POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Master of Science Course
in Materials Engineering

Master of Science Thesis

Bio-based epoxy resins and reinforcements for coating applications: review and project plan

Tutor	**Candidate**
prof. Marco Sangermano	Samuele Vitaglione

October 2020

Riassunto

Nell'arco del secolo scorso, la rivoluzione delle materie plastiche di tipo sintetico derivate dal petrolio ha coinvolto la quasi totalità degli ambiti industriali. Oggigiorno, questo tipo di materiali costituisce la scelta più vantaggiosa sia dal punto di vista tecnologico che economico per numerose applicazioni. Una tra le applicazioni maggiormente interessate è quella dei rivestimenti. Le resine polimeriche, ed in particolare quelle termoindurenti, costituiscono il componente chiave delle formulazioni dei rivestimenti di tipo polimerico. Esse svolgono il ruolo di leganti, ovvero di fase organica continua che ha la funzione di tenere insieme tutti gli altri componenti della formulazione (pigmenti, cariche, additivi, etc.) e di creare un film aderente al substrato sul quale viene applicato il rivestimento. Tra le varie opzioni di resine termoindurenti che vengono regolarmente impiegate come leganti, si è scelto di porre l'attenzione su quelle di tipo epossidico.

Nei decenni scorsi, l'utilizzo di queste resine ha stabilito un'innovazione, in termini di performance e costi notevolmente ridotti, tale da soppiantare completamente l'impiego delle risorse di origine naturale (polisaccaridi, grassi, oli vegetali, terpeni, etc.) che venivano precedentemente impiegate come leganti nelle formulazioni. Tuttavia, la crescita della domanda globale di rivestimenti polimerici derivati da petrolio e, soprattutto, gli effetti deleteri sull'ambiente della loro produzione, utilizzo e smaltimento hanno sollevato problematiche riguardo l'ecosostenibilità di queste resine.

Per questo motivo si è reso necessario un ritorno allo sviluppo di alternative *eco-friendly* a partire da risorse di origine naturale. Questo lavoro s'inserisce in questo contesto, proponendo la pianificazione di un progetto che ha come obbiettivo la produzione e lo studio di rivestimenti composti da resine epossidiche sintetizzate a partire da sostanze di origine naturale e rinforzate con nanocristalli di cellulosa. L'obbiettivo è quello di fornire uno schema per la realizzazione di un progetto di ricerca che possa contribuire alla definitiva sostituzione delle resine epossidiche derivate da petrolio con quelle derivate da fonti bio-rinnovabili.

Al fine di comprendere il significato del progetto, viene fornita una descrizione delle principali resine epossidiche derivate dal petrolio attualmente in uso nelle formulazioni dei rivestimenti polimerici (vedi Sezione 1), in modo da poterne conoscere le caratteristiche e proprietà che ne motivano un utilizzo commerciale così ampio. Successivamente, si riporta una rassegna delle più importanti fonti bio-rinnovabili dalle quali sono state sintetizzate e polimerizzate, in anni recenti, resine epossidiche adatte all'impiego in rivestimenti (vedi Sezione 2). In essa verranno evidenziate alcune delle loro limitazioni, riguardanti soprattutto aspetti termomeccanici. Per questo motivo, viene riportata una seconda rassegna delle possibili soluzioni in termini di cariche rinforzanti ugualmente derivate da fonti bio-rinnovabili (vedi Sezione 3). Di seguito si trovano i riassunti delle varie sezioni.

1. Resine epossidiche derivate da petrolio

Le resine epossidiche sono una classe di polimeri termoindurenti caratterizzati dalla presenza due o più gruppi epossidici, un etere ciclico in cui l'ossigeno è uno degli atomi di un anello a tre termini. Questa classe è particolarmente versatile e sebbene non venga utilizzata unicamente per la produzione di rivestimenti, questi ultimi ne costituiscono circa il 50% del loro impiego. Le resine epossidiche vengono generalmente categorizzate in due gruppi in base alle strutture chimiche: epossidiche tipo glicidil ed epossidiche non glicidil. Di seguito sono riassunte le proprietà delle resine più rilevanti a livello commerciale dal punto di vista dell'utilizzo nei rivestimenti.

1.1. Resine epossidiche glicidil etere

In generale queste resine epossidiche derivano dalla reazione in ambiente alcalino tra epicloridina e vari materiali contenenti un idrogeno attivo. Le rappresentanti più importanti di questa categoria di resine sono quelle a base bisfenolo A e le resine epossidiche novolac.

1.1.1. Resine epossidiche a base bisfenolo A

Dalla reazione tra bisfenolo A [2,2-bis-(4'-idrossifenil) propano] ed eccesso di epicloridrina si ottiene come prodotto il diglicidil etere di bisfenolo A (DGEBA). Dalle reazioni di auto-condensazione di questo pre-polimero derivano resine commerciali con numeri medi di unità ripetitive che variano, a seconda delle condizioni di reazione, tra 0 e 12. Quando sottoposto a reticolazione, il DGEBA produce un materiale che possiede elevate resistenza a corrosione e ad attacchi chimici, oltre ad un'eccezionale adesione. Le proprietà termomeccaniche (resistenza termica, modulo e resistenza a trazione) sono altrettanto ragguardevoli. Per questi motivi queste resine epossidiche rappresentano oltre il 70% dell'utilizzo globale di resine epossidiche. Tuttavia, dopo varie indagini, il bisfenolo A è stato inserito nell'elenco delle sostanze estremamente preoccupanti a causa delle sue proprietà tossiche per la riproduzione e di interferenza endocrina che causano probabili effetti gravi per la salute umana e nocivi per l'ambiente.

1.1.2. Resine epossidiche novolac

Le resine epossidiche novolac sono il risultato dell'epossidazione, che avviene tramite glicidizzazione per reazione con l'epicloridina, di resine fenoliche. Vengono utilizzate nei rivestimenti i glicidil eteri di resine fenoliche novolac (EPN), i glicidil eteri di resine *o*-cresoliche novolac (ECN) e il diglicil etere di bisfenolo F (DGEBF). Esse sono caratterizzate da una maggiore funzionalità rispetto alle resine epossidiche a base di bisfenolo A, grazie alla quale raggiungono una maggiore densità di reticolazione, che risulta in una maggiore resistenza chimica e termica. Inoltre, le resine a base bisfenolo F possiedono una viscosità minore, che previene problemi di cristallizzazione.

1.1.3. Resine epossidiche cicloalifatiche

Le resine epossidiche cicloalifatiche derivano dall'epossidazione di composti cicloalifatici insaturi tramite reazione con perossido d'idrogeno o acido peracetico. Questo gruppo di resine è particolarmente usato nelle formulazioni per fotoreticolazione cationica tramite irraggiamento UV. La loro viscosità è più bassa delle resine a base bisfenolo A ma quando reticolate presentano eccellenti proprietà elettriche e termiche, tali da renderle particolarmente utili nell'industria di coating di componenti elettroniche.

2. Resine epossidiche da fonti bio-rinnovabili

Il numero di sforzi in termini di studio e ricerca verso lo sviluppo di resine epossidiche da precursori naturali è stato via via crescente nello scorso decennio. Le opzioni esplorate coinvolgono una varietà di fonti di cui si riporta un elenco riassuntivo.

2.1. Oli vegetali

Gli oli vegetali vengono tipicamente estratti dai semi delle rispettive piante per via meccanica o chimica. Essi consistono in una miscela di trigliceridi, ovvero tre acidi grassi collegati da una

molecola di glicerolo, la cui composizione è molto variabile. Gli acidi grassi sono lunghe catene alifatiche le quali presentano gruppi funzionali e livelli d'insaturazione diversi a seconda della loro composizione; grazie a tali gruppi e soprattutto ai doppi legami carbonio-carbonio è possibile operare l'epossidazione degli oli con metodi quali l'epossidazione tramite peracidi, resine acide a scambio ionico, epossidazione enzimatica o tramite ossigeno molecolare. Il primo tra questi è il più comunemente utilizzato per la produzione di grandi quantità di oli vegetali epossidati (EVO).
L'olio di soia epossidato (ESO) è tra i maggiormente impiegati a livello industriale, anche grazie alla sua abbondante produzione, per la fabbricazione di lubrificanti, rivestimenti e bioplastiche. Anche l'olio di ricino epossidato (ECO) è stato ampiamente impiegato dai ricercatori per lo sviluppo di plasticizzanti naturali, prepolimeri, lubrificanti e adesivi. Meno sviluppati ma comunque oggetto di attenzioni recenti sono stati anche gli oli di Jatropha e Karanja epossidati. Tuttavia, se paragonati alle resine classiche, questi prodotti mostrano resistenza termica e proprietà meccaniche inferiori a causa delle lunghe catene alifatiche; le loro applicazioni pratiche sono perciò limitate a diluenti reattivi in miscele con DGEBA, nelle quali aumentano il contenuto di materiale *bio* ed elasticizzano il network del polimero reticolato.

2.2. Saccaridi

I saccaridi, o carboidrati, sono composti contenenti esclusivamente carbonio, ossigeno e idrogeno con formula empirica $C_m(H_2O)_n$. Alcuni derivati di polisaccaridi sono stati maggiormente studiati di recente per la produzione di monomeri epossidici. L'isosorbide è una molecola derivata dall'amido che ha riscontrato interesse in quanto possiede interessante rigidità e chiralità, grazie alle quali riesce a impartire una buona stabilità termica al network. Tuttavia, questa rimane inferiore a quella delle resine classiche, probabilmente a causa della sua struttura ad anello alifatico che non è rigida come quelle contenenti un anello aromatico. Altre molecole piattaforma sono i furani, composti derivati dalla cellulosa o emicellulosa, che hanno mostrato buona reattività per la produzione di polimeri la cui adesione al substrato è particolarmente stabile.

2.3. Polifenoli

I polifenoli naturali sono un'ampia classe di composti organici contenenti molteplici strutture fenoliche. La presenza di anelli aromatici è la principale responsabile per la capacità dei monomeri epossidici derivati da questi composti di conferire resistenza chimica, termica e una migliore stabilità strutturale alle resine epossidiche. I tannini sono i composti fenolici più abbondanti in natura dopo la lignina; una classe di composti derivabili dai tannini che sono state oggetto di studi recenti sono le catechine. Nonostante le difficoltà nel controllo dei prodotti secondari durante la loro epossidazione, i monomeri epossidici derivati dalle catechine producono una resina con temperature di transizione vetrosa (T_g) sufficientemente elevata. Il cardanolo è un altro composto fenolico (un lipide fenolico), di facile accesso e ampiamente studiato; da esso sono derivabili un'ampia varietà di monomeri epossidici e prepolimeri, grazie ai legami alchenici presenti sulla catena alifatica collegata all'anello aromatico. Tuttavia, questa stessa catena influisce sulle proprietà termomeccaniche delle resine prodotte che necessitano di miglioramenti.

2.4. Lignina e derivati

La lignina è un polimero naturale complesso, la cui struttura tridimensionale è composta da unità fenolpropanoiche. Attualmente l'utilizzo principale della lignina è quello di combustibile di bassa qualità; tuttavia, la consapevolezza del potenziale non ancora sfruttato di questa risorsa, specialmente per le industrie chimiche e dei polimeri, sta prendendo piede sempre più. Le difficoltà principali sono dovute ai metodi di estrazione e trasformazione chimica che necessitano di ulteriori miglioramenti per generare un prodotto adatto allo sviluppo di polimeri ad alto valore aggiunto. Alcuni tra i composti che possono essere derivati efficacemente dalla lignina sono la vanillina e l'eugenolo, le cui proprietà come precursori per la produzione di monomeri epossidici hanno attratto grande interesse. La vanillina in particolare è il fenolo monoaromatico puro attualmente più prodotto dalla lignina a livello industriale. Le resine epossidiche a base di vanillina possiedono uno scheletro molecolare rigido, responsabile per rigidità meccanica e T_g relativamente alta. Tuttavia, il gruppo metossi, che causa perdita di stabilità termica e di colore, è generalmente difficile da convertire in epossido a costi contenuti. Molti monomeri e pre-polimeri epossidici a base eugenolo sono stati sintetizzati e ingegnerizzati tramite vari metodi, regolandone la funzionalità, flessibilità, rigidezza e di conseguenza le proprietà finali della resina reticolata, che in generale risulta avere elevate proprietà termomeccaniche, talvolta addirittura superiori a quelle del DGEBA (es. T_g >200°C). Purtroppo, nella maggior parte dei casi sono necessari l'utilizzo di reagenti ossidanti piuttosto costosi, come l'acido meta-cloroperossibenzoico (mCPBA) e di solventi cancerogeni, come il diclorometano e il cloroformio.

3. Cariche rinforzanti da fonti biorinnovabili

Le resine epossidiche in generale mostrano i comportamenti tipici delle resine termoindurenti altamente reticolate, in particolare scarsa resistenza a impatto, fragilità e resistenza all'innesco e propagazione di cricche relativamente bassa. Nel caso di resine epossidiche da fonti rinnovabili le mancanze nelle proprietà termomeccaniche dei prodotti sono accentuate. Esistono però numerosi studi che evidenziano le capacità di diverse tipologie di cariche di apportare miglioramenti a vari aspetti della resina epossidica reticolata. Tra le numerose opzioni applicabili ai rivestimenti polimerici si è scelto di porre l'attenzione su tre tipologie di cariche rinforzanti la cui caratteristica principale è quella di poter essere ricavate da fonti biorinnovabili.

3.1. Gusci d'uovo

I gusci d'uovo sono compositi bioceramici naturali la cui frazione inorganica (95%) è quasi del tutto composta da carbonato di calcio. Rappresentano uno scarto di produzione il cui volume è decisamente considerevole, motivo per il quale se ne sono studiate le potenzialità in qualità di carica. L'aggiunta di particolato da gusci d'uovo in rivestimenti acrilici ha dato prova di migliorare le proprietà di ritardo alla fiamma di sistemi intumescenti. Altri studi hanno evidenziato i miglioramenti alla resistenza a trazione e durezza di resine DGEBA, in seguito a trattamenti superficiali delle particelle di gusci d'uovo con acido stearico per prevenirne l'aggregazione.

3.2. Nanocristalli di cellulosa

La cellulosa è il materiale polimerico più abbondante sulla Terra e rappresenta una risorsa biorinnovabile di enorme interesse tecnologico. Essa è ricavabile da un numero vastissimo di possibili fonti che spaziano dal legno delle foreste ai residui e prodotti secondari dell'agricoltura attraverso trattamenti di separazione tramite i quali è possibile rimuovere le altre componenti organiche (lignina, emicellulosa ed altri estratti). La sua struttura presenta unità di cellobiosio che formano delle catene organizzate in domini cristallini collegati tra loro tramite altri domini amorfi. Eliminando tali domini amorfi, solitamente attraverso idrolisi acida, si possono ottenere dei nanocristalli di cellulosa. Questo prodotto è stato impiegato per il rafforzamento di una grande varietà di materiali polimerici, sia termoplastici che termoindurenti, permettendo di migliorare notevolmente resistenza a trazione, rigidità e resistenza a corrosione, resilienza e contribuendo alla riduzione degli stress interni. Inoltre, la presenza di un gran numero di gruppi ossidrili sulla superficie dei nanocristalli permette di ingegnerizzare una varietà di modifiche superficiali in modo da promuovere collegamenti con la matrice epossidica e prevenirne l'aggregazione in cluster microscopici.

3.3. Carbonio

Qualsiasi sostanza organica costituisce una possibile fonte di carbonio, il quale può essere ricavato da esse e trasformato nella forma adatta all'utilizzo per una delle sue molteplici applicazioni. Il carbone attivo, ad esempio, è un prodotto a base di carbonio amorfo, dalla struttura altamente porosa che gli conferisce un'elevata superficie specifica. Nonostante il suo utilizzo sia principalmente quello di materiale assorbente per trattamenti di fluidi contenenti inquinanti, alcuni tentativi sono stati fatti per valutarne gli effetti sulle matrici epossidiche. È stato osservato come, in seguito a funzionalizzazione superficiale tramite ammine, sia possibile influenzare positivamente alcune proprietà come la T_g e la resistenza a corrosione. Tuttavia, vi sono stati negli scorsi anni molti più studi riguardanti un altro materiale a base di carbonio, ovvero il grafene. La struttura a strati monoatomici di atomi di carbonio ibridati sp^2 e disposti in un reticolo a nido d'ape conferisce al materiale la capacità di provocare, nei rivestimenti epossidici, un aumento delle caratteristiche meccaniche (quali resistenza a trazione), tribologiche (resistenza all'erosione), stabilità termica e maggiore protezione da corrosione (specialmente di metalli in ambienti marini). Nondimeno, vi sono prodotti derivati dal grafene, quali l'ossido di grafene (GO) e l'ossido di grafene ridotto (rGO), che presentano ulteriori vantaggi, tra i quali la migliore disperdibilità nella matrice e la maggiore possibilità di una funzionalizzazione più efficace.

