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Lignin-based nanocomposites with fire-retardancy properties: analysis and implementation of an innovative material

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To my family

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ABSTRACT DELLA TESI DI LAUREA MAGISTRALE IN ITALIANO

**"Lignin-based nanocomposites with fire-retardancy properties:
analysis and implementation of an innovative material"**

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Introduzione ed obiettivi del lavoro

Al giorno d'oggi è difficile immaginare la vita di tutti i giorni senza i materiali plastici. Le loro proprietà eccezionali e la loro versatilità ne fanno il materiale adatto per ogni genere di applicazione: si va dal packaging al settore automotive, il settore delle costruzioni, fino ai beni di consumo. Per questi motivi, la produzione e l'utilizzo della plastica tende a crescere esponenzialmente di anno in anno: si stima che seguendo l'andamento attuale, si passerà dalle 359 milioni di tonnellate prodotte nel 2018 a circa 800 milioni di tonnellate nel 2050. Inevitabilmente ciò comporta conseguenze negative sia per l'ambiente che per la salute umana.

Le plastiche sono prodotte a partire da combustibili fossili, considerati fonti non rinnovabili, visto che per rigenerarsi impiegano un tempo estremamente più lungo di quello con cui sono estratti e utilizzati.

Il primo problema è l'inquinamento: le materie plastiche di comune utilizzo non sono biodegradabili: quando disperse nell'ambiente non si decompongono per l'azione di batteri e microorganismi, ma possono rilasciare sostanze nocive che contaminano acqua e terra, entrando nella catena alimentare degli esseri viventi e quindi anche dell'uomo.

In secondo luogo, ci sono effetti negativi per quanto riguarda l'effetto serra: il processo di estrazione delle fonti fossili e lo smaltimento dei rifiuti plastici nelle discariche provocano un rilascio eccessivo di CO_2 nell'atmosfera, contribuendo al riscaldamento globale.

Per queste ragioni, negli ultimi anni è aumentato l'interesse nello sviluppo di polimeri "bio-based". Secondo la ASTM (American Society for Testing and Materials International), i materiali bio-based sono "materiali organici in cui il carbonio è derivato da una fonte rinnovabile tramite dei processi biologici". Ciò vuol dire che questa nuova classe di materiali è prodotta con fonti abbondanti in natura e rinnovabili, e rappresentano un'alternativa ai polimeri tradizionali, riducendo l'impatto sull'ambiente e sulla salute. Generalmente, le principali materie prime utilizzate sono derivanti da attività agricole, (come amido, cereali, patate, melassa) e dalla biomassa. Recentemente, l'attenzione si sta spostando anche sul recupero di scarti agricoli.

La European Bioplastics association propone una classificazione dei materiali plastici sulla base della loro origine (se fossile o bio-based) e sulla biodegradabilità. La **Figura (1)** mostra graficamente questa suddivisione, in base alla quale si possono trovare polimeri

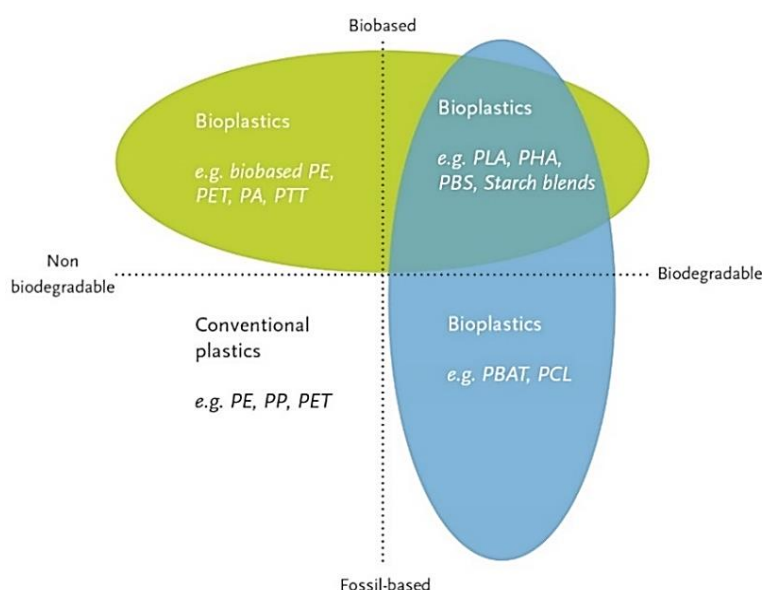bio-based ma non biodegradabili, polimeri convenzionali biodegradabili e polimeri bio-based e biodegradabili.

Figura (1) *Classificazione dei materiali plastici secondo la European Bioplastics association*

L'idea alla base del presente progetto di tesi è quella di produrre una plastica bio-based che abbia proprietà competitive se paragonata ai tradizionali polimeri. In particolare, l'obbiettivo è di studiare le caratteristiche di una resina epossidica a base di lignina, e utilizzarla insieme a dei silicati lamellari, per produrre un nanocomposito che abbia buone proprietà di ritardo alla fiamma. L'aggiunta di questa ulteriore caratteristica permette di associare questo materiale "bio-based" ad una fetta maggiore di mercato.

I silicati lamellari sono dei minerali di dimensioni nanometriche utilizzati principalmente come rinforzanti nella produzione di nanocompositi. Essi hanno una struttura costituita dall'alternanza di lamelle di SiO_2 con struttura tetraedrica e lamelle di Al_2O_3 con struttura ottaedrica, che si organizzano a formare pile separate da uno spazio chiamato galleria o interlayer. La sostituzione isomorfa che avviene tra le lamelle (Al^{3+} viene sostituito con Mg^{2+} o Fe^{2+}) genera una carica negativa che è controbilanciata dai cationi presenti nell'interlayer (e.g. Na^{2+}, Ca^{2+}). Questo fenomeno è responsabile delle principali proprietà che caratterizzano questi minerali, come la capacità di rigonfiarsi quando assorbono acqua e l'alta stabilità termica e chimica. Il loro largo utilizzo è dovuto anche alla loro abbondanza sulla terra e quindi al loro basso costo.

L'utilizzo dei silicati lamellari nei nanocompositi polimerici è vantaggioso perché permette di migliorare diverse proprietà della matrice polimerica tal quale. In primo luogo, per quanto riguarda le proprietà meccaniche, si nota un aumento del modulo elastico, della resistenza a trazione e dell'allungamento a rottura. In secondo luogo, i silicati lamellari sono molto importanti per il miglioramento della resistenza al fuoco. La **Figura (2)** mostra il loro funzionamento nella matrice polimerica. Durante la combustione si crea un gradiente di temperatura nel materiale che provoca la migrazione delle lamelle dal bulk alla superficie. Qui formano un "char", ossia uno strato ibrido

formato da carbonio e silicati, che agisce da barriera a calore e ossigeno, proteggendo il substrato da ulteriore degradazione.
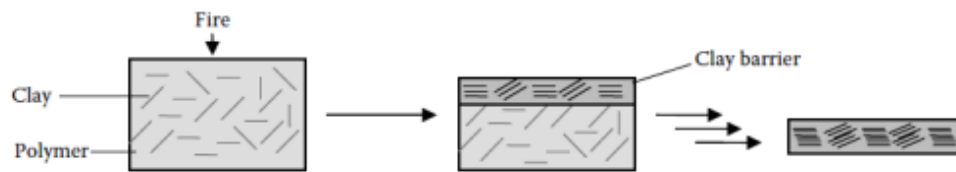
Figura (2) *Meccanismo di ritardo alla fiamma dei silicati lamellari nei nanocompositi*

Il buon funzionamento di questo tipo di tipo di filler dipende dall'interazione con la matrice polimerica. Poiché i silicati sono idrofili e il polimero è idrofobo, è possibile che le lamelle si aggreghino nella matrice. Di conseguenza, è essenziale rendere i silicati compatibili con il polimero modificandone la struttura con lo scambio degli ioni nell'interlayer. Il conseguente rigonfiamento della struttura consente al polimero di accomodarsi nell'interlayer. A seconda del grado di interazione fra le due componenti, è possibile identificare tre casi, mostrati in **Figura (3)**:

-nanocomposito con fasi separate: silicati lamellari e polimero sono incompatibili fra loro e non c'è una buona distribuzione delle lamelle nel polimero;

-nanocomposito con struttura intercalate: le catene polimeriche sono parzialmente intercalate tra le lamelle, formando pile alternate di polimero e silicati;

-nanocomposito con struttura esfoliata: le lamelle sono distribuite uniformemente tra le catene polimeriche.

Figura (3) *Tipologie di struttura di nanocomposito con silicati lamellari*

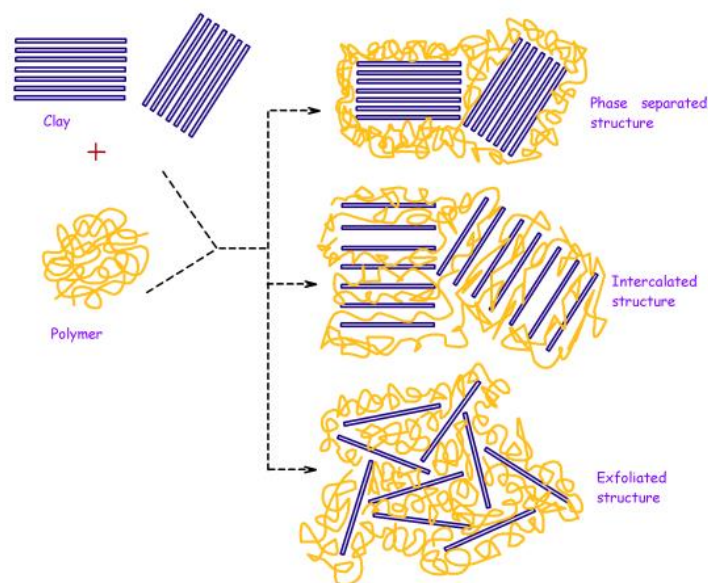Solo producendo una struttura esfoliata o intercalata si possono ottenere i miglioramenti nelle proprietà meccaniche e di ritardo alla fiamma.

Visti i numerosi vantaggi relativi all'utilizzo dei silicati lamellari, si è deciso di utilizzarli per ottenere un nanocomposito bio-based (per l'uso di una resina a base di lignina come matrice polimerica), e con buone proprietà di ritardo alla fiamma.

In origine, il progetto prevedeva la produzione delle resine presso il Royal Institute of Technology di Stoccolma e la creazione dei nanocompositi e la loro caratterizzazione presso il Politecnico di Torino, nella sede di Alessandria. Tuttavia, a causa dell'emergenza Covid-19, si è riusciti a svolgere solo la parte sperimentale a Stoccolma, portando quindi ad una modifica del progetto. A questo proposito, nella prima parte della tesi si descriverà il lavoro sperimentale svolto sulla lignina e il processo di produzione della resina epossidica; la seconda parte riguarderà l'attività di pianificazione per la produzione di questi materiali, evidenziando quali sono le attività principali del lavoro, con i loro specifici obbiettivi e i risultati che si intendono ottenere, e come si collegano l'una all'altra nel tempo. Infine, si analizzeranno i rischi che potrebbero compromettere una buona riuscita del lavoro.

Sezione sperimentale

In questo paragrafo si tratterà dell'attività sperimentale svolta presso il KTH di Stoccolma per preparare la lignina alla produzione della resina epossidica.

La lignina è uno dei biopolimeri più abbondanti in natura, essendo uno degli elementi costituenti di legno e piante, insieme a cellulosa ed emicellulosa. La sua struttura chimica è molto complessa ed eterogenea: è un composto aromatico ricco di unità fenilpropaniche e numerosi gruppi funzionali di diverso tipo che si combinano tra loro tramite legami diversi. I precursori della lignina sono essenzialmente tre: l'alcol p-cumarilico, l'alcol coniferilico e l'alcol sinapilico, chiamati rispettivamente p-idrossifenilpropano (H), guaiacile (G) e siringile (S) (**Figura (4)**).
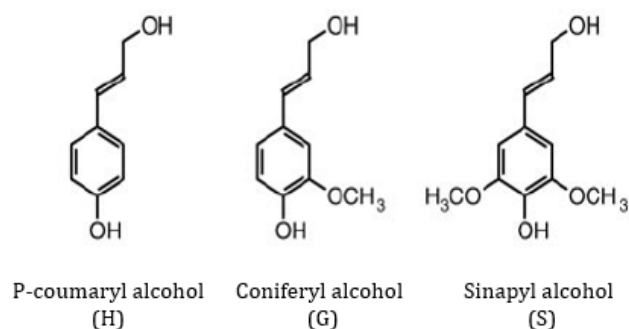
Figura (4) Precursori della lignina

A seconda del tipo di pianta, le suddette unità ripetitive saranno presenti in quantità diverse nella struttura chimica della lignina: nelle gimnosperme, la lignina è formata in

prevalenza da strutture guaiacile (G), nelle angiosperme da strutture sia guaiacile (G) che siringile (S).

È proprio per la complessità ed eterogeneità della lignina che prima di utilizzarla come materia prima per la produzione di biopolimeri deve essere sottoposta ad un'operazione di omogeneizzazione, cioè il frazionamento. Esso consiste in dissoluzioni sequenziali della lignina in diversi solventi organici, che portano ad ottenere frazioni sempre più omogenee in termini di polidispersità e peso molecolare, essendo essa solubile in modo diverso in ognuno di essi. Generalmente, i solventi utilizzati sono acetone, metanolo, etanolo, etilacetato e cloruro di metano.

La lignina impiegata nel presente lavoro di tesi deriva da abeti rossi (*Picea abies*), una delle specie più diffuse in nord Europa, appartenenti alla categoria delle angiosperme: La struttura chimica è essenzialmente composta da strutture guaiacile e unità idrossi-fenil-propaniche. La **Figura (5)** riassume tutte le fasi del trattamento preliminare della lignina.
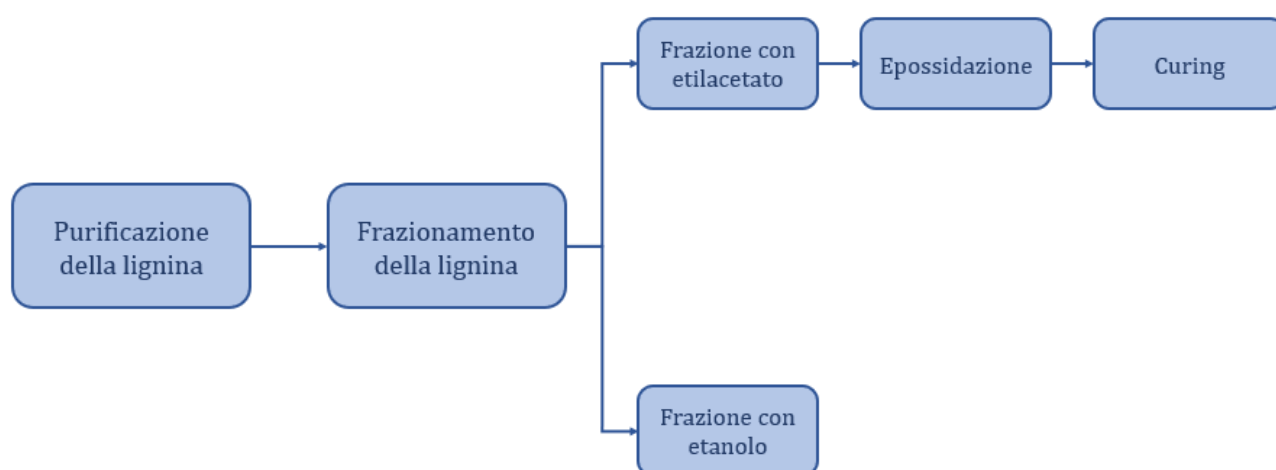
Figura (5) Fasi del trattamento preliminare della lignina

L'attività preliminare alla produzione delle resine inizia con la purificazione della lignina per eliminare eventuali sali o acidi presenti nella composizione e che potrebbero compromettere le successive fasi di frazionamento ed epossidazione.

I solventi organici utilizzati per il frazionamento sono due: etilacetato ed etanolo. La prima soluzione di lignina ed etilacetato viene mescolata per quattro ore a temperatura ambiente (**Figura (6)**). Successivamente, essa viene filtrata: si otterranno una soluzione con etilacetato e una parte insolubile. La prima viene sottoposta al freeze-drier per ottenere la lignina frazionata con etilacetato; il prodotto insolubile invece sarà sottoposto a frazionamento con etanolo.

Figura (6) *Frazionamento della lignina con etilacetato*

Al termine del secondo frazionamento, si ottengono tre frazioni di lignina: lignina frazionata con etilacetato, frazionata con etanolo e residuo finale insolubile. Essendo la resa della lignina frazionata con etilacetato maggiore (come mostrato dal grafico in **Figura (7)**), si è deciso di utilizzarla per la produzione della resina epossidica.
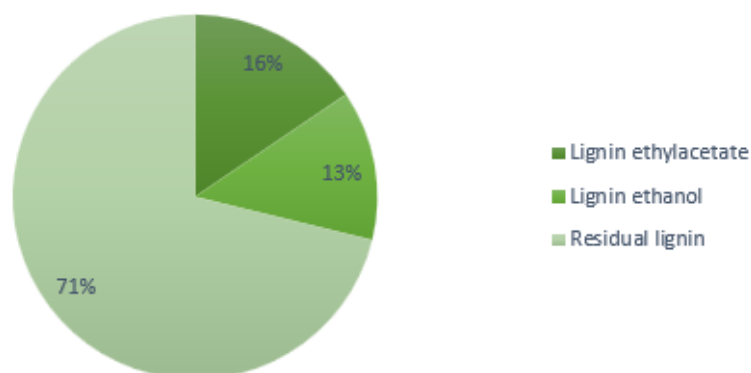
Figura (7) *Bilancio di massa della lignina frazionata*

Le analisi di cromatografia ad esclusione dimensionale (SEC) sono impiegate per verificare la corretta esecuzione del processo di frazionamento. Dal grafico ottenuto dalle analisi, mostrato in **Figura (8)**, si nota come la distribuzione di pesi molecolari si vada restringendo sempre più partendo dalla lignina originale (Lignoboost) e passando per il materiale frazionato prima con etilacetato e poi con etanolo. Ciò è accompagnato da una diminuzione dell'indice di polidispersione (da 2,25 a 1,21 e 1,42 rispettivamente per frazione con EtOAc e frazione con EtOH) e un aumento di peso molecolare.
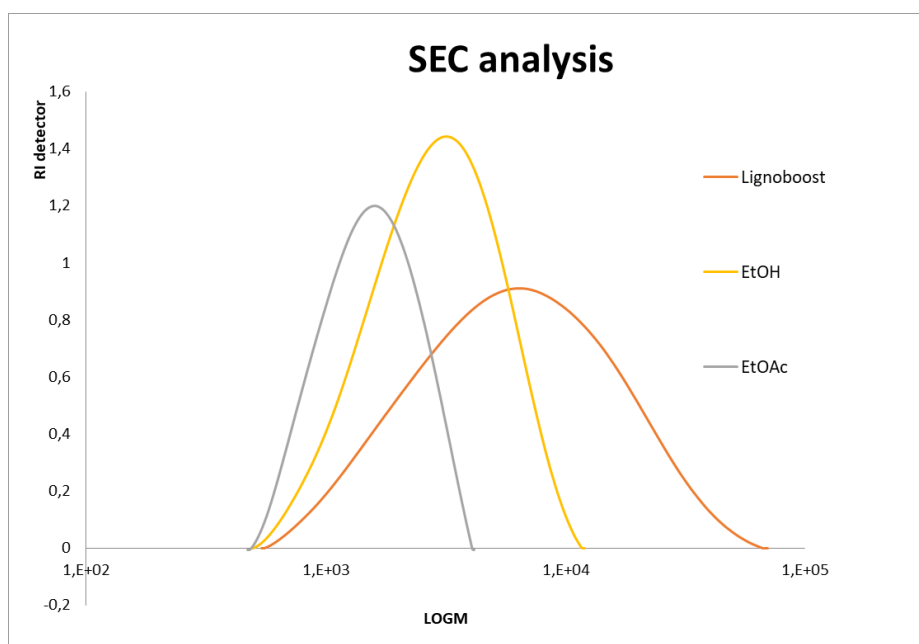
Figura (8) *Grafico risultante dalle analisi SEC relative a: lignina originale (Lignoboost), lignina frazionata con etilacetato e lignina frazionata con etanolo*

A seguire, la lignina frazionata con etilacetato viene sottoposta ad epossidazione. Per questa reazione sono necessari un composto costituito da gruppi idrossidi attivi, come fenoli o acidi dicarbossilici, in questo caso la lignina, e un composto contenente un gruppo epossidico, come l'epicloridrina.

La lignina è messa in soluzione con acqua e acetone in rapporto 50:50, tre equivalenti di NaOH e venti equivalenti di epicloridrina. La soluzione è messa a mescolare per cinque ore a 55°C. Una volta terminata la reazione, il composto è filtrato e sottoposto a freeze-drier per ottenere una polvere di lignina epossidata.

La tecnica di analisi NMR è utilizzata per avere informazioni di tipo quantitativo sui gruppi funzionali presenti, in particolare su fenoli, alcol alifatici e acidi carbossilici. Tramite la loro analisi è infatti possibile verificare se l'epossidazione si è svolta in modo corretto.

