Lignin epoxy resins: synthesis and evaluation as coatings and composites

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by

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Dear reader,

The thesis you have in front of you is the result of the work I carried out in collaboration with Westlake Epoxy for the past 9 months. However, the story started in September 2021 when I joined the company for an internship, during that time I learned a lot about epoxy resins and immediately decided that I would like to continue my thesis journey with them. My desire was to find a topic that would combine Chemistry and Material Science in a Sustainability topic, and this topic seemed to be the perfect option for this challenge.

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María Santana Martín
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Abstract

Epoxy resins are one of the most relevant and widely used thermosets in the market covering a wide range of applications. Industries are being forced to quickly transition towards sustainable alternatives due to the pressure from emerging environmental concerns, the depletion of petrochemical supplies, and compliance with environmental legislation. Since the primary component of epoxy resins is derived from petroleum (Bisphenol A (BPA)), companies like Westlake Epoxy have joined the search for innovative, environmentally friendly solutions. Many bio-based substitutes have surfaced in recent years, in efforts to eliminate or reduce the quantity of BPA in epoxy resins. Attention has been focused on lignin biomass as a viable feedstock in the manufacturing of these thermosets because of its large production volume and some structural characteristics.

This study addresses the synthesis of novel lignin-based epoxy resins and the evaluation of their potential application in the field of coatings and composites. For this research, different sources of technical Kraft lignin were employed. Since technical lignin is not very reactive due to the large molecular weight polymers, a Confidential Fractionation process has been developed. For its synthesis, both small- and large-scale glycidation processes were successfully implemented. To understand the chemical structure of lignin and its corresponding resins, different analytical techniques were used such as Gas Chromatography (GC), titrations, Nuclear Magnetic Resonance (NMR), Fourier-Transform Infrared Spectroscopy (FT-IR) and Gel Permeation Chromatography (GPC). Additionally, for the development and characterisation of coatings and composites, a variety of material testing techniques were employed, namely Differential Scanning Calorimetry (DSC), Dynamical Mechanical Analysis (DMA), Thermogravimetric Analysis (TGA), Interlaminar Shear strength (ILSS), Impact testing, Pendulum hardness, among many others.

Experimental results showed an average fractionation yield of 50-60% of technical Kraft lignin using the Confidential Fractionation process. Compositional differences in the fractionated lignin substrates studied via NMR analysis, predict some differences in the reactivity of these substrates towards glycidation, which is supported by different Epoxy Group Content (EGC) of the corresponding epoxy resins. The EGC of the lignin-based epoxy resin is significantly lower than that of the reference resin due to the presence of bulky moieties that hinder the reactivity of active sites. While lignin-based coatings exhibit comparable performance in hardness and direct impact resistance, however, its high viscosity and stiffness results detrimental in other areas. On the other hand, this high viscosity is a major challenge in the processes of prepreg laminates leading to poor adhesion of the fibres to the matrix, which has a negative effect when it comes to mechanical performance. However, adding lignin to epoxy resins has proved to improve the thermal stability of these materials.

1 Introduction

Rising environmental concerns and the rapid depletion of petrochemical resources are putting pressure on the chemical industry to explore and develop new alternatives. Some of the risks associated with the dependency on petroleum-based feedstock include increasing CO_2-taxes or related penalties in the near future on their use, demand for more renewable products, perception of society on chemical companies, limited supply, disruptions in the import process and fluctuating price and volatility of it. Consequently, bio-based feedstock has gained relevance over the last few years, becoming a competitor and promising alternative against conventional petroleum-based feedstock. In the polymer industry, this bio-based approach has been successfully implemented in the synthesis of thermoplastics, some of them even have been commercialized. This implementation has not reached thermosetting resins. Nevertheless, the fact that about 18% in weight of the overall production of polymeric materials corresponds to thermosetting resins [1], opens the possibility of a new field of investigation based on bio-based materials as the building block for thermosets.