4. Piano di progetto

Come già detto in precedenza, l'ultima Sezione di questo lavoro propone la pianificazione di un progetto che ha come obbiettivo la produzione e lo studio di rivestimenti composti da resine epossidiche sintetizzate a partire da sostanze di origine naturale e rinforzate con cariche anch'esse derivate da fonti biorinnovabili. Dall'analisi delle informazioni presenti in letteratura si possono fare tre osservazioni importanti ai fini della determinazione del progetto. La prima è che le resine epossidiche a base di composti aromatici manifestano proprietà termomeccaniche più simili a quelle del DGEBA rispetto a resine derivate da composti alifatici. La seconda è che vi è un'ampia disponibilità di dati e informazioni riguardo la reticolazione termica dei monomeri epossidici da fonti naturali, mentre studi e valutazioni sulle stesse resine reticolate tramite fotoreticolazione cationica sono ancora poco numerosi in confronto, nonostante quest'ultimo metodo presenti notevoli vantaggi rispetto al primo in termini di rapidità di processo e benefici ecologici. La terza osservazione che si può fare è che c'è una quasi totale assenza di studi, e di conseguenza dati, riguardo rivestimenti polimerici nei quali sia la componente legante che le cariche sono derivate da fonti biorinnovabili.
Pertanto, il progetto proposto consiste nella produzione monomeri epossidici a partire da tre diversi fenoli naturali, nello specifico l'acido ferulico, l'acido gallico e l'eugenolo (vedi **Fig.** 4.1, **Fig.** 4.2 e **Fig.** 4.3); nella sintesi di nanocristalli di cellulosa a partire da microcellulosa derivata dal cotone; e nella fotoreticolazione cationica per irraggiamento UV delle formulazioni. Il lavoro è stato perciò pianificato in quattro unità principali o "workpackage" riassunti qui di seguito.

1) *Sintesi di monomeri epossidati a base di composti naturali e relativa caratterizzazione*

Nella prima unità di lavoro si definiscono i metodi di sintesi di tre monomeri epossidici: il trisepossi triglicidil etere triferulato (GTF-EPO, vedi **Fig.** 4.1) sintetizzato a partire dall'acido ferulico; il tetraglicidil acido gallico (GEGA, vedi **Fig.** 4.2) sintetizzato a partire dall'acido gallico; ed il bisepossido 2,2’-diglicilil etere-3,3’-dimetossi-5,5’diallidifenilmetano (BEF-EP, vedi **Fig.** 4.3) sintetizzato a partire dall’eugenolo.

I procedimenti della sintesi delle tre resine vengono ripresi da quelli riportati in letteratura, in quanto l’obbiettivo, in questa fase di progetto, non è quello di studiare possibili modifiche a tali procedimenti, bensì quello di ottenere le resine di cui si propone di valutare, nelle successive fasi del progetto, la risposta alla fotoreticolazione cationica, gli effetti che le cariche avranno su di esse e le caratteristiche termomeccaniche complessive dei film rinforzati.

In seguito alla sintesi delle resine se ne verificheranno struttura, purezza e contenuto epossidico attraverso analisi spettroscopiche di risonanza magnetica (^{1}H NMR e C^{13} NMR), titolazione ^{1}H NMR e analisi spettroscopica infrarossa in trasformata di Fourier (FTIR).

2) *Sintesi di cariche biorinnovabili da cellulosa e relativa caratterizzazione*

Nella seconda unità di lavoro si definisce il metodo di sintesi dei nanocristalli di cellulosa, che verranno ottenuti eliminando dalla cellulosa microcristallina derivata dal cotone, disponibile commercialmente, le zone amorfe attraverso idrolisi acida.

I nanocristalli di cellulosa sono stati scelti per questo progetto, oltre alle loro proprietà di biodegradabilità, biocompatibilità e bassa espansione termica, per le loro trasparenza ottica, che dovrebbe facilitare la fotopolimerizzazione delle resine per irraggiamento UV.

In seguito alla sintesi, le particelle verranno caratterizzate tramite analisi FTIR per determinarne la purezza, osservazioni al microscopio a trasmissione elettronica (TEM) per una valutazione morfologica e dimensionale e analisi di diffrazione ai raggi X (XRD) per verificarne la cristallinità.

Infine, in seguito a liofilizzazione e dispersione meccanica delle nanoparticelle nelle resine, se ne valuterà il contenuto e la disperdibilità attraverso microscopia ottica; in base alle osservazioni si valuteranno modifiche superficiali per migliorarne la dispersione.

3) *Design e reticolazione UV delle formulazioni fotorecolabili rinforzate*

In questa terza unità di lavoro si stabilisce l’utilizzo del sale di triarilsolfonio esafluoroantimoniato come fotoiniziatore (in quanto più comunemente utilizzato) del quale verranno valutati contenuto e solubilità nelle formulazioni. Si pianifica l’utilizzo di tecniche di analisi quali la Real-Time FT-IR per lo studio della cinetica di fotoreticolazione e la photo-calorimetria a scansione differenziale (photo-DSC) per lo studio della reattività e della temperatura di transizione vetrosa delle varie formulazioni. Infine, saranno valutati i parametri migliori in termini di tempo di irraggiamento e intensità dei raggi UV.

4) *Caratterizzazione dei campioni reticolati*

Nell’ultima unità di lavoro sono stabilite tutte le tecniche necessarie alla caratterizzazione delle proprietà termomeccaniche delle resine rinforzate fotoreticolate. In particolare, si pianificano: analisi meccanica dinamica (DMA) per la determinazione dei moduli di conservazione (E’) e di perdita (E’’) e per la valutazione della temperatura di transizione vetrosa (T_g); analisi termogravimetrica (TGA) per la valutazione della stabilità termica; test secondo gli standard ASTM di adesione (ASTM D3359-09), resistenza all’abrasione (ASTM D4060-10), resistenza all’impatto e alla deformazione (ASTM D2794-10). Infine, verranno misurati gli angoli di contatto in test di bagnabilità per valutare l’idrofobicità dei rivestimenti e l’influenza dei nanocristalli di cellulosa su queste proprietà.

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Introduction

The development of polymers has greatly revolutionized many aspects of our society, both culturally and technologically, on a global scale. It is hard to think of an application in which polymeric materials have not been able to provide some sort of enhancement or solution. Thanks to their wide variety of properties, polymers have been used both as bulk material and as binders in coating formulations, providing the organic continuous phase that holds all the other components together. Polymers are not the only type of material than can be used in coating applications, in fact metallic and other inorganic materials such as ceramics are regularly implemented in the same field too. However, the main advantage over metallic and ceramic coatings is that polymeric coatings can be applied to almost any substrate with significant ease compared to the other types.

Polymers can be broadly divided in thermoplastics and thermosets. These last ones constitute the vast majority of advanced polymer coatings; the reason for this is found in their particular structure, consisting of a three-dimensional network of covalently interconnected macromolecules (**Fig.** I)[1], which imparts higher chemical and mechanical resistance to stresses than the thermoplastic counterpart.

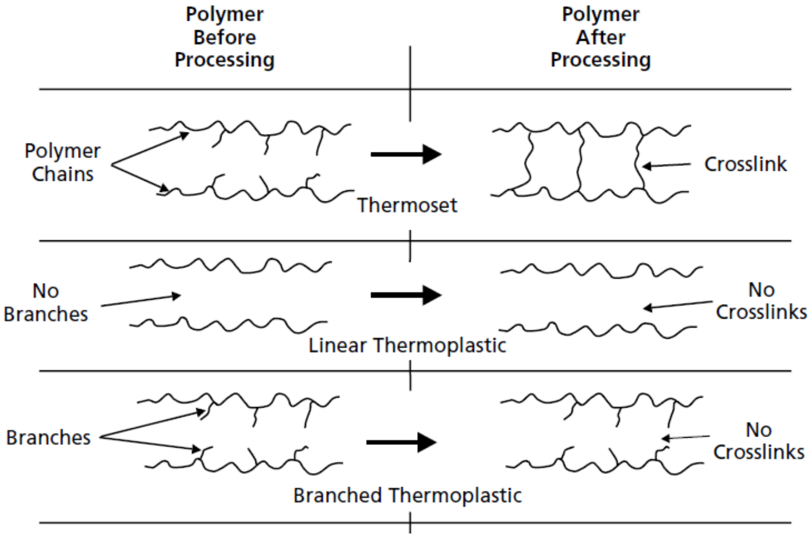

Figure I. Comparison of thermoset and thermoplastic polymer structure before and after thermal processing

The discoveries and following advances in petro-based chemistry, starting with the invention of Bakelite (the first fully synthetic plastic) by Leo Baekeland in 1907, have brought to life all the main types of thermosets that have been since used in coating formulations for over a century: phenol-formaldehyde (phenolics) urea-formaldehyde (aminos), epoxies, acrylates and acrylics, isocyanates, polyesters, alkyds.

Thermoset	**Year**	**Inventor**
Phenol-formaldehyde (*phenolics*)	1907	Leo Baekeland
Urea-formaldehyde (*aminos*)	1918	John Manns
Drying oils / *alkyd*	1925	Roy Kienle
Acrylates and acrylics	1927	Otto Röhm (Rohm & Haas)
Polyester	1929	Wallace Carothers
Isocyanates	1937	Otto Bayer
Epoxy	1938	Pierre Castan (CIBA)

Table a. Main types of thermosets used for coatings, with the year of discovery and inventor(s)

The low cost and incredibly wide diversity of petrochemicals have justified, economically and technologically, the loss of interest in the renewable resources (fats, plant oils, terpenes, minerals, polysaccharides) that had been regularly used as coating components before the very large supply of petrochemicals became industrially available. However, with the incredible growth of the world population over the past 50 years (**Fig.** II)[2] and the ever-increasing global demand of industrial coatings (estimated at ≈ 61.3×10^9 € in 2016 and projected to touch ≈ 87.6×10^9 € by 2022)[3], it has become more and more evident how unsustainable it is to rely on such a finite, quickly depleting supply of fossil resources. The overall environmental impact of the industry, from the extraction of raw materials, to their transformation, to item manufacturing and the final disposal of polymeric waste, has emphasized the sense of urgency for the need of a general technological shift towards renewable resources for the development of alternative bio-based, advanced coating components.

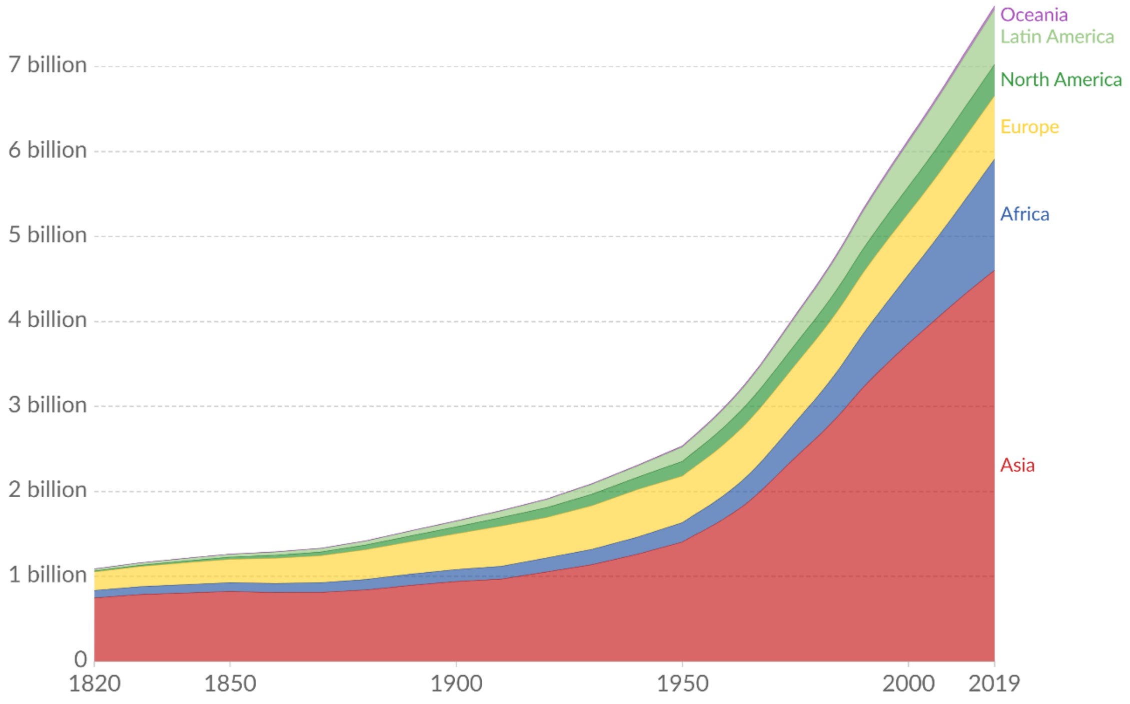

Figure II. World population by region between 1820 and 2019

This is particularly true for the case of epoxy thermosets. The need for alternatives to petro-based epoxy resins is all the more pressing when considering the fact that the majority of this type of thermoset contains Bisphenol-A (BPA), an industrial chemical that has been used since the 1960s for the production of the largest volume of petroleum-based epoxy resins, which has also been found to constitute a threat to human health because of its endocrine disrupting properties.[4] The resulting increasingly restrictive regulations regarding the use of BPA, particularly in materials in contact with foods for babies and children under three years of old, has further prompted the research towards safer, more sustainable alternatives.

In this work, a description of the most important petroleum-based epoxy resins currently implemented in coating formulations is presented in **Section 1**; there the reader may find information about their synthesis, properties and peculiarities that will give context to better understand how and why these resins occupy such a crucial place among the technologically advanced coating materials. What follows in **Section 2** is an overview of the latest and most advanced researches on the topic of bio-based epoxy resins, particularly those resins that have already found use in or have shown potential for coating applications; this Section presents the various, most technologically valuable renewable resources that are being studied with the goal of developing fully or partially bio-based alternatives to the petroleum-based epoxy resins, reporting on the progress and challenges that each of these alternatives poses.

The majority of these challenges are related to the properties of the final product which, unfortunately more often than not, fall short of the necessary standards to become a viable option. To overcome these imperfections, combinations of epoxy resins with fillers have also been studied over the past decades, resulting in the development of composite materials with greatly improved properties. **Section 3** specifically presents a selection of reinforcements that are also derived from renewable sources, thus keeping the focus on the most environmentally friendly solutions possible only; in this Section are information about how these materials have been implemented in various applications and fields, including that of coatings, and the enhancements they provide to the polymeric matrix.

Finally, the project plan outlined in **Section 4** represents the practical outcome of this work. Combinations of matrix and reinforcement derived from renewable resources are selected based on the previously presented information and all the necessary steps of the complete process of the composite preparation and characterization are mapped out.

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1. Epoxy resins from petroleum

Epoxy resins are a group of oligomeric materials which contain more than one epoxy (oxirane) groups per molecule.

