80	20	0
ELA2-J	2	308	81	19	0

Such a weight loss can be ascribed to the moisture loss absorbed by the natural fiber, because of hydrophilic groups present in their chemical structure. The subsequent weight loss of about 80% around 309°C is due to the degradation of the fibers (first) and the resin (then). Hence, during the isothermal step in oxidizing environment, the complete combustion due to the degradation of the carbon residue is achieved (Table 4.11).

Composites reinforced with carbon fibers, both VC than RC, show the first weight loss due to the resin degradation in the range 335-340°C, 30°C higher than natural fibers reinforced composites. Such a higher thermal stability shown by carbon fibers composites can be in part attributed to their better thermal conductivity that allows to avoid the formation of localized hotspots. Furthermore carbon fibers result more compatible with the epoxy matrix, thus the correspondent composites result more stable to heat. It is also worth noting that natural fibers have the intrinsic property to absorb moisture, as confirmed by TGA analysis, that could lead to a worse matrix fiber adhesion.

In oxidizing environment at 600°C RC fibers composites show a higher weight loss than VC fibers ones. Such a behaviour seems to suggest a deterioration of RC fibers that may be due to the thermal history of RC fibers in the pyrolysis process for their regeneration and reuse.

4.3.2 Study of the Epikote 828 - Adenine system

Given the excellent results obtained with the commercial infusion resin Elan-tron® EC 157, the possibility of using Adenine as crosslinking agent for commercial impregnation resins was investigated. In particular, the impregnation resin Epikote 828 (Hexion) was selected. Epikote 8282 possess an average molecular weight and viscosity similar to DGEBA, essential for prepregs production. Even if the crosslinking reaction of the impregnation resin will be less controllable, higher crosslinking heat and T_g could be achieved. On preliminary basis, different ratios of Epikote 828-Adenine have been investigated and different formulations have been prepared, in particular molar ratio ranging from 16 to 4 led to the best results, specifically EPA1 (2.3 w% - 15.25 mol / mol) ELA2 (4.5 w% - 7.61 mol / mol) and EPA3 (7.5 w% - 4.42 mol/mol) has been selected for further investigation (Table 4.2).

4.3.2.1 TGA analysis of Epikote 828 - Adenine system

As for the previous system, preliminary TGA analyses were carried out on EPA formulations and on plain resin in order to evaluate their thermal stability and the possible release of volatile compounds. TGA analysis have been performed on the epoxy precursor Epikote 828 and on EPA1, EPA2 and EPA3 systems. Analyses were performed for the three formulations EPA and the resin Epikote 828 using the same conditions reported in paragraph 4.3.1.1, and the results obtained are reported in Figure 4.6 and Table 4.12.

It can be observed that formulations EPA1, EPA2 and EPA3 display higher degradation temperatures compared to the plain resin. This is due to the fact that the Epikote 828 resin has formed a crosslinked system after the reaction with Adenine, and therefore a more rigid material, with a consequent intrinsic increased thermal stability, have been obtained.

The black curve, inherent to the Epikote 828 commercial resin, shows two weight losses associated with the degradation of the resin: the first one at 293°C (Onset I), and the second one at 365°C (Onset II). After the isothermal step in air (oxidizing atmosphere) the final residue observed is lower than 3%.

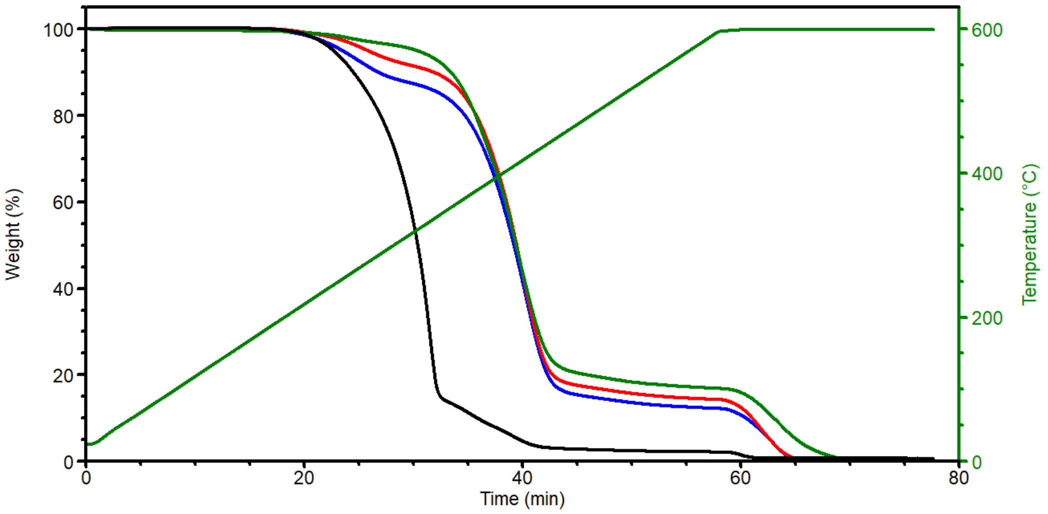


Figure 4.6: *TGA curves in nitrogen then air of Epikote 828 (**---**), EPA1 (**---**), EPA2 (**---**) and EPA3 (**---**) formulations.*

Concerning the formulations EPA1, EPA2 and EPA3, all show two weight losses, the first one with onset ranging between 280 and 340°C and the second one between 371 and 374°C. The first weight loss is probably referred to the release of low molecular weight compounds, while the second can be associated to the degradation of the crosslinked resin fraction.

Table 4.12: *Results of TGA analysis of samples Epikote 828 and formulations EPA1, EPA2, EPA3*

Sample	Weight Loss I (w%)	Weight Loss II (w%)	Onset I (°C)	Onset II (°C)	Residue (w%)
Epikote 828	86	12	293	365	2
EPA1	5	81	314	371	14
EPA2	5	80	313	374	14
EPA3	3	80	336	372	17

4.3.2.2 DSC analysis of Epikote 828 - Adenine system

Initially, in analogy with the previously tested samples, the three formulations EPA1, EPA2 and EPA3 were thermally characterized with DSC in dynamic mode. In particular a heating ramp of 1°C/min was applied in the first heating (to assess the crosslinking) and a 20°C/min ramp was selected for the second (to verify the complete curing reaction and define the final T_g); DSC thermograms and data are reported in Figure 4.7 and Table 4.13. In the first heating scan, all the analyzed formulations show a clear exothermal transition, ascribed to the epoxy resin precursor with Adenine, with a reaction heat ranging between 376-424 J/g, which grows as the amount of hardened added increases.

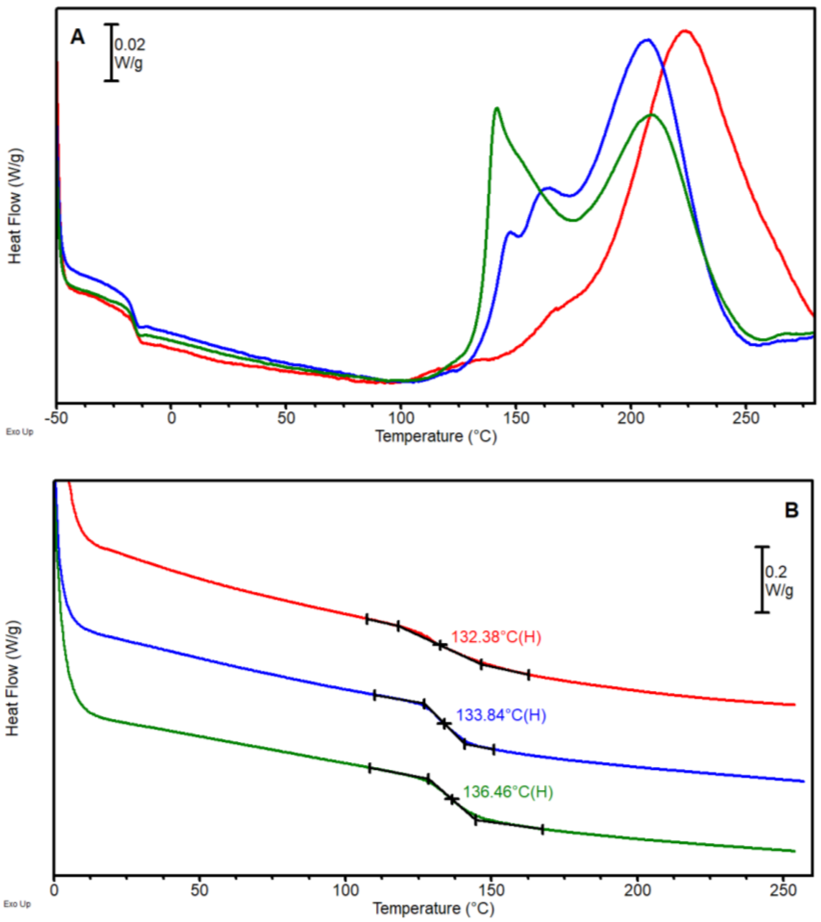


***Figure 4.7** DSC thermograms of the first heating scan (heating rate 1°C/min) (A) and second heating scan (heating rate 20°C/min) (B) for the EPA1(**---**), EPA2 (**---**) and EPA3 (**---**) systems*

Exothermal transitions of EPA samples, are characterized by the presence of multiple peaks of different shape and intensity dependent on the amount of Adenine in the systems; it suggests the presence of different reaction processes (with different kinetics) during the curing process. In the second scan a growing trend of T_g values towards higher temperature is reported when the amount of Adenine is increased.