La **Figura (9)** mostra i grafici relativi alle analisi P-NMR prima e dopo l'epossidazione. Sono evidenziati i picchi caratteristici dei gruppi citati: idrossili alifatici, 145-150 ppm, fenoli condensati, 140-144 ppm, fenoli non condensati, 139-140 ppm, e acidi carbossilici, 134-136 ppm. La scomparsa di questi ultimi dopo l'epossidazione indica che sono stati consumati durante la reazione con l'epicloridrina. Solo il picco relativo agli idrossili alifatici non scompare. Probabilmente ciò è dovuto al fatto che alcuni intermedi della reazione di epossidazione costituiti da alcol alifatici, non hanno reagito e rimangono nella composizione originando il segnale NMR.
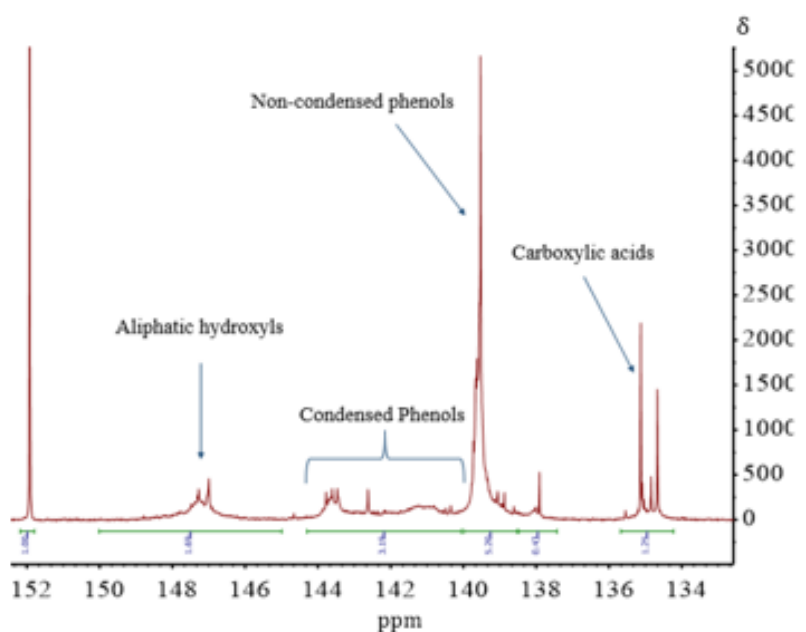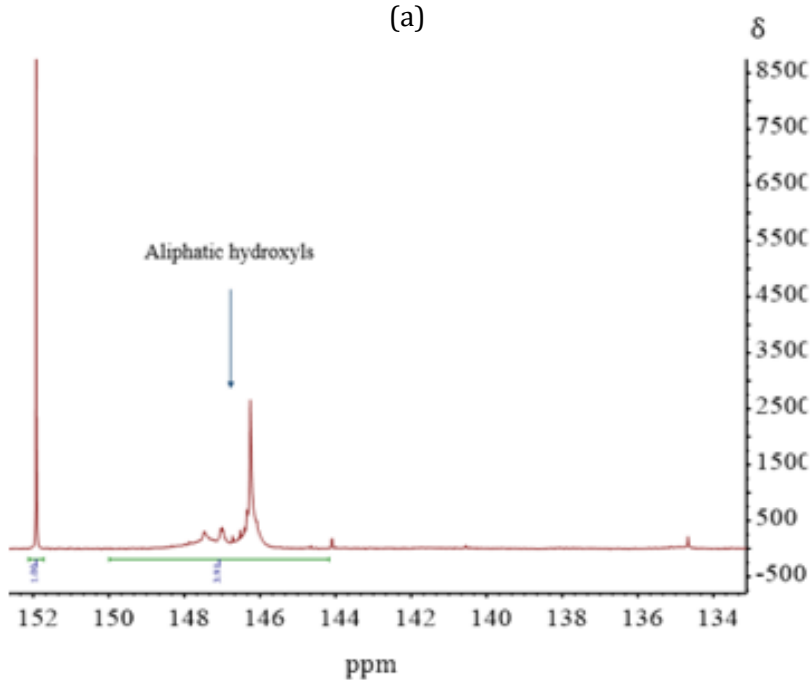
Figura (9) Analisi P-NMR: (a) prima dell'epossidazione; (b) dopo l'epossidazione

La reticolazione è l'ultimo step nella produzione della resina. La lignina epossidata viene messa in soluzione con un'ammina e la reazione tra quest'ultima e i gruppi epossidici da origine alla struttura tridimensionale reticolata. In questo caso, l'ammina scelta è una poli-ossipropilendiammina, la Jeffamine® D-400.

Lignina e Jeffamine D-400 sono mescolate in rapporto 2:1 in 300 µl di acetonitrile. Si è deciso di utilizzare questo rapporto perché ogni molecola di diammina reagisce con due catene del polimero. La soluzione viene inserita negli stampi in teflon per la produzione di campioni DMA e per test di combustione. Essi vengono inseriti in forno per completare

la reticolazione e le condizioni di temperatura sono: un'ora a 50 °C, due ore a 100 °C e due ore a 150 °C. In **Figura (10)** sono mostrati i campioni ottenuti.
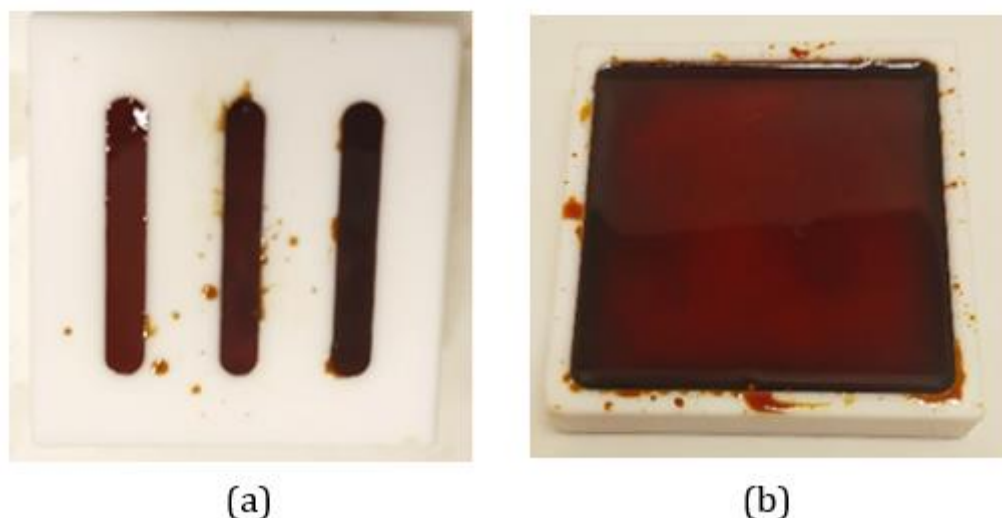

Figure (10) (a) campioni per DMA; (b) campioni per test di combustione

La caratterizzazione sui campioni di resina è stata effettuata con analisi DMA, con le quali si è calcolato il modulo elastico di 4500 Mpa, e la temperatura di transizione vetrosa, T_g, di 72,1°C. Quest'ultima ha un valore più basso se confrontata con le T_g di altre resine epossidiche (generalmente di circa 123°C). La ragione di questo valore inferiore è probabilmente spiegata dalla presenza di alcol alifatico che non ha reagito durante l'epossidazione. Ciò significa che non tutti gli anelli epossidici sono chiusi, portando alla formazione di un minor numero di reticoli e di conseguenza ad una T_g inferiore.

Sezione di pianificazione

La seconda parte della tesi presenta l'attività di pianificazione per la produzione del nanocomposito, con l'obbiettivo di fornire un percorso da seguire nell'ipotesi di riprendere il progetto a livello sperimentale.

Sono identificate le attività principali del progetto e per ognuna gli obbiettivi da raggiungere. Questa fase prevede la creazione di uno scaffold di un biopolimero e silicati lamellari in cui poi infiltrare la resina. È un espediente che permette di raggiungere una corretta distribuzione delle lamelle e quindi un più alto miglioramento delle caratteristiche meccaniche e di ritardo alla fiamma dei compositi.

Si considera un periodo di sei mesi per lo svolgimento del lavoro, tenendo conto del tempo richiesto dalla fase di ricerca bibliografica, dai tempi di esecuzione dei diversi test e degli eventuali rischi e imprevisti che potrebbero verificarsi. Sono impiegati due strumenti per la pianificazione dei progetti: diagramma di Gantt e diagramma di Pert.

Il diagramma di Gantt è utilizzato per comprendere come le attività sono collegate fra loro nel periodo di tempo stabilito, individuando le "milestones", ovvero gli obbiettivi chiave tramite i quali è possibile monitorare il corretto svolgimento del progetto. La **Tabella (1)**

riassume le attività del progetto, i tasks individuati per ognuna di esse e le rispettive milestones. Queste ultime verranno indicate nel diagramma di Gantt (mostrato in **Tabella (2)**) con una stella.

	Tasks	Milestones
1. Estrazione della lignina e selezione dei materiali per la produzione dello scaffold	1.2 Selezione dei materiali per produrre lo scaffold	Ottenere una o più formulazioni di biopolimero e silicati lamellari per produrre lo scaffold che esibiscano buona stabilità termica e alto residuo in peso dopo la degradazione termica.
2. Produzione dello scaffold	2.1 Produzione dello scaffold 2.2 Caratterizzazione dello scaffold	Ottenere uno scaffold con le seguenti caratteristiche: - Densità compresa fra 0,1 e 0,4 g/cm^3; - Porosità distribuita omogeneamente - Modulo di compressibilità $\simeq$ 4-6 Mpa - Stabilità termica e alto residuo in peso; - Autoestinguenza durante il test di infiammabilità.
3. Produzione del nanocomposito	3.1 Infiltrazione dello scaffold e curing 3.2 Caratterizzazione morfologica del nanocomposito	Ottenere un nanocomposito con struttura omogenea, con quantità minima di difetti
4. Caratterizzazione meccanica e del comportamento al fuoco.	4.1 Caratterizzazione meccanica 4.2 Comportamento al fuoco	- Aumento del 20-30% del modulo elastico; - Aumento del 40% della resistenza a trazione; - Aumento 10% della Tg; - Classificazione V-0 secondo lo standard UL-94; - Riduzione del 50% di pkHRR e TSR; - Resistenza alla penetrazione di fiamma per più di 5 minuti

Tabella (1) *Attività che compongono il progetto: per ognuna di esse sono identificate le principali tasks e le milestones*

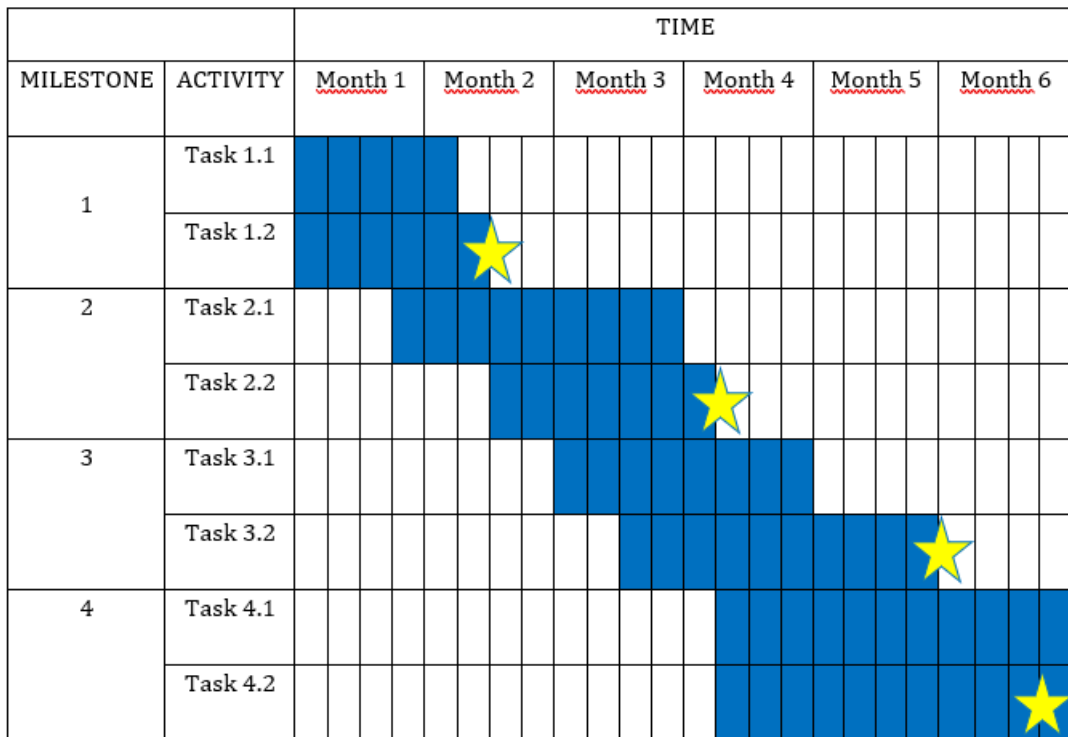|		TIME					
MILESTONE	ACTIVITY	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6
1	Task 1.1	██					
	Task 1.2	██ ★					
2	Task 2.1		██				
	Task 2.2			★			
3	Task 3.1			██			
	Task 3.2				██ ★		
4	Task 4.1				██		
	Task 4.2					★	

Tabella (2) Diagramma di Gantt

Il diagramma di Pert è invece impiegato per indicare le attività di feedback presenti tra un task e l'altro, ed è mostrato in **Figura (11)**.
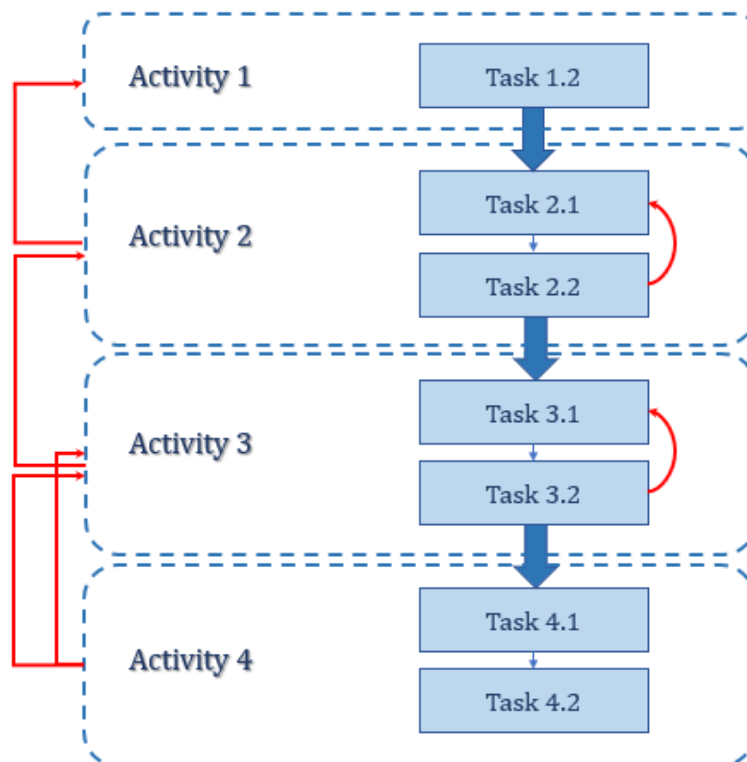

Figure (11) Diagramma di Pert

Infine, viene effettuata un'analisi dei rischi: essa rappresenta uno strumento importante per individuare tutti i fattori che potrebbero diminuire la probabilità di produrre un nanocomposito con le proprietà designate. L'analisi si riferisce solo alla produzione del nanocomposito; infatti il trattamento preliminare della lignina e la creazione della resina costituiscono delle attività già svolte secondo una procedura stabilita che non comporta rischi.

Tre sono i possibili rischi individuati, ognuno relativo a dei determinati task del progetto:

1. le proprietà meccaniche dello scaffold potrebbero non essere sufficientemente buone per resistere alla successiva infiltrazione di resina, portando al collasso della struttura (questo rischio è relativo ai task 2.1, 2.2 e 3.1);
2. la resina potrebbe essere infiltrata nello scaffold in modo errato: una sua distribuzione disomogenea porterebbe a cattive proprietà meccaniche del nanocomposito (questo rischio è relativo al task 3.1);
3. il comportamento al fuoco non è conforme ai requisiti desiderati (non ha classificazione V-0 secondo lo standard UL-94, ha un alto valore di pkHRR e TSR) (questo rischio è relativo al task 4.2).

Conclusione

Il presente progetto di tesi si è concentrato sullo sviluppo di nanocompositi a base di lignina e silicati lamellari con proprietà di ritardo alla fiamma. Si è deciso di suddividere il lavoro in due parti: una prima parte che descrive l'attività sperimentale riguardante il trattamento preliminare svolto sulla lignina, e una seconda parte volta alla pianificazione delle attività di produzione e caratterizzazione del nanocomposito finale (rimasta incompiuta a livello sperimentale per la sospensione delle attività a causa della pandemia da Coronavirus).

Dalla caratterizzazione svolta sulle resine epossidiche a base lignina ottenute, si è in grado di asserire che le proprietà risultanti analizzate sono paragonabili a quelle di una tradizionale resina epossidica derivata da fonti fossili.

Ma le proprietà ottenute sono sufficienti per sostituire un materiale convenzionale?

A questo proposito, a partire da questo lavoro di tesi si può ragionare su altri aspetti relativi alla vita di un materiale rispetto a quelli concernenti caratteristiche puramente fisiche e chimiche. Se si considera la suddetta resina a base lignina, nonostante il carattere naturale della materia prima principale, bisogna tener conto dei solventi chimici utilizzati per i vari step di frazionamento, epossidazione e curing che ne fanno un processo non interamente bio-based: etilacetato, epicloridrina, Jeffamine d-400 per citarne solo alcuni. Infatti, non solo il loro smaltimento rappresenta un problema a livello ambientale, ma anche la loro pericolosità e tossicità durante l'utilizzo non sono da sottovalutare. C'è bisogno di capire se un processo del genere abbia un impatto ambientale maggiore di quelli convenzionali. Inoltre, il grande numero di step che compongono l'attività ne fanno un processo complesso e al momento difficile da replicare su larga scala, che comporterebbe anche un costo maggiore per la maggior quantità di strumenti ed energia da impiegare. A tal proposito un'idea per un lavoro futuro potrebbe essere lo svolgimento di un'analisi del ciclo di vita (Life Cycle Assessment, LCA). Esso è uno strumento analitico standardizzato volto a valutare l'impatto di un materiale sull'ambiente e sulla salute umana, considerando il suo intero ciclo di vita, dalla realizzazione fino allo smaltimento.

In questo modo si potrebbe fare un confronto tra le analisi relative alla resina a base lignina e quelle di resine o altri polimeri convenzionali per valutare quale di loro ha un impatto ambientale maggiore.

La seconda parte della tesi è volta alla pianificazione delle attività di produzione e caratterizzazione del nanocomposito finale. Partendo dalla volontà di creare un materiale con delle determinate proprietà meccaniche e di ritardo alla fiamma, si è suddiviso il lavoro in diverse attività, ognuna con uno scopo ben preciso. Questo lavoro si è rivelato fondamentale per comprendere, a livello generale, quali sono le variabili da considerare e i passi da compiere quando ci si approccia ad un'attività di questo tipo. Infatti, questa analisi ha permesso di capire che se da un lato a livello teorico il lavoro sperimentale procede con tempi più o meno stabiliti, all'atto pratico bisogna tenere conto dei molti imprevisti e rischi che possono verificarsi e provocare ritardi nel suo svolgimento e individuare le possibili soluzioni. Strumenti quali i diagrammi di Gantt e Pert si sono rivelati fondamentali per organizzare il lavoro nel periodo di tempo scelto.

In conclusione, lo studio sullo sviluppo di nuovi materiali "bio-based" svolto in questa tesi rappresenta uno degli ambiti di ricerca più promettenti degli ultimi anni. Anche se i risultati ottenuti nella prima parte della tesi non danno informazioni su quanto sia conveniente, a livello ambientale, utilizzare la resina a base lignina rispetto ad una resina epossidica normale, è importante continuare a studiare per rendere questo processo sempre più sostenibile e più facile da implementare su grande scala.

1. INTRODUCTION AND THESIS GOAL

Nowadays, polymeric materials are fundamental in everyday life. Their versatility, together with other interesting properties such as strength, durability, lightness and the possibility to be moulded in different shapes, make them suitable for a wide range of applications. Packaging represents one of the largest end-use market for plastics, followed by the building sector and the automotive one. Other fields of applications are the agricultural one, the consumer's goods and electronics[1].

Due to plastic exceptional characteristics, the world production and consumption is increasing more and more every year, with inevitable consequences on human health and on the environment. It is estimated that in 2018, 359 million metric tons of plastics were manufactured, 62 of which produced only in Europe; this value is destined to double by 2050, reaching nearly 800 million tonnes per year[2][3].

The majority of plastics are produced from petroleum-based hydrocarbons; although only 4% of the world fossil fuel is used for this purpose, in future this percentage could increase significantly, due to the expected growth of plastic production[4]. The renewability of fossil fuel represents an issue: it could be considered a renewable source, since it can regenerate, however time necessary for regeneration is extremely longer than the rate at which it is extracted and used. For this reason, fossil fuels are considered non-renewable sources, that could run out in few decades.

Pollution represents another problem of the large use of plastic. Since the most commonly used polymers are not biodegradable, the waste disposal has a negative impact on the environment, as well as on the human health.

These concerns lead to the challenge of finding sustainable alternatives to petroleum-based plastic materials, which can reduce the dependency on fossil fuels. An answer to this problem is provided by the production of bio-based materials, generated from a renewable source. The raw material used mostly derives from agricultural feedstocks: corn, potatoes, molasses and other carbohydrate feedstocks; in recent year the attention shifted to lignocellulosic biomasses and on the recovery of organic waste. In every case, the possibility to have this kind of source is convenient because it is natural, abundant on earth and renewable.

The present project of thesis aims to produce and study the characteristics of a resin based on lignin, which is obtained from wood, being one of its main constituents together with cellulose and hemicellulose. Lignin constitutes a renewable and natural alternative to fossil fuels. The objective is to produce a material with competitive properties compared to conventional thermosetting resins and to analyse its fire retardancy behaviour, since this aspect is not discussed in literature. In this regard, the common strategies to increase the fire retardancy of polymers are discussed, with particular emphasis on which kind of additives are used for the resin.

Originally, the objective of the project was to produce a bio-based resin starting with the functionalization of lignin, which must undergo a process of purification and fractionation

before being actually employed for the resin production. It was expected to create samples of neat resin and samples of a nanocomposite made up of resin with montmorillonite, a clay used to improve the fire-retardant properties of the neat material. Finally, testing would be performed in order to analyse the mechanical, thermal, morphological and fire retardancy properties and confront the behaviour of the material with and without the clay.

Unfortunately, the suspension of all research activities due to the worldwide Coronavirus emergency prevented the continuation of the project as intended in the first place. Thus, only the first half of the work, which comprehends the treatment/extraction of lignin, has been carried out at the Royal Institute of Technology in Stockholm before the pandemic emergency. It is for this reason that the thesis has been modified to adapt to this new situation.

The new objective is to implement an activity plan for the production of the bio-based materials originally intended as the main outcome of the thesis work. The thesis structure is described in detail as follows.

Chapter 2 provides the bibliographical section focused on the state of the art on bio-based resins. Firstly, the definition of bio-based materials is given, explaining what they are and why they are developed. Then, the most important sources of such materials are cited, with particular emphasis on lignin, which is the main constituent of the resin that has to be produced. The main characteristics of the lignin-based resins are underlined, based on the literature available to date.

Chapter 3 explores the mechanism of fire retardancy and the additives used to improve this aspect. The focus is put on nanocomposites, their properties and their fire behaviour.

Chapter 4 provides the experimental section of the thesis with the description of the research activity carried out at KTH in Stockholm: lignin extraction, epoxidation step and the production of the resin. The second part focuses on the characterization techniques used to study the processed lignin.