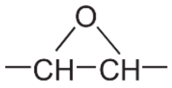

Figure 1.1 Epoxy group

This class of polymers is one of the most versatile, finding useful applications in many diverse fields such as metal can coatings, semiconductor encapsulants, printed circuit boards, adhesives, automotive primer and aerospace composites. The majority of cured epoxy resins yield amorphous thermosets with a unique combination of properties that is generally not found in any other single plastic material. These include excellent toughness and mechanical strength; superior chemical, moisture, and corrosion resistance; very interesting thermal, adhesive, and electrical properties; no volatiles emission and low shrinkage upon cure; and dimensional stability. Such outstanding performance characteristics, coupled with very handy formulating versatility and affordable costs, have made epoxy resins the materials of choice for a multitude of structural, bonding, and protective coatings applications. The production of a cross-linked structure requires bi- or multifunctional epoxides, which in fact constitute the vast majority of industrially important epoxy resins. Nonetheless, monofunctional epoxides are also in commerce and find primary use as reactive diluents, viscosity modifiers, or adhesion promoters.[1]

Based on their molecular structure and applications, epoxy resins can generally be categorized as one of two types: the glycidyl-type epoxy and non-glycidyl-type epoxy. Each of these two types can be further divided on the basis of the resins' structure. The glycidyl epoxy group encompasses glycidyl ether, glycidyl ester, and glycidyl amine resins; the non-glycidyl epoxy group encompasses aliphatic and cyclic epoxy resins. [2]

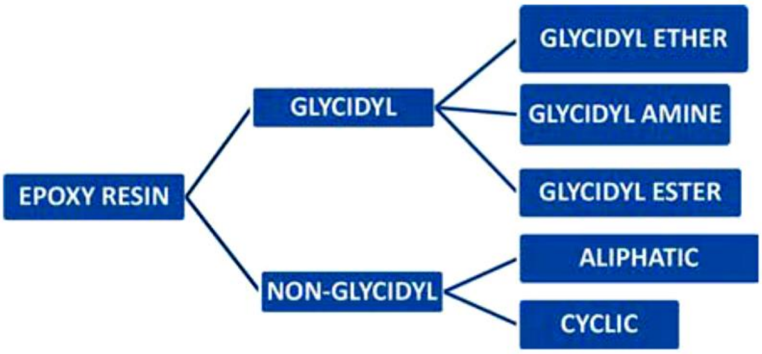

Figure 1.2 Categorization of Epoxy resins

To describe each and every one of these classes of resins would go beyond the scope of the present work. Instead, a description of the most commercially relevant epoxy resins will be made in the following paragraphs; particularly, the attention will be focused on those resins that find application as coatings.

1.1. Glycidyl ether epoxy resins

Glycidyl-based epoxies are derived from a condensation reaction of epichlorohydrin (1-chloro-2,3-epoxypropane or ECH) and various materials containing groups with active hydrogen (such as aliphatic hydroxyl, carboxylic acid, phenolic hydroxyl, or amine). The initial reaction yields a chlorohydrin, which is subsequently dehydrochlorinated to yield the glycidyl (epoxy) group.

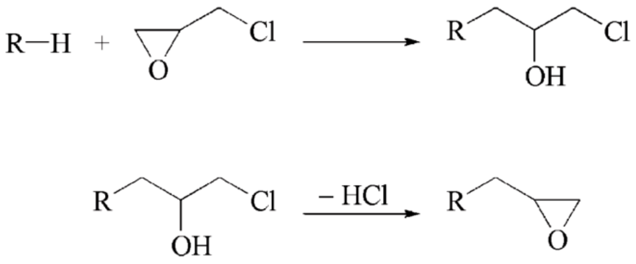

Figure 1.3 General scheme of epoxidation through epichlorohydrin

The most relevant classes of glycidyl-based epoxy resins are the bisphenol-A epoxy resins and the novolac epoxy resins.

1.1.1. Bisphenol-A epoxy resins

Bisphenol-A (2,2-bis(4-hydroxyphenyl)propane or BPA) is prepared from 2 moles of phenol and 1 mole of acetone; epichlorohydrin is usually prepared from propylene by chlorination to allyl chloride, followed by treatment with hypochlorous acid, which yields glycerol dichlorohydrin and is then dehydrochlorinated by sodium hydroxide or calcium hydroxide. The reaction of bisphenol-A with epichlorohydrin in the presence of a basic catalyst (usually NaOH) represents the common way of producing the diglycidyl ether of bisphenol-A (DGEBA). This resin dominates the scene by a very wide margin and accounts for over 70% of epoxy usage.[3]

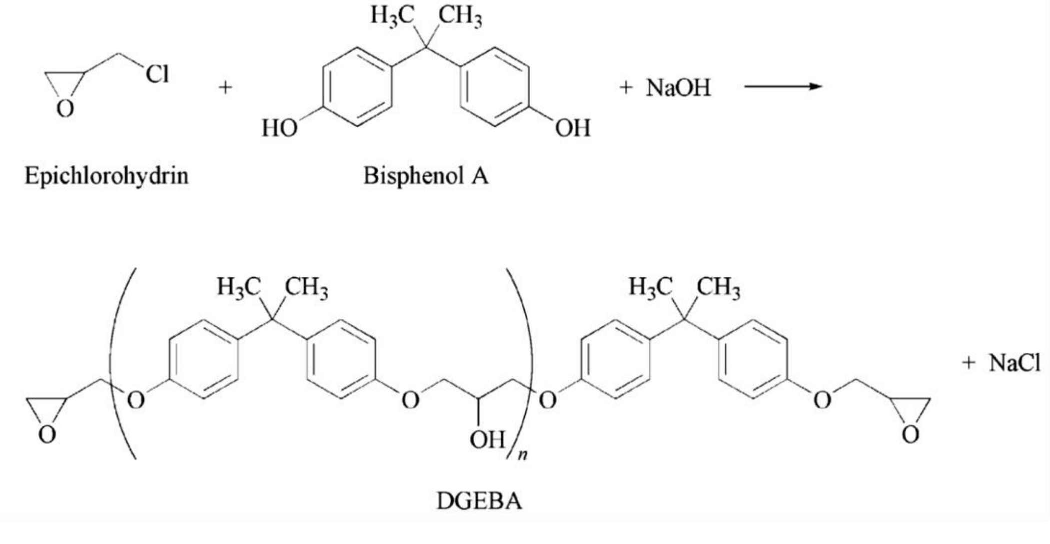

Figure 1.4 Scheme of DGEBA synthesis

The properties of the DGEBA resins can vary depending on the number of repeating units (*n*). The range of *n* value in commercial products goes from 0 to about 60. As *n* increases, so do the epoxy equivalent weight (EEW, the weight of resin required to obtain one equivalent of epoxy functional group) and the number of hydroxyl groups. For this reason, epoxy resins with low *n* values are generally cured by reaction of the epoxy group and resins with higher n values are instead cured by reaction of the hydroxyl functionality.

Resins with *n* values lower than 1 are viscous liquids and are mainly used in two-pack, ambient-temperature cure coatings, as well as in fiber-reinforced composites, flooring, electrical laminates and castings. Resins with *n* values ranging between 1-2 are low melting solids; they are used in solution in two-pack, ambient-temperature cure coatings. Resins having *n* values between 2-6 are solids; they do not sinter at room temperature and are predominately used in powder coatings. As previously mentioned, all of these applications are cured through the epoxy groups. Finally, the higher *n* value resins, particularly those with $n > 10$, find their use in solution and their greatest application in heat-cured coatings.

Coatings based on BPA epoxy resin are used in a wide variety of important end uses from a technological point of view, thanks to the unique combination of performance and characteristics they offer. Their exceptional adhesion and corrosion resistance motivated their use in corrosion-resistant primers and coatings since epoxy resins were first put in commerce. Additionally, an excellent chemical resistance has led to the formulation of epoxy coatings that can provide outstanding protection against severe corrosive environments, such as chemical plants, refineries, and marine equipment, such as offshore platforms and ships. Other important applications make almost exclusive use of epoxy resins coatings because of the corrosion protection they provide; these include aircraft, automotive, appliance primers and coatings for both the internal and external surface of pipelines.

However, coatings based on BPA epoxy resins exhibit significant weakness related to the resistance to ultraviolet (UV) exposure: exposition to direct sunlight causes the aromatic structure of the BPA backbone to absorb the UV energy and consequently degrade. As a result, their color turns to yellow and chalk. A common strategy to work around this weakness while taking advantage of the excellent corrosion resistance of the BPA epoxy resins is to use them as primers and subsequently topcoat them with coatings that are resistant to UV degradation.

1.1.2. Novolac epoxy resins

Phenol novolac epoxy resins (EPN)

Phenol novolacs are phenol–formaldehyde condensates that can be obtained from acid-catalyzed condensation of phenol and formaldehyde. By reacting phenolic novolac resin with epichlorohydrin the synthesis of epoxy phenol novolac resins, glycidyl ethers of phenolic novolac resins, is achieved.

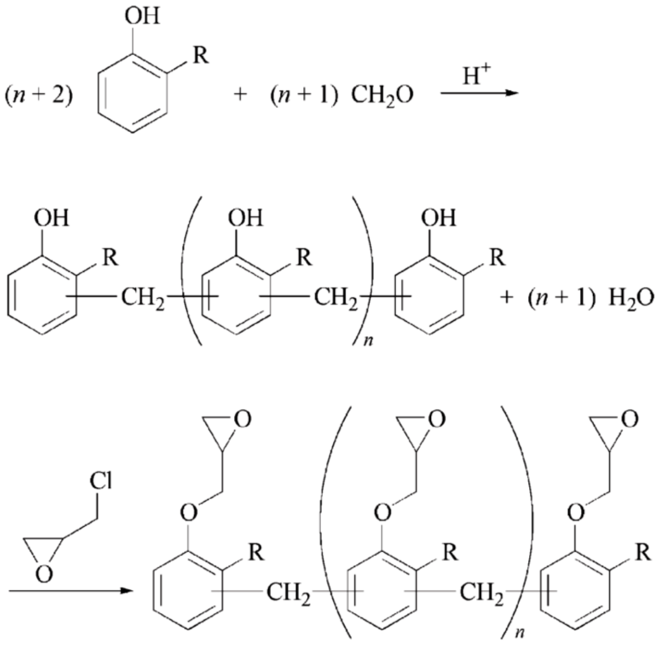

Figure 1.5 Scheme of epoxy phenol novolac's synthesis

Commercial Name	number of repeating units (n)	Epoxide Equivalent Weight	Viscosity, cP	Color, Gardner
EPN 1139[a]	0.2	175	1400[c]	1
EPN 1138[a]	1.6	178	35,000[c]	2
D.E.N. 439[b]	1.8	200	3,000[d]	2

Table 1.1 Typical properties of epoxy phenol novolacs
[a] The Dow Chemical Co.
[b] Huntsman Co.
[c] at 52°C, [d] at 100°C

An increase in the molecular weight of the novolac also induces an increase the functionality of the resin; this can be done by changing the phenol to formaldehyde ratio. The multifunctionality of these resins represents an important trait, since it provides higher cross-linking density, leading to improved chemical and thermal resistance properties over bisphenol A epoxies.

Bisphenol-F epoxy resins

Bisphenol-F (4,4'-dihydroxydiphenylmethane or BPF) is the lowest molecular weight member of the phenol novolacs. It is prepared with a large excess of phenol to formaldehyde, resulting in a mixture of *ortho*-, *para*- (*o,o'*, *o,p'*, and *p,p')* isomers. Through its epoxidation, diglycidyl ether of bisphenol F is obtained.

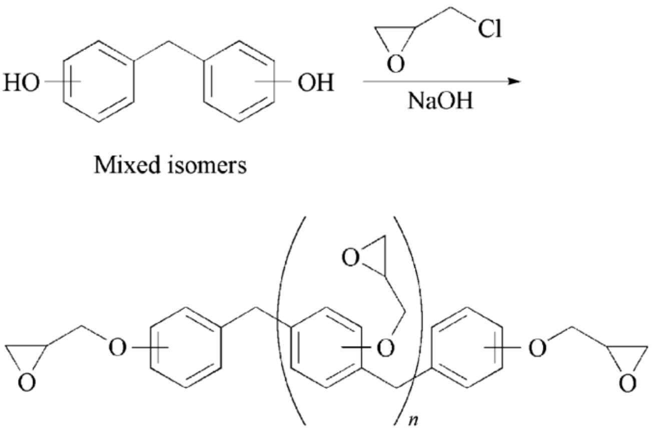

Figure 1.6 Scheme of DGEBF's synthesis

In its unmodified state, this low viscosity liquid resin (4000–6000 cP) exhibits slightly higher functionality than unmodified bisphenol A liquid resins, and as a consequence improved chemical resistance. Bisphenol F resin reduces crystallization, which is often a problem with liquid bisphenol A resins. For comparison, the standard commercial grade, liquid DGEBA's viscosity is about 120–140 Poises at 25°C, while that for a typical BPF liquid resin is about 25–45 Poises. These resins are commonly used in high solids, high build systems such as tank and pipe linings, road and bridge deck toppings, industrial floors, grouts, structural adhesives, coatings, and electrical varnishes.

Cresol novolac epoxy resins (ECN)

The *o*-cresol novolac epoxy resins (ECN) are analogous to phenol novolac resins. They possess better formulated stability and lower moisture adsorption than EPNs, although costs are higher. Typical properties of some commercial cresol novolac epoxy resins are shown in **Tab.** 1.2.

Commercial Name	**Molecular Weight**	**Epoxide Equivalent Weight**	**Softening Point, °C**	**Epoxide Functionality**
ECN 1235	540	200	35	2.7
ECN 1273	1080	225	73	4.8
ECN 1280	1170	229	80	5.1
ECN 1299	1270	235	99	5.4

Table 1.2 Typical properties of epoxy cresol novolac resins[a]
[a] Huntsman Co.

Epoxy cresol novolac resins are widely used as base components in structural molding compounds, castings and laminating systems, high temperature adhesives, tooling and, with increasing demand, high performance electronic. The semiconductor industry in particular has led to significant advances in the efficiency of the manufacturing technologies in reducing impurities content (mainly the ionic content, hydrolysable chlorides, and total chlorides) of ECN resin.

1.2. Non-glycidyl epoxy resins

Although glycidyl-based epoxy resins represent the largest volume of products, other non-glycidyl epoxy resins have gained more interest during recent years. These resins are generally prepared by epoxidizing unsaturated compounds using hydrogen peroxide or peracetic acid. Among them, cycloaliphatic epoxy resins are the one of greater relevance for coating applications.

1.2.1 Cycloaliphatic epoxy resins

Cycloaliphatic epoxy resins are characterized by a saturated ring structure that, in combination with high oxirane content and halogens' absence, gives important properties to coatings and other products made from them, such as high degree of weatherability, excellent electrical properties (dielectric constant, dissipation factor, dielectric breakdown voltage, etc.), high cured T_g. The main commercial cycloaliphatic epoxide is 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (**Fig.** 1.7). This and some other commercial cycloaliphatic epoxides are shown in Table with their physical properties.

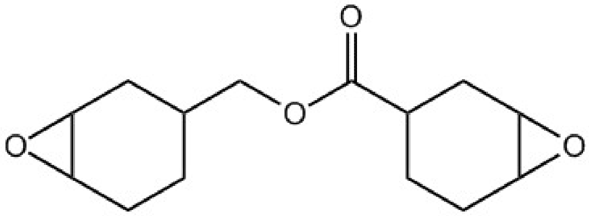

Figure 1.7 Structure of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate

Chemical Name	**Viscosity, cP at 25°C**	**Specific Gravity 25/25°C**	**Epoxide Equivalent Weight**	**Boiling Point, °C (mm Hg)**	**Vapor Pressure 20°C, mm Hg**	**Solidification or Glass Point, °C**
3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate	350-450	1.175	131-143	354 (760)	<0.1	-20
Bis(3,4-epoxycyclohexylmethyl) adipate	550-750	1.15	190-210	258 (10)	<0.1	9
2-(3,4-Epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-m-dioxane	7,000-17,000 at 38°C	1.18	133-154	>250 (760)	<0.01	>0
1-Vinyl-epoxy-3,4-epoxycyclohexane	<15	1.18-1.10	70-74	227 (760)	0.1	-55

Table Commercial cycloaliphatic epoxides and their physical properties

The polymerization mechanism involves a nucleophilic attack on the epoxide ring to form an ether linkage and a hydroxyl group on the ring, which is quite acidic in character and will readily open other cycloaliphatic epoxide groups. Usually polyols are used as flexibilizing agents for the highly cross-linked polymeric network resulting from their polymerization.

They are commonly cured via thermal or UV-initiated cationic cures. In fact, in the coatings industry, cycloaliphatic epoxides represent a major formulating ingredient in cationic, photocurable formulations [4], which usually include polyols, onium-salt photoinitiators, and other ingredients. Ultraviolet radiation causes the onium salts to photolyze and form strong protic acids that cause rapid polymerization of the epoxides as well as their copolymerization with active hydrogen compounds such as polyols.