***Table 4.13:** Relevant DSC data of Epikote 828/Adenine (EPA) samples*

Sample	**ΔH (J/g)**	**$T_{r\,max}$ (°C)**	**T_g (°C)**
EPA1	376	224	133
EPA2	408	207	134
EPA3	424	210	136

[a] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$, is the temperature corresponding to the fastest kinetic of the crosslinking reaction

The more the hardener, the more amine groups are capable of reacting with the commercial resin, leading to a higher reaction heat, due to the opening of more epoxy rings, and a greater number of crosslinking points in system, leading to an increase in the intrinsic rigidity of material and higher T_g values.

Based on the data obtained through dynamic DSC tests, isothermal DSC analyses were performed at 160, 180 and 200°C. The results obtained in isothermal DSC mode are shown in Table 4.14 and Figure 4.8.

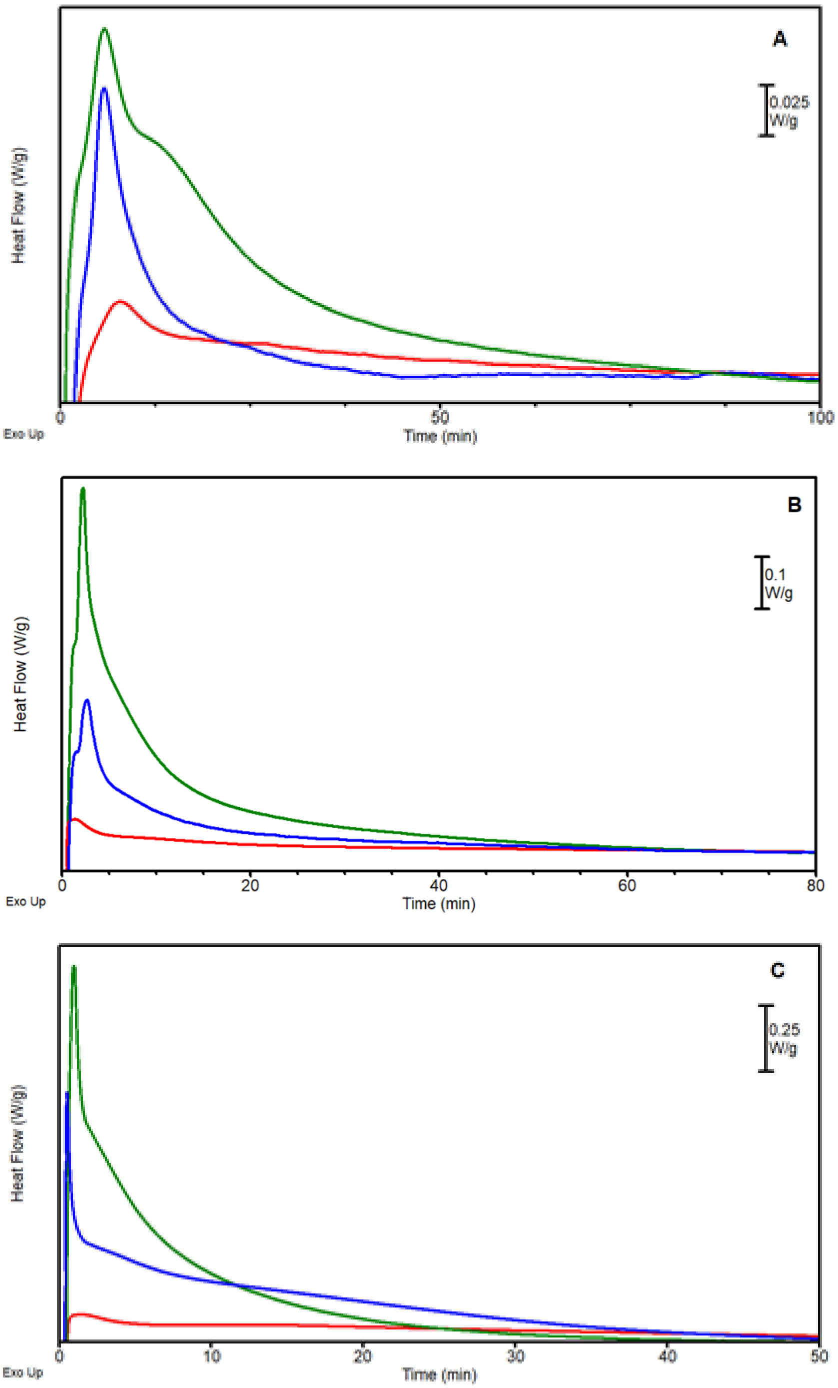


Figure 4.8: *DSC thermograms of the isothermal step of the systems at 160°C (A),180°C (B) and 200°C (C) of EPA1 (---), EPA2 (---) and EPA3 (---) systems.*

It is possible to highlight, as the isotherm temperature increases, a clear shift towards shorter times of both the maximum crosslinking speed and of the time necessary to complete the reaction. Both these events are dependent on the temperature at which the isothermal processes have been conducted; in fact, more the temperature increases, more the hardener reacts faster with the resin.

Table 4.14: *Relevant isothermal DSC data of EPA1 EPA2 and EPA3 samples at 160-180-200°C*

Sample	***T iso (°C)*** [a]	***Time peak (min)*** [b]	***Time tot (min)*** [c]	***ΔH (J/g)*** [d]	***T_g(°C)***
EPA1	160	7.82	168	82	/
EPA2	160	5.77	106	91	/
EPA3	160	5.81	181	321	110
EPA1	180	1.37	143	106	52
EPA2	180	1.74	186	373	168
EPA3	180	2.27	129	391	187
EPA1	200	1.45	165	313	102
EPA2	200	0.53	133	514	153
EPA3	200	0.96	133	563	164

[a] T iso, is the temperature chosen for the curing process, [b] t peak, is the time corresponding to the maximum speed of the crosslinking reaction, [c] t tot, is the time needed to achieve a complete crosslink of the resin system, [d] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener.

At 160°C the crosslinking is slow, the shape of the reaction peaks of all formulations appears to be broaden and only for EPA3 sample a T_g is observed. Both EPA1 and EPA2 formulations display low exothermal heat and short curing time since the crosslinking reaction was not completed. It is possible to observe that the total reaction time relative to the EPA3 formulation is higher than the one related to EPA1 and EPA2. This event is due the isothermal temperatures that are not high enough to achieve a complete crosslinking of the formulations EPA1 and EPA2, which consequent need of shorter curing times.

At 180°C, EPA1 sample still displays low reaction heat and final T_g value, while both EPA2 and EPA3 formulations show high reaction enthalpies and T_g, indication of a complete crosslinking process. Also at 180°C it can be observed that the EPA2 sample needs longer time than the EPA1 to complete the curing process, as the latter does not completely crosslink and consequently requires a short process time.

Finally, at 200°C all formulations display high reaction enthalpies and T_g, confirming the complete crosslinking of the resin.

It is possible to observe a decrease of the T_g for the formulations EPA2 and EPA3, when the isothermal temperature is increased to 200°C. A plausible explanation for this phenomenon could be that, considering the high temperatures used and the high quantity of Adenine present, unexpected parasitic or secondary reactions will occur. Secondary reaction, such as the opening of the aromatic cycle due to the presence of free Adenine, could lead to a loss of rigidity and therefore to a lowering of T_g of the final system. In general, in this system enthalpy and T_g, are similar when compared to the DGEBA based systems and higher than the results obtained with the Elan-tron® EC 157 resin.

4.3.2.3 Production and characterization of Epikote 828 - Adenine chopped fibers reinforced composites

Also for the impregnation resin, the more promising formulation (EPA2) was selected in order to produce SCFRP with hot press process. Composite materials were produced with the same manufacturing method used for ELA2 system (see paragraph 4.2.2.3). The system selected was EPA2 since EPA1 system displayed low thermal properties while some issues in the mixing process of EPA3 formulation were reported.

For all the carbon reinforced composite panels, the average resin content was estimated to be around the 42 w%, while for the natural fiber reinforced products it was ranging between 28-36 w%, as reported in Table 4.15.

Table 4.15: Results and fiber content of the composite material produced with EPA2 resin system.

Sample	*Fiber content (w%)*	*Resin content (w%)*	*AAD (g/cm^3) [a]*
EPA2-VC	58	42	1.34
EPA2-RC	58	42	1.36
EPA2-F	72	28	1.13
EPA2-J	64	36	1.01

[a] Average Apparent Density (AAD) determined as the average of the ratio between measured weight and volume of the single bars as cut in the convenient dimension for mechanical tests.

Again, for the obtained samples the Apparent Density (AD) was measured in order to obtain an index of the compactness of the sample. Carbon fiber composites possess close average densities ranging from 1.34 to 1.36 g/cm^3. The results are a little lower than the expected density for a quasi-isotropic epoxy CFRP (1.55 g/cm^3) [193] and it is probably due to possible defect or non-homogeneities obtained during the production process. Flax and jute reinforced composites displayed densities, 1.13 to 1.01 g/cm^3 respectively, similar to ELA2 samples and lower than VC and RC products, which are reinforced with carbon fibers which possess higher density than natural fibers.