Epoxy resins are high-performance materials and exhibit exceptional properties such as high mechanical strength, remarkable adhesion, and thermal and chemical resistance [2]. Due to these outstanding attributes, epoxy resins account for almost 70% of the market of thermosetting resins [1], dominating applications such as composites and coatings. The main drawback lies in using Bisphenol A (BPA) or Bisphenol F (BPF) which are petroleum-based organic compounds associated with potential health hazards such as suspected endocrine-disrupting effects. The transition towards more renewable products is already a trend within the industry. Companies are currently developing and trying to implement new sustainable alternatives into their processes. Westlake Epoxy wants to seize this opportunity to add new bio-based epoxy resins in their portfolio.

With an estimated production of 200 billion tons, lignocellulose is the most abundant natural biomass on the planet [3]. Lignocellulosic biomass can be described as any organic material derived from biological origin that is not used for food or feed [4], also defined as plant structural material with high cell wall content [5]. Depletion of fossil resources and arising concerns towards climate change, added to its easy availability, reduction of carbon dioxide emission [3] and better compliance with collection and transportation [6], has made of lignocellulosic biomass promising feedstock. Although lignocellulosic biomass is produced in various industries, it is particularly abundant in the agricultural sectors, especially in broad-acre crops like wheat, corn. Furthermore, municipal organic solid wastes such as food waste and wastewater treatment contain biomass [6]. In the paper industry and biorefineries, lignin is also a by-product of the pretreatment and separation process of distinct components of lignocellulosic biomass, generating annually 50-70 million tons of what is defined as technical lignin [7]. Despite this, the annual valorisation rate of lignin is less than 2%, remaining one of the most underused renewable feedstocks, implying that technological improvement is required to capitalize and gain some revenue on lignin as a valuable feedstock [8]. The current practice is to incinerate or landfill the generated lignin waste, which implies a waste of resources that carries additional environmental risks. It is expected that lignin might contribute significantly more to biorefinery if it is used for purposes other than energy recovery.

When it comes to lignin, there are both advantages and downsides. The aromaticity of lignin is probably the most noteworthy structural feature. The aromatic rings provide stiffness to the system which will shift the T_g of the resulting epoxy resin towards higher temperatures [9]. The structural stiffness will be advantageous in applications such as composites since epoxy resins are used as matrices for fibre reinforcement which usually requires high tensile modulus. Aromaticity will also influence the thermal stability of the epoxy resins; it is reported that aromatic epoxy resins exhibit better thermal performance than aliphatic ones [10]. Crosslink density is another factor that controls the thermal stability. Lignin structure is three-dimensional and contains several hydroxyl groups which allow to establish crosslinks between polymer chains, enhancing the crosslinked network of the thermosetting system. Thus, the aromatic structure of lignin is expected to enhance the stiffness and thermal stability of the epoxy resin. The presence of phenolic hydroxyl groups in the lignin chemical structure is similar to those found in BPA, which suggests its value as a possible substitute [11] [12]. The presence of different moieties in the lignin structure presents active sites that can be transformed into epoxy groups [13]. The potential of lignin to be introduced and used as a building block in epoxy resins is reflected by the increasing number of articles that published over the years (*Figure 1*).