The planning activity of the project is discussed in detail in chapter 5. Firstly, a brief overview of the whole project is reported. Then the main activities and their objectives are identified; Gantt diagram and Pert diagram are employed to show how the different activities are connected, and the time required to accomplish them.

An evaluation of risk is presented in chapter 6 to study the problems that might arise during the development of each phase and what are the possible solutions to them.

Finally, chapter 7 provides the conclusion of the thesis work with particular focus on possible future developments on this research area.

2. STATE OF THE ART: BIO-BASED POLYMERS

The first bio-based products appeared in the 1980s in Great Britain, they were made from poly(hydroxyalkanoate) and used for packaging and agricultural applications [5]. In the last decades, bio-based materials have attracted more and more attention, due to the need to substitute petroleum-based plastic with something natural and sustainable, that can offer similar properties and can be employed in a wide range of applications.

But what does "bio-based" means?

There are several definitions of bio-based material: according to the Sustainable Biomaterials Collaborative (SBC), a bio-based plastic is a "*plastics in which 100% of the carbon is derived from renewable agricultural and forestry resources such as corn starch, soybean protein and cellulose*"[6]. Another definition is provided by ASTM (American Society for Testing and Materials International) that defines a bio-based plastic "*an organic material in which carbon is derived from a renewable resource via biological processes*" [7]. Out of the two definitions, the latter seems more appropriate to describe the bio-based resin that this project aims to analyse, because although most of the raw materials used are natural and renewable (like lignin and clay), other chemicals employed for the production process aren't. Nonetheless, it is convenient to have a material like this, even if is not 100% bio-based, to substitute non-renewable fossil resources.

From a general point of view, bio-based plastics allow to save fossil fuel by using biomass as a raw material because it is abundant in nature and can renew periodically. In addition, they can reduce the impact on the environment especially for what concerns the CO_2 released. Plastics have a big carbon footprint during their life cycle because all the stages of production (from the extraction and distillation of fuel to the processing), and the waste disposal release a high amount of greenhouse gas, contributing to the global warming[8]. Bioplastics represent a positive answer to this problem: in fact, there's a balance between the CO_2 released during the production of the material, its utilization and disposal, and the CO_2 consumed during the growth of the biomass [9].

Although bio-based plastics are produced from renewable sources, they are not necessarily biodegradable. A polymer is biodegradable if its properties undergo physical and chemical deterioration when exposed to microorganisms, carbon, methane and water [10]. This property is linked to the chemical structure of the material, not to its source. This makes it possible to have a petroleum-based plastic more biodegradable than a bio-based one.

The association European Bioplastics provides a graph, shown in **Figure 2.1**, to better understand the common types of conventional plastics and bioplastics. The distinction is on the origin of the material (fossil-based or bio-based) and on the biodegradability. For instance, according to this classification, a fossil-based plastic can be biodegradable, while a bio-based one is not.
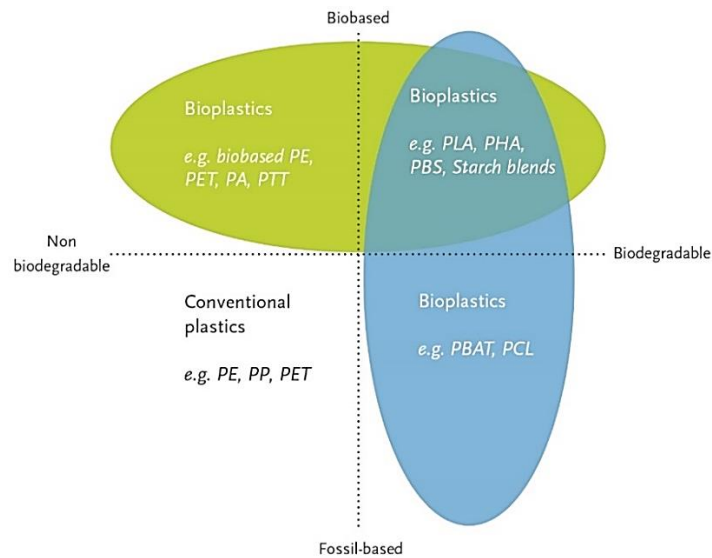
Figure 2.1 *"Material coordinate system of bioplastics" from the European Bioplastics association* [11]

Generally, bio-based plastics are divided into two main categories: "Old economy" and "New economy."

"Old economy" bioplastics represent materials used before the advent of petrochemicals, they are based on modified natural compounds, like rubber, gelatine or cellulose.

"New economy" bioplastics indicate those plastics with a natural and renewable resource developed as alternative to petrochemical materials. They divide into two sub-categories, according to their chemical composition. The first category is the one of "Chemical novel", which have a chemical structure that is completely new with respect to the conventional polymers. Examples of this kind of materials are PLA (Polylactic acid) and PHA (Polyhydroxyalkanoates). The second group is the one of "Drop-ins": they keep the same chemical structure of traditional polymers but are bio-based; the most known are bio-based PET (Bio-PET), bio-based polyethylene (Bio-PE) and bio-based epoxy resins [12].

The different types of biopolymer can be collocated in the groups of the graph in **Figure 2.1**: "Old economy" polymers are part of the top right group, bio-based and biodegradable polymers, together with "Chemical novel" polymers. "Drop-ins" polymers are part of the top left group, because they are not biodegradable.

2.1 MARKET'S DATA AND SUSTAINABILITY

At the moment, bioplastics represent 1% of the global market of plastics, and this value is expected to increase, since the demand for such materials is constantly growing in every field of application. According to the association of European Bioplastics, it is estimated that the growth in production of bioplastics will increase from approximately 2,1 million tonnes to 2,4 million tonnes by the end of 2024, as shown in **Figure 2.2**.
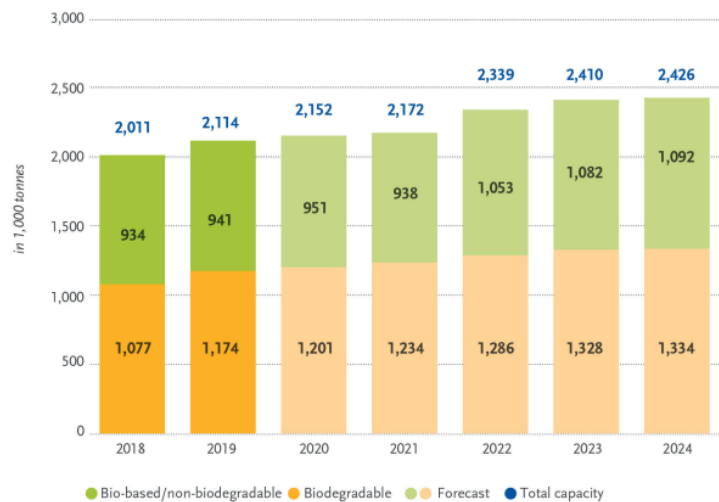
Figure 2.2 *Trend for the global bioplastics production capacity*[13]

Asia is the main producer, holding 45% of the bioplastics global market, followed by Europe and America [13].

The large-scale production of bio-based plastics is advantageous from an environmental point of view, since their life cycle allows to reduce greenhouse gas emissions, that would be much higher by using fossil resources. But can bio-based plastics be defined as sustainable materials in all cases? A material is sustainable if it reduces the impact on public health and on the environment throughout its life cycles [7]. Several factors must be considered in order to state whether a material is sustainable or not: what is the source used, what production process is implemented and what is its disposal at the end of the life cycle. Whilst bioplastics can be considered sustainable for the above reasons, there is an important factor that might compromise this aspect. Indeed, the use of toxic pesticides and other dangerous additives to maximize the production at industrial level can eventually contaminate water and soil thus limiting the sustainable and environmentally friendly characteristics of bio-based plastics. Moreover, the high exploitation of arable lands can cause loss of habitats and biodiversity and water shortage and can lead to deforestation. In this perspective, a new definition of sustainable bioplastic can be provided: "*a material produced from a source grown without genetically modified organisms (GMOs), hazardous pesticides, certified as sustainable for the soil and ecosystems, and compostable into healthy and safe nutrients for food crops*" [7].

Another important negative factor is the one related to the quantity of land used to produce the renewable feedstock: there's the concern that it may compete and even reduce the land needed for the cultivation of food and feed. This doesn't appear to be a problem at the present time, since land used for bioplastic feedstock is only 0.02 % of the global agricultural area. However, it can grow into a real problem in the future, when the bioplastic production is expected to considerably increase [12].

The solution proposed to solve this problem is the implementation of a second generation of natural feedstock focused on lignocellulosic biomass and waste from agricultural production, different from the first generation (constituted by sugar, corn, etc.) that

5

further complicates the competition for the use of lands. The use of such raw material not only give them a new economic value, but also allows to have a lower cost[9].

2.2 PRODUCTION PROCESSES AND MAIN BIO-BASED PLASTICS

This paragraph analysis what are the fundamental methods to produce bioplastics and presents the most important and used types, underlining their main properties and applications.

There are three main ways in which bio-based plastics can be obtained:

1. The modification of natural polymers without the alteration of their backbone structure. This approach is used with plastics based on starch and cellulose.
2. The second way consists of two steps: in the first one the bio-based monomer precursors are produced with chemical transformation; then, the second step is characterised by their polymerization. The materials obtained by means of this process are the "New economy" and "Drop-in" plastics. This is the most used approach to transform an agricultural source into a bioplastic.
3. The final method consists in the production of bio-based plastics via chemical processes that involve microorganisms or plants, like fermentation or photosynthesis. Although this gives the possibility to have a plastic ready to use without further modifications, the process is very complex due to environmental issues, so it is not very used[5].

The above production methods make it possible to obtain both thermoplastic and thermosetting polymers. In this paragraph the most important bio-based plastics are mentioned, underlining their major characteristics.

PLA or Poly(lactic acid) is the most important and most produced commodity bio-based polymer. It is produced exploiting the third approach mentioned above, by the fermentation of sugar obtained from corn starch or sugarcane. The advantage of this polymer is that not only it is based on a fully renewable source, but it is also biodegradable and compostable.

Figure 2.3 shows the life cycle of PLA: pellets are obtained from the renewable raw material and are processed with conventional manufacturing techniques (extrusion, injection molding) to create objects. After their utilization, there are different options: recycling, incineration, with the energy recover, and biodegradation or compost.
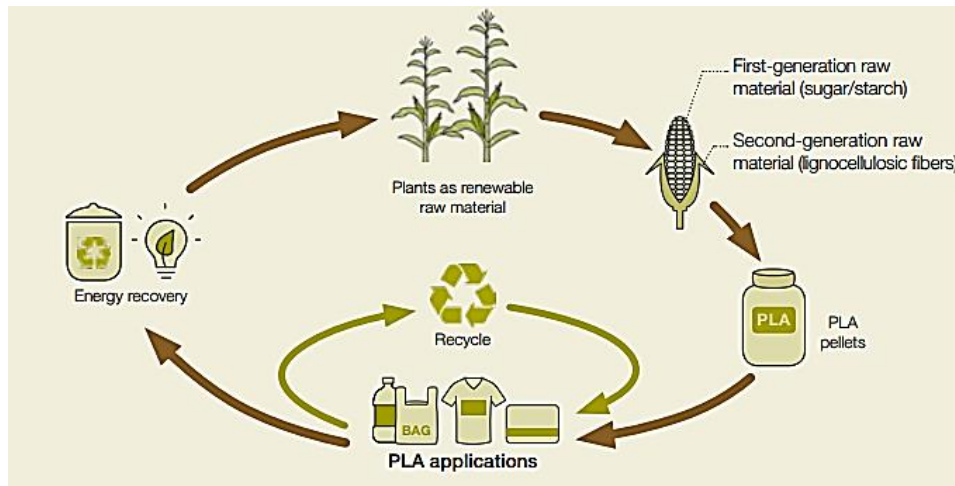
Figure 2.3 *Life cycle of PLA: from the raw material to the fermentation to produce PLA pellets and finally consumption and recycle* [14]

PLA presents several interesting properties that put it at the same level with traditional fossil-based polymers: it has good barrier properties to odours that make it suitable for packaging applications, optimal torsional and bending behaviour and good UV resistance. Some drawbacks are present too. PLA is a brittle material, with less than 10% elongation at break: this limits its applications, since it cannot endure high stresses[15]. Moreover, the thermal resistance is quite low, around 60°C, making it difficult to find its optimal processing conditions. Generally, nanofillers, such as MMT, graphene or zinc oxide, are employed to improve these characteristics: they increase the impact strength and the Young modulus as well as the oxygen barrier properties[16].

PLA is employed in a wide range of applications: agricultural field, electronic, building and constructions and medical sector but, above all, the excellent barrier properties and the biodegradability make it the perfect material for packaging, like disposable plates, cups, cutlery, bags, etc.

Another example of bio-based plastic is the one obtained from starch: it is called thermoplastic starch (TPS). The raw material is a biodegradable polysaccharide, very abundant in nature, since it can be found in numerous plants. It exists as a granular hydrophilic polymer that must undergo a process of injection molding or extrusion in presence of water to form TPS. Indeed, by heating the granules with water for a given amount of time while applying a mechanical force, the structure is disrupted and plasticized to form a homogeneous melt, achieving a thermoplastic material[17].

Thermoplastic starch is a fragile polymer, its Tg is relatively high, approximately 200°C, and this compromises the mechanical properties[18]. To improve them, plasticizers such as water, formamides, urea, acetamide, sugar and other natural additives are often used. This is needed to preserve the natural character and the biodegradability of the material[19]. Moreover, TPS is a hygroscopic material: its Tg can vary according to the atmospheric humidity. This problem is usually solved by making TPS blends with other polymers (like PLA), or using coatings that protect the material[20].

Commercialisation of thermoplastic starch is growing more and more every year, most of all for what concerns the packaging sector, with bags, films and coatings for the food industry.

Not only bio-based thermoplastic polymers are produced, but also thermosetting ones. Above all, it is important to consider the production of bio-based resins. This kind of material allows to have better performances in other fields of applications, like adhesives and coatings, due to the higher stability and rigidity. Several natural sources have been used to produce bio-based resins: lignin, rosin, sugar, vegetable oils[21].

Furan resins represent an example of bio-based thermosetting polymer. The raw material used for their production is furfuryl alcohol, an organic compound obtained from biomass like sawdust, sugarcane and wheat bran. It undergoes condensation polymerization in the presence of strong acids to create the furan resin. Due to their high resistance to temperature and chemicals, these resins are mainly used for foundry applications as cements and binders[22]. They are also utilised as matrices in the composite production. One of the main attractive of this kind of resin is its high fire resistance. Furan resins are able to create a char that inhibits further degradation of the material. There are several types of resins with these characteristics like the phenolic resins that are the most used ones. Furan resins constitutes an advantageous alternative to them since they are natural materials and the level of toxicity of the furfuryl alcohol used to produce them is less dangerous that formaldehyde, used to synthetize phenolic resins[23].

Epoxy resins constitute another large group of materials that can be produced with natural resources. In addition to the need to have bio-based materials for environmental issues, in this case there is another aspect to consider, which is human health. In fact, 75% of the world production of epoxy resin is synthesized using Bisphenol-A[21]; it is demonstrated that its impact on human health is negative, since it is an EDCs (Endocrine Disruptor Compounds), a compound that modifies endogenous hormonal activity. These alterations through exposure to EDCs are dangerous for the structure and function of the brain itself and also to the regulation of hormones. Generally, exposure to Bisphenol-A occurs via food in contact with BPA-containing materials[24]. For this reason, epoxy resins based on natural sources are gaining more and more attention. Rosin, soybean, cardanol are only a few among the most used raw materials for epoxy resins. One of the most important is lignin, which is also the main component of the resin analysed in the present project of thesis.

2.3 LIGNIN

Lignin is the second most abundant biopolymer on earth, being one of the main elements of wood and plants, together with cellulose and hemicellulose. The first time lignin was presented as a biopolymer was in 1960, when Brauns described it as plant polymer made from phenylpropanoid building units[25]. Years later this definition was revised by Brunow, who provided a more complete overview of the lignin's chemical features: "Lignin is a biopolymer consisting of phenylpropanoid units with an oxygen atom at the

para-position (i.e., –OH or –O–C) and with none, one, or two methoxyl groups in the para-position to this oxygen atom" [25].

Lignocellulosic biomass is made up of three components as function of the source: cellulose (30-50%), hemicellulose (20-35%) and lignin (15-30%)[26]. In the plant structure, lignin acts as a binder between the plant tissue providing mechanical strength and rigidity to the biomass cell structure. While the first two components are largely utilised in the production of biofuels and chemicals, lignin is the most underused of them. Indeed, on the 40-50 tonnes available every year, only the 2% is exploited commercially, while the rest is burnt as a low-value fuel[27]. Despite of this, lignin has a huge potential to be used as a raw material to create new bioplastics, since it is available in great quantity, it is natural and biodegradable and can be easily processed to produce new monomers.

This chapter provides an overview of the fundamental properties of lignin from a chemical and compositional point of view, and a description of all the main processes to extract and treat lignin and convert it into a biopolymer.

2.3.1 CHEMICAL PROPERTIES

The structure of lignin is very complex and heterogeneous: it is an aromatic and optically inactive compound with phenylpropane units and different functional groups that combine by means of several linkages. The precursor monolignols are three: cumaryl alcohol, coniferyl alcohol and sinapyl alcohol, also called respectively p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) (**Figure 2.4**). What changes between them is the number of methoxy groups attached in ortho position to the aromatic ring (no metoxy group for "H", one for "G", two groups for "S").
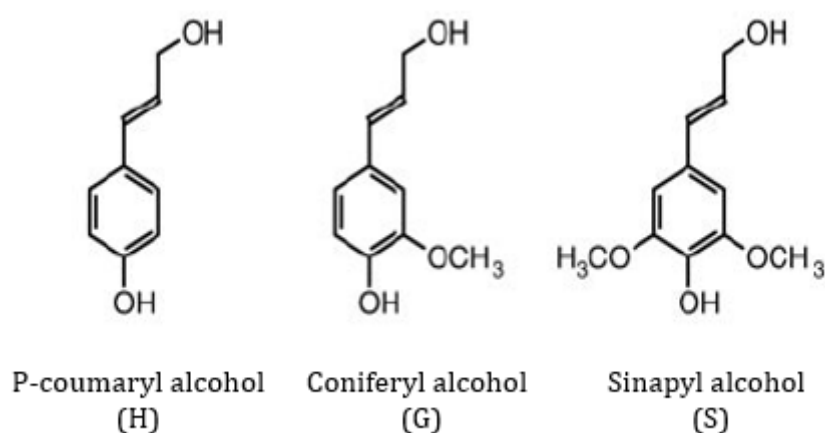

Figure 2.4 Lignin monolignols[28]

The content of lignin, and the monolignols present in the structure, can vary according to the type of plant: for example, in softwoods (Gymnosperm lignins), lignin is mainly

composed by guaiacyl structure, in hardwoods (Angiosperm lignins), it contains both guaiacyl and sinapyl structures, in grasses it has all the three units[25]. These differences depend also on other factors, like the plant growth, the climate conditions in which it exists and the illumination to which it is exposed[29]. Also, the type of functional groups and their content may change. Generally, the main functional groups present in lignin are alcohol hydroxyl group, phenolic hydroxyl group, carbonyl group, carboxyl group, methoxyl, and sulfonic acid. Their determination is important in order to know the characteristics of the polymer, like optical properties or the chemical reactivity. There are many carbon-carbon bonds between the structural units, however the most frequent link between the monolignols is the 4-O-β ether bond. The most recurring bonds in lignin structure are shown in **Figure 2.5**.
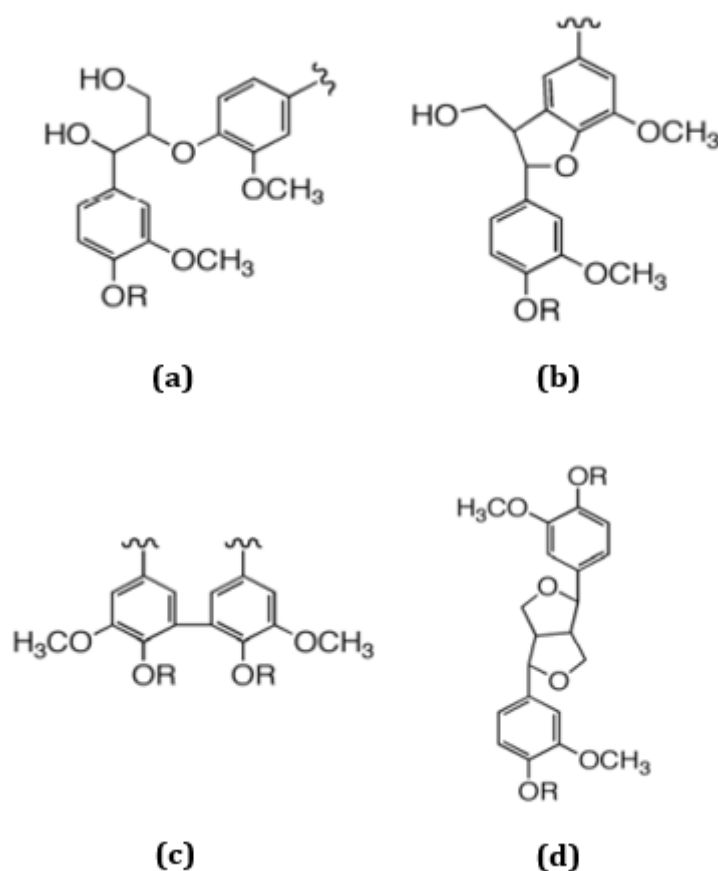
Figure 2.5 *Typical bonds in the lignin structure: (a) β-O-4, (b) β -5, α-O-4, (c) 5-5, (d) β -β*[30]

The great diversity of monomer content and type in every species of plant and the variability of chemical bonds between them make the determination of the exact chemical composition of lignin extremely hard. This heterogeneity constitutes the main obstacle for the production of polymers and can be overcome only with pre-treatments that decrease the naturally high polydispersity.

2.3.2 TREATMENT OF LIGNIN: EXTRACTION AND CONVERSION

In recent years, the number of scientific papers describing different procedures on how to extract and treat lignin into a high value biopolymer has increased.