All the obtained results suggested the possibility to achieve the production, even with a manual lab scale process, of composites with high fiber dosage and a good matrix - fiber interaction.

The DMA results obtained for all the composite materials produced are reported in Figure 4.9 and Table 4.16 and for each kind of sample, three specimens have been tested.

Concerning carbon fiber reinforced composite materials, they display comparable E′ modulus values. This behaviour suggests the possible use of recycled carbon fibers at industrial scale also without sizing application, since the partial oxidation of fibers, obtained during the recovering process, is able to enhance the fiber-matrix adhesion. Natural fiber reinforced materials display promising E' modulus (Figure 4.9) but lower than carbon fibers, as expected. Also for EPA2 formulation, the best results with natural fibers have been obtained with flax fibers, which display a modulus twice the one obtained with jute fibers.

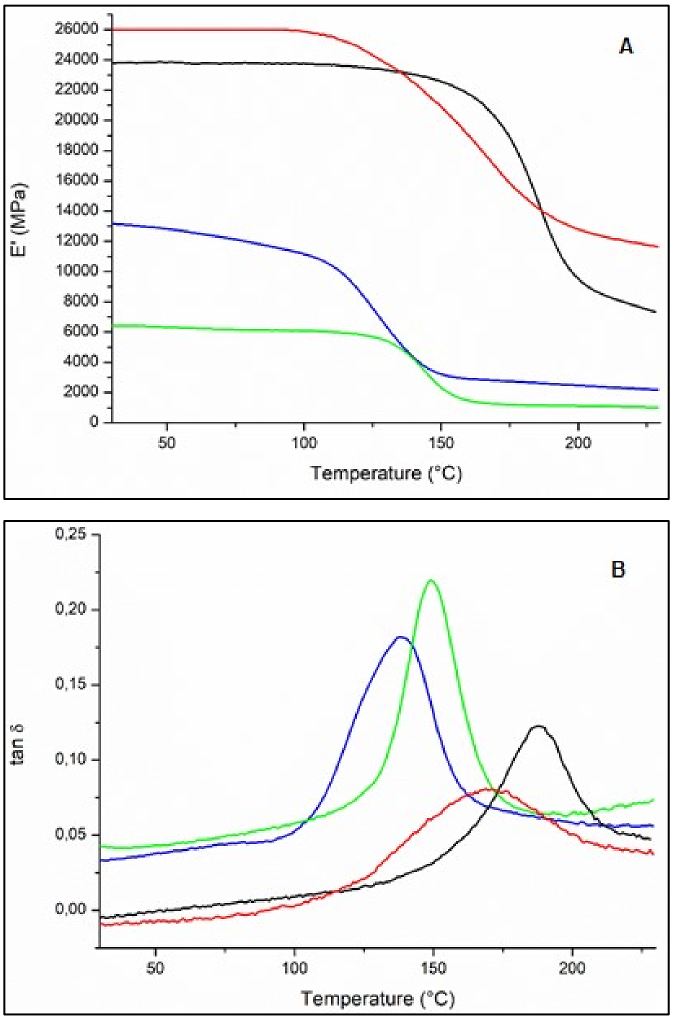


Figure 4.9: *DMA analysis of EPA2-VC (**---**), EPA2-RC (**---**), EPA2-F (**---**) and EPA2-J (**---**) samples.*

Analyzing E' onset temperatures of the composites (E' onset), virgin fibers displayed higher values than recycled ones while for natural fiber the highest onset was obtained with flax fibers. The highest E' onset temperatures have been obtained with carbon fiber products, probably depending on a better heat distribution to the resin during the curing process if compared to natural fibers.

***Table 4.16**. Results of DMA analysis of the composite material produced with EPA2 resin system.*

Sample	***E'$_{30}$ (MPa)***	***E' onset (°C)***	***tan δ peak (°C)***
EPA2-VC	22900±1800	166	188
EPA2-RC	23300±3100	136	177
EPA2-F	10900±2500	119	142
EPA2-J	5600±700	135	152

The tan δ curves are plotted as a function of temperature in Figure 4.9 B. All the composites show a main relaxation process (T_α), corresponding to their T_g after the curing, whose position depends on the type of fibers added. Again the best results have been obtained when carbon fibers have been used and all the products displayed tan δ peak over 140°C.

In general, all the results obtained confirm a good adhesion and interactions between all fiber kind and the EPA2 systems and the possibility to produce composite materials with high T_g and high mechanical properties.

Comparing EPA2 with ELA2 composites two values trends can be highlighted, in particular ELA2 products displayed higher E’ moduli while EPA2 samples presented the highest E’ onset temperatures and tan δ peaks. These events are probably due to the different resin systems used. Probably a better fiber-matrix interaction have been achieved with ELA2 formulation, resulting in higher mechanical properties, while the presence of more aromatic groups in EPA2 systems led to higher thermal properties and stability.

In order to define the composite materials behavior at high temperature, the samples produced with EPA2 matrix were tested through TGA analysis and the values and thermograms obtained are shown in Figure 4.10 and Table 4.17.

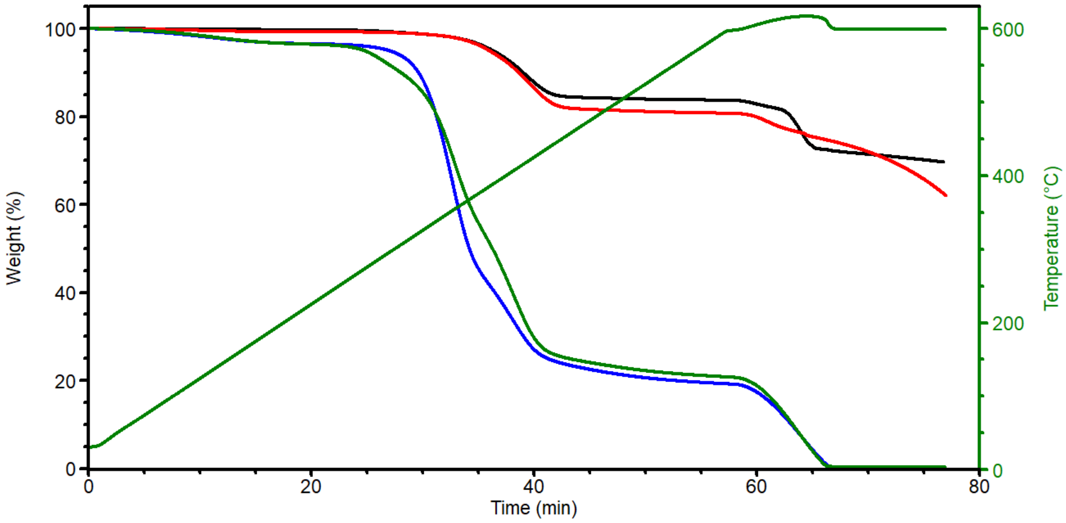


***Figure 4.10**:* TGA thermograms of *EPA2-VC (---), EPA2-RC (---), EPA2-F (---) and EPA2-J (---) samples.*

The curves show different weight losses at different temperatures depending on the type of reinforcement used (natural or carbon). The samples reinforced with flax and jute fibers show a weight loss (about 3%) around 160°C, which is not present on the thermograms of carbon fibers reinforced composites. Such a weight loss can be ascribed to the moisture loss absorbed by the natural fiber, because of hydrophilic groups present in their chemical structure. The subsequent weight loss of about 77% around 324°C (flax) and 321°C (jute) is due to the degradation of the fiber (first) and the resin (then). Hence, during the isothermal step in oxidizing environment, the complete combustion due to the degradation of the carbon residue is achieved (Table 4.17).

Table 4.17: TGA results of EPA2 fiber reinforced composite materials.

Sample	*H_2O loss at 100°C (w%)*	*T onset (°C)*	*I weight loss (w%)*	*II weight loss (600°C) (w%)*	*Residue (w%)*
EPA2-VC	/	374	16	14	70
EPA2-RC	/	374	19	19	62
EPA2-F	3	324	77	20	0
EPA2-J	3	321	76	21	0

Composites reinforced with carbon fibers, both VC and RC, show the a single weight loss due to the resin degradation at 374°C, 50°C higher than natural fibers reinforced composites, with a value of 16 w% (VC) and 19 w% (RC) respectively. Again the increase in thermal stability can be in part attributed to their better thermal conductivity of carbon fibers and the better interaction between fiber and matrix.

It is also worth noting that natural fibers has the intrinsic property to absorb moisture, as confirmed by TGA analysis, that could lead to a worse matrix fiber adhesion.

In oxidizing environment at 600°C CR fibers composites show a higher weight loss than CV fibers ones. Such a behaviour seems to suggest a deterioration of CR fibers that may be due to the thermal history of recycled carbon fibers in the pyrolysis process for their regeneration and reuse.

4.4 Conclusions

Two different commercial epoxy resins (infusion and impregnation resins) have been successfully crosslinked using Adenine as bio-based curing agent.

Both the resins, Elan-tron® EC 157 and Epikote 828, confirmed the possibility to use Adenine as crosslinking agent and produce high performance epoxy resin systems characterized by high thermal properties.