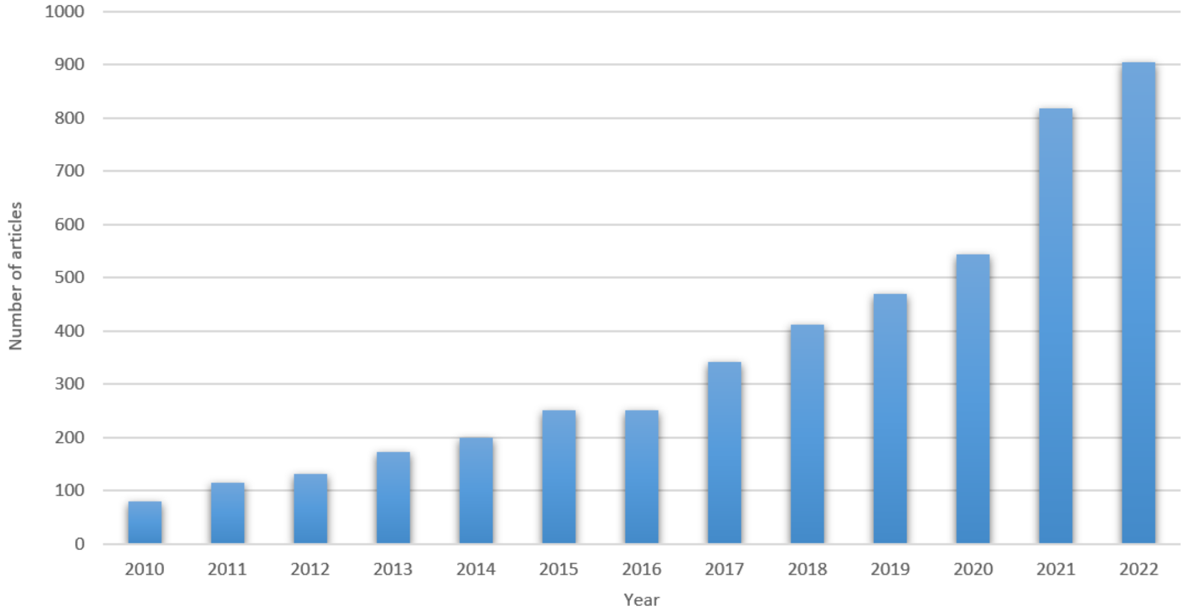


Figure 1. Articles published over the years containing the terms "lignin epoxy resin" in their titles.

Some of the challenges in substituting BPA with lignin are related to its chemical structure. These are the polydispersity index, molecular weight, different types of hydroxyl groups and the limited solubility of lignin in organic solvents and water, which will decrease the reactivity of lignin towards ECH [14]. The heterogeneity and complexity of lignin generated by the biosynthesis and extraction methods limits its application in polymer systems. The lack of structural characterisation techniques along with the lack of control over the molecular structure after the synthesis and extraction remains one of the most significant challenges in the up-scaling of lignin-based epoxy resins [15]. It is imperative to address the heterogeneity of lignin before scale-up of production since industries must be supplied with reproducible and constant quality stream of lignin. However, technical lignin is not as reactive due to the large molecular weight of lignin polymers. The degradation of lignin into phenolic products or monolignols is an energy-intensive procedure, which is why lignin is usually considered to have more value as fuel than as a feedstock. Methods that could use lignin as a source to synthesize new materials without further degradation would be useful and environmentally favourable. Solving this issue is essential to assess the potential that lignin can play in the use of its epoxy resins in the field of coatings and composites. Ultimately, understanding the relationship between chemical structure and performance is necessary.

The scope of this research is to find answers to the following questions that are listed below:

1. Technical sources of lignin are used for the synthesis. Can a depolymerisation method be developed to have a reactive system for synthesizing epoxy resins? If so, it is essential to understand the yield of this process as well as characterising the substrate obtained from it.

2. So far, the lignin-based epoxies have been synthesized on a small scale; however, translating this process to a larger scale is still challenging. What are the reaction conditions and process to follow to produce a realistic epoxy resin from lignin derivative? Different process conditions will be tested, and the obtained products will be characterised to choose the most suitable reaction conditions.

3. How can lignin epoxy resins be implemented in the field of coatings and composites? What is the mechanical and thermal performances of the synthesized lignin epoxy resins? What is the performance of these lignin epoxy resins compared to reference epoxy resins?

4. Understand the relationship between the chemical structure of the lignin and its epoxy resin and the performance they exhibit as coatings and composites.

2 Literature Research

This literature research presents the available literature and background knowledge concerning lignin and corresponding epoxy resins made from it.