The largest end uses in order of volume are conformal coatings in the electronics industry, which require water permeability and excellent electrical flammability properties, as well as exterior can and other packaging coatings, paper and metal printing inks overprint varnishes.

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[4] Koleske J. V., “Miscellaneous Materials and Coatings” in *Paint and Coating Testing Manual:15th. ed of the Gardner-Sward Handbook*, West Conshohocken, PA, ASTM International, **2012**

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2. Epoxy resins from renewable sources

The number of activities, involving both academic and industrial actors worldwide, dealing with renewable resources and covering all aspects of macromolecular science and technology has been ever increasing over the past decade. Bio-based thermoplastics have been the first class to benefit from a great number of technological advancements. However, the potential of the same or yet unexplored renewable sources as precursors for bio-based thermosets has become more and more apparent and appealing to researchers. Reports investigating the use of many different sources as precursors for the preparation of epoxy resins and their characteristics have been published with increasing frequency.

In this Section, a description will be made of the main renewable sources that have been studied with the goal of creating epoxy resins and derivates which could potentially replace the predominant petroleum-based epoxy resin currently on the market, DGEBA, more specifically in coating applications. Those renewable sources are vegetable oils; saccharides; phenols and polyphenols; natural resins; lignin and lignin derivatives. For each one of them, the most recent advancements will be highlighted in the corresponding sections, by referring to recent studies and the results that have been reported on the subject.

2.1. Vegetable oils

Vegetable oils are typically extracted from the plant seeds via either mechanical extraction using an oil mill or chemical extraction using a solvent. They mainly consist of a mixture of triglycerides, three fatty acids attached to a glycerol molecule (**Fig**. 2.1), the composition of which can vary much depending on factors such as the type of plant or even its growing conditions.[1],[2] Composition of fatty acids in some commonly used vegetable oils are shown in **Fig.** 2.2

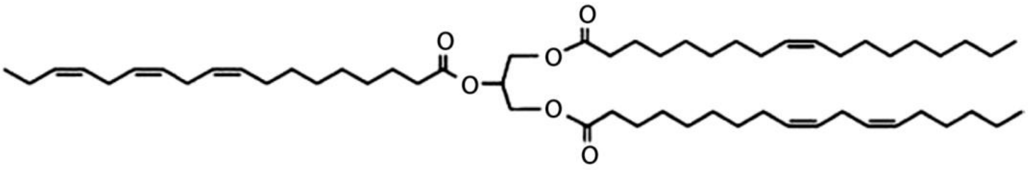
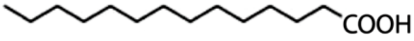
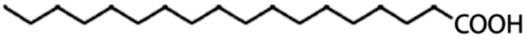
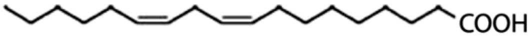
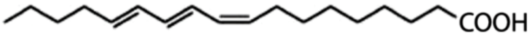
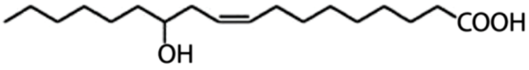
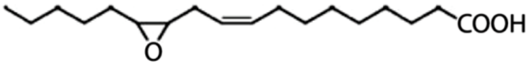


Figure 2.1 The triglyceride structure

As shown in **Tab.** 2.1, different fatty acids present different additional functional groups, which can markedly influence some of the oil's properties. For example, although the composition of fatty acids contained in linseed and castor oil is largely identical, the latter contains rinoleic acid while the former contains oleic acid instead. Rinoleic acid presents an additional hydroxyl group which is absent in oleic acid; this alone increases the lineseed oil's viscosity and suitability for use in lubricating oils and grease applications.[3]

Table 2.1 Structures of important fatty acids

Fatty acid	Formula	Structure
Caprylic	$C_8H_{16}O_2$	
Capric	$C_{10}H_{20}O_2$	
Lauric	$C_{12}H_{24}O_2$	
Myristic	$C_{14}H_{28}O_2$	
Palmitic	$C_{16}H_{32}O_2$	
Palmitoleic	$C_{16}H_{30}O_2$	
Stearic	$C_{18}H_{36}O_2$	
Oleic	$C_{18}H_{34}O_2$	
Linoleic	$C_{18}H_{32}O_2$	
Linolenic	$C_{18}H_{30}O_2$	
α-Eleostearic	$C_{18}H_{30}O_2$	
Ricinolic	$C_{18}H_{34}O_3$	
Vernolic	$C_{18}H_{32}O_3$	

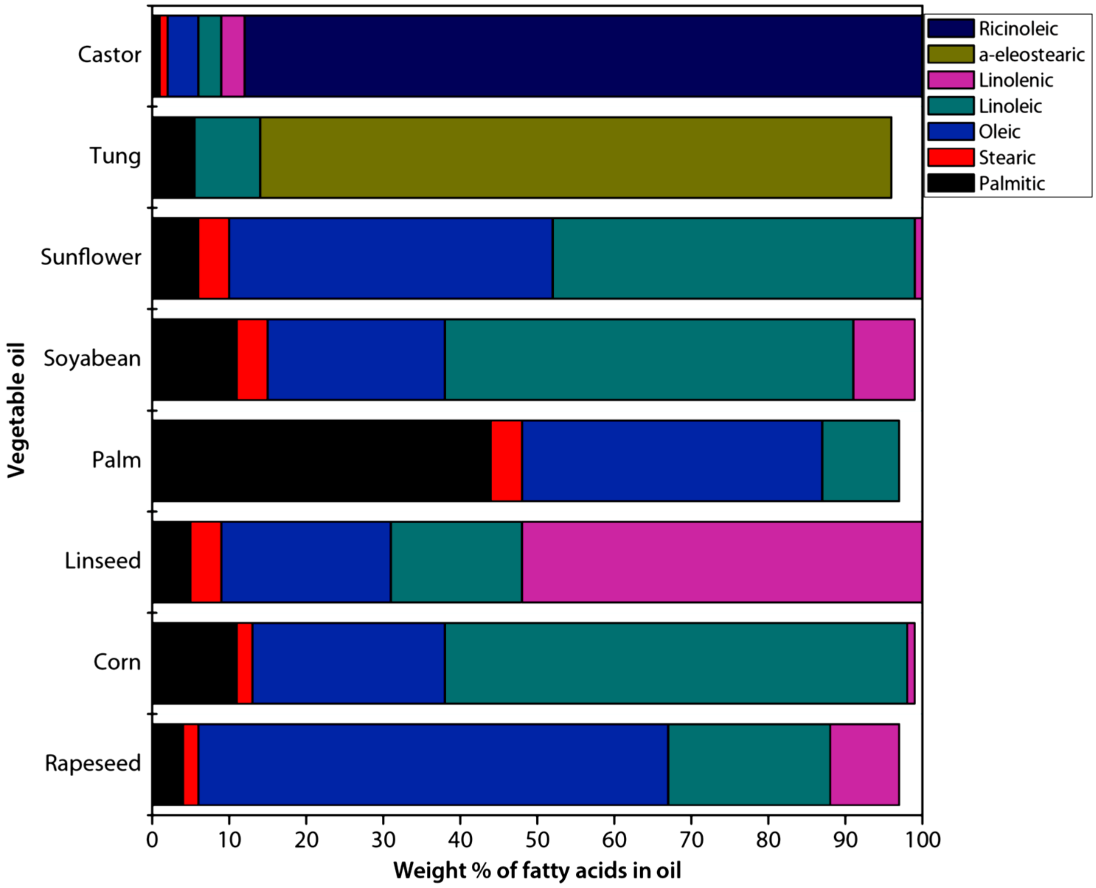


Figure 2.2 Composition of fatty acids in some commonly used vegetable oils

Another aspect that differentiates the various vegetable oils is their degree of unsaturation, which can be expressed through an iodine value. Commonly used oils and their iodine values are shown in **Tab**. 2.2 Oils with iodine values above 150 belong to the class of drying oils; some examples are linseed and tung oils. These have high level of unsaturated fatty acids [4] and can form a tough, elastic film [5], and therefore they are commonly used in paints and enamels. Oils with iodine values between 100-150 belong to the class of semi-drying oils; some examples are soybean, sunflower, and corn oil, all of which are typically used in food applications.[5],[4] Finally, oils with iodine values under 100 fall into the class of nondrying oils; examples are palm, rapeseed and castor oils, all of which are quite greasy and tend to rot.[4],[5]

Table 2.2 Physico-chemical properties of commonly used vegetable oils

Vegetable oils	Kinematic Viscosity at 38-40°C	Flash Point, °C	Saponification Value, (mg·KOH·g^{-1})	Iodine Value, (mg I_2/g Oil)
Castor Oil	293	250	175-187	82-88
Tung Oil	115	>110	188-197	166-170
Sunflower Oil	41	316	188-193	120-134
Soybean Oil	32	317-324	188-195	125-128
Palm Oil	38	314	195-205	50-55
Linseed Oil	30	222	189-196	170-204
Corn Oil	34[a]	332-338	187-193	127-133
Rapeseed Oil	37	275-290	188-192	110-126

As explained in the previous paragraphs, the use of the plant oils and the exact physical and chemical properties are determined by the alkenyl unsaturation and the triglycerides' fatty acid compositions.[1],[2],[4] Most of the global seed oil production (about 75%) is currently destined to food use; the rest is implemented in diverse industrial applications, such as adhesives, inks, plasticizers, cosmetics and coatings.[1] The great number of carbon-carbon double bonds allows for the production of thermoset resins from plant oils, as these bonds provide the starting site for polymerization.[7],[8] In fact, one of the available ways of transforming plant oils to be used in bio-based polymers is the direct polymerization of the fatty acid's double bonds; another path is the transformation of the double bonds into functional groups through which subsequent polymerization can proceed. Alternatively, the oils triglycerides may be transformed into simple fatty acids or diglycerides, which can then act as base monomers for the polymer's synthesis.[6]

2.1.1. Soybean oil

A triglyceride molecule derived from unsaturated acids (such as linoleic acid (55%), oleic acid (22%) and linolenic acid (7%))[9],[10], soybean oil presents nonconjugated C=C double bonds, which can be used as reactive sites and functionalized by acrylation, transesterification, and epoxidation.

Soybean oil and especially its derivatives, epoxidized soybean oil (ESO) and acrylated epoxidized soybean oil (AESO) have been widely applied in the UV curable coatings.[11],[12] Efforts were made to improve the mechanical, thermal and coating properties of acrylated epoxidized soybean oil (AESO) by J. Dai *et al.*; in their study, a UV-curable unsaturated monomer was synthesized from itaconic acid and glycidyl methacrylate (GMA) and was used as a crosslink agent to copolymerize with AESO. The UV-cured coatings that were prepared showed a significant improvement not only in tensile strength and modulus, but also in coating performances in terms of hardness, flexibility, adhesion and solvent resistance.[13]

Approaches toward improving the performance and bio-renewable content of soybean oil based coatings were made by R. Liu *et al.*; a novel kind of soy-based UV-curable branched oligomer was synthesized by chemically introducing cashew nutshell liquid (CNL) onto the epoxidized soybean oil backbone, followed by epoxidization and acrylation.[14]

Finally, the potential of ESO polymeric composites as a way to enhance the performances of multiplex organic coating systems has been investigated by S. Ammar *et al.*, who attempted different loading ratios of epoxy resin and epoxidized soybean oil were introduced into acrylic–silicone polymeric blend with the presence of polyisocyanate (NCO) as the curing agent.[15]

2.1.2. Jatropha oil

With a high oleic (44.7%) and linoleic (32.8%) fatty-acid composition[16] and the presence of toxic chemical constituents such as phorbol ester and curcin[17], which make it nonedible, Jatropha oil has drawn attention from researchers in the preparation of polymeric resin; therefore coating and film properties of Jatropha seed oil-based polyurethane have been studied.[18] More recently, attempts were made to improve Jatropha-oil based epoxy acrylate (AEJO) resin's coating anticorrosion properties by Min M. A. *et al.*, blending the resin with nano zinc oxide to make hybrid nanocomposites.[19] The result was a significant enhancement of corrosion resistance as well as coating performance.

2.1.3. Karanja oil

Karanja trees grow wildly across coastal and fluvial regions of Japan, India, and Sri Lanka [20]; from its seeds can be derived the nonedible Karanja oil. The progress of its industrial use is not, at the present time, as advanced as the one of soybean oil. Nevertheless, some recent developments, such as a more performing method of epoxidation which makes use of peroxy formic acid, are bringing it closer to being a more viable solution.[21] A study by A. Kadam *et al.* reported the production of a biodegradable biobased epoxy resin from karanja oil and its potential to be a bio-based replacement for paper coating and lamination was concluded.[20]

2.1.4. Castor oil

Consisting of ricinoleic acid, which covers 85−90% of the content (see **Fig.** 2.2), and of unsaturated functionality, making it reactive and versatile, castor oil is yet another nonedible oil which is used to form prepolymers or polymers.[22] In fact, epoxidized castor oil (ECO) is being widely used by researchers worldwide as a biobased plasticizer, coating material, prepolymer, lubricant, additive, and adhesive due to its functionalities.[23]-[25] In particular, studies have focused on blends of ECO and diglycidyl ether of bisphenol A (DGEBA)−epoxy resin. Sushanta K. S. *et al.* recently reported the toughening effects of using epoxy methyl ricinoleate (EMR), obtained through the transesterification of ECO, as a less viscous diluent for copolymerization with the DGEBA matrix.[26]

2.2. Saccharides

Also known as carbohydrates, saccharides are compounds containing exclusively carbon, oxygen and hydrogen, with the empirical formula $C_m(H_2O)_n$ (where *m* may be different from *n*); plants and animals use these molecules as their primary source of energy.[27] A categorization of saccharides into four chemical groups can done based on the amount of single sugar molecules that are linked together in their structure: monosaccharides (or single sugars), such as fructose or glucose (**Fig.** 2.3), are carbohydrates with the lowest molecular weight (the general chemical formula of an unmodified monosaccharide is $(C\bullet H_2O)_n$), cannot be hydrolyzed to smaller carbohydrates and constitute the unit for all other saccharides; disaccharides, such as lactose or sucrose, are composed of two sugars; oligosaccharides, such as maltodextrins, raffinose and stachyose, are chains of up to 10 sugars; polysaccharides, such as starch, cellulose, and hemicellulose, are complex, long polymeric chains of carbohydrates.[28]

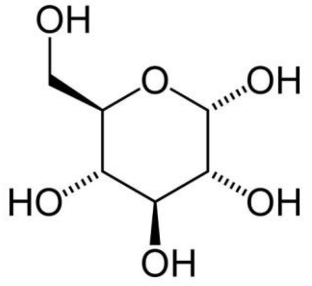


Figure 2.3 Structure of a glucose molecule

Saccharide derivatives have proved useful in multiple fields of research, as hydrogels in biomedical applications and biopolymer adsorbents in wastewater treatment.[29],[30] Saccharide-based epoxy resins have been studied materials for applications in the adhesives, composites, and coatings industries where the requirements for epoxy resins' curing and physical properties are higher.[31] Among these derivatives are isosorbides and furans, which have been used in the attempt of creating alternative epoxy resins with desirable properties.

2.2.1. Isosorbide

Isosorbide is a bicyclic chemical compound, a diol consisting of two furan rings fused together. The preparation from starch is done through multi-step process in which the hydrogenation of glucose is followed by the dehydration of sorbitol. A scheme of that conversion is shown in **Fig.** 2.4 [28],[34] Isosorbide possesses interesting rigidity and chirality; thanks to these characteristics the resulting thermosetting polymer network can be both stiff and thermally stable.[32],[33] Other important aspects are the fact that the isosorbide molecule is nontoxic and water soluble.