The obtained systems, named ELA (Elan-tron® EC 157 - Adenine) and EPA (Epikote 828 - Adenine) have been characterized by TGA with the aim to assess their thermal stability, and by DSC, both in dynamic than in isothermal mode. Such analysis were fundamental to evaluate the total reaction heat, how different amounts of hardener can influence the reaction and to obtain information on the resin crosslinking speed, the time taken to complete the crosslinking reaction at different temperature conditions and the final T_g achievable after the curing process. ELA systems displayed interesting heat of reaction (250 J/g) and T_g values, ranging between 108-116°C, suggesting the feasibility of using Adenine as a novel curing agent for the commercial epoxy infusion system Elan-tron® EC

157. Also for the Epikote 828 resin, the possibility to use Adenine as crosslinking agent was confirmed by the considerable heat of reaction and final T_g over 130°C obtained for the systems tested. In general, the new systems produced are very promising since Adenine is a biocompatible, non-toxic and environmentally friendly molecule and also adding only 2,3% in weight of the hardener satisfactory results were obtained.

The studied resins have been reinforced with different kinds of chopped fibers. In particular short carbon fibers (both virgin and recycled), flax and jute fibers were added to ELA2 and EPA2 systems in order to obtain new sustainable composites by a hot-press compression molding.

The thermo-mechanical properties of the produced composites have been evaluated by DMA analysis. All the obtained composites have a high fibers amount, good thermal stability and T_g higher than 100°C for infusion resin and 140°C for the impregnation resin.

In particular, concerning E' modulus, the best results have been obtained with ELA2 carbon fiber composites, which displayed values 30% higher than EPA2 formulation. Instead, regarding E' onset temperatures and tan δ peaks, the best results have been obtained with EPA2 systems. These events are probably due to the different resin chemical structure and fiber-matrix interaction achieved by the formulations.

Considering all the data obtained from the various analysis techniques and from the industrial simulations of the treatment process, it can be stated that the Elan-tron® EC 157- Adenine and Epikote828-Adenine systems are suitable for the production of composite material with high thermal and mechanical properties. Moreover, the data obtained with Recycled carbon fibers and natural fibers suggest them as a valid compromise and alternative to oil-based fibers for high performance materials where high temperatures of application, adequate flexibility and good mechanical properties are required.

Chapter 5- Study and production of fully bio-based composite materials

5.1 Introduction

Excellent mechanical and thermal properties are usually displayed by composite materials made from glass or carbon fibers and epoxy resins, making them widely applicable in various industrial fields. However, these materials have serious end-of-life disposal, cost and health issues. As a result, in the last years, a renewed interest in natural composite materials, that are environmentally safe, has grown [125]. Bio-based composite materials derived from a new category of products including one or more components such as reinforcing agents and resins, obtained from a sustainable resource [124]. In the new sub-category defined as 'Green composites', both resins and fibers are most commonly derived from plants, making them fully sustainable [124]. The greener composites combine degradable fibers with non-degradable resins and the idea of bio composites made from cellulose-based reinforcement agents and bio-based resins appears to be the best route to achieve 'green' composites [126].

The resin phase of the composites can be classified as either thermoset or thermoplastic. Thermoset resins derived from petroleum include polyesters, vinyl esters, epoxies, bismaleimides and polyimides, while thermoset epoxies make up most of the current resin market for advanced composites. A green resin is a product derived fully or partially from biological, mostly plant, sources. Even considering the high cost of the manufacturing process used to convert renewable sources into the monomers essential to produce the resin, thanks to the greening of the global economy, carbon footprint sensitivity, increased awareness on sustainable systems, bio-based resin feedstocks derived from plants are now a commercially developed and expanding product.

Concerning the reinforcement agents, natural fibers can be subdivided into three broad categories: vegetable (plant-based), animal, and mineral fibers. Plant-based fibers can be classified as either wood or non-wood fibers. Non-wood fibers may be further subdivided into bast, leaf or seed hair fibers, depending on their origin [132] in the plant, and wood fibers can be further subdivided into softwood and hardwood fibers. All plant-based fibers, whether from wood or non-wood origin, are composed of three main cell wall polymers: cellulose, lignin and polysaccharide resins constituted of pectins and hemicelluloses [135]. In addition to these, several nonstructural components, such as waxes, inorganic salts and nitrogenous substances, broadly referred to as extractives, are also present in plants [132].

Fibers may be converted to various suitable textile forms/ structures and may be used separately or can be combined to tailor the properties of the composites. In particular, they may be in various textile forms including fibers, yarns, woven or nonwovens mats and knitted fabrics or may also be chopped to the desired length and added to the resin to fabricate composites. Textile structures are among the most efficient reinforcements for composite materials and allow the manufacture of composites in complex shapes in a single operation or process. Obtaining such parts with desired properties is not easy since the shapes depend on the orientation and mechanical behavior of the textile forms during the forming process. Fibers. In order to design a structural material, an experimental investigation is required to understand the mechanical parameters of the chosen materials to be used in the manufacture of the composite (matrix and reinforcement).

The major interest in natural cellulosic fibers depends on their eco-friendly advantages, low production cost, worldwide availability and higher specific strength/stiffness compared to their traditional synthetic counterparts [136–138]. Moreover, the manufacturing process of bio-based composites is health-friendly and provides better working conditions [142]. Although the great number of advantages offered by natural fibers over synthetic products, they display some not negligible disadvantages [145] such as possible water/moisture absorption, low thermal stability and unavailability of fibers in continuous form, unless spun into yarns [146–149]. However, considering the overall properties the advantages of natural cellulosic fibers outweigh their disadvantages [150].

Given the high importance developed in the production of completely bio-based composite materials, it could be of great interest testing different kinds of fibers, some obtained from renewable sources, with a fully bio-based resin system in order to produce a “Green Composite”. In previous works the possibility to use Adenine as epoxy resin hardener, both for commercial impregnation and infusion systems, was validated (see Chapters 2 and 3). Good results have been obtained with the commercial formulations and the composite materials produced both with synthetic and natural fibers, displayed excellent mechanical and thermal properties. For these reasons, for further implementation of the final products, it was decided to test Adenine as a crosslinking agent of a commercial bio-based epoxy resin already used at industrial level. The chosen resin, SUPER SAP® CLR (Entropy Resin), displays characteristics similar to Elan-tron® EC 157 resin (tested in Chapter 3) thus, good crosslinking heat, high T_g, a controllable reaction and a low intrinsic rigidity of the system are expected. The main aim of this work was initially to verify the feasibility of Adenine as a crosslinking agent for commercial bio-based resin, achieving high T_g crosslinked products. Hence the more promising formulations, one for each type of resin, was coupled with carbon (virgin and recycled), flax and jute fibers in order to produce short fiber reinforced composite materials. The use of recycled carbon fibers and natural fibers was performed in order to study the possibility to produce composite materials reinforced with fibers obtained from renewable resources. The resin formulations and the composite products obtained have been tested through Thermogravimetric Analysis (TGA), Dynamic Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA).

5.2 Experimental

5.2.1 Materials

SUPER SAP® CLR (Entropy Resin) resin, was purchased from Entropy Resin and used as received without further purification.

Adenine (99% pure) was purchased from Alfa Aesar and used as received.

Virgin chopped carbon fibers (VC) (25 mm) were obtained cutting down Unidirectional Fabric UC 301 based on Toray T700S 12K dry fabrics. The recycled chopped carbon fibers (RC) (25 mm) were obtained from pyrolyzed Toray T700S 12K based carbon fiber post-treated at 500°C for 60 minutes under an oxidizing atmosphere. Both virgin and recycled carbon fibers are used without any other treatment.

Flax and jute fibers, kindly supplied from Assen University, Netherlands, were manually chopped at a length of 25 mm and used without any further treatment.

5.2.2 Formulation preparation

SUPER SAP® CLR - Adenine systems (CA): different amounts of Adenine (2.3 – 4.5 – 7.5 w%) were added to SUPER SAP® CLR resin. The obtained formulations were mechanically stirred with a speed of 300 rpm at 75°C until complete homogenization of the hardener with the resin. When the mixture appeared completely homogenous, the flask was cooled and used for the preparation of the TGA and DSC samples. Different mixtures were produced and labeled according to the list reported in Table 5.1.

Table 5.1: Compositions of the different thermosets formulations of SUPER SAP® CLR with Adenine investigated

Sample	CLR (w%)	Adenine (w%)	CLR (g)	Adenine (g)
CA1	97.7	2.3	10	0.235
CA2	95.5	4.5	10	0.471
CA3	92.5	7.5	10	0.810

5.2.3 Composite materials production

Chopped carbon fiber reinforced composite materials production:

Virgin (VC) and Recycled Carbon (RC) fibers of the average 25 mm length (15 g) were mixed with the pre-mixed Adenine-SUPER SAP® CLR system (50g) at 75°C in order to obtain a uniform wetting of the fibers and avoid an increase of the resin viscosity during the mixing phase. In Table 5.2 are reported the fiber/resin weight ratio used for the production of chopped carbon fiber composites.

Table 5.2: Fiber/resin weight ratio used for composite production.