2.1 Definition and chemistry of lignin

Lignin is the second most abundant polymer after cellulose, a constituent in plant cell walls, with a three-dimensional heterogeneous aromatic structure formed by three main phenolic units. This is known as native lignin [16]. In the paper industry and biorefineries, lignin is a by-product of the pre-treatment and separation process of distinct components of lignocellulosic biomass, known as technical lignin [17]. Substantial differences in composition and structure will arise not only between technical and native lignin, but also within these two categories. The chemical properties (molecular weight, composition, molecular structure) of lignin vary based on the source of origin and on the extraction, procedures used on plant biomass, resulting in distinct forms of lignin [17]. As a result of the molecular complexity and diversity in structural composition, a definitive definition of lignin has yet to be determined.

Although lignin is not a very precisely defined compound, it does have several structural features that can be identified. Its highly complex architecture derives from the oxidative coupling of primarily three hydroxycinnamyl alcohols that act as a building block, also referred to as monolignols [18]. These monolignol species are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The position of the methoxyl group in the aromatic ring is the fundamental difference between these units [17]. P-coumaryl alcohol lacks a methoxyl group in its structure, whereas coniferyl alcohol has one at position C3 in the aromatic ring and sinapyl alcohols have two at positions C3 and C5. These aromatic alcohol precursors contain p-hydroxyphenyl (H unit), guaiacyl (G unit) and sinapyl (S unit) moieties [19], which will be the aromatic residues in the polymer (*Figure 2*).

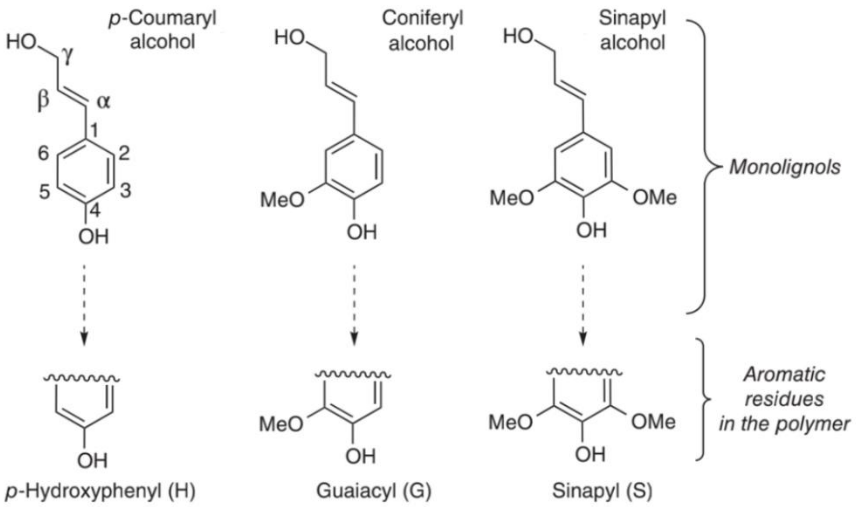


Figure 2. Chemical structure of monolignols species [17].

Lignin can be classified based on two main criteria: plant taxonomy and chemical structure. Although there is a relation between taxonomy and its corresponding chemistry, the chemical classification is preferable [16].

- Type-G: lignin that exhibits abundance of guaiacyl residues, such as the case of gymnosperm lignin (softwood).
- Type-G-S: lignin which presents mainly guaiacyl and sinapyl residues, e.g., angiosperm lignin (hardwood).
- Type-H-G-S: lignin that incorporates a mixture of the three aromatic residues, such as herbaceous or grass lignin.

The bonds between monolignol units can be divided into carbon-oxygen or carbon-carbon interatomic bonds. Nomenclature of the links is noted as follows: aromatic rings carbons are denoted with numbers, whereas carbons in the side chains are described with Greek letter that begin with the one closest to the aromatic ring [16]. If the interatomic link is C-O, then an O is added between the Greek letter and numbers, in case of a C-C bond, no letter is signified (*Figure 3*).

- C-C bonds: β-β, β-5, β-1 and 5-5.
- C-O bonds: β-O-4, α-O-4 and 4-O-5.
- C-C and C-O bonds: β-5/α-O-4 and β-β/α-O-γ.