The general process starts with the isolation of lignin from the source, that can be constituted by the by-product of the paper industry, the lignocellulosic biomass or agricultural waste. The extracted lignin undergoes a conversion step that consists of thermochemical reactions to obtain aromatic compounds, which are the raw material to produce lignin-based polymers. A schematic overview of the process, with all kinds of reactions that can be performed, is shown in **Figure 2.6**.
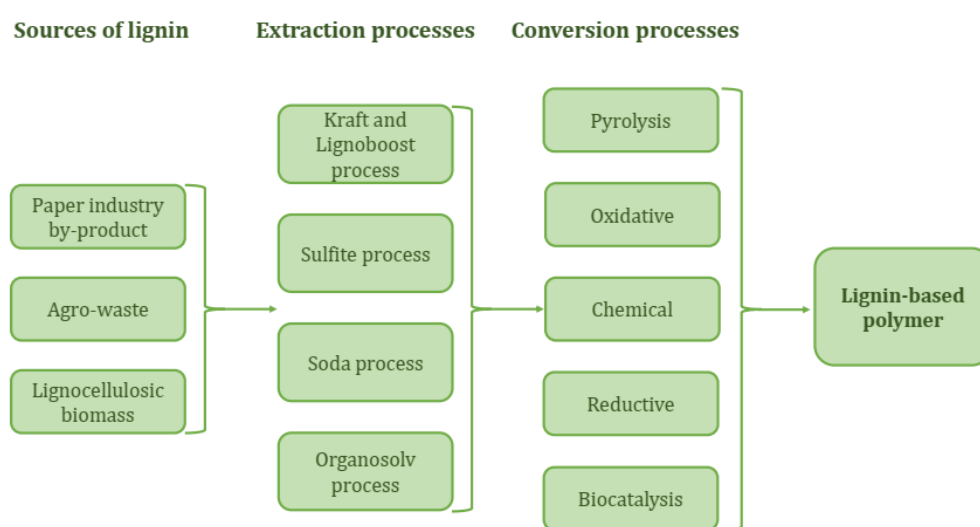

Figure 2.6 *Overview of all the types of processes used to transform lignin into a biopolymer*

A great number of methods are implemented to treat lignin. This paragraph focuses on the main extraction and conversion processes industrially employed, underlining their major characteristics.

The first process that the lignin undergoes is the isolation from the source: the objective is to separate pure lignin from the other lignocellulosic biomass components. The use of reactants consents to break the bonds with cellulose and hemicellulose, allowing the recovery of the pure material. The final properties of the extracted lignin depend on the kind of method used, since every one of them is characterised by the use of different reactants and conditions.

There are two main groups of processes to isolate lignin, one involves sulphur while the other does not. The first group comprehends Kraft process and Sulphite process; the second group includes Soda process and Organosolv process[26].

The Kraft process is the most widely used process, delivering over 98% of the lignin currently on the market (in total more than 1 million ton of lignin)[31]. It allows to isolate lignin from the cellulose pulp, which is used to produce paper. The lignocellulosic biomass

is treated under high temperature (150-180°C) with aqueous soda (NaOH) and sodium sulphide (Na_2S)[32]. The strong alkaline character of the solution causes the degradation of lignin and hemicellulose. The pulp obtained at the end of the treatment is separated from the cooking solution, which is called Black Liquor, typically made up of 40%–45% soaps, 35%–45% lignin, and 10%–15% of other organic materials[33]. There are several ways of isolating pure lignin from the black liquor, but the most important is the Lignoboost process. This process has been introduced only recently to the market producing 27000 tonnes of Kraft-lignin in 2013[26]. It consists in the filtration of the heterogeneous solution enhanced by the use of CO_2 that lowers the pH; this passage is repeated twice, and it causes the precipitation of lignin. At the end of the process, the mixture is re-filtered and washed[34].

The Sulphite process is the other method normally employed to isolate lignin that involves sulphur. In this process, the lignocellulosic biomass is dissolved in a solution of sulphur dioxide (SO_2) and sulphite base salts. Sulfuric acid is produced with the reaction between SO_2, biomass and water at a temperature around 120-150°C. According to the types of salts used, the solution has a different pH. At the end of the process, an aqueous mixture is obtained, known as "special pulp", from which lignin is recovered using different techniques, like precipitation, ultrafiltration or fermentation. The recovered product is called "lignosulfonate"[32].

Kraft lignin and lignosulfonate have a sulphur content generally higher than 5% and mainly ascribed to the presence of hydrosulfonyl groups. This can constitute a problem when lignin is employed as an energy fuel, since the removal of sulphur from the combustion gases requires expensive scrubbing. For this reason, an alternative to the previous extraction methods capable of producing sulphur-free lignin were developed and are known as the Soda and Organosolv processes.

The Soda process is typically used for non-wood-based biomass, like agricultural waste biomass. The source is put in a solution containing sodium hydroxide at high pressure (0,06 bar) and temperature around 160-170°C. NaOH breaks the α-ether bonds starting the delignification process with the decrease of the molecular weight and the increase of the lignin solubility. The obtained lignin fragments can be isolated from the mixture via precipitation and the purity of the material obtained is higher than the one from the Sulphite process.

Lastly, the Organosolv process is the most recent one and consists in using an aqueous organic solvent that breaks the alpha aryl-ether of the lignin structure into fragments that are soluble in the solvent. The most common organic solvents employed are ethanol, methanol, and acetone. The process can be improved by using acid catalysis at low temperature. The advantage of such a method is the possibility to isolate lignin, hemicellulose and cellulose simultaneously, obtaining a higher purity with respect to the Kraft lignin. It is also more environmentally friendly than the previous processes since it operates at room temperature and pressure and does not employ sulphur. Despite these aspects, the Organosolv process has not reached the commercial scale because the recovery of the material has not been optimised yet, making it more expensive than the traditional methods[26].

Once obtained a soluble and isolate product from the previously described processes, generally known as "technical lignin", the conversion step can start. It involves thermochemical processes that degrade lignin into aromatic monomers of high added value, that constitute a suitable renewable feedstock to substitute petroleum aromatics in the production of plastics. The main lignin conversion strategies are investigated in this paragraph.

Pyrolysis is a promising process for the conversion of lignin into biomaterials. Lignin is heated to high temperature (generally around 450-500°C) in absence of oxygen and is thermally degraded into several products, like solid char, liquid oil and gases[35]. According to the conditions used (e.g. temperature and heating rate), these conversion products are present in different proportions. It is the liquid oil, full of aromatic compounds, that represents the raw material for the plastic production. There are two main types of pyrolysis: fast pyrolysis and catalytic fast pyrolysis. The first one is conducted with a heating rate higher than 100°C/s which causes a gradual degradation of lignin. The catalytic fast pyrolysis differs for the use of a catalyst which is able to convey the production of a certain lignin by-product and increase the yield of the process. Zeolites and metal catalysts are the most exploited for this task[32]. A variant of this process is hydrogenolysis: it is a pyrolysis but performed in the presence of hydrogen. Lignin is treated with an active hydrogen-donating solvent, such as sodium formate, formic acid or tetralin, leading to higher conversion grade and less char formation, if compared with the traditional pyrolysis. It allows to achieve phenols from lignin[36].

Oxidation is an alternative process to isolate aromatic compounds from lignin. In the presence of oxidants like nitrobenzene, metal oxides, and hydrogen peroxide, modifications of the chemical structure occur. They cause the opening of the lignin rings and the breaking of the side chain group, producing aromatic aldehydes and carboxylic acids[36]. This process can be improved by the use of a catalyst that can avoid over-oxidation and increase the yield.

Although pyrolysis and oxidation are efficient processes used for the conversion of lignin, their drawback is the fact that the reaction products contain oxygen, which can compromise the stability of the final polymer and hence a refinement step is needed before the application. A solution to this problem is represented by the reductive conversion, that utilizes H_2 for the depolymerization and deoxygenation of lignin.

The two last conversion processes are the chemical-based conversion and the biocatalysis. In the chemical process, depolymerization of lignin can be implemented by the use of bases or acids: the difference lays in the kind of bonds that are broken in the structure. Biocatalysis is different from the previous methods for the use of microbes and enzymes to obtain the aromatic compounds from lignin; this improves the reaction selectivity and reduces the char formation[32].

The aromatic monomers obtained from the conversion step, mainly phenolic and aliphatic substances, are ready for the biopolymer synthesis (**Figure 2.7**).
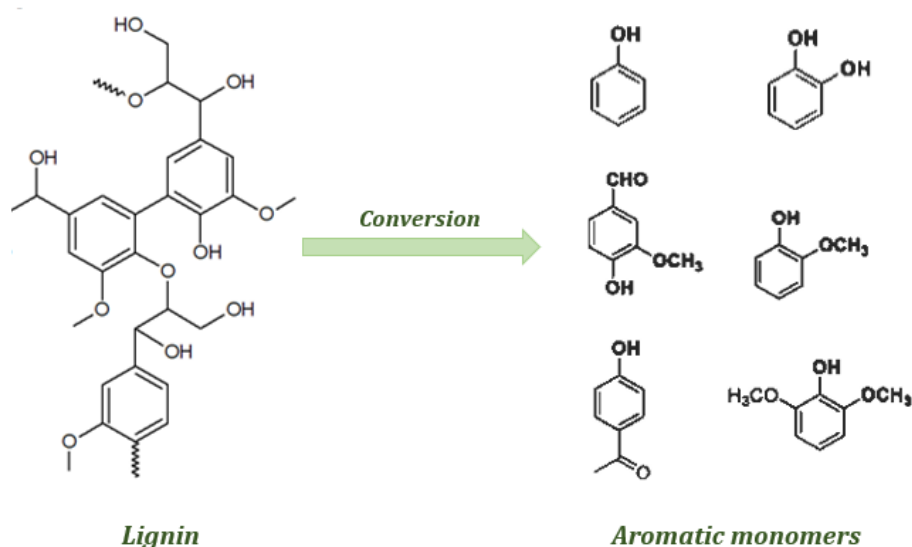
Figure 2.7 *Main aromatic monomers obtained by the lignin conversion process*

The final properties of the polymers are a function of the kind of processes that lignin was subjected to. Since at this point lignin is still a heterogeneous compound, insoluble in most of common solvents, a step of molecular fractionation is necessary to have a narrow polydispersity and more homogeneity and make it ready for the material production[37].

Lignin-based biopolymers include polyolefins, polyesters, polyurethane and epoxy and vinyl ester resins. Generally, lignin can be blended with several thermoplastic polymers, like polypropylene, poly (vinyl alcohol) or polyethylene, to create a material with improved properties with respect to the neat polymers. These lignin-based material show higher tensile strength and toughness, and an increased durability[38].

Interesting is the case in which lignin is blended with polymers like PLA or PHA: not only the impact strength and the thermal stability of the materials are improved, as well as resistance to UV irradiation, but also the biodegradability is preserved.

However, the production process of such plastics is not easy for the compatibility of the polymers, since the large number of polar functional groups in lignin causes self-interactions between the molecules[32].

For what concerns the thermosets, lignin is used to produce a wide range of resins, from polyurethane resins to phenol formaldehyde ones, but epoxy resins represent the most important type.

2.4 LIGNIN-BASED EPOXY RESINS

Epoxy resins are one of the most used kind of thermosetting polymer[39]. The curing process it undergoes introduces crosslinks between the chains that give the material its peculiar properties: high strength, chemical and solvent resistance, low shrinkage, excellent adhesion to various substrates, resistance to corrosion[39]. These

characteristics make it suitable for several applications. Its major use is as an adhesive or coating. The second largest use for epoxy resins is the one of composites: it is used as a matrix in composite materials reinforced with fibers or fillers. This combination enhances the material's properties, making it very versatile: applications can vary from the production of automotive components to communication satellites, sporting goods, structural use[40].

Lignin is used to produce bio-based epoxy resins in three ways:

1. In blend with the traditional fossil-based epoxy resin, even though there can be problems for the compatibility of the two polymers;
2. Lignin is put in a reaction with epichlorohydrin, causing the epoxidation of the hydroxyl groups of its structure; then, the epoxidized lignin can be cross-linked with the amine curing agent, forming the resin;
3. In the third method, lignin undergoes a chemical modification (e.g. phenolation, hydromethylation) before the epoxidation step[41].

The second method is the one considered in the present project to produce the resin samples.

The use of lignin to produce bio-based epoxy resins causes a general improvement of mechanical and thermal properties. More specifically, the final characteristics of the material are a function of the type of lignin employed and the way it is chemically treated. For instance, the molecular weight (Mw) of lignin is strongly related to the Young modulus of the final resin: the higher Mw, the higher the modulus[37]. Mw depends on the treatment lignin received before the epoxidation step, which is called fractionation. After the extraction step, lignin has a heterogeneous and complex structure, characterized by high polydispersity, that makes its utilization very challenging. A schematic representation of the process is shown in **Figure 2.8**.
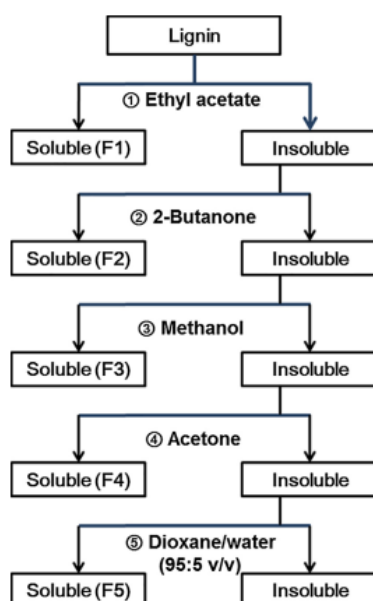

Figure 2.8 *General process of lignin fractionation using several organic solvents*[42]

The fractionation process consists in the sequential dissolution of lignin in different organic solvents, obtaining fractions more and more homogeneous in terms of polydispersity and functional groups, that are easier to use for the material production. The most used organic solvents for this task are methanol, ethanol, ethylacetate, methane chloride and acetone. The reason why several organic solvents are employed is that the solubility of each lignin fraction is different in them, being a function of its Mw and its functional groups[42].

According to the fraction employed for the resin production, the final material will exhibit different mechanical and thermal properties. Generally, lignin-based resins show a higher toughness and strength than the traditional petroleum-based ones, and this effect is more pronounced when the Mw of the lignin used is higher. A similar effect is observed for the Tg of the resin: when it is used a fraction with high Mw, the mobility of the polymer decreases and this causes an increase in the Tg of the material and in its thermal stability[37].

For what concerns the fire retardancy of these lignin epoxy resins, the existing information are not exhaustive; in fact, when speaking about the fire behaviour of epoxy resins, lignin is commonly employed as a flame-retardant additive (a filler). So, it is something external to the material, while in the bio-based epoxy resins lignin represents its main constituent.

It is for this reason that this project of thesis aims to analyse the flame retardancy of a lignin-based epoxy resin and the ways to improve it with the use of natural additives, in order to keep the material bio-based.

3. FLAME RETARDANCY OF POLYMERS AND POLYMER NANOCOMPOSITES

Fire behaviour of materials represents a topic of great interest due to the need to decrease the risk of fire growth and increase the safety of flammable goods. Polymeric materials are almost always the first item that ignites, so it is necessary to study a way to delay the ignition of the flame and reduce the consequences on people and on the environment. This is an important aspect to take into account when speaking about biopolymers: besides mechanical and thermal properties, the flame retardancy is essential to guarantee a place in the market to this kind of material.

The first part of this chapter explores how polymeric materials react to fire and what are the main strategies used to improve their resistance. In the second section, the characteristics of clay nanocomposites are described: they are materials that unite good mechanical properties to exceptional fire behaviour and represent the main focus of the present thesis.

3.1 POLYMER COMBUSTION CYCLE

Plastics represent one of the major sources of fire in homes, commercial environments and transportation. They are carbon-based materials that can burn easily, degrading and producing volatile products and smoke. In addition to this, the risk is increased by the fact that the most flammable polymers are the less expensive ones, the commodity polymers, that represent the most used for consumer's goods, electronics, home furnishings, automobiles.

When evaluating the level of risk of a possible fire scenario, several factors need to be considered. First of all, the chemistry of the material: in the case of polymers, their chemical structure will determine their behaviour when exposed to heat and how many and what kinds of volatiles are produced. For instance, the heat release during combustion is higher for aliphatic polymers than for aromatic ones, which can resist more to the ignition[43]. Other aspects to consider are the physical characteristics of the object in exam, like its density, its shape that can influence the fire behaviour, and finally the external factors: the characteristics of the fire scenario are important to understand how fire develops. All these elements are enclosed in the definition of "fire risk": it is the evaluation of the conditions for which an object can catch fire. It differs from "fire hazard", that regards the consequences of a fire on people and objects and on the environment[44].

For combustion to take place, three conditions must exist simultaneously: fuel, oxygen and heat; only acting on one of these factors fire can be extinguished. They are represented by the so-called "fire triangle", shown in **Figure 3.1**.

Fuel represents the material available to burn; a heat source is necessary to ignite the fuel, and the "flash point", which is the lowest temperature at which there can be ignition, is different for each material[45]. It must be considered that heat is produced also by the

combustion reaction itself, so it tends to increase the fuel's temperature. Finally, oxygen is the factor necessary to sustain the combustion by reacting with the fuel, with the release of carbon dioxide and heat. Only removing one of these factors (particularly oxygen and heat) the combustion reaction can be stopped.
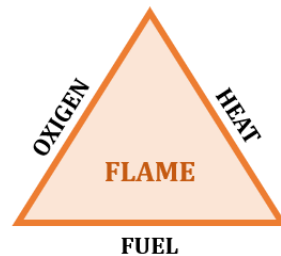

Figure 3.1 *Fire triangle: it shows the conditions necessary for fire to occur*

For what concerns polymers, the so called "combustion cycle" explains well what happens to the material during a fire. Two phases are to be taken into account: the condensed phase, constituted by the polymer, and the gas phase, constituted by air and volatile products. As a result of the application of heat, the polymer increases its temperature and starts to degrade into volatile products. It is when these volatiles react with oxygen in air and the flash point temperature is reached, that the combustion begins. The process is self-sustained if the volatile products continue reacting with oxygen, generating heat that starts the cycle again. Only when the condensed phase is completely consumed, the combustion stops (**Figure 3.2**).

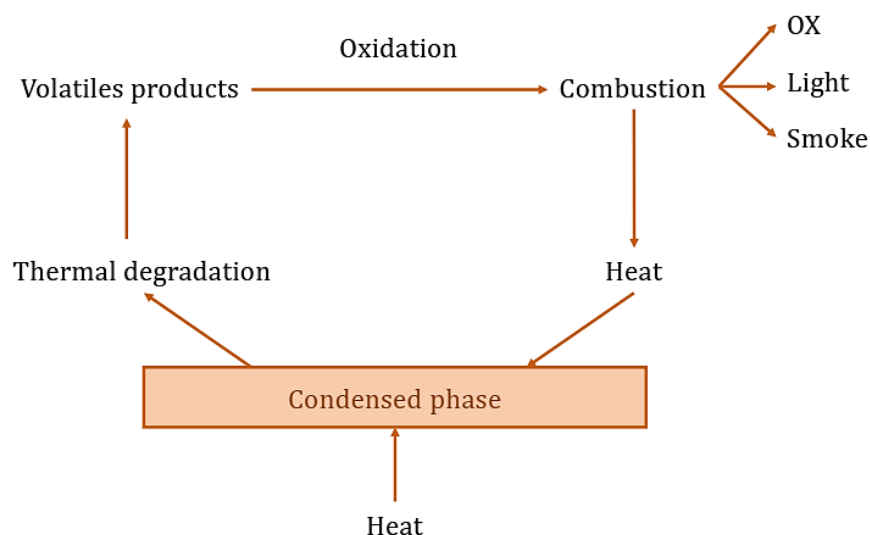*Figure 3.2* *Scheme of the polymer combustion cycle*

To better understand the dynamics of a fire scenario, Time-Temperature curves are utilised (**Figure 3.3**). They allow to identify the moments in which it is possible to intervene to extinguish a fire. First of all, the Time to Ignition (TTI) corresponds to the point where combustion starts, temperature remains stable after that. It is possible to

intervene on the fire until the Flash-over point is reached: from this point on there is a rapid increase of temperature that makes it impossible to extinguish the fire. It is necessary to have a system that can either act on the TTI or on the Fire growth time to Flash-over (time between the ignition of the flame and the flash-over point), respectively to prevent or delay the ignition and to decrease the combustion rate.
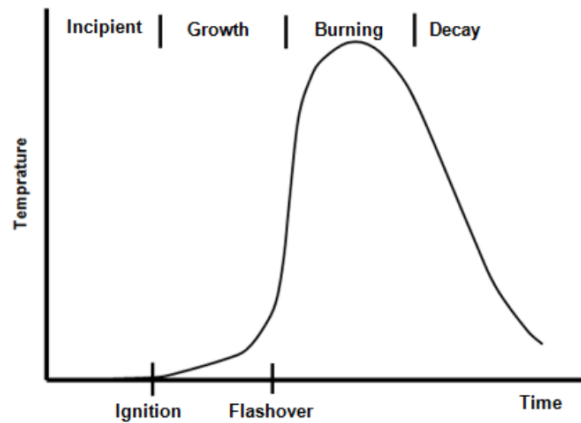

Figure 3.3 *Time-Temperature curve for a polymer*[46]

3.2 FLAME RETARDANT TYPES

There are three main approaches to protect a material from fire. The first one consists in using a fire protection coating to put on the object and protect it from the flames. Although it is the easiest and cheapest method, it is the less effective, since if the protection is moved, the object is exposed to fire.

The second way involves the use of inherently flame retarded polymers, which already have a chemical structure that provides high thermal stability and fire protection. The flame retardant compounds, that can contain nitrogen, halogen or phosphorus, are directly attached to the main chain through stable chemical bonds[47]. An example is given by PLA in which 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), a phosphorus compound, is incorporated. This system provides an improvement in fire behaviour with respect to the neat PLA, with a lower heat release peak and a reduction of the melting drip[48]. However, the cost of such materials is high and there are difficulties in their disposal and recycle that make them suitable only for niche applications.

The last approach is the addition of flame-retardant additives to the polymer that are easy to incorporate and cheap, allowing to have more versatility. Their function is to act on the polymer combustion and degradation rate reducing it, avoiding the dripping of the material and decreasing the smoke emissions.

Flame retardants are gathered in three macro-groups according to the type of mechanism they use to fulfil their function: gas phase flame retardants, endothermic flame retardants and char-forming flame retardants[44].

Gas phase flame retardants act on the gas phase with a chemical mechanism, with a reaction with the free radical present, reducing their concentration and the quantity of

heat released, and eventually stopping the combustion. Halogenated systems and phosphorus compounds are flame retardants that work in this way. They are constituted by aliphatic or aromatic molecules based on halogens, like Cl, Br and on phosphorus (**Figure 3.4**). When thermal degradation starts, the polymer releases hydrogen halides H-X that react with the radical present in the gas phase, like H· and OH·, generating X·. Since the radicals that sustain the flame are neutralised and X· is a stable molecule, the combustion is inhibited. The efficiency of this kind of system is high because the radical X· can take a H from the polymer chain, producing a new H-X that begins the entire process again.