Sample	Fiber content (w%)	Resin content (w%)
CA2-VC	55	45
CA2-RC	55	45
CA2-F	50	50
CA2-J	50	50

The mixture was stirred until complete uptake of the resin by the CFs, then the resin/Carbon fiber mixtures (33 g) was poured into a 60 x 60 x 10 mm mold and hot-press (DAN12T4CPT model, produced by Monti Sistemi, equipped with water cooling plates) according to the following procedure: the mold was inserted in the press with the plates already heated at 140°C, where it was kept in isotherm for 45 minutes with an applied pressure of 1 bar. After the isothermal step, the temperature was raised at 180°C and the applied pressure was increased up to 50 bar. The sample was kept in this isothermal condition for 200 minutes. Finally, before opening the hot-press plates, the mold was cooled at RT and then the pressure was decrease and the mold removed from the press. After cooling down to RT, the composite panel was cut for the preparation of the different specimens in order to perform thermal and mechanical characterization.

Chopped natural fiber reinforced composite materials production:

The epoxy resin system CA2 was prepared in a considerable amount (30g) by adding and stirring the selected amount of Adenine to SUPER SAP® CLR. Then flax (F) or jute (J) fibers (10 g respectively) were added and carefully hand-stirred with pre-mixed systems kept at 75°C in order to obtain a uniform wetting of the fibers and avoid an increase of the resin viscosity during the mixing phase (Table 5.2). Each one of the randomly oriented resin/natural fiber mixtures (20 g) was transferred into an iron mold with a 60 x 60 x 10 mm cavity, which was closed with a counter-mold designed to allow the come out of the resin excess from the edges. Hence, the system, closed in the mold, was placed in a hot-press and cured according to the following procedure: the mold was inserted in the press with the plates already heated at 160°C, where it was kept in isotherm for 45 minutes with an applied pressure of 1 bar. After the isothermal step, the temperature was raised at 190°C and the applied pressure was increased up to 50 bar. The sample was kept in this isothermal condition for 200 minutes. Finally, before opening the hot-press plates, the mold was cooled at RT and then the pressure was decrease and the mold removed from the press. After cooling down to RT, a 60 x 60 x 4 mm composite panel was removed from the mold and the samples obtained was post-cured at 180°C for 120 minutes in order to complete the crosslinking reaction of the resin. Thus, it was possible to obtained composite materials containing flax and jute fibers using infusion and impregnation resins crosslinked with Adenine. Every composite panel was cut for the preparation of the different specimens in order to perform thermal and mechanical characterization.

5.2.4 Characterization

- Thermogravimetric analyses (TGA) were carried out on a TA Instruments SDT Q600, in nitrogen atmosphere (flow rate: 100 ml/min) heating from RT to 600°C at 10°C/min, followed by a switch to oxidizing atmosphere (air) and an isothermal step of 20 min.
- The thermal behavior of the reacting mixtures was evaluated by Differential Scanning Calorimetry (DSC, Q2000 TA Instruments) and the measurements have been carried out in dynamic and isothermal mode. Dynamic DSC analyses were performed, under nitrogen flow, heating the samples at a heating rate of 1°C/min from -50 to 280°C. After the first heating, the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation. Isothermal DSC analyses were performed at 160, 180, and 200°C and the sample was introduced in the furnace already heated to the experimental temperature. After the isothermal step, the samples were cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation.
- Dynamic mechanical analysis (DMA) were performed with NIETZCH 242 E Artemis instrument, in Three Point Bending mode with 20 mm sample holder. The following conditions, in mixed control, were used during the analysis: heating ramp at 3°C/min from RT up to 250°C, frequency 1 Hz, maximum amplitude ± 10 μm,

maximum dynamic force 10 N, additional static force 0.5 N and proportional factor (Fstat/Fdin) = 1.1.

5.3 Results and discussion

With the aim of verifying the feasibility of Adenine as crosslinking agent for commercially bio-based epoxy resin, it was tested with the product SUPER SAP® CLR from Entropy Resin. The selected resin possesses viscosity and properties similar to the infusion resin Elan-tron® EC 157. To determine the optimal ratio between the bio-based epoxy precursor SUPER SAP® CLR (called CLR) and Adenine, in order to obtain excellent thermal and mechanical properties, different formulations of the two have been prepared by hot mixing at 75°C. The best homogenization results were obtained with percentages of Adenine between 2% and 7% by mass (CA1, CA2 and CA3 in Table 5.1).

5.3.1 TGA analysis of SUPER SAP® CLR - Adenine system

A preliminary TGA screening was carried out on the bio-based epoxy precursor and CA1, CA2 and CA3 formulations, in order to assess their thermal stability, the possible release of volatile compounds and define the operating conditions of the parameters to be used in the simulations of the curing cycle (Figure 5.1 and Table 5.3).

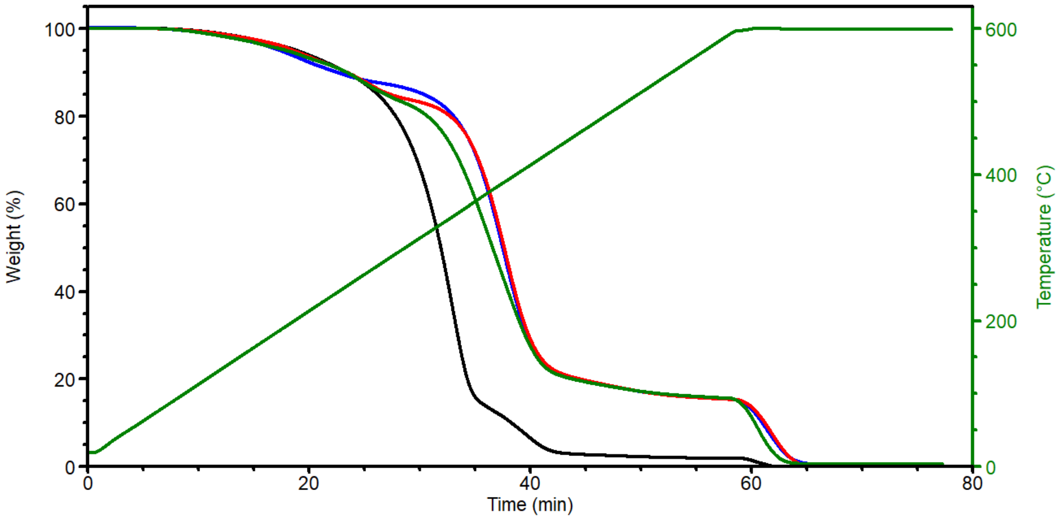


Figure 5.1: *TGA curves in nitrogen then air of CLR resin (---),CA1(---), CA2 (---) and CA3 (---) formulations*

The thermogram of the plain CLR resin (Figure 5.1) shows a first weight loss between 120 and 250°C due to the release of volatile substances, and two weight losses with onset at 295°C and 393°C due to the degradation of the resin; at the end of the heating step a residue of less than 3% is observed. After the isothermal step in an oxidizing atmosphere, the final residue is completely degraded, confirming that the epoxy precursor does not contain inorganic additives in significantly detectable quantities.

In analogy, the three resin formulations CA1, CA2 and CA3 (Figure 5.1 and in Table 5.3) display the same behavior as CLR up to 250°C and a second weight loss with an onset, associated with the component degradation, between 347 and 364°C. The latter position is shifted by about 100°C to higher temperatures when compared to CLR resin. This important increase in thermal properties is due to the crosslinking reaction between the epoxy precursor and Adenine achieved during the analysis heating phase.

Table 5.3: *Results of TGA analysis of samples CLR and formulations CA1, CA2, CA3*

Sample	Weight Loss I (w%)	Weight Loss II (w%)	Onset I (°C)	Onset II (°C)	Residue N_2 (w%)
CLR	86	12	295	393	2
CA1	16	68	187	364	16
CA2	12	72	194	359	15
CA3	16	68	210	347	16

All CA formulations show less than 16% of carbon residues after the heating in nitrogen atmosphere and are completely degraded in the isothermal step in air at 600°C.

5.3.2 DSC analysis of SUPER SAP® CLR - Adenine system

The thermal characterization of the not yet crosslinked formulations CA1, CA2 and CA3 was performed by DSC analysis in constant speed heating mode (hereinafter called "dynamic conditions"), with a first heating rate of 1°C/min (which will be referred to below as R1) to determine the maximum crosslinking temperature and the temperature range in which it occurs. The first heating was followed by a fast cooling down to 0°C and a further heating in the second scan at 20°C/min to verify the T_g obtained during the crosslinking process and the presence of any residual crosslinking, observable as an exothermic signal present at temperatures higher than the obtained T_g. The results obtained from DSC analysis in dynamic mode are shown in Figure 5.2 (A and B) and in Table 5.4.

In the first heating all the analyzed formulations show an exothermic transition associated to the crosslinking reaction between the components of the mixture, with a reaction enthalpy between 315-350 J/g which increases as the quantity of hardener increases. Furthermore, it is possible to observe a shift towards lower temperature values (142°C) of the peaks related to the maximum reaction speed, depending on the amount of Adenine used. The exothermal transition of the analyzed samples is characterized by different shape and intensity based on the different amounts of hardener added. Analyzing the formulations CA1 and CA2, it can observed that only one crosslinking signal of different intensity, probably due to the different quantity of Adenine, is present in both the systems. The CA3 formulation, instead, is characterized by an exothermic transition composed of several signals. This phenomenon is due to the presence of several consecutive reactions, with different and lower activation energy than the other two formulations. In Table 5.4 are reported the relative total crosslinking enthalpy values, the temperature values corresponding to the maximum reaction speed and the T_g of CA1, CA2 and CA3 formulations.