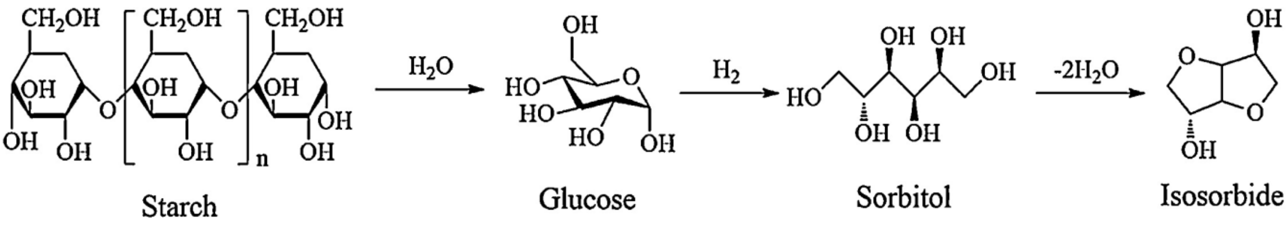


Figure 2.4 Scheme of the conversion of starch into isosorbide

The work to reach the status of commercially viable polymer is still ongoing. In 2015, Lorenzini *et al.* copolymerized isosorbide diglycidyl ether (DGEDAS) with poly(3-hydroxyalkanoate)-diepoxy (PHA-diepoxy) and create a bio-based epoxy network using a photo-polymerization technique. [33] The network showed a decrease in T_g, indicating enhanced flexibility, and an increased weight loss when tested through hydrolytic degradation; this higher degradability is appealing when envisioning the production of a biodegradable thermosetting polymer. Further studies, such as the one by Fertier *et al.* modified a starch derived with (meth)acryloyol chloride to obtain isosorbide di(meth)acrylate; by intense UV irradiation, ISDA-based crosslinked materials were produced and compared to other (meth)acrylated derivative monomers incorporating polycaprolactone and poly(tetramethylene glycol) segments (CAPDA, PEGDA). The comparison showed that ISDA-based materials had a higher glass transition temperature and modulus. However, the researchers also studied UV curing formulations from ISDA/PEGDA and ISDA/CAPDA, increasing the number of biobased monomers.[35]

2.2.2. Furans

Furans are chemical compounds containing five-membered aromatic rings with four carbon atoms and one oxygen. The two most important aspects that draw researchers' interest to furanyl building blocks are their aromaticity and availability. Furanyl chemicals are generally derived from pentose (such as xylose), hexose (such as glucose) or other polysaccharides (**Fig.** 2.5). [36] Furfural (F) and 5-(hydroxymethyl)22-furfural (HMF) are two of such chemicals derived from biomass-based polymeric carbohydrates; they can be transformed into 2,5-furandicarboxylic acid (FDCA) and furfuryl alcohol (FA), both of which are precursors of furan-based green polymers.[36],[37]

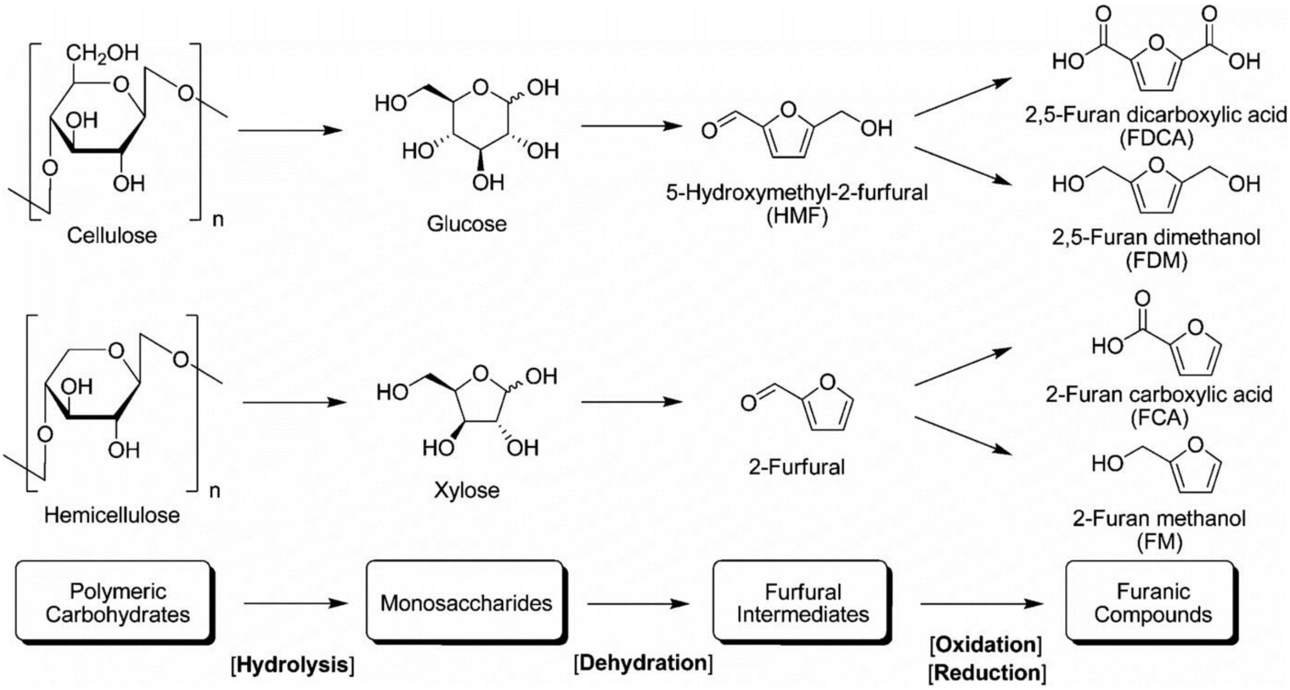


Figure 2.5 Synthesis pathways of furanic compounds prepared from biomass-based polymeric carbohydrates

However, due to their inability to develop networks via crosslinking, these precursors need to undergo further modification in order to become usable furanic based epoxy monomers. The potential of furanyl building blocks to rival against petroleum-based phenyl building blocks has emerged from several studies which have focused on the development of multifunctional furanyl based epoxy resins.

Cho *et al.* [38] reported the preparation of two furan based epoxy monomers: a monofuran diepoxide (2,5-bis[(2-oxiranylmethoxy)methyl]-furan (BOF)), and a bis-furan diepoxide, using 2,5-bis(hydroxymethyl)furan (BHMF); the group investigated their applicability as adhesives and conducted shear tests on polycarbonate plates that had been bonded with the synthetized compounds through cationic photo-curing. The bonds' tensile-shear strength was increased in the case of both systems compared to the petroleum-based phenyl analogue.

Palmese *et al.* [39] further reported that 2,5-bis[(2-oxiranylmethoxy)methyl]-furan (BOF) shows good miscibility with DGEBA and is able to improve its T_g, although BOF thermosets samples would show lower T_g than DGEBA-based ones, due to the methylene groups between the aromatic ring and the glycidyloxy group.

2.3. Polyphenols and Phenols

Natural polyphenols are a class of organic chemicals containing multiple phenol structural units. They come in a wide variety of origins, biological functions and complex chemical structures.[43] The broadest organization of this class of compounds divides them into two groups: flavonoids and nonflavonoids. The flavonoids group comprises compounds synthetized by plants, consisting of two phenyl rings connected by a heterocyclic ring; the nonflavanoids group comprises compounds that do not have this particular structure and can be subdivided into many groups, of which phenolic acids, stiblins, phenolic alcohols, and lignans are the main ones.[40]

Phenolic compounds have shown the ability to enhance the chemical and temperature resistance of epoxy resins, as well as provide better structural stability.[42] In the following paragraphs the attention is brought to the development of epoxy resins from two phenol derivatives in particular, namely tannins and cardanol.

2.3.1. Tannins

Tannins belong to the nonflavanoids group of phenolic compounds. They can be categorized into condensed and hydrolysable tannins, both of which are used for the preparation of epoxy monomers, though the reactivity of condensed tannins is usually higher than that of hydrolysable ones.[44],[45] These compounds are generally extracted from plant components such as trees' bark, as well as leaves and nuts [46], and have been of interest for composite applications. In 2017, Udangshree B. and Niranjan K. have synthesized a hyperbranched epoxy resin using bio-based tannic acid (**Fig.** 2.6) as a branch generating moiety. This resin served as a matrix in the production of a nanocomposite with different doses of reduced graphene oxide. [48]

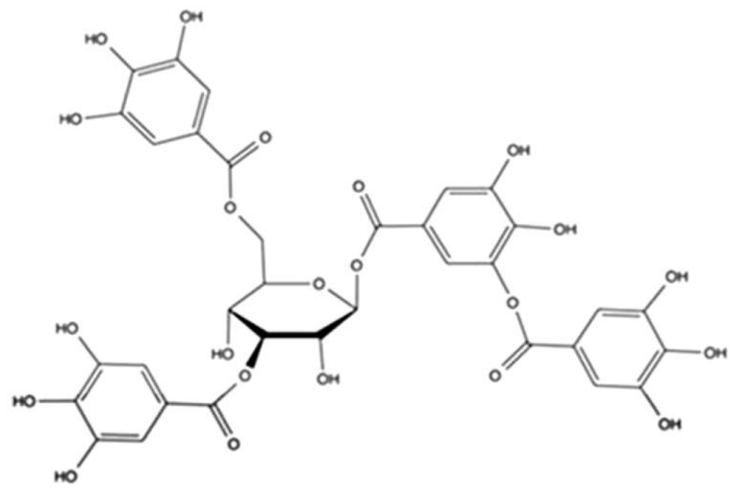


Figure 2.6 Tannic acid

Catechin is a tannin-derivative that can be found in many fruits, herbs, vegetables, algae, beverages, and confectionary items; it has been much studied for use in epoxy resins.[45] In 2013 Benyaha *et al.* provided some comparisons between the polymer formation of epoxidized catechin extracted from green tea and bisphenol-A based resin systems; the study of thermal-mechanical properties highlighted how the first system possessed higher storage moduli compared to the latter.[49] However, the same also exhibited a reduced T_g; this result was attributed to functional groups which are present in green tea extract catechin but are absent in straight catechin-based resins.[49] Another example is a 2015 study by Basnet *et al.* which reported on the epoxidation and curing of catechin from green tea.[50] The curing agent was lignin extracted from eucalyptus, soluble in methanol, and was used to also cure BPA-based epoxy resins. The results showed that the catechin-based resin could reach T_g values comparable to that of the petroleum-based counterpart, as well as similar heat resistant temperatures.[50]

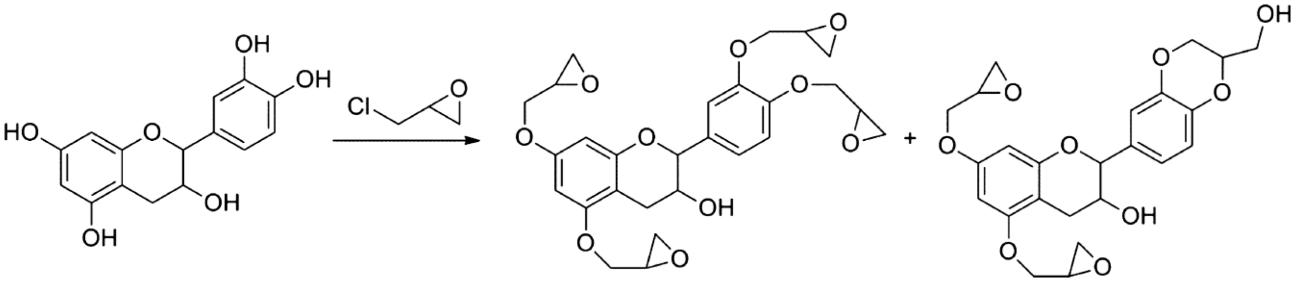


Figure 2.7 Epoxy Monomer (Glycidyl ether of Catechin) and Byproduct from Catechin Epoxidation

2.3.2. Cardanol

Cardanol is a phenolic lipid, more precisely it is a mixture of four *m*-alkylphenols, each presenting an aliphatic chain with different degrees of unsaturation (**Fig.** 2.8). It is obtained from anacardic acid, the main component of cashew nut shell liquid (CNSL) and a byproduct of cashew nut processing.[51]

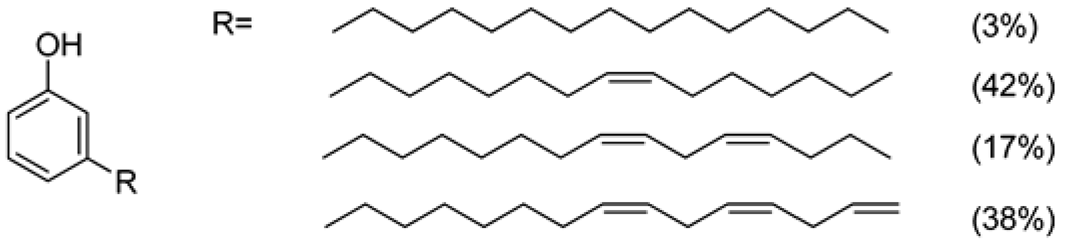


Figure 2.8 Structure of cardanol

Despite its large production, given the corresponding large amount of yearly cashew crops (about 2.7 million tons/year) [52], only a fraction of it finds use in industrial fields. Nevertheless, studies have been conducted to assess its applicability in various polymer applications, including bio-based epoxy resins.[51]-[53]

When Jaillet *et al.* reported on the curing of epoxidized cardanol resins and the polymeric networks they had obtained, results showed that the resin's thermomechanical properties were still insufficient in order to replace bisphenol A-based materials, specifically that T_g was too low and crosslinking densities were very scarce compared to DGEBA analogues.[55]

Following this trail, Darroman *et al.* proposed the use of bio-based saccharides, specifically sorbitol and isosorbide, as epoxidized reactants in the cardanol-based system, with the goal of increasing the durability of the resulting material.[51] Epoxidized sorbitol was found to be particularly able to increase both the T_g and the hardness of the cured polymer at a lower weight ratio, whereas epoxidized isosorbide would need to be added in higher quantities.[51] The study did provide an insight on a pathway to produce cardanol blended resins with acceptable thermomechanical properties.

2.4. Natural Resins

A variety of plants and trees (particularly, pine and conifer trees) produce natural resins in the form of vicious liquids and secrete them through either the bark, the buds or the flowers. [56] Their composition is mostly made of terpenes; some resins contain high proportion of resinic acids. Fresh resin may also be heated, causing the evaporation of the volatile fraction of terpene-based compounds called turpentine, thus obtaining a solid residue called rosin.[57] The focus of the following paragraphs will be on the studies that have involved the use of terpenes and rosin as precursors for bio-based epoxy resins.

2.4.1 Terpenes

Terpenes are a large class of organic compounds that plants (particularly conifers) produce and can therefore be derived from their seeds, leaves, stems and roots. They are based on isoprene units (2-methyl-1,3-butadiene, **Fig.** 2.9) and are characterized by strong, generally pleasant odor and taste, which is the reason why they also find large use in fragrances and flavor industries. [57] Terpenes are classifiable based on the number of isoprene units (hemiterpenes are composed of a single unit, monoterpenes consist of two, sesquiterpenes have three, and so forth) and on their structure (acyclic, monocyclic, bicyclic, etc.)[58]

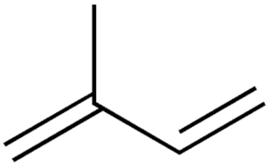


Figure 2.9 Structure of isoprene

A 2014 study by Wu *et al.*[59] reported the production of a polyurethane/epoxy resin composite coating, which had the goal of combining the flexibility and tenacity of the polyurethane with the heat resistance and rigidity of the epoxy resin. A terpene-maleic ester-type epoxy resin (TME, **Fig.** 2.10) was synthetized from turpentine and constituted the base material; an anionic polyol was prepared from it and crosslinked with polyisocyanate. The study led to the production of a flexible and transparent film, with good thermal stability and good antifouling properties, thus qualifying as a potential alternative for current coatings.

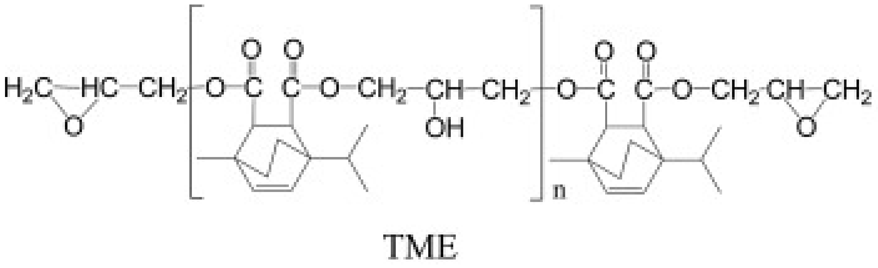


Figure 2.10 Chemical structure of Terpene-maleic ester type epoxy resin

The properties and potential of a waterborne dispersion of TME (WTME) as bio-based replacements of BPA-based epoxy resins had already been investigated by the same group. Unfortunately, results showed that the crosslinked networks' mechanical properties would fall short of target values. [60] The proposed solution was the make of a thermoset nanocomposite through the incorporation of cellulose nanowhiskers (CNWs) within the WTMEs matrix. The combination proved successful, as storage modulus, Young's modulus and tensile strength of the networks all saw an increase.