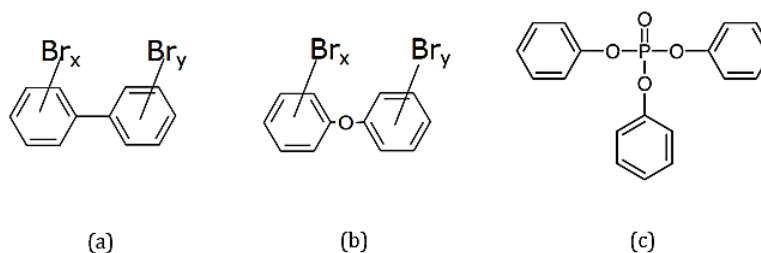(a)   (b)   (c)

Figure 3.4 Main types of halogen and phosphorus flame retardants: (a) Polybrominated biphenyl (PBB); (b) Polybrominated diphenyl ethers (PBDE); (c) triphenyl phosphate (TPP)

Despite of this, recent years saw a decrease in the use of such compounds because of their toxicity and threat to the environment. They can persist after their use, accumulating in plants and in animals' organisms, and cause effects on human health, interfering with hormones activity[49]. Considering their large employment in consumer goods, like mattresses, couches, chairs and electronic devices, they cannot be eliminated but need to be substituted by other types of flame retardants, halogen-free ones, that have no effects on human health (e.g. phosphorus compounds, inorganic hydroxides)[50].

Endothermic flame retardants constitute the second group and comprehend the inorganic hydroxides. They act on the condensed phase, unlike the halogenated compounds, decreasing the polymer's temperature with the formation of water. Under fire conditions, a dehydration reaction occurs and forms oxides and water. The oxides accumulate on the surface of the polymer, acting as a thermal shield that isolates the material from the flame; in the meantime, water cools down the system, causing the decrease of the degradation rate. Usually aluminium $Al(OH)_3$ and magnesium $Mg(OH)_2$ hydroxides are utilised. The reactions in which they are involved are the following:

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$$

$$Mg(OH)_2 \rightarrow MgO + H_2O$$
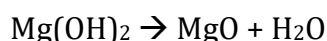
They have low impact on the environment, but the efficiency is low and high concentrations are needed for the system to work (50-60%). Their main application field is the one of wires and cables. It is important to guarantee their fire safety; for this reason, a strict regulation regarding their characteristics (smoke emissions, flame propagation, heat release, etc.) is applied to them [51].

The last category is the one of char-forming flame retardants, represented by the intumescent systems: they operate on the condensed phase providing a surface protection from the flame. Under heating conditions, they are able to form a char, which is an expanded carbonized layer, thermally stable, that isolates the polymer underneath from the heat and slows down the transfer of volatiles from the material to the gas phase. Intumescent system are formed by a carbon source, an acid catalyst that causes its crosslinking and the formation of a thermally stable carbon compound, and a spumific agent, responsible for the foam generation[44]. A scheme of their functioning is shown in **Figure 3.5**.
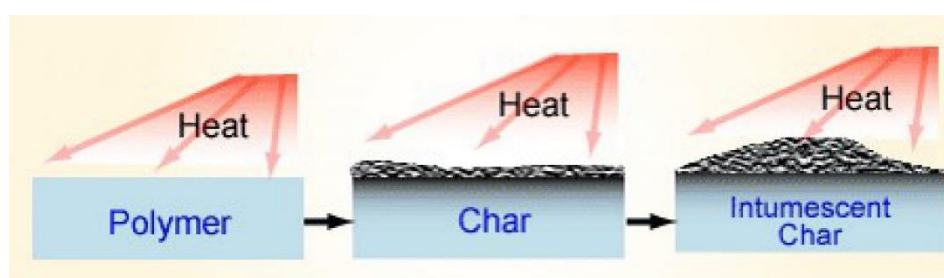
Figure 3.5 Functioning of intumescent systems[52]

There is another system that works in a similar way to intumescent flame retardants: polymer nanocomposites and in particular layered clay nanocomposites. The clay present in these materials allows the formation of a carbonaceous-silicate char during combustion, that protects the material. The next paragraph explores the world of nanocomposites, underlining their major characteristics and how they behave under fire conditions.

Figure 3.6 shows a summary of all the types of flame retardants described in this paragraph.

Figure 3.6 Summary of all types of flame retardants

3.3 NANOCOMPOSITES

A nanocomposite is a material made up of two phases, one of which has a dimension in the order of nanometres. A first example appeared in 1985 when Toyota researchers realised a belt cover for car with Nylon-Montmoril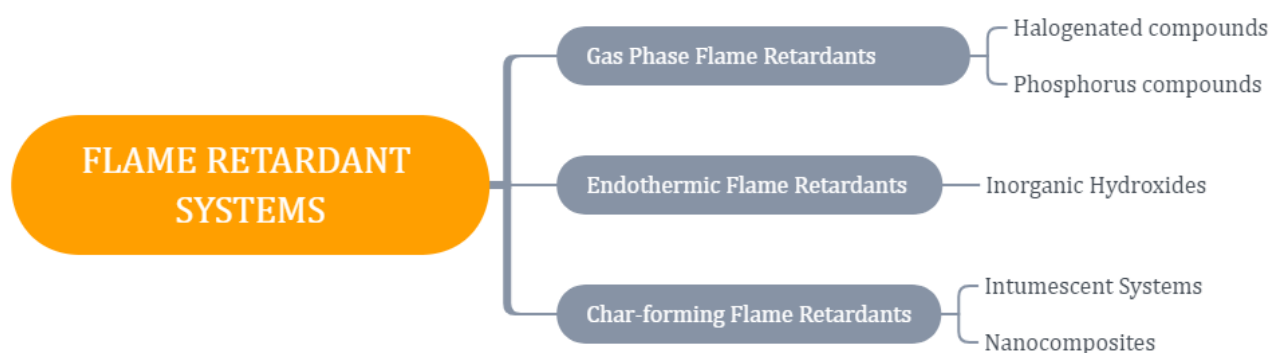lonite nanocomposites, which were called "Hybrids". Since then, research in this field has become increasingly important due to the excellent properties that this kind of material exhibits[53].

Having a dimension in the order of nanometres means a higher surface to volume ratio of the reinforcing phase which leads to improvements in the matrix properties: the tensile strength is enhanced as well as the modulus, the thermal stability is improved, their gas permeability is reduced and the flame retardancy is improved[54]. These advantages make the nanocomposites suitable for a wide range of applications, such as catalysts, sensors, coatings, structural materials, electronic, optical, magnetic, mechanical and energy conversion devices[55].

Generally, the matrix in nanocomposites can be ceramic, metal or polymeric, but the latter is the most used; in particular, epoxy resin represents the majority of polymeric matrices[39]. For what concerns fillers, there are three fundamental characteristics that they must have in order to fulfil their function: firstly, they must possess good mechanical properties, like an high Young's modulus; then, the aspect ratio must be high as well as the surface area, in order to facilitate the interaction with the polymer matrix; finally, the fillers must be well dispersed to avoid agglomerations. The combination of these three key factors makes it possible to have a better material than the neat polymer. In particular, a good dispersion of nanofillers leads to a better load distribution between polymer and filler, and the increased interfacial area due to the nano size allows to have an improvement in strength.

There are three types of nanofillers, according to their dimensions (**Figure 3.7**):

-1D lamellae, like phyllosilicates, phosphates, graphene, clay;

-2D nanotubes, like carbon nanotubes (CNT), fibers, whiskers;
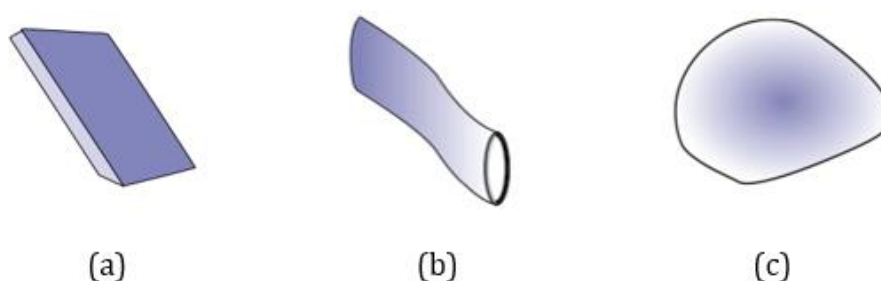
-3D particles, like silica, metallic particles[56].

(a)   (b)   (c)

Figure 3.7 *Types of nanofillers: (a) lamellae; (b) nanotubes; (c) particles*

Clays, carbon black, glass fibers, metal powders are the most used as nanofillers. This paragraph focuses on the description of clay nanocomposites that show interesting properties in relation to the fire behaviour.

3.3.1 CLAY NANOCOMPOSITES

The term "clay" refers to a material made up of fine grains, characterised by a certain plasticity caused by the water content[57]. From a morphological point of view, clays have a layered structure composed by silicon oxygen tetrahedral (SiO_2) sheets and metal-oxygen (Aluminium or Magnesium) octahedral sheets organized into two kinds of structures (**Figure 3.8**): 1:1, where tetrahedral sheets alternate to octahedral sheets by sharing one oxygen atom; kaolinite and serpentine belong to this group. The 2:1 structure consists in a octahedral sheet sandwiched between two tetrahedral sheets; montmorillonite, talc and hectorite have this morphology[58].
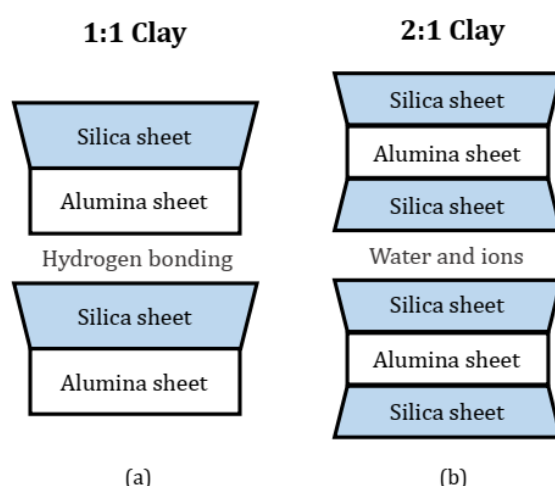

Figure 3.8 *Clay structures: (a) 1:1 clay, (b) 2:1 clay*

The 2:1 clay, also known as "layered silicate", is commonly used in nanocomposites. These layers organize themselves to form stacks and the gap between the layers is called interlayer or gallery. The isomorphic substitution of Al^{3+} with Mg^{2+} or Fe^{2+} between the layers, generates negative charges, which are counterbalanced by positive alkali or alkaline cations in the gallery, like Na^+ or Ca^{2+}. They are responsible for some peculiar properties of the material such as swelling properties, the possibility to have ion-exchange, ease of synthesis, a high chemical and thermal stability, and a base catalysis character [59]. These characteristics together with the clay's natural abundancy on earth and low cost, are responsible for the success of this material.

The good working of this kind of filler depends on the interaction with the polymer matrix. Since the clay is hydrophilic and the polymer is hydrophobic, there can be agglomeration of the clay platelets into the matrix. Consequently, it is essential to make the clay compatible with the polymer by modifying its structure with the exchange of the ions in

the interlayer by organocations. The consequent swelling of the structure allows the polymer to accommodate in the interlayer area. According to the different level of interaction between polymer and clay, it is possible to distinguish three types of composite structures, showed in **Figure 3.9**:

-Phase-separated nanocomposite (or micro-composite): the interaction and compatibility between the two components is weak and the intercalation of the polymer in the clay layers cannot be achieved;

-Intercalated-nanocomposite: the polymer chains are partially intercalated between the clay layers resulting in an ordered stacking of alternating polymer and clay;

-Exfoliated-nanocomposite: there is a complete exfoliation of clay layers that results in a homogeneous dispersion into the polymer matrix[53].
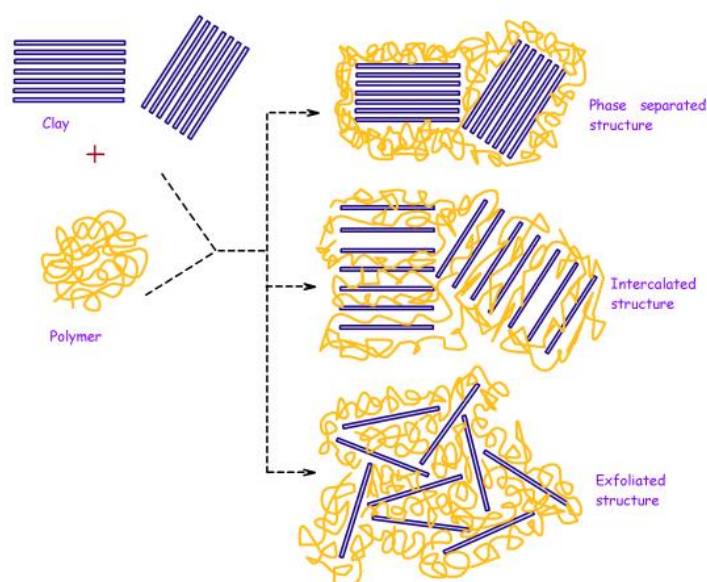

Figure 3.9 *Possible types of polymer/clay nanocomposite structures*[53]

It is not convenient to have the first structure because the distribution would not be optimal, compromising the properties, that can be even worse than the neat polymer ones. The exfoliated structure is the ideal one, but it is indeed very challenging to reach such a high level of dispersion; so, it is easier to find the intercalated structure in nanocomposites[57]. The strategies to produce clay nanocomposites all aim to achieve it.

The main production methods are three: intercalation of polymer from solution, in situ intercalative polymerization and melt intercalation[60].

The intercalation of polymer from solution consists in dispersing the silicates in a solvent in which the polymer is soluble; the most common solvents are water, chloroform, or toluene. When the polymer is added to the solution, it intercalates between the clay platelets, displacing the solvent which then is removed through evaporation, leaving the intercalated structure of a nanocomposite. Usually, because of safety and economic reasons, the most employed solvent is water[61].

In the in situ intercalative polymerization method, the silicates are not dispersed in a solvent, but in a monomer solution so that polymerization occurs directly between the clay platelets, leading to the production of a well-exfoliated nanocomposite.

The last strategy is the melt intercalation that starts with a mixture of polymer and an organically modified clay that are heated above the softening point of the polymer: this causes the diffusion of the molten polymer into the silicate gallery to form the intercalated structure. This method shows two main advantages with respect to the previous ones: it is the most convenient to use on an industrial scale since it is compatible with conventional processes, like extrusion or injection molding; it is environmentally friendly due to the lack of organic solvents[58].

The use of nanoclays as fillers in polymer matrices improves several properties. The following paragraphs report some examples of the major improvements seen in bio-based clay nanocomposites. According to the clay content and the level of dispersion into the polymer matrix, effects on mechanical, thermal and barrier properties are observed.

An example is provided by a study on an epoxy-clay nanocomposite, where the resin is derived from soybean oil. It is observed a general improvement in mechanical properties. For instance, the higher the clay concentration, the higher the modulus. This characteristic is also related to the dispersion rate of the clay. A good dispersion means that the interfacial contact area between clay and matrix is increased, resulting in a higher modulus and a better mechanical behaviour under load[62].

Another case is the one of thermoplastic starch, used as matrix in a clay nanocomposite. With a concentration of 5 wt% of sodium montmorillonite, the tensile strength is increased (from 2,6 to 3,3 MPa), as well as the elongation at break, making the TPS a more resistant material[63].

For what concerns the thermal stability, clay has a positive influence causing the increasing of the temperature at which degradation occurs. This is due to the formation of a clay char that reduces the oxygen uptake into the material and the heat transfer, and enhances the barrier properties of the nanocomposite[62].

Besides the enhancements seen in mechanical and thermal properties, clay is extremely efficient when it comes to improving the fire behaviour. As seen in paragraph 3.2, nanocomposites constitute one of the most used fire-retardant systems. Combustion creates a temperature gradient in the material that causes a migration of the clay particles from the bulk to the surface, helped also by their lower surface free energy. The particles accumulate to form a thermally insulative surface layer called "char", a hybrid layer made up of carbon, derived from the polymer degradation, and clay that acts as a barrier to heat and oxygen, protecting the substrate from further degradation[58]. **Figure 3.10** shows a schematic representation of the described mechanism.
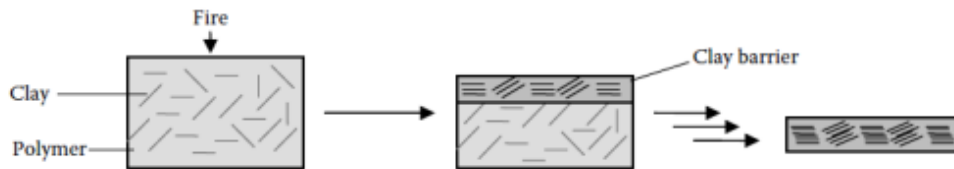
Figure 3.10 *Illustration of the fire-retardant mechanism of a clay nanocomposite*[64]

The production of char occurs only after the combustion has started because they act on the time to flash-over, the period of time in which fire can still be extinguished. In order to improve the efficiency of the system, they are usually combined with other flame retardants, like inorganic hydroxides or phosphorus compounds, obtaining a synergic effect: in this way the TTI is significantly increased and the peak of heat released is reduced[44].

3.3.2   WATER-BASED NANOCOMPOSITES

In recent years, a new frontier in the field of nanocomposites is taking hold, that is water-based nanocomposites. Their production takes inspiration from the brick-and-mortar structure of natural nacre: aragonite platelets are kept together by soft polymers (like proteins), leading to better mechanical properties like higher stiffness and strength (**Figure 3.11**). The same principle is used for creating a bio-inspired material, where the "bricks" are represented by the clay platelets, and the "mortar" is constituted by a polymer.
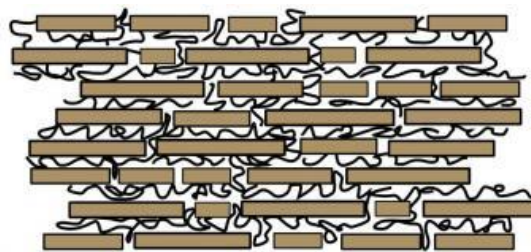
Figure 3.11 *Representation of a typical nacre structure*[65]

The use of this kind of material encounters the need to have "green" alternatives to reduce the use of petroleum-based plastics because its main constituents are natural and abundant in nature. Generally, the polymeric part is made up of biobased polysaccharides and proteins, such as chitosan, casein, cellulose, alginate, natural rubber and lignin, all derived from renewable resources[66][67]. Each of them influences the final features of the nanocomposite, improving mechanical properties like stiffness and modulus and fire behaviour. For what concerns the clay, smectite and montmorillonite are the most employed.

Among the mentioned polymers, cellulose is the most used, since it is the most abundant polymer on earth and its cost is low. In particular Cellulose Nanofibrils (CNF) are employed for nanocomposites. They are the main reinforcing element of the wood cell wall and are obtained from the disintegration of wood pulp fibers. Their nanoscale geometry, typically 3–15 nm in diameter and 0.7–3 μm in length, and good mechanical properties (high modulus, low density and high tensile strength), make them suitable to be used as a reinforcement in nanocomposites [68][69].

An important alternative to CNF is constituted by Alginate, the main constituent of the cell wall of brown algae. It can be found in several forms: hydrogels, fibers and films. Thanks to its non-toxicity and biocompatibility, alginate is largely employed for tissue engineering and for the production of carriers for drug delivery, other than for the production of nanocomposites[70]. Moreover, the alginate fibers are characterized by good fire behaviour, being the limiting oxygen index (LOI) 48.0 and peak heat release rate (PHRR) of 4.99 kW/m^2: they are better values compared to the ones of viscose fibers (LOI=20.0 and PHRR= 168.75 kW/m^2), that make alginate an inherently flame retardant material[71].

The production of water-based nanocomposites starts with a suspension of polymer and clay. The biobased polymer has an important role because it allows the orientation of the clay platelets in-plane, preventing their agglomeration and increasing the possible content of clay that can be inserted in the composite up to 70% (much higher with respect to conventional nanocomposites where the clay content is generally less than 10% wt.)[72][73]. This leads to a reinforcement of the whole structure, increasing tensile strength, Young modulus, and toughness. Also, fire-retardant properties are significantly improved by this structure firstly because the better gas barrier properties hinder the passage of oxygen through the polymer, reducing the thermal degradation and the combustion. Moreover, the orientation of clay platelets due to the presence of the polymer, promotes a good dispersion of them, maximizing the contact between clay and cellulose and enhancing the production of char[73]. In this way it is possible to have a material which is inherently flame retardant, without the need to add other additives.
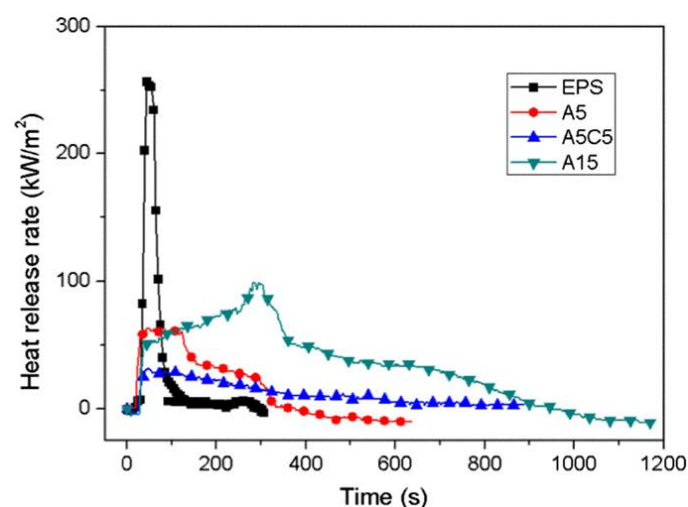

Figure 3.12 *Heat release rate of neat alginate and clay/alginate aerogel*[74]

Figure 3.12 shows the heat release rate (HRR) of alginate/clay aerogels in comparison to other materials. The green curve refers to neat alginate, the blue one to alginate/clay aerogel: it can be seen that the nanocomposite shows a halved value of PHRR with respect to pristine alginate, since it is reduced from 64 kW/m^2 to 32 kW/m^2[74]. It is worth to note the difference with expanded polystyrene (EPS) (black curve): its peak value is much higher not only in comparison with clay/alginate composite but also with respect to alginate alone, making it more convenient to use this biobased polymer, which is inherently flame retardant, in place of conventional plastic materials.

So, despite similarities with traditional nanocomposites (both have good mechanical properties, high thermal stability, excellent fire behaviour), water-based nanocomposites constitute an evolution of the conventional materials for the improvements seen thanks to this particular structure.