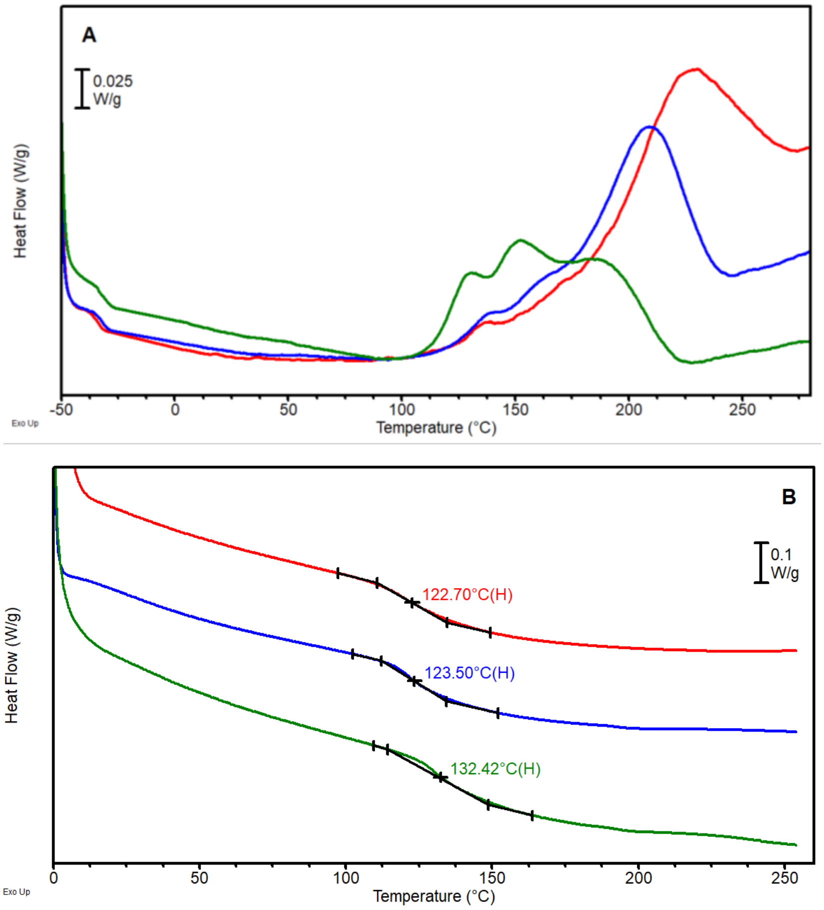


Figure 5.2: *DSC thermograms of the first heating scan (heating rate 1°C/min) (A) and second heating scan (heating rate 20°C/min) (B) for the CA1(---), CA2 (---) and CA3 (---).*

An increasing trend of the reaction heats and of the T_g (123-132°C), respectively for the formulations CA1, CA2 and CA3, is observed as the quantity of Adenine increases. The increase of T_g and reaction heat is due to the extent of crosslinking in the system, as a greater quantity of hardener involves a higher number of reactive amino groups able to open the epoxy rings of the polymer precursor. This will result in a greater heat developed, a higher number of crosslinking points of the system, which will correspond to higher T_g values and an intrinsic rigidity of the final product. In general, based on the values of heat generated (all over 300 J/g) and the T_g obtained, it is possible to confirm the use of Adenine as a new promising hardener for the SUPER SAP® CLR epoxy system.

Table 5.4: Relevant DSC data of CLR resin/Adenine (CA) samples

Sample	***ΔH (J/g)*** [a]	***$T_{r\,max}$ (°C)*** [b]	***T_g (°C)***
CA1	316	217	123
CA2	325	207	124
CA3	350	142	132

[a] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener, [b] $T_{r\,max}$, is the temperature corresponding to the fastest kinetic of the crosslinking reaction

Based on the results obtained from the dynamic DSC analysis, it was possible to determine a temperature range suitable to perform isothermal DSC analysis of CA1, CA2, and CA3 samples to study and optimize the curing cycle. The isothermal temperatures were chosen in dependence on the position of the exothermal peak shown in the dynamic DSC analysis, which represents the maximum reaction speed. For this reason, three temperatures have been selected: 160 and 180°C, which fall within the optimal range of thermal stability of the material, and 200°C since it represents the maximum crosslinking peak speed of the formulation with the lowest Adenine content. This type of analysis is fundamental to define the reaction enthalpy, the speed and time required to obtain complete crosslinking in conditions close to those of industrial production. Once the isotherm step at the selected temperature was completed, the samples were rapidly cooled and then heat up from 0 to 260°C at 20°C/min to determine the T_g of the resin achieved after the isothermal step and confirm the absence for any residual crosslinking. All this information is necessary to optimize the parameters of the industrial curing process of each formulation and the subsequent composite production process parameters. The obtained results are reported in Table 5.5 and in Figure 5.3 (A, B, C).

As shown in Table 5.5, it is possible to highlight, as the isotherm temperature increases, a clear shift towards shorter times of both the maximum crosslinking speed and of the time necessary complete the reaction. Both of these events are due to the different temperatures at which the isothermal processes have been performed. The higher the temperature applied for the isothermal step, the greater the reaction speed between the functional groups of the hardener and the epoxy resin. It is also possible to observe an increase in reaction ΔH, keeping the isotherm temperature constant, as a function of the concentration of hardener present in the resin. This is caused, as already mentioned above, by the dependence of the activation energy and the crosslinking speed of the resin on the quantity of amino groups able to react with the epoxy groups at the selected isothermal temperature.

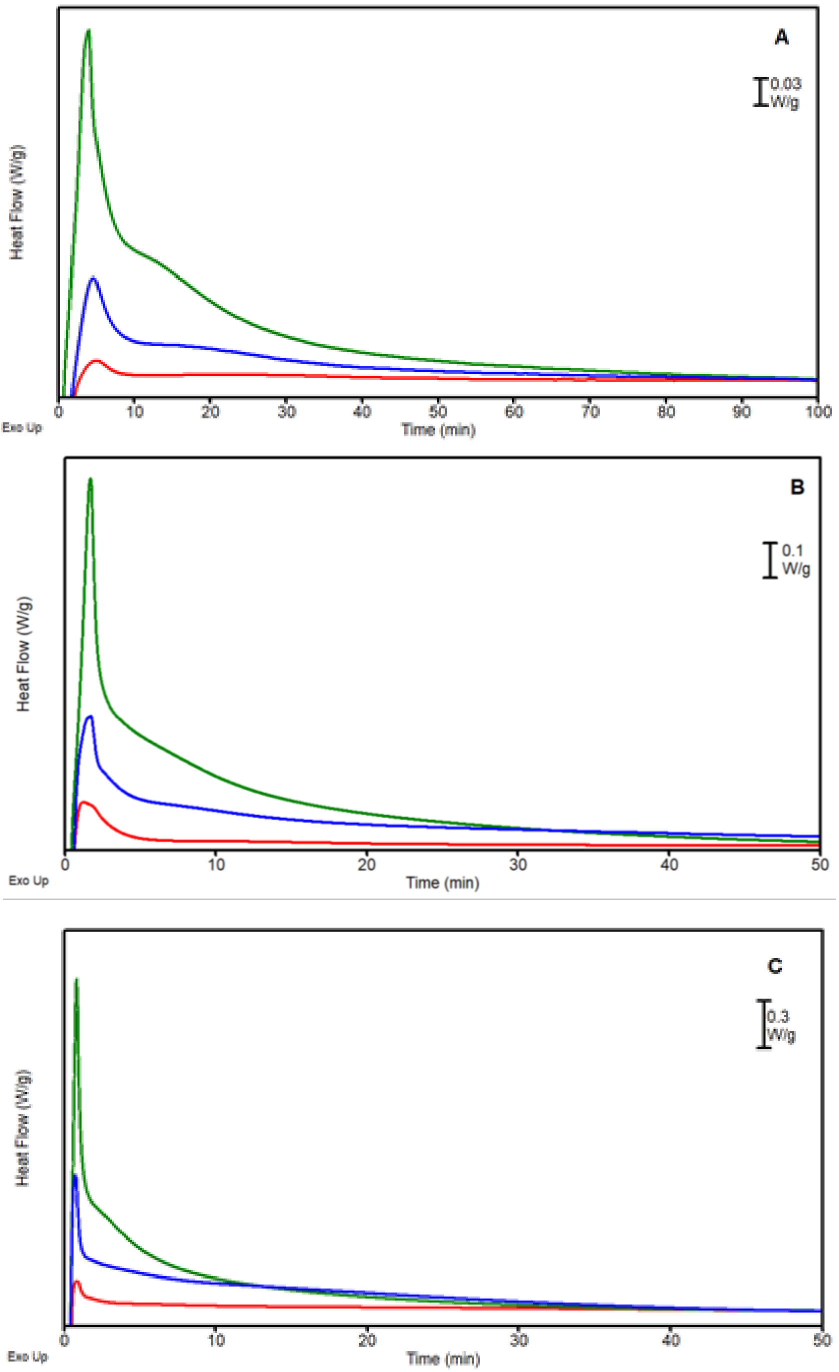


Figure 5.3: *DSC thermograms of the isothermal step of the systems at 160°C (A), 180°C (B) and 200°C (C) of the CA1(---), CA2 (---) and CA3 (---) systems.*

At 160°C the crosslinking reaction is slow, the shape of the reaction peak appears to be broaden and only in large excess of hardener (formulation CA3) T_g and reaction enthalpy value can suggest a complete curing process. The CA1 and CA2 formulations show low crosslinking heat, which indicates the non-completeness of the crosslinking process due to a temperature that is too low to promote the complete reaction of the system. During the second scan, which starts at 0°C, no T_g value is observed for CA1, while for CA2, a T_g value of 57°C is reported. Moreover, residual crosslinking is observed in both formulations confirming that with low hardener contents 160°C conditions are not enough to achieve a complete crosslinking.