Limonene is another building block that has been used in the production of general terpene-based epoxy resin. Starting from naphtol and limonene, a hybrid epoxy resin (glycidyl ether of a limonene alkylated naphtol-formaldehyde resin) was reportedly synthetized and cured back in 2004.[61] The crosslinked polymer showed improved T_g and thermal stability compared to DGEBA resins, indicating potential in becoming a bio-based replacement. Even so, later and more recent research with limonene has aimed at improving the control over the crosslinking of terpene-based precursors used in the production process of thermosets for coatings applications.[62],[63]

2.4.2. Rosin

As previously mentioned, rosin is derived from evaporating the volatile fraction of turpene-based compounds, which are abundantly present in trees such as pines and conifers. When these trees' matter is processed in pulp and papermaking industries, the waste becomes a great source of biomass from which rosin can be obtained as a byproduct.[64]

The substance is composed of a complex mixture of neutral materials and rosin acids of high molecular weight (mainly abietic acid and its isomers, **Fig.** 2.11). [65],[66] In the past, rosin has been widely used in applications such as inks, coatings, soaps, and adhesives; the rigidity of the phenanthrene ring and the substance abundance have sparked increasing interest in the use of rosin and its derivatives as additional feedstock for polymer synthesis.[67] Some recent studies are an example of this trend.

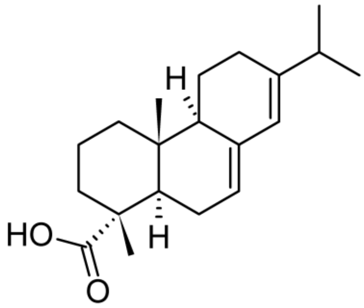


Figure 2.11 Structure of abietic acid

In 2013, a rosinic acid oligomer polygral was epoxidized and blended with DGEBA to function as coreactant. The addition proved to decrease the cured polymer's T_g by almost 30°C and the storage modulus by $6 \cdot 10^8$ MPa when reaching 60 wt%. Nevertheless, T_g would still be higher than that of systems derived from plant oils reported in previous studies and it would also be comparable to that of DGEBA materials used in liquid-solution products. [69]

A 2015 study reported on the epoxidation and curing of rosin derivatives with a rosin-based crosslinker; the resulting polymers exhibited comparable storage moduli and significantly higher T_g than those of commercial BPA-based resins.[68]

2.5. Lignin and lignin derivatives

Lignocellulose is plant biomass representing the most abundant natural polymer on the planet. It consists of three components: two carbohydrate polymers, cellulose and hemicellulose, accounting for 30-50 and 15-30% of lignocellulose dry mass respectively; and a third non-carbohydrate phenolic polymer, lignin (**Fig.** 2.12). It mainly imparts strength and rigidity to the plant's cell walls. [70],[71]

When dry land plant biomass is processed, for example through paper mills in papermaking industry, the three constituents of lignocellulose are separated and destined to different uses. [72] Lignin's primary use is that of low-grade fuel [70]; in fact, as of 2010, 50 million metric tons of lignin have been extracted yearly and about 98% of it has been burnt for energy, while only the small remaining fraction has been used for dispersing or binding agents, or low-value products of similar kind. [73]

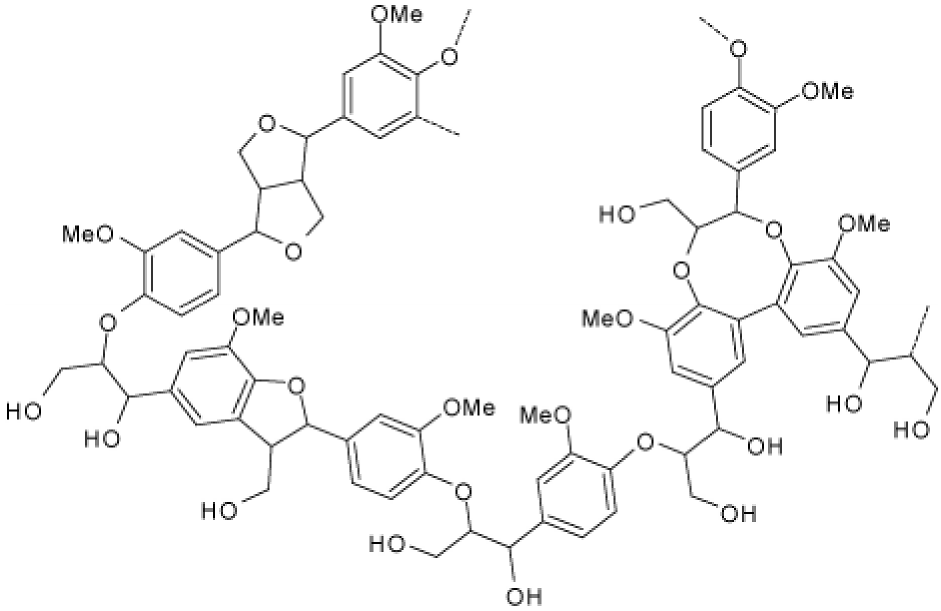


Figure 2.12 The most common types of linkages within the lignin molecule

There is an increasing awareness about the untapped potential for the use of such an abundant and renewable resource, especially from chemical and polymer industries. [71] In fact, much research is being done to develop better bioengineering methods for lignin's recovery and chemical transformation under appropriate biorefinery conditions, in order to isolate the resource and use it for the production of high-value polymers and foams. [74] The separation and processing methods largely determine the uses and products that can be obtained from lignin. [73] The kraft process is a well established, currently dominant technology of pulp and paper industry. This process uses aqueous solutions of sodium sulfide and sodium hydroxide to separate the wood chip's lignin from the cellulose. [75] The organosolv process is a different, more environmentally friendly method, which uses an organic solvent to achieve the separation.[75] In both cases, the resulting lignin is a suitable starting material for the production of activated carbon and carbon fibers, phenolic resins, phenol derivatives and vanillin. [73]

The natural feedstock also plays a role, although there is a vast choice among the dry land plants from which lignin can be obtained and utilized in polymer applications. Asada *et al.* [76] reported on the extraction of low molecular weight lignin from three different biomasses (cedar, eucalyptus and bamboo) and its epoxidation; the lignin-derived epoxy resins were further cured with biomass-derived lignin, in order to produce almost fully lignin-based polymers. When comparing the three resulting networks with commercial DGEBA, the group found that these exhibited slightly lower thermal decomposition temperatures, yet good enough heat-stability properties to perform well in electronics applications. [76]

2.5.1. Vanillin

Vanillin (4-hydroxy-3-methoxybenzaldehyde, **Fig.** 2.13) is a monoaromatic phenolic aldehyde, commonly used as flavour and aroma agent in the food industry, therefore it is, of course, nontoxic; it is a lignin derivative currently available for commercial production which has been recently explored as a platform chemical for polymer synthesis.

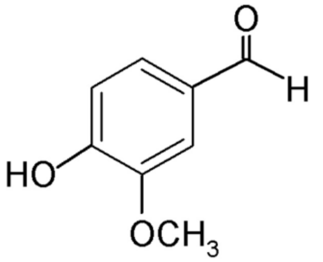


Figure 2.13 Chemical structure of vanillin

Fache *et al.* [77] were able to adapt an existing synthesis strategy used for BPA-based resins for the development of bio-based epoxy thermosets from vanillin-derived oligomers. The group synthesized diglycidyl ether of methoxyhydroquinone from vanillin and crosslinked it with a diamine agent (IPDA). [78] The thermal properties of the epoxy thermoset, such as the T_gs, were high (between 80 and 110°C) in comparison to bio-based thermosets found in literature, showing much potential. However, the necessity of future work in order to better investigate other mechanical properties was concluded. [77]

A more recent study explored the possibility of producing readily degradable thermosets using this renewable resource. Yuan W. *et al.* introduced two epoxy groups onto erythritol acetalized vanillin through the reaction with epichlorohydrin. The fully bio-based monomers were cured, resulting in a resin with high glass transition temperature, hardness and modulus. The dicyclo diacetal structure that becomes part of the epoxy network imparts the desired degradability in acidic solutions. [79]

2.5.2. Eugenol

Eugenol (1-allyl-3-methoxy-4-hydroxybenzene, **Fig.** 2.14) is a natural phenol, a flavoring component of herbs with antioxidant and antimicrobial properties. It is the major compound of clove oil, from which it is currently mainly obtained. However, eugenol can also be derived from lignin through depolymerization [80]; this is one of the reasons why it has drawn interest as a candidate aromatic building block for the synthesis of novel biobased monomers.

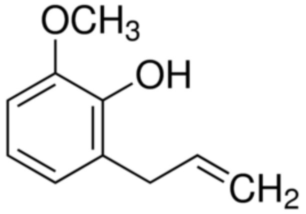


Figure 2.14 Chemical structure of eugenol

A good number of studies have looked into the preparation of epoxy derivatives from eugenol. Notably, in 2015, Zhao and Abu-Omar [81] reported the production of epoxy nanocomposites starting from dihydroeugenol (DHE), a lignin-derived compound, which was modified and epoxidized; the introduction of nanoclay significantly helped improve the thermal stability of the polymers. The study mainly provided insight on an effective route for the fabrication of a high-performance polymer using building blocks from direct catalytic lignin conversion.

Soon after, Wan *et al.* [82] synthetized a novel bio-based epoxy resin with high net bio-based content (70.2%); following its curing with diamine agent, the resulting network exhibited high rigidity and low flammability, with chain motions at the glassy state and high-temperature charring ability.[13]

Finally, a 2019 study by Jiang *et al.* [83] focused on reducing the estrogenic activity and further increasing the biocontent of the resin. The group used eugenol as the starting material for the synthesis of a renewable bisepoxide monomer, 2,2'-diglycidyl ether-3,3'-dimethoxy-5,5'-diallydiphenylmethane (BEF-EP); the estrogenic activity manifested by the eugenol-based bisphenol monomer was extremely lower than that of commercial bisphenols (BPA and BPF).[83] Furthermore, vanillin was used for the preparation of the hardener; the effect on the epoxy material was that of enhancing the crosslinking density and improving its rigidity to a larger extent in comparison to conventional and renewable hardener.[83]

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3. Reinforcements from renewable sources

In **Section 1**, epoxy resins have been shown to generally manifest a remarkable combination of properties and characteristics. However, specific necessities of various fields of application and product requirements motivated industrial research for ways to further improve one or more of said properties. For example, epoxy resins show typical mechanical behavior of highly cross-linked thermosets, namely rigidity, brittleness and relatively poor resistance to crack initiation and growth; this limitation to their use in applications such as structural materials has led to numerous attempts at improving their physical properties through toughening or strengthening agents.

The appropriate dispersion of thermoplastic components such as poly(acrylonitrile-co-butadiene-co-styrene) (ABS), poly(ether sulfones) (PES), poly(etherimides) (PEI), polysulfones (PSF), poly(ether ketone) (PEK), and polyimides (PI), into the epoxy matrix results in thermoplastic-modified epoxy systems with improved toughness. [1]-[4] The addition of inorganic particles can reportedly increase the modulus, hardness, and fracture toughness of the resulting epoxy/inorganic composite. [5]-[8] Low concentrations of surface-treated clays also enhance the resins' mechanical strength; furthermore, epoxy/clay nanocomposites exhibit marked improvements of other important properties, such as thermal stability, permeability, and flammability, compared to pristine epoxy matrices and traditional micro/macro composites.[9]-[11]

However, the concern for the reinforcing agent's source with regards to their positive or negative environmental impact has only become a more prominent aspect to take into consideration in more recent years. This led to the important development of biocomposites which use natural fibers such as jute, Kenaf, or Ramie as reinforcement, often in combination with more than one type of reinforcement, both of inorganic and organic materials, to form what is known as a hybrid composite. For example, natural fibers such as jute and coir have been combined with polypropylene, viscose rayon, as well as high performance fibers such as carbon and Kevlar.[12]

Howbeit, the aforementioned kind of fiber reinforcement, though derived from renewable sources such as biowaste, does not find application in the field that is the focus of this work, namely coatings and alike. The main reason is of course the inappropriate dimensions of the reinforcing agent itself. In this chapter, other, more fitting candidates will be presented. From an analysis of current literature, it emerges that eggshell, cellulose nanocrystals and carbon products (activated carbon, graphene and graphene derivatives) are reinforcements derived from renewable sources which show the greatest potential overall for achieving coating products with superior properties.

3.1. Eggshell

Eggshells are natural composite bioceramics. They contain, for the most part (95%), inorganic components and a minor fraction (5%) of organic components. Calcium carbonate represents about 96 wt% of total inorganic components, the remaining include mainly magnesium oxide and, to a lesser extent, oxides of sulfur, phosphorus, aluminum, potassium, chlorine, strontium, and silicon (a representative chemical composition analysis of different crude eggshells is shown in **Tab.** 3.1).[59] The constituents of the organic fraction are materials such as type X collagen, sulphated polysaccharides and other proteins.[13],[14]

Table 3.1 Chemical composition analysis of crude eggshells

Compounds	Raw chicken eggshells (wt%)	Raw duck eggshells (wt%)	Raw bird eggshells (wt%)
$CaCO_3$	96.46	96.35	96.23
MgO	-	0.10	1.12
SiO_2	-	0.01	0.04
P_2O_5	0.80	0.46	1.19
SO_3	1.79	0.96	0.98
Cl	-	-	0.6
ZrO_2	-	0.02	-
K_2O	0.21	0.20	0.11
SrO	779 ppm	0.0.2	0.02
Na_2O	-	<0.1	0.23

The eggshell represents an industrial byproduct that is produced in very large quantities. The hatchery industry for both egg and poultry meat production is where the quantity of eggshell to be disposed of becomes most considerable.[15] In recent years, the necessity of finding alternatives to the landfill disposal of biowaste has met the search by the polymeric industry for potential substitutes for existing additives. Widely available, inexpensive, eco-friendly chicken eggshell has become a promising candidate as reinforcing agent in polymers; in fact, it has already been used in this way, as reported by many studies.[16]-[19]

Further research by Boronat *et al.*[14] aimed at imparting the same improvements in the mechanical characteristics (stiffness, hardness, flexural and tensile modulus) exhibited by petroleum based polymeric matrix to a biobased polymer, namely polyethylene obtained from sugar cane. The study concluded that, though there be an increase in viscosity, with the proper attention given to process conditions, eggshell could be used as filler in order to obtain a new environmentally friendly material.

However, the group also highlighted how the behavior of filled polymers is a complex issue since the composite is influenced by many factors such as filler characteristics, filler content and interfacial adhesion. In the case of their study, coupling agents were tested in order to achieve a greater interaction between the hydrophobic polyethylene matrix and the hydrophilic eggshell filler. Their role was to provide a hydrophobic surface to the filler, thus increasing the adhesion.[20]

The same issue was addressed by Shah *et al.*[20], coupled with the necessity of reducing agglomeration and improving dispersion of the filler in the matrix, by treating the eggshell particles with stearic acid. The study highlighted agglomeration as another critical factor when eggshell particles are reduced in size (particularly in the production of composites for coating applications) and the loading is increased in order to reach higher mechanical characteristics. Therefore, it investigated the use of stearic acid for the treatment of eggshell particles to use as reinforcement in a DGEBA epoxy matrix; it was found successful with loadings as high as 20 wt%.[20]

Finally, eggshell proved to have the potential to act as intumescent flame-retardant in acrylic coatings. A study by Yew *et al.*[13] produced 5 formulations, mixing three halogen-free flame-retardant additives (phase II ammoniumpolyphosphate, APP, the acid source; pentaerythritol, PER, as the carbon source; melamine, MEL, the blowing agent) with acrylic resin and different flame-retardant fillers. The addition of 5.0 wt% and 2.5 wt% eggshell bio-filler into 2 of the 5 formulations, successfully improved fire protection due to char formation, with better morphology, height and structure of the protecting shield.[13]

3.2. Cellulose nanocrystal

As the most abundant polymeric raw material on earth, cellulose represents a fascinating and sustainable feedstock. Its annual production is estimated to be between 10^{10} and 10^{11} t, of which only a portion (6×10^9 t) is utilized by a number of industrial fields such as textile, chemical, papers and material industries.[21]

Cellulose's basic structure consists of repeating β (1,4)-bound D-glucopyranosyl units (anhydroglucose unit, AGU) disposed in the $^4C_1$-chain configuration, where every monomer unit is corkscrewed at 180° compared to its neighbors (**Fig.** 3.2) [60]. The resulting cellobiose units are linked together, thus producing a crystalline structure of cellulose known as elementary fibrils. Bundles of these fibrils produce micro-fibrils, which in turn form macro-fibrils.[22] Native cellulose presents both disordered (amorphous) and ordered (crystalline) domains (**Fig.** 3.3) [61]. Its degree of crystallinity can vary between 40 to 70% depending on the natural source and the extraction procedure.