The initial suspension can undergo two different processes to produce two different kinds of materials: if it is filtered, thin films are obtained; if it is freeze dried, then aerogels are achieved. In both cases the mechanical behaviour and the fire retardancy are better than the neat polymer, for the above reasons.

Films are commonly employed for the production of protecting coatings, also exploiting their high optical transparency that allows to preserve the aesthetics of the underlying material[75].

Clay aerogels nanocomposites, instead, constitute a different class of materials characterized by low density, high surface area and high porosity, low thermal conductivity and high insulation property. Considering also their biocompatibility and sustainability and the excellent fire behaviour, this kind of aerogel have the potential to be employed as substitute of the traditional petroleum-based insulating materials like, for instance, polyurethane foams for the thermal insulation of buildings. Polyurethane foams are the main material used for this application because of their low thermal conductivities, low density and low cost; despite of this, they are highly flammable, so it is necessary to add a flame-retardant protection coating or additives to improve their fire behaviour[76]. The ignition of these foams is one of the main causes of home fires and death, like the one happened in London in 2017 to the Grenfell tower that caused the death of 72 people. In that case, the building insulation was constituted by PU foams coated with an aluminium panel cladding with a PE core, a system that was employed because it would have considerably reduced the cost with respect to the use of a composite fire-retardant material (it has saved about 300.000 pounds)[77]. During fire, the aluminium panels fell, leaving the PE core and the PU foams exposed to flames that spread to the top of the building in a very short time. Water-based foams represent a "green" alternative to the conventional PU foams because they are bio-based materials that can thermally isolate the building and at the same time guarantee a better fire protection.

The main drawback of aerogels is that, having a highly porous structure, the mechanical properties are not optimal. The intrinsic cell wall brittleness can be reduced by controlling the morphology of the pore structure by means of modification of freeze-drying conditions or by changing the composition of the composite. It is preferable to have a

homogeneous structure with close pores because of their higher strength with respect to open pores. Moreover, the composition of the nanocomposite can be modified in order to have optimal mechanical properties; to this end it is possible to add a third polymeric phase, preferably a water-soluble polymer like PVA[78]. It is necessary to control the content of each of the constituents to obtain a more homogeneous porous structure and consequently higher stiffness and yield strength. There must be a good balance between the content of the two polymeric phases and the clay so that their interaction allows to have a crosslinked structure that reduces the intrinsic cell wall brittleness of the foam[78]. This also influences the fire behaviour: for instance, if considering a CNF/PVA/clay nanocomposite, the content of PVA must not be higher than 30% because this would compromise the natural ability of cellulose to form char by reducing the interactions between clay and cellulose[72].

Considering the numerous advantages that this kind of material offers, it is born the idea to unite a water-based nanocomposite with a bio-based epoxy resin, to create a new unique material that combines the best characteristics of the two structures. The objective of this project of thesis is to plan the production of such material, with a lignin epoxy resin, CNF and montmorillonite. It is a bio-based nanocomposite, since all the main constituents are natural and renewable; it exploits the presence of clay and CNF to improve the mechanical properties of the resin and the fire retardancy.

4. PRELIMINARY EXPERIMENTAL ACTIVITY

This chapter presents the experimental work carried out at the Royal Institute of Technology in Stockholm. It comprehends the preliminary treatment of lignin (reassumed in **Figure 4.1**), and its characterization.
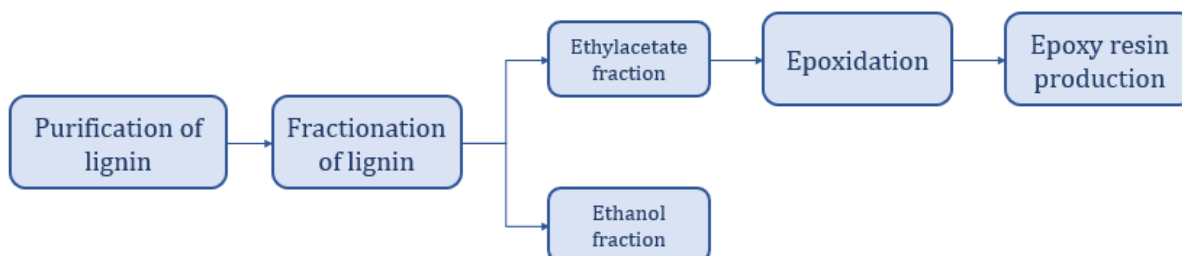

Figure 4.1 *Scheme of the preliminary treatment of lignin*

4.1 PRELIMINARY TREATMENT ON LIGNIN

4.1.1 FRACTIONATION

In order to produce the resin samples, lignin must be chemically treated with a fractionation process to obtain a less complex structure with lower polydispersity.

The lignin employed for this project is a spruce Kraft lignin, obtained from the black liquor by means of the LignoBoost process. The Norway Spruce (Picea abies) is one of the most important coniferous species diffused in northern, central and eastern Europe. It belongs to the category of hardwoods, so the chemical structure of this kind of lignin is essentially made by the repetition of guaiacyl units and hydroxy-phenyl-propane units[79].

Before fractionation, Kraft lignin has to be purified in order to eliminate any salts or acids present in the composition that could interfere with the following steps of the process (like epoxidation). 100 g of lignin were put in 2L of water; the solution stirred for two hours at 80°C. pH must be controlled: it must be low so that the phenolic groups contained in lignin wouldn't dissolve, since their pk is 10. For this reason, pH is normally adjusted from 5 to 3 by adding HCl to the solution. After stirring, the solution is filtered. The filtration is repeated twice to have a higher grade of purity. Finally, lignin powder is obtained by putting the solution in the vacuum oven at 40 °C for one night.

The purified lignin powder is ready for fractionation. In this case, the organic solvents employed are ethylacetate and ethanol.

Figure 4.2 *Stirring of lignin with ethylacetate during the fractionation step*

Ethylacetate is the first solvent used: 39,861 g of lignin are immersed in 750 ml of ethylacetate and the solution is put to stir for four hours at room temperature. At the end of the process, the solution is washed with ethylacetate and filtered. A soluble product and an insoluble one are obtained.

The soluble product is a solution of lignin and ethylacetate. The instrument Rotovapor® is employed to eliminate the ethylacetate from the solution by overcoming its boiling temperature, and prepare it for the freeze drier, that allows to obtain ethylacetate-lignin powder.

The insoluble part obtained from the filtration of lignin undergoes fractionation with ethanol. The procedure is the same as described above: 35 g of material are put in 700 mL of ethanol to stir for four hours at room temperature. After the elimination of ethanol with the Rotovapor® and the use of the freeze drier, the powder of lignin fractionated with ethanol is obtained.

At the end of this step, three fractions are obtained from the 100 g of lignin employed at the beginning of the process: ethylacetate fraction, ethanol fraction and the insoluble residual lignin obtained after the second fractionation done with ethanol. The mass balance of all the obtained fractions and of the residual lignin is shown in **Figure 4.3**.
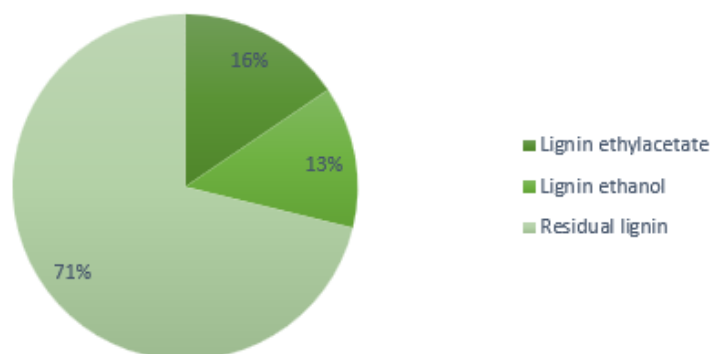

Figure 4.3 *Mass balance of the lignin fractions*

Due to the larger output of the ethylacetate fraction (16% against the 13% of the ethanol fraction), it was selected for the production of the resin samples.

In order to study how molar mass distribution of lignin changes after each fractionation step, Size-Exclusion Chromatography (SEC) analysis are employed. They are performed using a SEC 1260 infinity (Polymer standard service) equipped with a PSS precolumn, PSS column 100 Å and PSS GRAM 10000 Å analytical columns thermostated at 60°C. The detection system included a UV detector in series with a refractive index detector.

SEC samples are prepared by making a solution of lignin and dimethyl sulfoxide (DMSO); the original LignoBoost lignin, the ethylacetate fraction and the ethanol fraction are examined.

The Size-Exclusion Chromatography consists in the separation of polymeric molecules based on their size. This is carried out by means of a gel made up of spherical beads containing pores; according to the ability of the molecules to pass through the pores, the distribution of molecular weights of the polymer can be determined.

The process is conducted in a column, a hollow tube containing the beads: larger molecules, being unable to enter the pores, do not encounter obstacles to their flow and go through the column in a short time; smaller molecules can diffuse through the pores, taking longer time according to their size.

SEC analysis are performed on three fractions of lignin: the initial LignoBoost, ethylacetate fraction and ethanol fraction. Results show how fractionation has worked in obtaining a less complex polymeric structure and composition.

The sequence in which fractionation was conducted shows a progressive decrease in the polydispersity index (D) and an increase in the molecular weight (Mw). As reported in **Table 4.1**, EtOAc lignin constitutes the fraction with lower Mw, 1650 g/mol, while EtOH fraction presents a higher value, 3300 g/mol. The initial value of polydispersity is 2,25 in LignoBoost, for the higher complexity of the chemical structure, that decreases to 1,21 and 1,42 respectively for the ethylacetate and ethanol fractions. These values are typical of epoxy resin precursors [83].

	LignoBoost	**EtOAc**	**EtOH**
M_n	4050	1400	2350
M_w	9050	1650	3300
M_z	17200	1950	4400
D	2,25	1,21	1,42
M_p	5200	1500	2900

Table 4.1 *Molar mass analysis by SEC*

Figure 4.4 shows how the distribution of molecular weight changes going from the heterogeneous structure of LignoBoost lignin to the more homogeneous compositions of

the EtOAc and EtOH fractions; the peak in the EtOH curve indicates the higher molecular weight of this fraction.
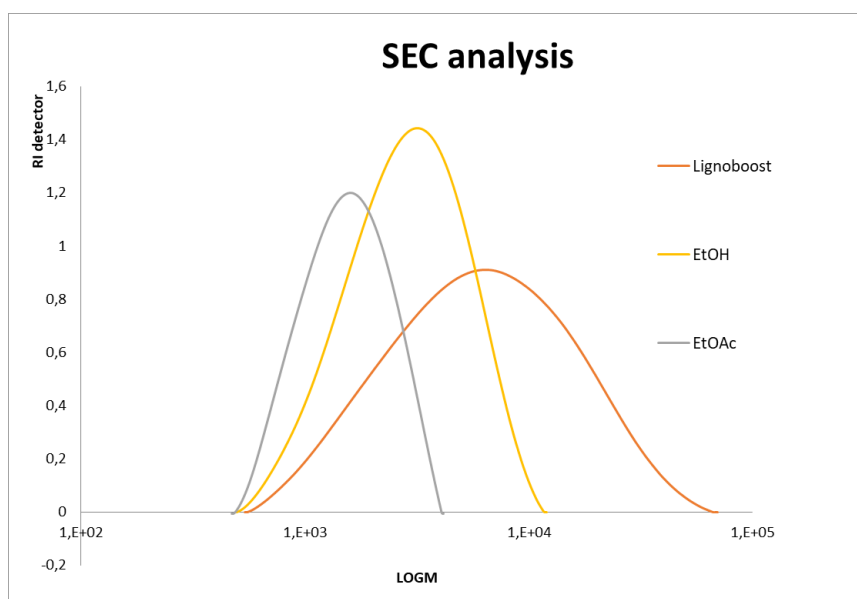

Figure 4.4 *SEC analysis performed on LignoBoost, ethylacetate fraction and ethanol fraction*

4.1.2   EPOXIDATION

Epoxidation of lignin represents the next step. Epoxy resin production generally starts with two types of compounds: one containing active hydrogen groups, like phenols, dicarboxylic acids or polyols, and the other containing an epoxy group, like epichlorohydrin. Usually the reaction is catalysed by a strong base catalyst, such as NaOH or KOH. Epoxidation comprises two steps: the first one consists in the opening of the epoxy ring thanks to a nucleophilic substitution, forming chlorohydrin; in the second step a new epoxy group is created by a dehydrochlorination, with elimination of water and hydrochloric acid. This creates functional monomers that react among themselves to start polymerization of the resin[80].

A typical epoxidation reaction is showed in **Figure 4.5**: Bisphenol A is used with epichlorohydrin to create epoxy resins. In the present work, bisphenol A is substituted by the previously obtained lignin fractionated with ethylacetate. The procedure employed is based on the one described in the article "*Tunable Thermosetting Epoxies Based on Fractionated and Well Characterized Lignins*"[37].
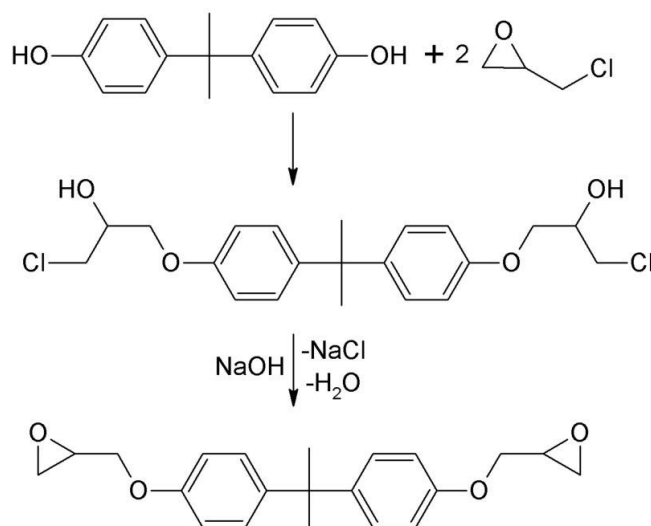
Figure 4.5 *Epoxidation of Bisphenol A and epichlorohydrin*[81]

Lignin powder is put in a round bottom flask together with a mixture of 45 mL of water and acetone at a 50:50 ratio, 3 equivalents of NaOH and 20 equivalents of epichlorohydrin. The solution is stirred at 55 °C for five hours.

At the end of the reaction time, the solution is washed with water and the pH is lowered to approximately 3.5 in order to facilitate the following filtration step. The filtered product is then dissolved in acetone, precipitated with water and then freeze dried. The powder obtained by this process is the epoxidized lignin which will be used to create the resin samples.

Lignin is analysed before and after epoxidation with NMR techniques, in particular with P-NMR, 2D-NMR and H-NMR. The analysis is recorded at room temperature on a Bruker Avance III HD 400 MHz instrument with a BBFO probe equipped with a Z-gradient coil for structural analysis. MestreNova (Mestrelab Research) is utilized for processing data using 90° shifted square sine-bell apodization window; baseline and phase correction was applied in both directions.

P-NMR samples are prepared by putting lignin in solution with Dimethylformamide, pyridine, internal standard (with concentration of 60,2 mg/ml), phosphorus compound and chloroform.

2D-NMR and H-NMR samples are prepared with lignin mixed with DMS-D (deuterated dimethyl-sulfate) and the internal standard for the H-NMR analysis.

NMR analysis gives quantitative and qualitative evaluation of the functional groups present in the lignin fraction used to produce the epoxy resin, the ethylacetate one. It is needed to quantify the hydroxyl groups present in the structure for the calculation of epichlorohydrin equivalents and NaOH equivalents to use in the epoxidation of lignin and to verify the correct execution of the reaction: the presence of hydroxyl groups and their consumption during epoxidation is studied.

P-NMR provides a quantitative analysis of the functional groups present in the structure, in particular of phenols, aliphatic alcohols and carboxylic acids (all groups containing -

OH). In order to better understand what happens during epoxidation and what functional groups are involved, a preliminary analysis is performed on the ethylacetate lignin fraction before epoxidation. The resultant spectrum is showed in **Figure 4.6**. The characteristic peaks of the main groups are underlined: aliphatic hydroxyls, 145-150 ppm, condensed phenols, 140-144 ppm, non-condensed phenols, 139-140 ppm, and carboxylic acids, 134-136 ppm.

As it can be seen in **Figure 4.7**, after the epoxidation, the peaks related to all phenols (condensed and non-condensed) and carboxylic acids disappear, meaning that they are consumed during the reaction with epichlorohydrin.
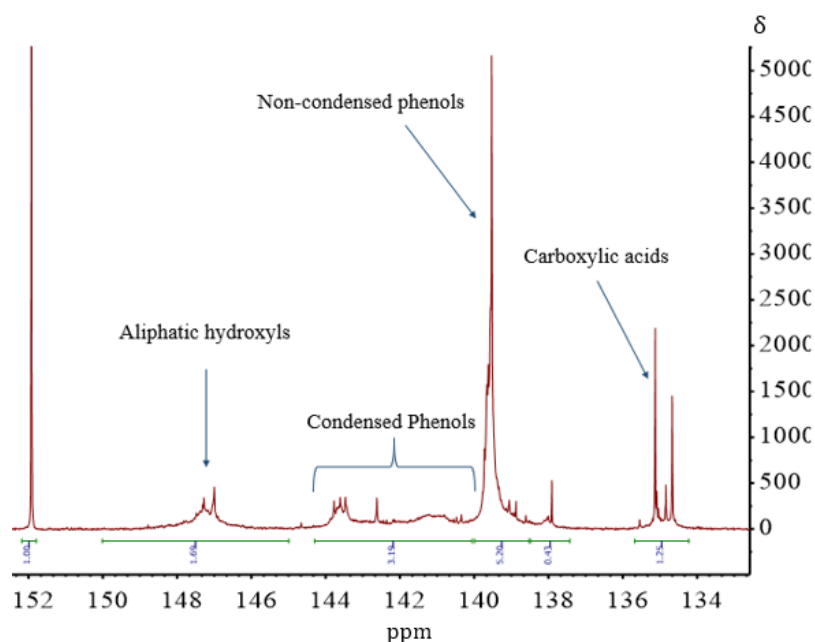

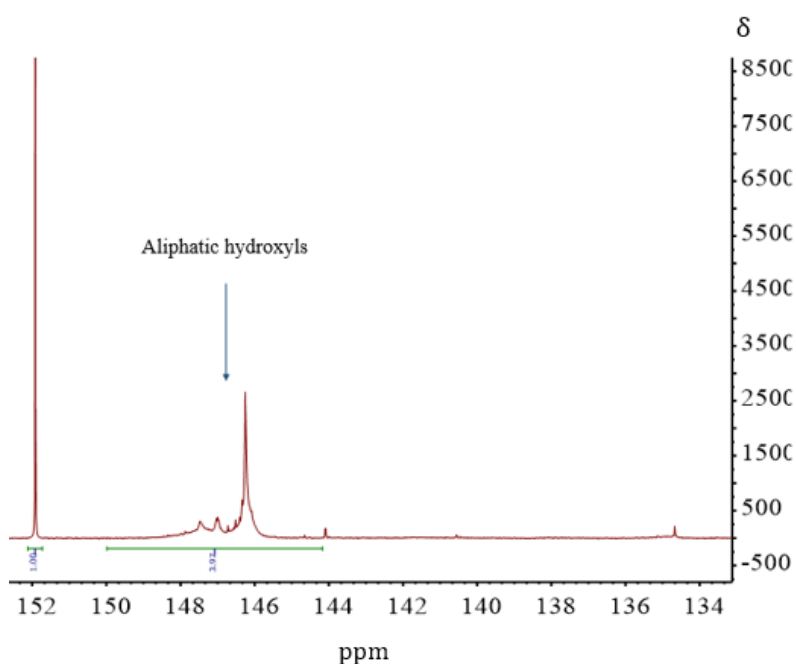*Figure 4.6* P-NMR spectrum of LignoBoost lignin before epoxidation

Figure 4.7 P-NMR spectrum of ethylacetate lignin fraction after epoxidation

Table 4.2 reports the quantification of the functional groups in the ethylacetate fraction of lignin before and after the epoxidation. The values are calculated knowing the concentration (mmol/g) of lignin in the P-NMR sample, the integral value of the peaks obtained from the spectra and the dry content of lignin.

As seen in the spectra, the consumption of hydroxyl groups during the reaction with epichlorohydrin was successful, since there is a decrease of carboxylic acids and phenols in the composition. There is, instead, an increase in the aliphatic alcohol concentration. If considering the epoxidation reaction (**Figure 4.5**), the intermediate product is an aliphatic alcohol; the higher quantity seen after epoxidation is probably due the fact that some of them did not take part in the reaction and remain in the composition originating the NMR signal.

	Aliphatic-OH (mmol/g)	Carboxylic acids (mmol/g)	Total phenols (mmol/g)
Before epoxidation	0,94	0,69	4,88
After epoxidation	2,45	0,00	0,00

Table 4.2 *Hydroxyl groups concentration in ethylacetate lignin quantified by P-NMR before and after epoxidation*

A further control on the good outcome of epoxidation is given by the H-NMR analysis. In the obtained spectrum the series of peaks between 2,5 and 3 ppm indicates the presence of the oxirane group, typical of the epoxy structure.

The value of total phenols present is used to calculate the equivalent weight of epichlorohydrin and NaOH to use for the epoxidation. Firstly, it is calculated how many mmol of phenols are present considering the weight of lignin employed in the reaction; the resultant quantity is then multiplied for the number of equivalents required for the established procedure (20 equivalents of epichlorohydrin and 2 equivalents of NaOH) and then for their molecular weight to obtain the mg to put in the solution.