At 180°C, the CA1 sample still shows a low reaction enthalpy and a low T_g, even if the results obtained are higher than those achieved at 160°C condition. Furthermore, the presence of residual crosslinking in the second scan of CA1, confirms that the reaction is not completed in the analysis conditions. Formulations CA2 and CA3, on the other hand, show higher reaction heat in first heating and high T_g, indicating the completeness of the reaction. The reaction enthalpy shows an increasing trend depending on the greater quantity of hardener present in the resin system. Concerning reaction times, a decrease is observed in function of an increase in concentration of hardener in the systems, in both in the time necessary to reach the maximum crosslinking speed and in the time required to return to the baseline.

Finally, at 200°C, all three formulations show reaction enthalpy and T_g data indicating a complete resin crosslinking reaction. Also in this case it is possible to notice the presence of a dependence of T_g and of the reaction heat on the amount of hardener added. Furthermore it is possible to point out that CA2, at 180 and 200°C shows a 10°C decrease of the final T_g. This event could depend on secondary parasitic reactions. Similarly, the formulation CA3 shows a decrease in T_g as the cure temperature increases from 160 to 180°C probably due to the same phenomenon discussed above.

Table 5.5: Relevant isothermal DSC data of CA1, CA2 and CA3 samples at 160-180-200°C

Sample	*T iso (°C)* [a]	*Time peak (min)* [b]	*Time tot (min)* [c]	*ΔH (J/g)* [d]	*T_g(°C)*
CA1	160	5.3	137	62	/
CA2	160	4.7	111	93	57
CA3	160	4.0	240	391	168
CA1	180	1.2	232	161	68
CA2	180	1.7	198	345	152
CA3	180	1.7	104	424	147
CA1	200	0.8	289	339	117
CA2	200	0.7	107	425	142
CA3	200	0.8	84	443	147

[a] T iso, is the temperature chosen for the curing process, [b] t peak, is the time corresponding to the maximum speed of the crosslinking reaction, [c] t tot, is the time needed to achieve a complete crosslink of the resin system, [d] ΔH, is the heat generated by the crosslinking reaction of the epoxy resin precursor with the hardener.

In conclusion, at 160°C the resin does not crosslink completely and at 200°C hot spots can form activating parasitic reactions of the resin and of the hardener, which display higher activation energy than the main reaction. For example the loss of aromaticity due to the opening of the Adenine rings can happen, leading to a significant decrease in rigidity and a decrease in the system's T_g [198]. Furthermore, it is worth noting that the formation of any hot spots can affect the structure of the fibers, especially the natural ones that are thermolabile, thus negatively influencing the thermal and mechanical properties of the final composite. At 180°C the reaction takes place more slowly than at 200°C, with less possibility to form hot-spot and allowing a better control over the exothermic crosslinking process. The latter temperature was selected as optimal for the curing process.

5.3.3 Composite materials of SUPER SAP® CLR - Adenine system production and characterization

Short fiber reinforced composites (SFRPs) are applied in a variety of fields, as they exhibit isotropic properties and allow a simpler manufacturing process than long fiber composites [13, 193–195]. The final properties of SFRPs depend on various factors such as production process, type of matrix and fiber used, fiber concentration, fiber length, fiber orientation and matrix adhesion [186, 187, 196, 197]. Based on the results obtained in the previous study, in order to confirm the possible use of the bio-based resin system / Adenine for industrial purposes, it was decided to proceed with the production of fiber reinforced composite materials. In particular, carbon fibers (recycled RC, and virgin VC for comparison), flax fibers (L) and jute (J) were used to produce new sustainable composites [132, 191]. Natural fibers have been used as they represent a potential starting point for the design and production of high-performance composite materials, completely obtained from renewable sources. The composite materials were produced using a steel mold, specially manufactured for this study, and the curing process was performed by hot-press compression molding. In particular, of the three systems analyzed above, only the CA2 formulation was tested as a matrix for composite materials since CA1 displays low thermal properties while for CA3 some problems have been reported in the resin mixing process and a low crosslinking reaction control.

Since it is well known that part of the resin present in the feed can be expelled from the mold after the application of pressure before it can reach the crosslinking, which blocks the resin flow, in order to determine the actual fiber / resin ratio, after the curing process, each composite panel was weighed. Assuming that the fraction of fiber cannot flow out the mold, and the weight of the reinforcement remains therefore constant, for the composite panels in carbon fiber an average resin content of around 24-26% by weight, corresponding to a fiber content of about 75-77%, has been estimated. For composites in natural fibers, on the other hand, the estimated average fiber content is about 60-70% with a respective resin percentage of about 30-40%.

Therefore, for each of the obtained samples the Apparent Density (AD) was measured in order to obtain an index of the compactness of the product and to provide information about the overall homogeneity. As reported in Table 5.6, the produced carbon fiber composites possess Average Apparent Densities (AAD) ranging from 1.45 to 1.49 g/cm^3, in agreement with the expected density for a quasi-isotropic epoxy CFRP (1.55 g/cm^3) [193]. Both natural flax and jute fiber reinforced composites displayed lower density values, in the range 1.15 g/cm^3 (flax) and 1.03 g/cm^3 (jute), if compared to Carbon fiber reinforced product since the density of natural fibers is lower than carbon fibers. The determined AAD suggest that a good compaction has been reached for all the composites produced, although a manual lab scale process was used, and in presence of a high fiber dosage (about 60-80%). It is also worth noting that, besides the untreated VC fibers, none of the other fibers has been subjected to a sizing treatment, thus lacking a surface coupling agent helping to promote adhesion toward the polymer matrix in the composite production.

Table 5.6: Results and fiber content of the composite material produced with CA2 resin system.

Sample	*Fiber content (w%)*	*Resin content (w%)*	*ADD (g/cm^3)* [a]
CA2-VC	77	23	1.45
CA2-RC	75	25	1.49
CA2-F	70	30	1.15
CA2-J	62	38	1.03

[a] Average Apparent Density (AAD) determined as the average of the ratio between measured weight and volume of the single bars as cut in the convenient dimension for mechanical tests.

In order to determine the final thermomechanical properties of the products, the produced composite materials were characterized by Dynamic Mechanical Analysis (DMA). The DMA results obtained for all the composite materials produced are shown in Figure 5.4 (A and B) and Table 5.7.

Table 5.7: Results of DMA analysis of the composite material produced with CA2 resin system.

Sample	*E'(MPa)*	*E' onset (°C)*	*tan δ peak (°C)*
CA2-VC	33800±1600	119	144
CA2-RC	25900±1500	120	147
CA2-F	7200±1500	95	116
CA2-J	8700±2100	101	120

The carbon fiber reinforced materials show a great elastic modulus (E') at 30°C and, in particular, the highest value of module E' was obtained for virgin carbon fibers. The samples containing recycled fibers displayed a lower modulus, probably due to the lack of sizing, that are present on the virgin ones. The sizing agents, in fact, are generally used to facilitate the handling of the fibers and promote their adhesion to polymeric matrices. The possible use of sizing also on recycled fibers would therefore allow us to hypothesize an improvement in the performance of the composite. Despite this, the results obtained can be considered satisfactory for the application of recycle fibers as reinforcing agents. Materials reinforced with natural fibers show a promising elastic modulus, lower than carbon fibers, as expected. The best results have been obtained with jute fibers, whose composites show a higher modulus than the flax-based analogues.