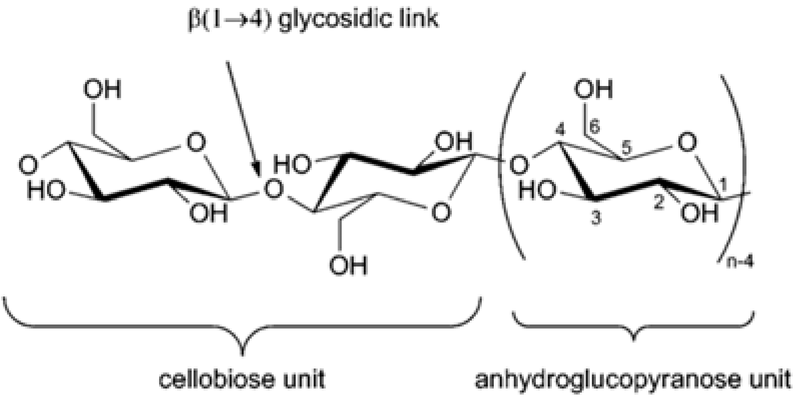

Figure 3.2 Cellulose chain showing the anhydroglucose unit and glycosidic link

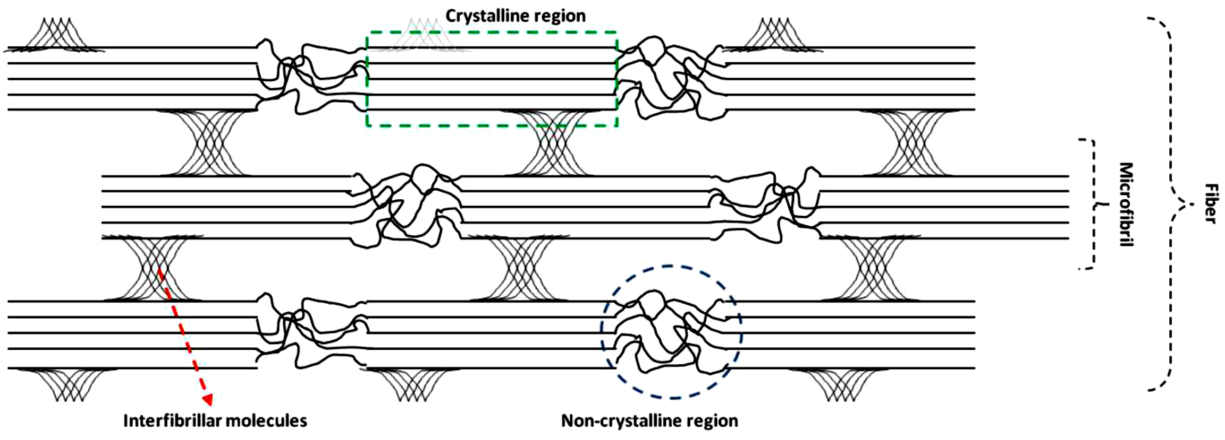

Figure 3.3 Part of a cellulose fiber with crytalline and amorphous regions

Plant sources alone cover a great number of possibilities, spanning from the wood of forest resources (soft wood, hard wood, and recycled newspaper and magazine fiber) to non-wood lignocellulose (e.g., sisal, coir, hemp, flax, jute, ramie, kenaf, cotton, and algae) to agricultural residues/by-products (e.g., corncob, risk husk, sugarcane bagasse, banana, and crop straw).[23]
The preparation of nanocellulose from cellulose can typically be divided into two main stages: the first stage involves feedstocks' pretreatments necessary to obtain pure cellulose; based on specific pretreatment methods, extractives (monomers, dimers and polymers of fat, free sugar, tannins, resin, rosin, flavonoids, terpenoids, terpene, waxes, fatty acids, etc.), hemicelluloses and lignin are partially or totally eliminated from the feedstocks; the second stage is usually dedicated to the production of cellulose nanocrystals, via the elimination of amorphous domains form pristine cellulose, giving rise to the production of cellulose nanocrystals (CNCs).[24] Cellulose nanocrystals are usually produced by acid hydrolysis, consist of cylindrical, elongated, less flexible, and rod like nanoparticles with 4–70 nm in width, 100–6,000 nm in length, and 54–88% crystallinity index.[25]

The employment of CNCs as reinforcing agent, particularly in polymers, is the object of intense research in the composite field. This material has gained visibility as an interesting nanofiller due to its chemical structure (specifically the abundance of -OH groups, which imparts great reactivity), high specific surface area (given the nanometric size and aspect ratio), mechanical, thermal and optical properties, even when incorporated at low concentrations.[26] The range of polymer matrixes, both thermoplastic polymers and thermosets, that have been reinforced with CNCs is wide. The aim in combining CNCs and thermosets (such as unsaturated polyesters, some polyurethanes, epoxy and phenolic resins) in nanocomposites is to couple useful features from each compound in a synergetic manner. These nanofillers provide better strength and stiffness along with resistance to corrosion;[27] moreover, they appear to be beneficial in reducing the internal stresses introduced during curing process, have proven to increase the cross-linking density and can impart nanocomposites with significantly improved toughness.

However, the full potential performance of CNCs as nano-building blocks may only be unlocked through surface modification. As previously mentioned, CNCs surfaces expose a high density of –OH groups, which possess high chemical reactivity. It is through these groups that the crystal's surface can be readily modified by various techniques, which are here broadly categorized into five distinct strategies: adsorption of molecules onto the particles surface, introduction of electrostatic charges, bacterial modification, chemical modifications and physical modifications.[28] Surface modification can influence the homogeneity of the dispersion of the filler within the matrix, a key factor in improving the final properties of the system; it also potentially eliminates the need for a solvent and dispersant, easing the process and reducing volatile organic compounds emissions.
Peng *et al.*[29] reported how acetyl grafted CNCs improved Young's modulus, tensile strength, and work of fracture of neat DGEBA epoxy. More notably, Yue *et al.*[30] have pointed out that the use of CNCs functionalized with an amino trimethoxy silane allowed for an additional reaction with a biobased epoxy resin derived from diphenolic acid, enabling physical interlocking points in the cured epoxy matrix restricting chain mobility, significantly enhancing storage modulus and glass transition.

3.3. Carbon products

3.3.1. Activated carbon

Activated carbon (AC) is a carbonaceous solid product, specifically a graphite-based material in which networks of three-dimensional (3D) arrangement of graphene layers form highly developed porous structures. The material is mainly characterized by a large number of micropores (smaller than 2 nm), which contributes to its high specific surface area, along with physical and chemical stability.[31]

Commercially available activated carbon is produced from natural materials such as wood or coal, the processing of which still results highly expensive. Alternatively, cheaper, renewable resources such as forestry wastes, agricultural residues, and sewage sludge are available in large quantities and therefore they are considered as important precursors.[32]

In fact, numerous studies on low-cost agricultural solid waste-based activated carbon reported its production from agricultural waste such as coconut shell, bamboo, jute fiber, cassava peel, rice husks, plum kernels, fruit stones, palm tree cobs, bagasse, nutshells, date pits, olive stones, peach stones, oil palm shell, corn shell, rattan sawdust, orange peel carbon, and vegetable fiber.[33]

Activated carbons, either in granular or powdered form, are widely used as effective industrial absorbents for the removal pollutants from gases and liquids. Yet, the effects of its use as reinforcing material within epoxy matrices have been investigated, yielding some fairly interesting results. In a study by Wang and Su [34] it was found that, after an initial improvement, the comprehensive mechanical performances of AC/epoxy composites (tensile strength, elongation at break, impact strength) would just decrease when exceeding a small amount of loading (0.3%wt). This suggested that the physical interaction between the resin and filler due to the large specific surface area and porous structure was not enough.

In an attempt to further improve the reinforcing effect of activated carbon, a simple, efficient, economic, and eco-friendly treatment with aqueous ammonia solution was performed. The results indicated that the introduction of nitrogen groups could contribute to a better mechanical performance through the reaction between the formed ammonium carboxylate species and the epoxy group of AC during the curing process.

Vaithilingam *et al.* [35] showed another example of the use of amine functionalized activated carbon in two similar studies. In the first study, carbon derived from cashew nut shell was used as a reinforcing agent in a eugenol benzoxazine-DGEBA blend matrix, while in the second one, the carbon was derived from palm flower and used as a reinforcing agent in a cardanol benzoxazine-DGEBA blend matrix. In both studies the composites exhibited higher values of glass transition temperature and improved anticorrosion properties, showing value as coating materials for high-performance applications.

3.3.2. Graphene and graphene derivatives

Unanimously called the wonder material of 21st century, much like plastic in the 20th century, since its discovery graphene has in many ways revolutionized every sector from energy, to health, to environment.

Structurally a single-atom thick sheet of sp2 hybridized carbon atoms arranged in a honeycomb lattice (**Fig.** 3.4)[62], this 2D material exhibits outstanding properties such as high surface area, strong mechanical strength, good chemical stability and high thermal and electrical conductivity.[36]-[39] These valuable properties led researchers to study, among numerous other fields of applications, the effects of graphene as nanofiller in polymer nanocomposites. When used to modify epoxy coatings, the resulting nanocomposites were found again and again to have superior anticorrosion behavior, especially for the protection of metal surfaces in marine environment.[40] Not only that, but the nanofiller greatly improved mechanical characteristics such as Young's modulus and erosion resistance, as well as the coatings' thermal stability.[41],[42]

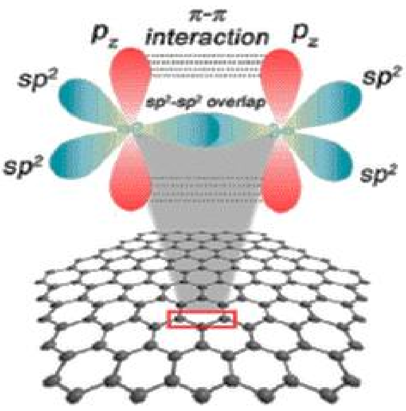

Figure 3.4 Structure of graphene with sp2-hybridized carbon atoms

However, it was also pointed out that pristine graphene presents some challenging aspects such as poor solubility [43] and agglomeration in solution due to van der Waals interactions.[44] A poor distribution of the nanomaterial negatively influences the potential positive effects on the resulting nanocomposite. Graphene derivatives such as graphene oxide (GO), reduced graphene oxide (rGO) and graphene quantum dots (GQDs) have offered a way around those challenges thanks to their ideal material properties and dispersibility in polymer matrices.

Graphene oxide (**Fig.** 3.5) has a similar hexagonal carbon structure to graphene but also contains hydroxyl (OH), carbonyl (CO), alkoxy (COC), carboxylic acid (COOH) and other oxygen-based functional groups; reduced graphene oxide is the form of GO that is processed by chemical, thermal and other methods in order to reduce the oxygen content and repair the defects in GO; graphene quantum dots represent another class of graphene derivative that has recently emerged and are essentially graphene sheets of <100 nm in their lateral dimension, thus taking advantage of the unique edge effects of graphene.[45]

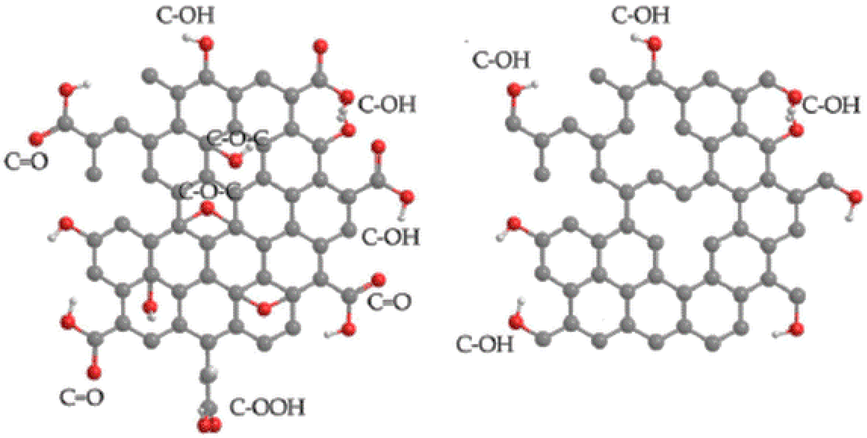

Figure 3.5 Structure of graphene oxide (left) and reduced graphene oxide (right)

Generally, the two fundamental sources for the preparation of graphene are graphite and organic molecules, in the form of hydrocarbons in gas or liquid phase. However, these non-renewable resources represent a sustainability issue that is being addressed over the past few years, during which biomass feedstocks have become popular benign precursors for carbon-based materials.

Lignocellulose has been used as a source of graphene and graphene-like nanostructures by implementing a green chemistry top-down approach.[46] Ruan *et al.* [47] grew graphene from food, insects, and waste by chemical vapor deposition (CVD). Researchers were able to synthesize well-aligned graphene layers from seaweed, nori biomass, *Pinus kesiya* sawdust, pine wood sawdust, poultry litter and wastewater biosolids, bacterial cellulose, biomass residues of the olive oil industry, soybean oil precursor, coconut shell, natural chitosan and glucose.[48]-[58]

All the mentioned various biomass sources are inexpensive and readily obtainable in high quantity and quality, in addition with being available in abundant morphological and structural varieties. Despite the fact that the synthesis of graphene, graphene-oxide, reduced graphene oxide and all their doped analogues from biomass could result in unwanted impurities (along with the desired doping), the conversion of waste into high value products, such as green epoxy coating nanofillers, represents one of the greatest possibility of our century.

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4. Project plan

This final section builds upon the information presented in the previous sections, in which the topics of epoxy resins derived from petroleum and renewable sources, of biobased reinforcements and their applications in the coating industry have been reviewed. It contains a practical proposition, in the form of a project plan, that has the overall goal of bringing the scientific and industrial communities one step closer to replacing unsustainable products with eco-friendly, performing, advanced materials for coating applications.

The aim of the project is the production of bio-based epoxy resin coatings reinforced with bio-renewable fillers and their characterization. For this purpose, three different bio-based monomeric phenols (namely ferulic acid, gallic acid and eugenol) have been selected among the numerous options based on three criteria.

First and foremost, aromatic poly-epoxides have proven to be more able to compete with DGEBA in terms of thermomechanical properties, becoming of primary interest for renewability. Secondly, even though research groups reported on the synthesis of the aromatic moieties, their epoxidation and thermal curing, information about their reactivity towards cationic photopolymerization process is still missing. The disproportion in the amount of reported data about epoxy resins thermal curing versus UV-curing is generally true in scientific literature. However, the photopolymerization method can be considered the most rapid and environmental method to transform a solvent-free liquid monomer into a crosslinked polymer.[1] Thirdly, the effects of biorenewable reinforcements such as the ones presented in Section 3 on these resins are also yet to be investigated. For this purpose, cellulose nanocrystals have been selected based on their availability, high mechanical performance and (specifically to facilitate the UV-curing process) optical transparency.

The plan is outlined in four workpackages, each identifying a main objective and listing the specific tasks that are necessary in order to reach it.