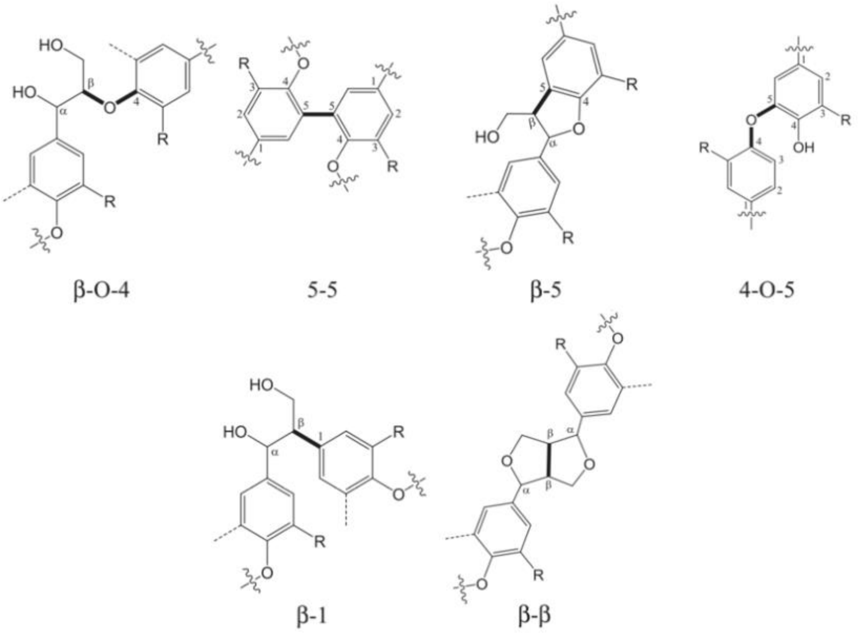


Figure 3. Scheme of the most common linkages in the lignin [20].

2.2 Lignin sources

The main constituents of plant biomass or lignocellulosic biomass are cellulose, hemicellulose, and lignin, and additional trances of pectin, protein, extractives, and ashes. On average by dry weight, cellulose and hemicellulose make up 70–80% of the total, whereas lignin makes up 10–25% [21]. The most common sources of lignocellulose biomass are agricultural and forestry wastes, lignocellulose biomass can be divided into two categories: woody biomass (softwood and hardwood) and non-woody biomass (agricultural residues and native plants). These sources are native lignin sources. Lignin can be derived from industrial sources, yielding technical lignin. Technical grade lignin is a by-product of the different pretreatments and isolation processes on lignocellulosic biomass in the production of pulp and bioethanol [17]. In the paper-making industry, lignin is chemically separated from the lignocellulosic biomass by a process called pulping [22]. Various processing methods to separate lignin from lignocellulosic biomass have been devised. However, due to the nature of the substrates that will be used in this project, the focus will be on Kraft lignin.

Kraft lignin

In the late 1980s, the Kraft process produced the most lignin as a by-product of the paper industry, with around 75 million tons produced worldwide [23]. Nowadays, 85% of the global production of lignin is produced by this industrial method, with a production of 630,000 tons per year, becoming the dominant technology for extraction of lignin. This process uses a mixture named white liquour as main reagent, made up from sodium hydroxide (NaOH) and sodium sulfide (Na_2S) at temperatures between 140 and 170 ºC. As a result of the delignification process in which linkages of lignin are broken via cleavage [24], a black liquour is obtained which contains the degraded lignin, which is isolated by precipitation followed by acidification, and finally a drying process that results in a solid form of lignin [16].