A qualitative analysis of lignin chemical composition is provided by 2D-NMR. This allows to detect all the varieties of linkages that characterizes the complex chemical structure of lignin. The obtained spectrum is shown in **Figure 4.8**: the majority of them is constituted

by βO4 interunit, followed by guaiacyl units (respectively indicated on the spectrum by A1, Ar-2, Ar-6) and oxirane groups after the reaction with epichlorohydrin.
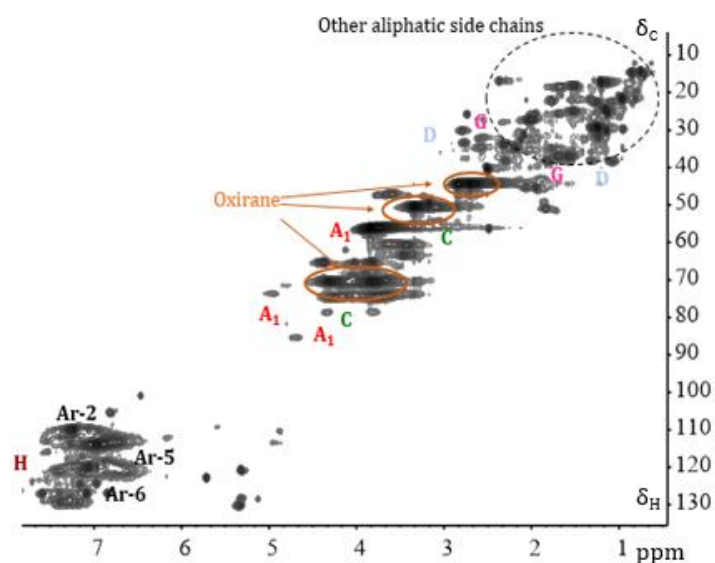
Figure 4.8 *2D-NMR spectrum of epoxidized ethylacetate lignin*

4.1.3 CURING

Curing is the reaction employed to obtain the three-dimensional cross-linked structures that give the epoxy resins their good mechanical properties. The epoxidized material reacts with a hardener, generally an amine, at temperatures up to 150 or 200°C. The reaction between the epoxy group and the amines creates a crosslinked polymer. In this case, the hardener employed to react with the epoxidized lignin is Jeffamine® D-400, a Polyoxypropylenediamine (**Figure 4.9**).
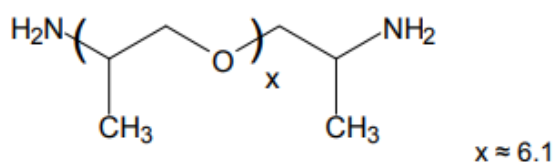
Figure 4.9 *Chemical structure of Jeffamine D400*[82]

The epoxidized lignin and Jeffamine D-400 are mixed in a 2:1 ratio together with acetonitrile. It is decided to use this ratio because each diamine molecule reacts with two chains of the lignin polymer. The solution is put in the Teflon moulds for producing DMA and cone calorimeters samples (**Figure 4.10**). The curing conditions are already known: one hour at 50 °C, two hours at 100 °C and two hours at 150 °C[37].
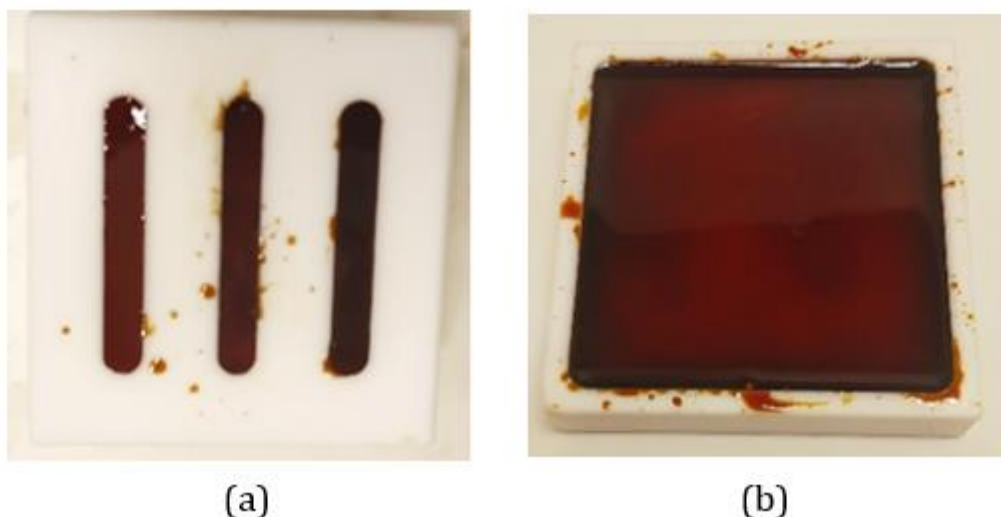
Figure 4.10 *(a) DMA samples; (b) Cone calorimeter samples*

Dynamic mechanic analysis (DMA) is employed to study the modulus of the resin and its glass transition temperature. The DMA measurements are carried out according to the Standard Test Method for Plastics: In Flexure (Three-Point Bending) ASTM D5023-07 at a constant frequency (1 Hz), amplitude of 20 mm. The samples are subjected to a temperature ramp, from -50°C to 180°C, with a heating rate of 2-3 °C/min, and a strain rate of 0,1%.

The experiment consists in applying a sinusoidal oscillating stress to the sample. The response of the material will be different according to whether it has elastic behaviour or not: for an elastic material the resulting strain will be in phase with the applied stress ($\delta=0°$); for a viscous material the resulting strain will not be in phase ($\delta=90°$). Viscoelastic materials, like polymers, have an intermediate behaviour: the strain phase δ is between 0° and 90°. Knowing these values, it is possible to determine the Storage Modulus of the material E', the Loss Modulus E'' and tanδ that is the ratio between them.

Figure 4.11 shows the graph obtained from the analysis.

The storage modulus can be obtained from the first trait of the green curve: it is 4500 MPa. The glass transition temperature T_g is determined by observing the peak of the tanδ curve (blue curve): the value is 72,1°C.

Based on information derived from literature, T_g is lower than the typical value observed for conventional epoxy resins (72,1°C vs the typical average value of 123°C)[83]. The reason for this lower value is probably explained by the presence of aliphatic alcohol that did not react during epoxidation (as seen in paragraph 4.1.2). This means that not all the epoxy rings are closed, leading to the formation of a lower number of crosslinks and consequently to a lower T_g.
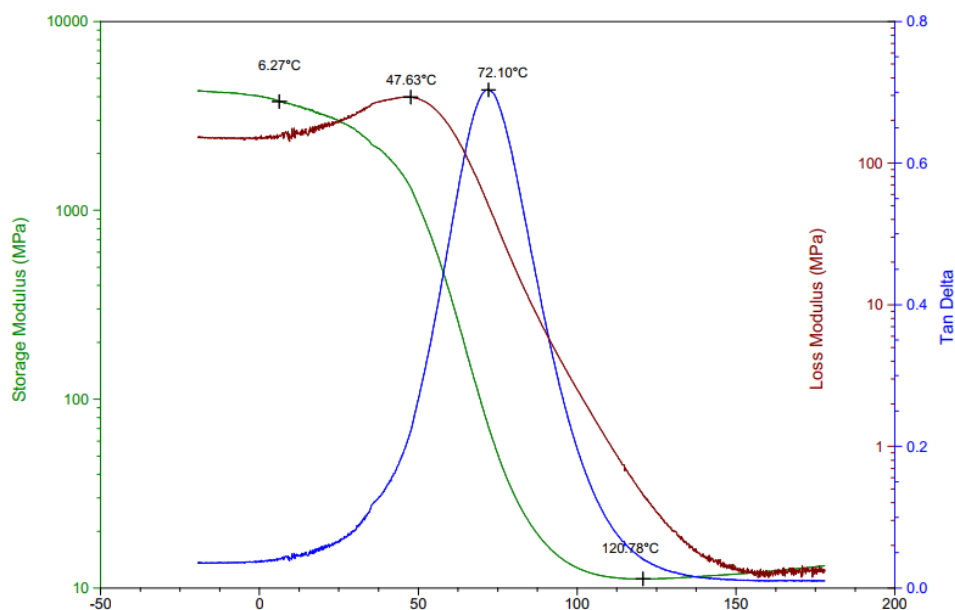
Figure 4.11 *DMA spectrum*

Moreover, the type of hardener employed during the curing step strongly influences T_g: the higher its molecular weight, the higher the flexibility of the resulting resin, which will have a lower T_g. Polyoxypropylenediamine D-400 is used in this project: the resulting resin is in a glassy state at room temperature. As can be verified by the data present in literature, if Polyoxypropylenediamine D-2000 were the hardener, the T_g would have been much lower (approximately between -50°C and -30°C)[37][84]. The difference between the two diamines stands in their molecular weight (400 g mol^{-1} for D-400, 2000 g mol^{-1} for D-2000) and consequently in their chemical structure, since Jeffamine D-2000 is constituted by longer chains and less amines that react with the epoxy rings of lignin. This results in a less crosslinked structure with lower T_g but higher flexibility. The will to create a resin with good mechanical properties lead to the choice of Jeffamine D-400 as hardener.

After the production of these lignin-based epoxy resin samples, the aim was to create nanocomposites samples, where the montmorillonite clay is used to enhance the fire-retardant behaviour of the resin. However, the suspension of all activities due to the Coronavirus emergency made it impossible to pursue the original aim of the project.

5. SCAFFOLD AND NANOCOMPOSITE PRODUCTION ACTIVITY PLAN

This chapter describes the activities that were originally planned for the development of lignin-based clay nanocomposites. Given that due to the Coronavirus emergency it is impossible to carry out this part of the work in laboratory, the description of the steps required for the production of the nanocomposite is presented as an activity plan with the aim of resembling a methodology section of a scientific project proposal. The main tasks of each activity and the expected results are identified; for each of them, a detailed analysis of the references from the literature will be performed in order to understand and support the proposed approach, aiming at obtaining the activity specific goals. In doing so, the resulting activity description will provide a detailed roadmap that can be followed in the hypothesis of taking up the present thesis project and carrying it forward.

The nanocomposite development starts with the selection of the materials that will be employed; then, the production of the foam, or scaffold, in which the lignin-based epoxy resin (produced with the process described in chapter 4) is infiltrated and cured, takes place. The scaffold must have good mechanical and thermal properties and must contain clay in the composition, so that the fire retardancy is improved. Clay has the ability to form a carbonaceous-silicate char on the material surface during combustion, that acts as a barrier that protects the substrate from further thermal degradation[60].

In order to guarantee the correct preparation of the scaffold and of the nanocomposite, the process is divided in a sequence of activities; each of them will be briefly described and the expected results will be identified as well as the way to achieve them. The duration of the activity is estimated to be 6 months in total, considering the time to perform the work, the bibliographic research phase, contingencies and risks (the latter will be further discussed in chapter 6).

In this regard, a Gantt chart is employed; it is an instrument that allows to analyse a project plan by representing each task as a bar and putting them on a time schedule, to better understand how they are interconnected in time. It is important to identify the milestones, that is to say the key activities that help to monitor the progress of the project.

The Gantt chart related to the present thesis is showed in **Table 5.1**. The milestones are represented on the diagram as stars and are related to the tasks whose fulfilment is mandatory to complete the project. They main activities are the following: the choice of the material to create the scaffold and its production; the process to create the nanocomposite; mechanical characterization and study of its fire behaviour.

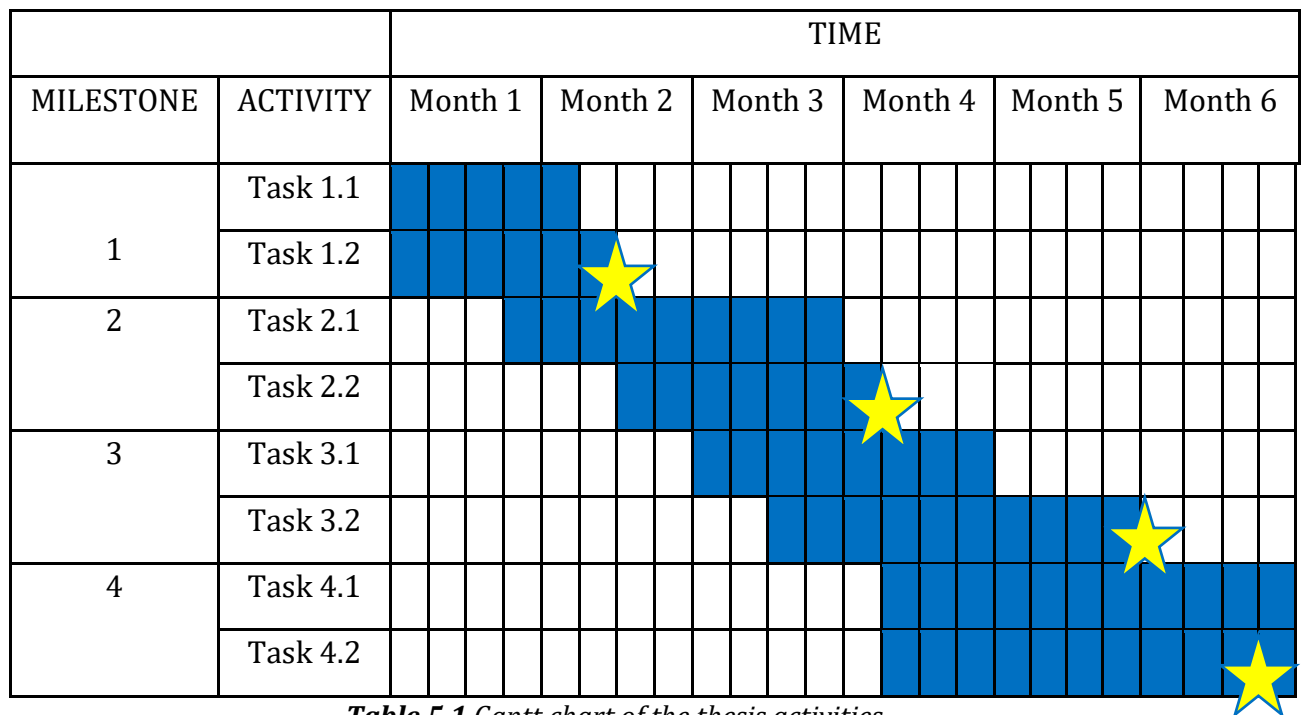| MILESTONE	ACTIVITY	TIME																							
		Month 1				Month 2				Month 3				Month 4				Month 5				Month 6			
1	Task 1.1	▪	▪	▪	▪																				
	Task 1.2	▪	▪	▪	▪	★																			
2	Task 2.1				▪	▪	▪		▪	▪	▪	▪													
	Task 2.2								▪	▪	▪	▪	★												
3	Task 3.1									▪	▪	▪	▪	▪	▪	▪									
	Task 3.2												▪	▪	▪	▪	▪	▪	▪	▪	★				
4	Task 4.1														▪	▪	▪	▪	▪	▪	▪	▪	▪		
	Task 4.2																	▪	▪	▪	▪	▪	▪	▪	★

Table 5.1 *Gantt chart of the thesis activities*

Pert diagram is used to understand the interconnection between the tasks. The one related to this project is shown in **Figure 5.1**: the feedback activity between the different tasks are underlined by the red arrows and are described as follows.
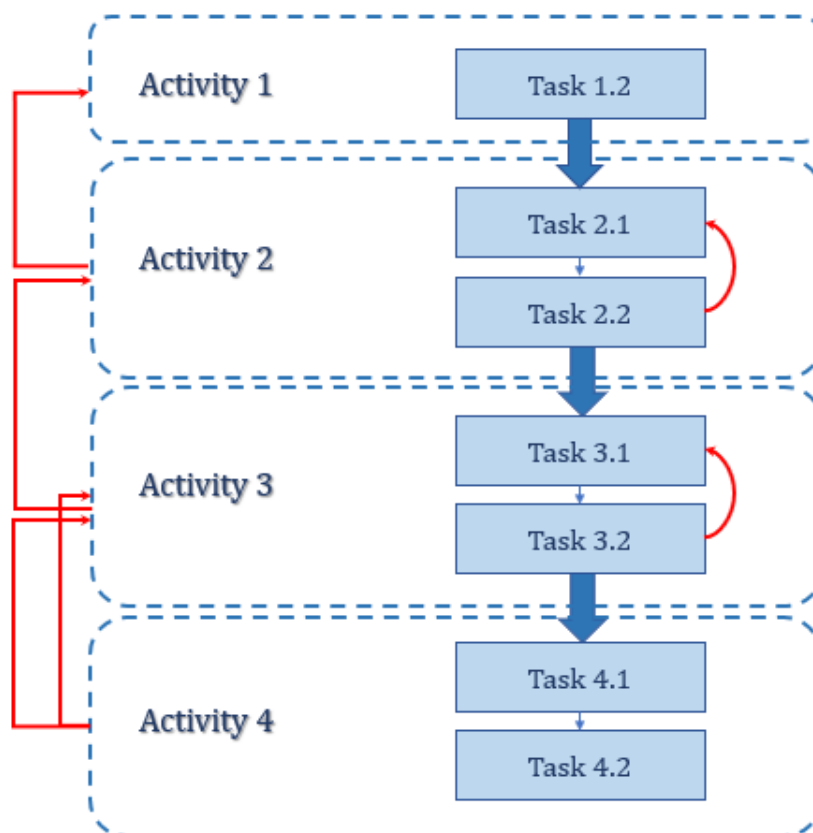

Figure 5.1 Pert chart of the activity

Firstly, connections between tasks belonging to different activities are identified:

- During task 2.2 (characterization of the scaffold), it is possible to see if the formulations chosen during task 1.2 are correct and allows to achieve the desired properties;
- Task 3.2 (the morphological characterization of the nanocomposite) gives a feedback to task 2.1: if the properties are not correct, it is necessary to go back to modifying the processing conditions for the scaffold production;
- Task 4.1 and 4.2 (the general characterization of the final material) directly relate to the nanocomposite production process (task 3.1).

For what concerns the feedback responses within the activities:

- Task 2.2 (the scaffold characterization) is directly dependent to the processing conditions (task 2.1);
- Task 3.2 (the nanocomposite morphological characterization) is directly dependent to the processing conditions (task 3.1).

5.1 ACTIVITY 1: Extraction of lignin and selection of materials for the production of nanocomposites

The right materials for the development of the nanocomposite must be produced (lignin extraction and functionalization as described in chapter 4) and selected (components for the scaffold): this is the objective of the "Activity 1". There are important requirements that need to be considered. Activity 1 can be divided in two tasks.

TASK 1.1 - Treatment of Lignin

This task regards the processes of extraction and preparation of lignin for the epoxidation step and the production of the epoxy resin. The procedure is known and is the one employed for the experimental activity carried out at KTH in Stockholm (see chapter 4). This means that all the parameters and conditions regarding the different phases have already been established and the resulting resin has all the right properties to be employed for the production of the nanocomposite.

TASK 1.2 - Selection of The Components for The Scaffold

- Objectives of task 1.2: obtain one or more formulations comprising a natural polymer and clay to employ for the production of the scaffold.

  This task focuses on the selection of the materials to be employed for the production of the scaffold that is capable of conferring flame retardant properties.

In order to create a scaffold, the material must be able to dissolve in water or in an aqueous solution to form a gel that will subsequently undergo a freeze-drying process, forming a porous structure. As already reported in the literature, the materials employed as structural components can be synthetic (i.e. polyethylene glycol (PEG), polyhydroxyethyl methacrylate (PHEMA)) or natural (i.e. chitosan, cellulose, alginate, gelatine)[85][86]. Since one of the main goals of the project is the creation of a bio-based alternative to petroleum-based polymers, the raw materials have to be abundant in nature and should renew periodically (according to what has been said in chapter 2).

Moreover, the contribution to the fire-retardant properties of the resulting material needs to be considered. To this aim, the use of inorganic nanoparticles such as clays has been demonstrated important in these regards since their inclusion acts as a thermal insulator, delaying the thermal degradation and increasing the char yield from the organic components of the scaffold[87]. The flame retardancy of the produced structure can be further improved by the employment of a polymer that already possesses the ability to form char and that help achieving a uniform distribution of the clay particles.

On the basis of these requirements and the literature background, the possible options are two natural polysaccharides, cellulose and alginate. Although biopolymers like chitosan and pectin are widely employed for the production of bio-based scaffolds (mostly used in the tissue engineering field), the information present in literature regarding their fire behaviour are not exhaustive. Chitosan, for instance, is a positive polyelectrolyte, hence when put in water in the presence of clay, that is negatively charged, it forms insoluble compounds, making it impossible to produce a foam[88]. For this reason, a modification step, like acylation and phthaloylation, would be necessary in order to avoid complex formation.

On the other hand, cellulose-based materials and alginates behave as negatively charged polyelectrolytes and thus would be suitable to be combined with clays that normally show a negative charge in water. In addition, they are very abundant in nature: the first is one of the main constituents of the biomass while the latter is derived from brown seaweeds, making them cheap; then, they are renewable, non-toxic, biocompatible and biodegradable. For these reasons, there are plenty of examples of clay aerogels produced with cellulose or alginate[87][67][71]. This is an advantage because it gives the possibility to have a comparison of data with other works while also providing a preliminary scrutiny on the foam processing conditions.

In addition, cellulose is able to form char when subjected to fire, and this capacity is enhanced by the presence of clay[87]. Alginate, as presented in chapter 3.3.2, is an inherently flame-retardant polymer, with a LOI value of 48: even without clay, the system has already an excellent fire behaviour[71].

It is possible to use different forms of alginate and cellulose that can lead to solutions, and consequently to foams, with different characteristics.

For what concerns the choice of the clay, it is demonstrated that no great differences are seen in the use of montmorillonite, kaolinite or aluminium hydroxide nanoparticles[89]. Montmorillonite is the most common choice for this kind of material. Its high-aspect ratio and high-surface area make it possible to enhance the mechanical properties of the material and the ability to form stable suspension in water and water-soluble polymers is suitable for the scaffold production process[90]. Within this task vermiculite and kaolinite will also be evaluated.

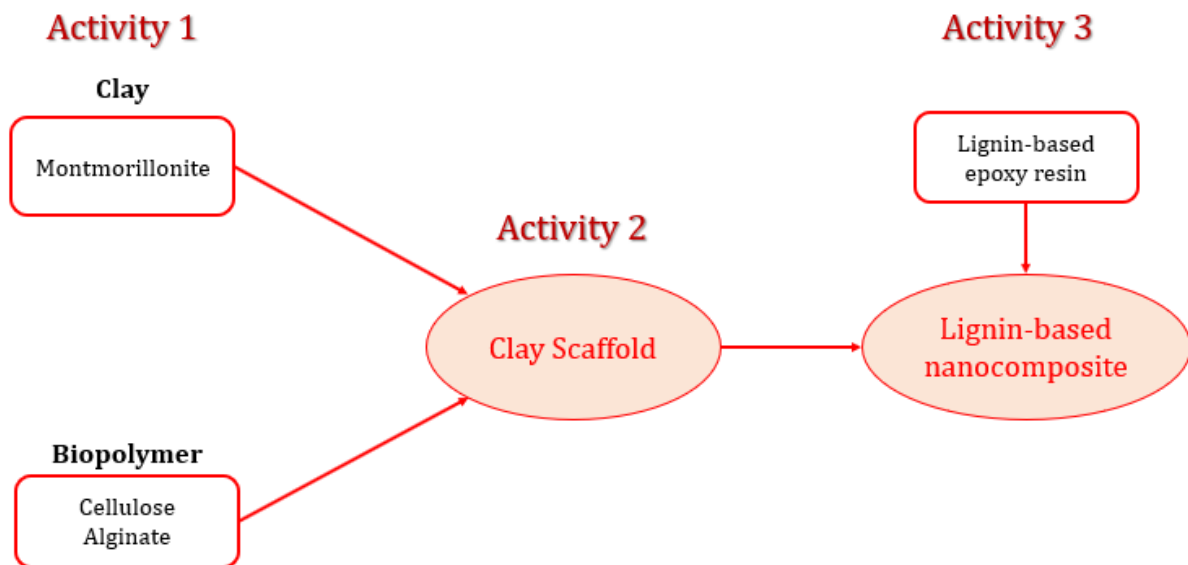**Figure 5.2** sums up the choices made for the production of the clay scaffold.