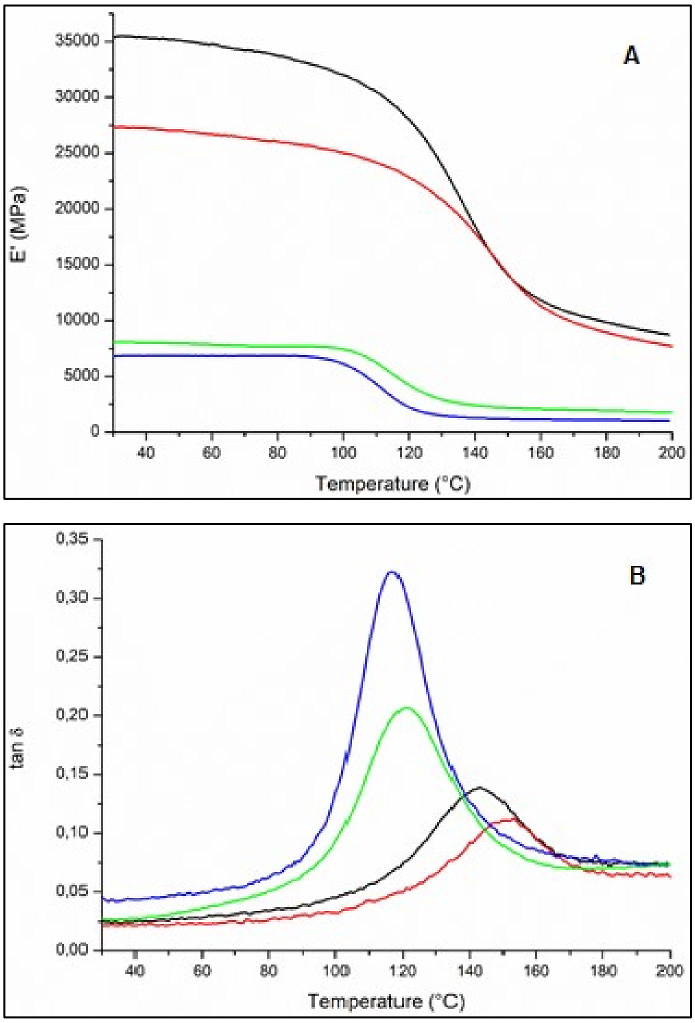


Figure 5.4: *DMA analysis of CA2-VC (**---**), CA2-RC (**---**), CA2-F (**---**) and CA2-J (**---**) samples.*

Analyzing the E' onset temperatures (E' onset) of the composites, the samples with virgin and recycled carbon fibers show a similar behavior; in the same way the results obtained with flax fibers are similar to those obtained with jute fibers. The highest E’ onset temperatures (Table 5.7) were obtained with carbon fiber materials (Figure 5.4, A). This is probably due to the greater efficiency in the distribution of heat to the resin during the crosslinking process compared to natural fibers (carbon fibers are good conductors of heat, unlike cellulose fibers such as jute and linen).

The tan δ curves have been reported as a function of the temperature in Figure 5.4, B. All the analyzed composites show a single relaxation process (T_α) that can be associated with the glass transition of the resin (T_g), whose position depends on the type of fiber / resin system. Once again the best results were obtained when virgin and recycled carbon fibers were used. The two composites derived from synthetic fibers show a tan δ peak of 144°C (CA2-VC) and 147°C (CA2-RC) while products with natural fibers show a tan δ peak higher than 115°C (Table 5.7).
In conclusion, the overall obtained results confirm a good adhesion and interaction between all types of fibers and CA2 system; furthermore, the possibility of producing composite materials with good T_g and high mechanical properties is confirmed.

Lastly, in order to evaluate the thermal stability and the behavior at high temperature, all the composite materials produced were tested through TGA analysis using the same method previously applied for the resin systems. These analysis were useful to verify the quality of the materials produced, identifying the decomposition temperature and the presence of any residue after degradation. The results and thermograms obtained are shown in Figure 5.5 and in Table 5.8.

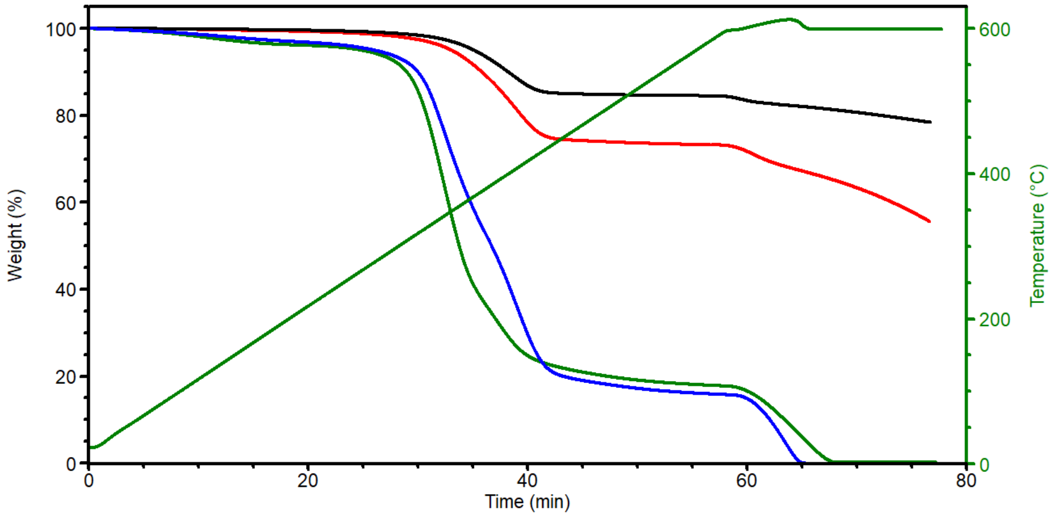


Figure 5.5: *TGA thermograms of CA2-VC (---), CA2-RC (---), CA2-F (---) and CA2-J (---) samples.*

The curves show different weight losses at different temperatures depending on the type of reinforcement used (natural or carbon). The samples reinforced with flax and jute fibers show a weight loss (about 3%) around 100°C that is not present on the thermograms of carbon fibers reinforced composites. Such a weight loss can be ascribed to the moisture loss absorbed by the natural fiber, because of hydrophilic groups present in their chemical structure. The subsequent weight loss of about 80% around 316°C is due to the degradation of the fiber (first) and the resin (then).

Table 5.8: *TGA results of ELA2 fiber reinforced composite materials.*

Sample	H_2O loss at 100°C (w%)	T onset (°C)	I weight loss (w%)	II weight loss (600°C) (w%)	Residue (w%)
CA2-VC	/	359	15	6	79
CA2-RC	/	356	25	18	57
CA2-F	3	316	80	16	1
CA2-J	3	318	78	18	1

Hence, during the isothermal step in oxidizing environment, the combustion due to the degradation of the carbon residue is achieved with a final residue up to about 1% (Table 5.8). Composites reinforced with carbon fibers, both VC than RC, show the first weight loss due to the resin degradation in the range 356-359°C, 40°C higher than natural fibers reinforced composites. Such a higher thermal stability shown by carbon fibers composites can be in part attributed to their better thermal conductivity that allows to avoid the formation of localized hotspots. Furthermore carbon fibers results more compatible with the epoxy matrix, thus the correspondent composites result more stable to heat. It is also worth noting that natural fibers has the intrinsic property to absorb moisture, as confirmed by TGA analysis, that could lead to a worse matrix fiber adhesion.

In oxidizing environment at 600°C RC fibers composites show a higher weight loss than VC fibers ones. Such a behaviour seems to suggest a deterioration of RC fibers that may be due to the thermal history of recycled carbon fibers in the pyrolysis process for their regeneration and reuse.

5.4 Conclusions

With the aim to develop a completely green resin-hardener system and producing composite materials with various natural fibrous reinforcing agents, the commercial bio-based epoxy resin SUPER SAP® CLR was crosslinked with Adenine as a hardener. Three formulations were tested, named CA1 (2.3 w% Adenine), CA2 (4.5 w% Adenine) and CA3 (7.5 w% Adenine) and TGA analysis have been carried out in order to assess the thermal stability of the systems. DSC analysis pointed out a dependence of the reaction kinetics, the crosslinking enthalpy and the T_g on the Adenine amount used. Such a behavior can be ascribed to the greater degree of crosslinking achievable in presence of higher quantity of hardener, which allows the formation of a more compact and rigid three-dimensional lattice. Based on the results obtained from the dynamic analysis, the conditions for DSC in isothermal mode were defined and in particular, the formulations were tested at temperatures of 160, 180 and 200°C. With this method, it was possible to obtain information on the resin crosslinking speed and on the time taken to complete the crosslinking reaction. At 160°C the formulations CA1 and CA2 show a minimal crosslinking with low values of reaction heat (60-90 J/g) and T_g. At 180°C a complete crosslinking is observed for formulations CA2 and CA3 while the CA1 sample is not yet completely cured. Finally, at 200°C the formulations show, in terms of both enthalpy of reaction and T_g, a complete crosslinking for all three samples, but they present hot-spot and low homogenization problems of the hardener in the resin.

Finally, the composites of CA2 resin were produced with virgin and recycled carbon fibers and jute and linen fibers, using the hot press forming process. The virgin carbon fibers have been used as a reference of the maximum value achievable with this type of resin system, since they display greater mechanical performances. The recycled carbon fibers have been tested as they represent a more sustainable and ecological choice as they are a second raw material compared to their virgin analogous, while linen and jute fibers represent a potential starting point for the design of high performance composite materials, obtained from totally renewable sources. The curing cycle was optimized for both carbon fiber and natural fiber reinforced materials, with the aim to achieve the better final properties. The trend of the elastic modulus (E') and the T_g of all the composites were studied through DMA analysis. The obtained data confirm the possibility of producing composite materials with good mechanical properties and excellent T_g values . As for the E 'module, the best results have been obtained with carbon fiber composites, as they show a better interaction between fiber and matrix and intrinsically possess a greater rigidity than natural cellulosic fibers. To improve the properties of completely bio-based materials, in the future, a study to avoid the natural water absorption of cellulose fibers could be conducted. Considering all the data obtained from the various analysis techniques, it can be stated that the Adenine / SUPER SAP® CLR system is suitable for the production of composite materials resistant to high temperatures and with good mechanical properties. Moreover it is possible to manufacture composites completely obtained from renewable sources and which, therefore, represents a valid alternative to traditional composite materials. Furthermore, it has been shown that Adenine may represent a viable alternative as a hardener from renewable sources for epoxy resins in the future.

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