Workpackage n°1

Synthesis of biorenewable epoxidized monomers from aromatic moieties and their characterization

Task 1.1 Epoxidation of ferulic acid

Ferulic acid (4-hydroxy-3-methoxycinnamic acid, FA) is a phenol derivable from lignocellulosic biomass which shows no endocrine disruptive activity; it presents highly reactive hydroxyl and carboxyl groups, making the compound a good starting material for epoxy functionalization. The synthesis of the trisepoxide triglycidyl ether triferulate (GTF-EPO) monomer will be achieved following a three-step procedure described in the works by Ménard *et al.*[2] and Hollande *et al.*[3] and shown in **Fig.** 4.1. The first step is the synthesis of ethyl dihydroferulate from solubilizing ferulic acid in ethanol in the presence of a strong acid (such as hydrochloric acid), followed by a palladium-catalized hydrogenation. After the solvent removal, the crude product is purified by silica gel flash chromatography. The second step is a lipase (CAL-B)-mediated transesterification with glycerol which leads to the formation of the precursor glycerol triferulate (GTF). The third and final step is the glycidation with epichlorohydrin under alkaline conditions, using triethylbenzyl ammonium chloride (TEBAC) as phase transfer catalyst.

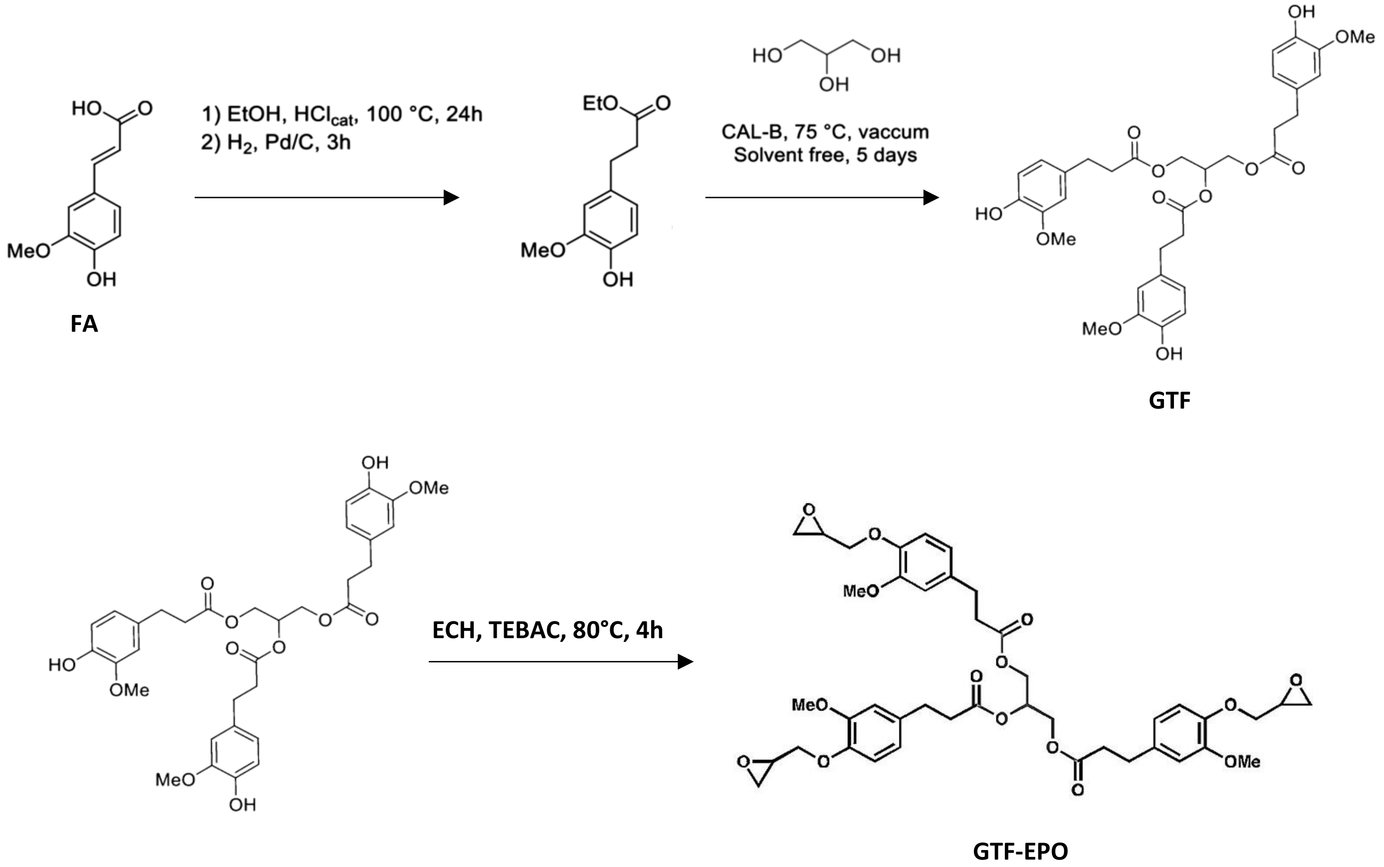

Figure 4.1 Three-steps synthetic route of triglycidyl glyceroltriferulate (GTF-EPO)

Task 1.2 Epoxidation of gallic acid

Gallic acid (3,4,5-trihydroxybenzoic acid, GA) is a phenolic acid with antioxidant properties and is the only mono-aromatic compound with four functionalities that can be glycidated. Tetra-glycidyl ether of gallic acid (GEGA) is the epoxy monomer which will be synthetized from gallic acid following a two-step procedure described in the work by Tarzia *et al.*[4] and shown in **Fig.** 4.2. The first step is the alkaline assisted allyation of hydroxyl groups, from which the precursor tetra-allylated gallic acid (AGA) will be obtained. The second step is the epoxidation of the double bonds which can be achieved through an oxidizing agent (such as m-chloroperbenzoic acid, MCBA).

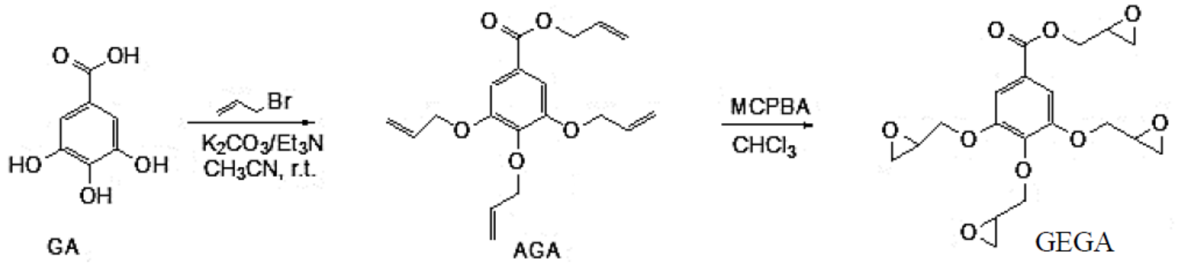

Figure 4.2 Two-steps synthetic route of 3,4,5-tris(allyoxy)benzoate (GEGA)

Task 1.3 Epoxidation of eugenol

Eugenol is a phenolic compound known to be safe, non-carcinogenic and non-mutagenic; it also exhibits pharmacological properties such as anesthetic, antioxidant, and antimicrobial activities. Bisepoxide 2, 2'-diglycidyl ether-3, 3'-dimethoxy-5, 5' diallydiphenylmethane (BEF-EP) is the epoxy monomer which will be synthesized from eugenol following a two-step procedure described in the work by H. Jang *et al.*[5] and shown in **Fig.** 4.3. The first step is the reaction of eugenol with formaldehyde in the presence of a strong acid (such as phosphoric acid), which will yield the precursor bisphenol 2,2'-dihydroxy-3,3'-dimethoxy-5,5' diallydiphenylmethane (BEF). This product has been tested and shown to exhibit a far lower estrogenic activity than commercial bisphenols A and F. The second step is the direct glycidylation with epichlorohydrin in the presence of tetrabutylammonium bromide (TBAB) as the phase-transfer catalyst followed by a post treatment with sodium hydroxide.

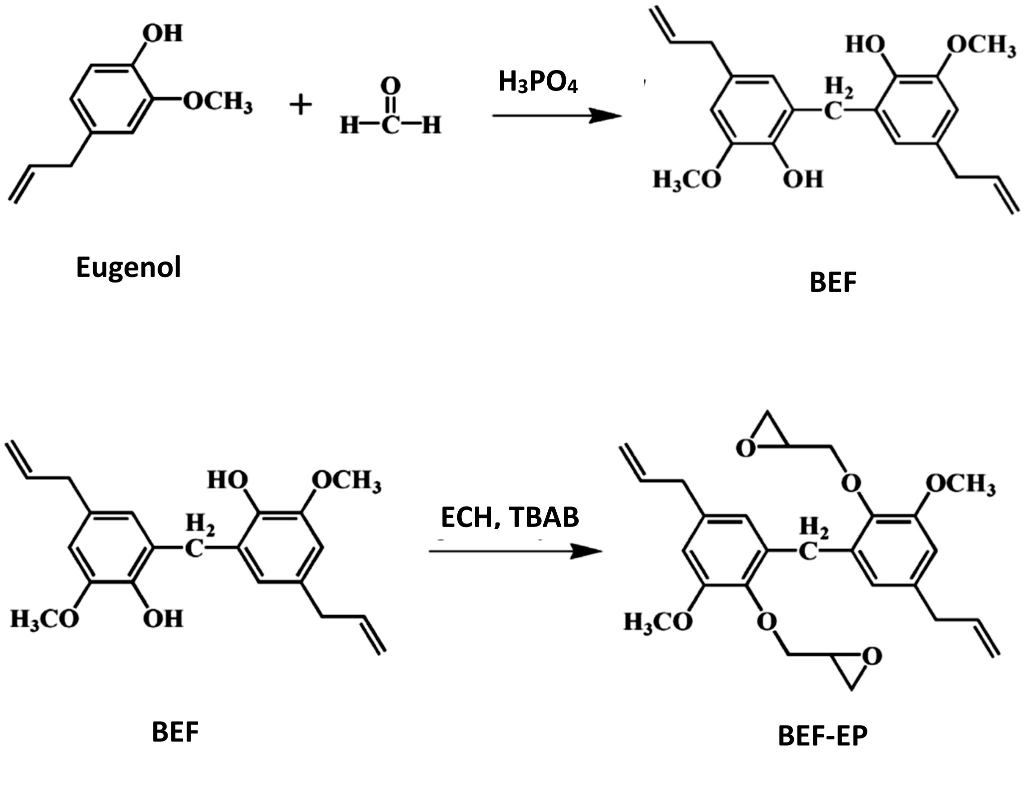

Figure 4.3 Three-steps synthetic route of bisepoxide 2,2'-diglycidyl ether-3,3'-dimethoxy-5,5' diallydiphenylmethane (BEF-EP)

Task 1.4 Characterization of the resins

Following washing, drying, filtering and vacuum evaporation, the epoxy content of each resin will be evaluated with proton nuclear magnetic resonance (^{1}H NMR) titration. The chemical structure of the monomers will also be evaluated through ^{1}H NMR, carbon nuclear magnetic resonance (^{13}C NMR) and Fourier transformation infrared (FTIR) analysis.

Workpackage n°2

Synthesis of biorenewable fillers from cellulose and their characterization

Task 2.1 Crystal nanocellulose isolation

Crystal nanocellulose (CNC) is a bio nanomaterial which can be used as filler in order to provide advanced mechanical resistance and thermal stability to the matrix; besides its reinforcement function it also possesses important properties such as biocompatibility and biodegradability, low thermal expansion and optical transparency. This last property represents an additional value for the purposes of UV-curing methods, since it lowers the hindrance of the radiation's energy absorption by the formulation. The CNCs will be prepared from cotton-derived, commercially available microcrystalline cellulose (MCC) through strong acid hydrolysis, using sulphuric acid, which will remove the amorphous domains.

Task 2.2 CNCs Characterization

Samples of CNCs will be lyophilized and analyzed through FTIR spectrometer in order to determine the purity of the nanoparticles. Morphological and dimensional evaluation of nanocellulose samples will be carried out using transmission electron microscopy (TEM) on a drop of (ultrasonicated) aqueous solution following the complete evaporation of the water. Crystallinity of the lyophilized CNCs will be evaluated by means of an X-ray power diffraction (XRD) analysis.

Task 2.3 Characterization of CNC/epoxy suspensions

The filler content and its dispersibility in the uncured matrix will also be evaluated by means of optical microscopy. Based on these observations, the need for the nanoparticles surface modification to prevent agglomeration will be taken into consideration. Furthermore, rheological properties of the suspensions will be measured during this task.

Workpackage n°3

Design and UV-curing of reinforced photocurable formulations

Task 3.1 Design of photocurable formulations

During this task different photocurable formulations will be studied in terms of photoinitiator (triarylsulfonium hexafluoroantimonate) content and its solubility. The photocrosslinking kinetics will be evaluated by Real-Time FT-IR analysis. Furthermore, the reactive behavior and glass transition of all formulations will be characterized by photo-differential scanning calorimetry (photo-DSC).

Task 3.2 UV-curing

Samples of the various formulations will be coated on various substrates (such as glass and polypropylene) and covered with a transparent foil to protect it from external humidity. The best parameters in terms of UV irradiation time and intensity will be evaluated during this task.

Workpackage n°4

Characterization of cured samples

Task 4.1 Thermomechanical properties

During this task dynamic mechanical analysis (DMA) will be conducted on cured samples of the reinforced and neat resins, to obtain information about the storage (E') and loss (E'') moduli and the glass transition temperature (T_g); thermal stability will be evaluated by means of thermogravimetric analysis (TGA) to measure the decomposition temperatures of 5% and 10% weight loss ($T_{d5\%}$ and $T_{d10\%}$), as well as the decomposition temperature for the maximum rate of weight loss (T_{dmax}). The influence of CNCs on the epoxy matrix will be highlighted by performing ASTM standard tests: adhesion (ASTM D3359-09), abrasion resistance (ASTM D4060-10), impact and deformation resistance (ASTM D2794-10)

Task 4.2 Determination of wettability

Contact angle tests will be conducted on cured coating samples to determine the hydrophobicity of the surface and the CNCs influence on this property

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5. Conclusions

This work examined the current scene on the subject of bio-based epoxy coatings and fillers obtained from natural, renewable sources. The overview of the industrial materials currently implemented for the production of epoxy coatings showed that petroleum-derived substances are the main protagonists for this application. The different types of chemicals involved in the production of epoxy resins (bisphenol A-based, novolacs and cycloaliphatic epoxy resins) were described, together with the main characteristics of each type of resin. It appears clear that petroleum-based epoxy resins offer a great combination of properties and versatility; it is also made evident that there are heavy ecological implications, as well as threats to human health, in the widespread use of such chemicals, hence the need for replacement.

The overview of the bio-based alternatives for the fabrication of epoxy resins for coating applications showed that a great amount of work has been done by researchers with interesting results and a good number of natural sources, such as vegetable oils, saccharides, polyphenols, natural resins, lignin and its derivatives, manifest potential. However, it emerged that, all these sources still feature major drawbacks. Epoxidized vegetable oils, despite their vast volume of production and availability, present long aliphatic chains which compromise thermomechanical properties; glycidyl ethers derived from polysaccharides monomers are hygroscopic and the presence of water may compromise the network; polyphenols and lignin derivatives possess aromatic structures imparting the best thermomechanical properties to the polymeric network out of all the alternatives, yet biorefining processes that are sufficiently ecofriendly and effective for large-scale production are still lacking.

The review of bio-based potential fillers in epoxy coatings showed that eggshell particles, cellulose nanocrystals and carbon products, such as activated carbon, graphene, graphene oxide and reduced graphene oxide, are currently the most viable options. However, it appears that these materials have been extensively studied in combination with bulk polymeric materials and DGEBA resins, yet not much data is available regarding their effects on bio-based epoxy resins derived from the natural sources previously described.

Finally, a project plan has been presented, in which three natural phenolic resources, namely ferulic acid, gallic acid and eugenol, have been selected for the synthesis of epoxidized monomers, to be combined with cellulose nanocrystals and cured via cationic UV-curing. The results of the characterization of the reinforced coatings will provide more data to move forward the active search for replacements to petroleum-based epoxy coatings, as well as a framework for future studies sharing the same purpose.