Figure 5.2 Summary of the material chosen for the clay scaffold

Cellulose NanoFibers (CNF) are the type of cellulose generally employed for the nanocomposite production. They are produced from wood pulp, which is put in high-pressure homogenizers and subdued to a mechanical disintegration to obtain fibers. In order to increase the yield of this process, special treatments are used, like 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation and enzymatic hydrolysis[91]. According to the kind of pre-treatment employed, the resulting CNF will show different properties. From a morphological point of view, TEMPO fibrils have a lower diameter and are shorter compared to enzymatic fibrils (respectively 3-5 nm against 10-20 nm)[73]. This leads to a higher compaction of the first, and consequently to higher density and better mechanical properties for the final structure obtained, whether it is a clay nanopaper or an aerogel. However, the carboxyl groups present on TEMPO fibrils make them less thermally stable than enzymatic fibrils that has no surface groups[91].

For what concerns alginate, its properties are a function of the composition. Alginate is a copolymer where the repetitive units are β-D-mannuronate (M) and α-L-guluronate (G). The monomers can form homogeneous sequences like G-G or M-M or can alternate forming heterogeneous sequences M-G (**Figure 5.3**)[92].
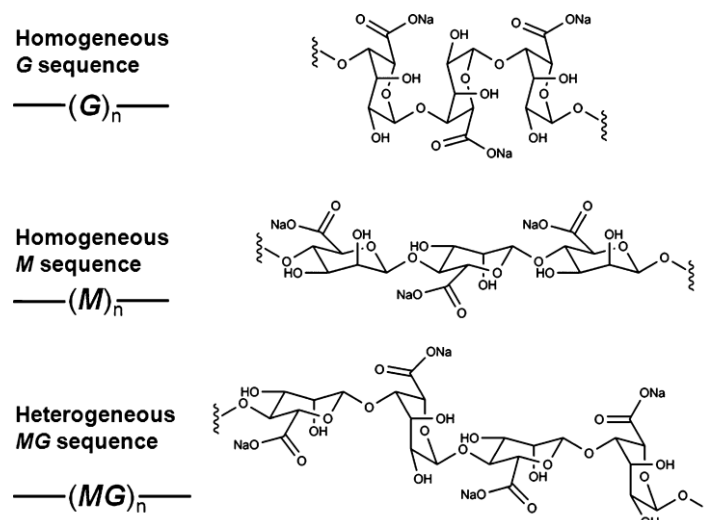
Figure 5.3 *Typical monomer blocks of alginate*[92]

The ratio of the two monomers present in the composition affects the final properties of the solution. For instance, a composition with a higher amount of monomer G (so a lower M/G ratio) results in a higher viscosity of the solution and in higher strength of the structure[93]. This can affect the processability of the prepared solutions/suspensions and will thus be carefully evaluated. To this extent TGA is performed on both the components as such and on their dried suspensions to study their thermal stability and mass residue percentage; rheometer is then employed to measure the viscosity of the suspensions to predict their processability and the possible mechanical properties of the foam.

Considering the broad literature background available, different formulations can be used in order to achieve the best properties in the final scaffold.

Milestone 1: to obtain one or more formulations of polymer and clay that exhibit improved polymer thermal stability/char yield and good processability.

5.2 ACTIVITY 2: Scaffold production

After the choice of the materials, the objective of the activity 2 is to produce the porous scaffold that will be impregnated with the lignin-based resin. In order to produce the scaffold, the freeze casting technique will be employed. The general procedure employed comprehends three steps:

1. the polymer/clay suspension is prepared: firstly, the chosen biopolymer and water are mixed; a clay suspension is prepared separately via centrifugation and sonication in order to avoid aggregations of the particles. Finally, the two suspensions are mixed together.
2. The polymer/clay suspension is frozen at low temperature by means of liquid nitrogen, leading to the nucleation of ice crystals into the solidified material.
3. Sublimation of the ice occurs at low pressure, obtaining a porous structure[89].

Figure 5.4 *Schematic representation of the scaffold production process*[89]

This method is called freeze drying. It is worth to note that other two alternative drying processes exist, ambient drying and supercritical drying. The ambient drying method is the easiest one that employs ambient pressure and room temperature, however, in order to prevent collapsing upon drying and to obtain a strong material, a step of surface modification must be performed prior to drying, generally by means of silylating agents and organic solvents, increasing the pre-treatment time[94]. Supercritical drying, instead, employs temperatures in the range of 300-600°C and pressures between 50-100 bar; there is no pre-treatment to do on the suspension, which is made up of organic solvent and not water, making it one of the most used drying methods on industrial scale. Besides this, it is not convenient to use it for the present project since the use of these critical conditions and the employment of organic solvents would increase the cost and the risks of hazards[86][95].

Freeze drying employs pressures lower than 100 mbar and temperatures between −70°C and −20 °C, it is easy to prepare, without the need to treat the suspension further and has a low cost, thus it is the most suitable for the production of the clay scaffold.

On this basis the conventional freeze drying is employed, and the following tasks are foreseen.

TASK 2.1 – Scaffold production

- Objective of task 2.1: to choose the best freeze-drying condition for the production of the scaffold.

It is important to consider the characteristics that the foam must have in order to be used in the nanocomposite production before deciding which freeze drying conditions to employ. First of all, the scaffold is a porous material, generally with an average density of 0,1 g/cm^3, with porosity around 92%, and pores dimensions of tenths of microns[89][96]. Since the creation of the nanocomposites requires the infiltration of the resin inside the pores of the scaffold, it is necessary to have a higher porosity with bigger pores, distributed uniformly, also to guarantee good mechanical properties. This can be achieved by tailoring the freeze-drying conditions, like cooling rate and temperature, and by modifying the clay content.

Firstly, viscosity of the initial suspension must be controlled: a higher viscosity means a higher density and consequently higher toughness and modulus [97]. Increasing the clay content up to 70-80% helps achieving this result, leading to a structure with a uniform pore distribution and good mechanical properties. At the same time, density must not be too high not to have a brittle structure. In addition, the freeze-drying parameters are to be considered. When freezing the suspension, ice crystals are formed by water, moving polymer and clay into the interstices. The sublimation of ice crystals creates the pores. The crystals dimension can be controlled by temperature: a higher temperature and a slower cooling rate lead to a low number of crystals of big dimension, and so big pores but lower density[72].

Therefore, these parameters must be tailored to control the final properties of the clay scaffold: it needs to have pores that are big enough to facilitate a correct resin infiltration but at the same time, density must not be too low, otherwise it would result in a brittle structure that would break during the infiltration.

TASK 2.2 – Characterization of the scaffold

- Objective of task 2.2: perform the characterization of the scaffold properties in order to validate the processing conditions

After the scaffold creation, a characterization step is necessary to check the good outcome of the process.

First of all, morphology must be studied through SEM analysis in order to calculate the density, the pore size and control if pores are distributed homogeneously. To this extent, it is convenient to produce scaffolds with different density values (in a range of 0,1-0,4 g/cm^3) to find out which are the composition and the processing conditions that lead to the best mechanical properties[67]. To analyse them, a compressive test is necessary to know the compressive modulus and toughness of the scaffold. Generally, the compressive modulus for clay aerogels is in the range of 4-6 MPa[67][98]. TGA is then needed to analyse the thermal stability and residue percentage of the foam. Preliminary flammability tests will be performed in order to evaluate the reaction to a direct flame application of the scaffold.

Milestone 2: obtain a clay scaffold with the following characteristics:

- a density in the range of 0,1-0,4 g/cm^3;
- big porosity homogeneously distributed;
- compressive modulus approximately of 4-6 MPa;
- thermally stable and increased residual mass;
- self-extinguish characteristics.

5.3 ACTIVITY 3: Composite production

Activity 3 aims to produce the final nanocomposite by combining the epoxy resin and the foam together. It is important to underline which are the characteristics expected from the material. In order to have good mechanical properties, the foam must be uniformly distributed into the resin matrix: the fact that the inorganic component is embedded into the scaffold is advantageous because it reduces the risk to have aggregations of the particles into the material. Moreover, the overall density of the material should be comparable to the value of the neat resin (1,07 to 1,22 g/cm^3) as a result of a correct infiltration process[99]. **Figure 5.5** graphically describes the procedure employed in this activity.
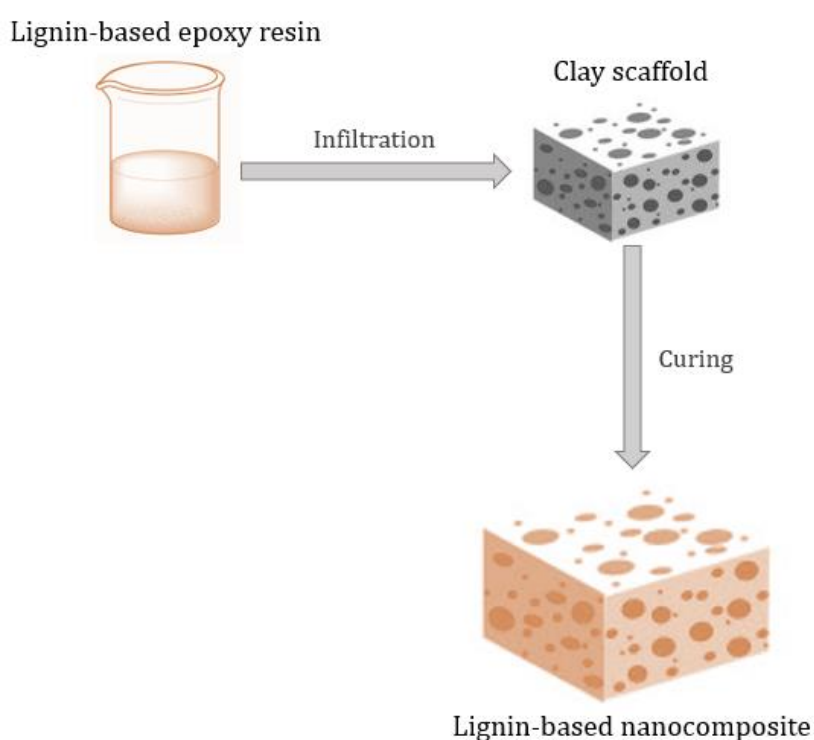

Figure 5.5 *Schematic representation of nanocomposite production process*

TASK 3.1 – Preparation of the infiltrated scaffold

- Objective of task 3.1: obtain a nanocomposite where the produced scaffold accounts for 10-30% of the composite)

The preparation of the nanocomposite begins by putting the scaffold in the mould of the same shape as the wanted samples (DMA, cone calorimeter and TGA and DSC samples). Then the solution of epoxy resin, hardener and acetonitrile is poured into the mould and infiltrated into the scaffold. The system is put in the oven where curing is carried out with the same conditions employed for the production of the neat resin (see chapter 4.1.3).

The obtained material will be characterized by a certain porosity and a certain content of the clay scaffold into the resin. The idea is to produce several samples in which the scaffold content is progressively increased to analyse how the properties change and what is the best composition that guarantees a homogeneous porosity and less defects in the structure. This can be achieved by modifying the scaffold thickness. For instance, if porosity of the scaffold is 90% of the volume, then the final nanocomposite will be 10% scaffold and 90% resin. By compressing the foam, the free volume inside can be reduced: this allows to have less content of resin in the final composite and more scaffold. Therefore, the more the scaffold thickness is reduced, the higher its content in the nanocomposite will be. It is important not to have a very thin scaffold otherwise the porosity would be too small to infiltrate the resin, making it impossible to obtain the nanocomposite.

TASK 3.2 – Preliminary characterization of the nanocomposite

- Objective of task 3.2: analyse the morphological properties of the nanocomposite

The nanocomposite must have a structure with no pores, since every pore of the scaffold should be occupied by the infiltrated resin. Moreover, it is important to verify the absence of voids in the structure, that could be caused by a non-perfect adherence between resin and scaffold. A SEM analysis will be performed to study these morphological aspects.

Another aspect to consider is the crosslinking of the resin. DSC analysis will be performed to confirm the proper occurrence of the curing process.

Since SEM and DSC work with small portions of material, the samples produced for this task will be smaller than the ones destined for the mechanical and flame retardancy characterization.

Milestone 3: to obtain a nanocomposite with a homogeneous structure characterized by the absence of defects and voids.

5.4 ACTIVITY 4: Functional properties of the produced nanocomposites

The lignin-based nanocomposites produced in activity 3 are tested to analyse which are their mechanical and thermal properties as well as fire behaviour. It is expected that the presence of the inorganic component into the nanocomposite would lead to important changes in the characteristics with respect to the neat lignin-based epoxy resin.

TASK 4.1 – Mechanical characterization

- Objective of task 4.1: to characterize the mechanical properties of the prepared infiltrated nanocomposite.

The mechanical characterization of the nanocomposite consists in two different tests that allow to evaluate the most important properties of the material.

Firstly, a tensile test is performed on the samples in order to calculate the elastic modulus E and the tensile strength. Then, Dynamic mechanic analysis (DMA) is employed to evaluate the T_g.

An increase in the elastic modulus and in the tensile strength should be noted. Starting from the resin characterized in chapter 4, an increase of at least 20-30% is expected. The increase varies according to how well the clay platelets are distributed into the scaffold and how well the scaffold is distributed into the epoxy resin. The more homogeneous the distribution, the better the mechanical properties[57].

For what concerns the tensile strength, its value generally increases in clay nanocomposites based on epoxy resin. Above a critical value of clay concentration, there is aggregation of clay particles and consequently an abrupt reduction of strength[100]. However, in this case the fact that clay was firstly dispersed in a polymer to form a foam in which the resin is infiltrated allows to have a more homogeneous dispersion of the particles, reducing the risk of aggregations and allowing to use a higher clay content. It is expected to have an increase of 30-40% in the tensile strength value (generally neat epoxy resin have a value in the range of 40-50 MPa)[101][102].

The same reasons might lead to an increase in the T_g value of 10%: a good dispersion of clay allows to have a lower mobility of the epoxy network and consequently a higher rigidity and thermal stability[103].

TASK 4.2 –Fire behaviour

- Objective of task 4.2: to evaluate the thermal and fire behaviour of the prepared nanocomposites

Thermal stability can be related to the fire behaviour of the nanocomposite. The increased ability to form char could potentially lead to a higher fire resistance. In this regard, it is important to study the thermal stability of the material and, above all, the residue percentage after thermal degradation by using of a TGA analysis[104].

For what concerns the fire behaviour, three types of test can be performed in order to have a more complete overview on how the lignin-based nanocomposites react to the exposition to fire.

The vertical flammability test or UL-94 is employed to evaluate the ability of the material to develop fire. A flame is applied to the sample for ten seconds; the reaction of the material allows to define a classification according to the standard UL-94: V-0, if the flame extinguish within ten seconds with no dripping, V-1 if the flame extinguish within thirty seconds with no dripping, V-2 if the flame extinguish within thirty seconds with dripping[105].

In order to analyse the material behaviour in the case in which fire has already developed, forced combustion test is used, in particular the cone calorimeter test. The sample is exposed to an external heat source that makes the combustion start. Several important parameters can be achieved by this analysis: the heat release rate peak (pkHRR) which is an index of the severity of a fire, the TTI, the mass loss rate, the total smoke release (TSR)[106].

An additional test that can be performed is the flame penetration test. It studies the resistance of the material when subjected to a standard flame for five minutes. Information like the mass loss and the quantity of gas released during the fire test can be obtained. These kinds of tests are conducted on the basis of two different standards: ISO2685:1998(E) and FAR25.856(b):2003[2]. The difference between them stands in the conditions used, like the type of burner, the type of fuel, the temperature of the flame. They are generally employed to verify if the material can be used for aircraft structural applications[107].

As explained in the previous chapters, the presence of clay in the composition enhances the fire behaviour of the neat resin thanks to the barrier effect to the thermal degradation and the capacity to migrate to the surface of the material to form a silicate-carbonaceous char that protect the substrate. Therefore, it is expected that, during the flammability test, the nanocomposite would extinguish the flame in a better way with respect to the neat resin and result in a V-0 classification, according to the UL-94 standard. This means that no dripping should be seen, and the flame should be extinguished in few seconds.

The properties expected from cone calorimeter test are a heat release rate of 50% lower compared to the resin alone and also a halved value of TSR (from approximately 4800 m^2/m^2 of the pristine resin)[108].

<u>Milestone 4</u>: to obtain at least one formulation capable of granting the main mechanical and flame retardant properties as summarized in **Table 5.2**. It also reports the possible application fields suitable for such a material.

	Improvements with respect to the neat resin	*Applications*
Mechanical properties	- Increase of 20-30% of elastic modulus - Increase of 40% of tensile strength - Increase of 10% of T_g	- Transport industry - Structural applications - Adhesives, protective coatings[109] - Aerospace sector, in particular aircraft structural applications, if

Fire behaviour	• V-0 classification (according to UL-94) • 50% reduction of pkHRR • 50% reduction of TSR • Resistance to the penetration of an impinging flame for more than 5 minutes	compliant to the standards ISO2685:1998(E) and FAR25.856(b):20032[107]

Table 5.2 *Summary of the expected properties of the final nanocomposite*

6. RISK ANALYSIS

This chapter assesses the risks that are most likely to impact the good working of the process. By means of this analysis the probability of succeeding in producing nanocomposites with the designated characteristics can be increased.

The risk analysis refers only to the scaffold and nanocomposite production and on its characterization. The treatment on lignin is not included because it is an experimental activity already carried out in accordance with a well-established procedure and does not involve any risk.

Table 6.1 is employed for the risk analysis. For every identified risk, there will be a brief description and one or more solutions will be proposed.

	Risk	Description of the risk	Solutions
Task 2.1-2.2-3.1	• The produced scaffold shows bad mechanical properties	The scaffold is not tough enough to withstand the resin infiltration and collapses during the process.	1 - Crosslinking of the organic component of the scaffold can enhance the compressive modulus and the strength up 30 times[71][110]. It is possible to use substances like divinyl sulfone (DVS), boric acid (which can also be used as a flame retardant) as crosslinkers. The disadvantage is that the addition of these substance decrease the bio-based content into the nanocomposite, being them not natural.
			2 - Functionalization of the clay with organic compounds: the clay particle surface is functionalised in order to improve the interfacial interactions between the filler and the polymeric matrix, leading to better resistance of the foam[111]. The main drawbacks are three: the organic compounds employed are not natural, decreasing the bio-based content; there is an additional step that increase the duration of the process; the cost ascribed to the functionalized clay can be high.

Task 3.1	• The resin is not distributed homogeneously in the nanocomposite	The resin is poured into the mould where the clay scaffold is located. The scaffold maintains structural integrity, but the resin is not distributed uniformly, leading to voids and defects that compromise the nanocomposite mechanical properties.	- Use of an infiltration procedure employing high pressure (e.g. Resin Transfer Moulding (RTM)). This solution employs high pressure to inject the resin in the mould, obtaining a more uniform distribution and less voids in the structure. It is a low-cost process, even if it should be adapted to the production of small components (it is generally used for components of big dimensions)[112].
Task 4.2	• Fire behaviour of the final nanocomposite non-compliant to the objectives	The nanocomposite results a flammable material, does not classify V-0 (UL-94 standard), has a high value of pkHRR and TSR.	- The inclusion of conventional flame retardant of flame retardant additives in the resin. The fact that clay is already present in the formulation allows to insert a concentration of additive smaller than that which is usually employed aiming for a synergistic effect. Since the employment of the usual flame retardant additives (like phosphorus compounds) would decrease the bio-based character of the material, an option would be the use of bio-based flame retardants. An example is provided by tannic acid, a compound derived from wood, which has been successfully used as flame retardant in several works[113].

Table 6.1 *Risk analysis*

7. CONCLUSIONS

The present project of thesis focused on the development of lignin-based clay nanocomposites with improved fire behaviour. The project aims to seek for an alternative to traditional petroleum-based plastic to limit the issues related to their employment. The work is divided into two parts: the first one describes the experimental activity concerning the preliminary treatment carried out on lignin, and the latter develops the activity plan for the production and characterization steps of the final nanocomposites.

The laboratory activity has been carried out at KTH in Stockholm. From the characterization carried out on the lignin-based epoxy resins obtained, it is possible to assert that the resulting properties are comparable to those of a traditional epoxy resin derived from fossil sources.

But considering only the properties is enough to prefer a bio-based material to a conventional one?

To this extent, starting from this thesis, it is possible to reflect on other aspects related to the life of a material, other than its chemical and physical properties. If considering the aforementioned lignin-based resin, despite the natural character of the main raw material, it is necessary to take into account all those chemical solvents employed for the steps of the process (like fractionation, epoxidation and curing) that make it not entirely bio-based: ethylacetate, epichlorohydrin, Jeffamine just to name a few. Not only is their disposal an issue from the environmental point of view, but their dangerousness and toxicity cannot be underestimated. It is necessary to understand if a process like this has a higher environmental impact than conventional ones. Moreover, the numerous steps that compose the process increase its complexity and make it difficult to implement it on large scale, making it more expensive for the higher quantity of instruments and energy to employ. In this regard, an idea for future work could be carrying out a life cycle analysis (Life Cycle Assessment, LCA). It is a standardized analytical tool aimed at assessing the impact of a material on the environment and human health, considering its entire life cycle, from construction to disposal. In this way, a comparison could be made between the analysis relating to the lignin-based resin and those relating to conventional polymers to evaluate which of them has a greater environmental impact.

The second part of the thesis aims to plan the production and characterization activities regarding the final nanocomposite. Starting from the will to create a material with certain mechanical and flame retardant properties, the work was divided into different activities, each with a specific purpose. This work proved to be fundamental for understanding, on a general level, what are the variables to consider and the steps to be taken when approaching an activity of this type. Indeed, this analysis made it possible to understand that if on one hand the experimental work proceeds with more or less established times on a theoretical level, in practice it is necessary to take into account the many unforeseen events and risks that can occur and cause delays in its development and identify the possible solutions.

Tools such as Gantt and Pert charts proved to be crucial in organizing the work over the chosen time frame.

The study on the development of new bio-based materials carried out in this thesis is located in one of the most promising research areas of recent years. Even if the results obtained in the first part of the thesis do not give information on how convenient it is, on an environmental level, to use the lignin-based resin compared to a normal epoxy resin, it is important to continue studying to make this process more sustainable and easier to be implemented on a large scale.

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