2.3 Valorisation of lignin

Governments are presenting additional incentives in the last years to establish a long-term renewable energy alternative to fossil fuels. Lignin is the most abundant aromatic building block in nature, and it is emerging as a feedstock for the synthesis of bio-based compounds. However, there are few wellestablished procedures for adding value to it, due to its structural complexity and chemical inertness. Kraft lignin accounts for 85% of the global lignin production, producing 630,000 tons annually [25]. Despite this, the annual valorisation rate of lignin is less than 2%, which means it is one of the most underused renewable feedstocks, implying that technological improvement is required to allow its valorisation [8]. Due to the insoluble nature of Kraft lignin, the current practice is to incinerate or landfill the generated lignin waste, which implies a waste of resources that carries additional environmental risks. It is expected that lignin might contribute significantly more to biorefinery if it were used for purposes other than energy recovery. Therefore, it is important to develop and optimise a value-chain for lignin that can potentially allow its revalorisation (*Figure 4*).

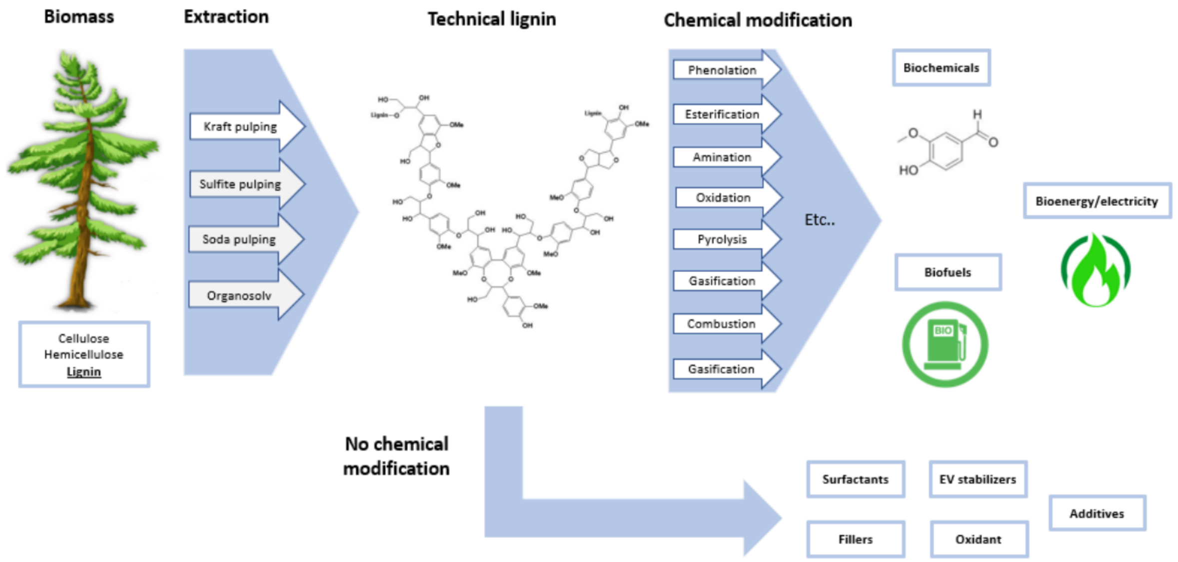


Figure 4. Value chain of lignin for its valorisation.

Developing a successful lignin-based value chain is no easy task, especially since many challenges arise from it, such as the significant knowledge gap on the structure and properties of different type of lignin, the effect of extraction methods in its structure, etc. Economic viability is required to implement a value-chain of lignin in biorefineries beyond energy recovery applications. The wide range of potential applications (surfactants, coatings, biocomposites, resins, etc.) and the economic and environmental benefits of lignin valorisation are the driving forces for exploiting this raw material in the transition towards a bio-based economy.

2.4 Properties of Kraft lignin

As the knowledge of heterogeneous physical and chemical properties is still limited, it is fundamental to understand the chemistry of lignin and the physicochemical transformations and properties achieved in different processing methods. Lignin presents detrimental or damaging properties that limit its applications in other polymer materials, such as a rather high molecular weight, steric hindrance, poor solubility in organic solvents and low reactivity due to one or more methoxy groups present in its structure [17].

When it comes to solubility, Kraft lignin is soluble in alkaline solutions (pH > 10.5), dioxane, acetone, dimethylformamide and 2-methoxyethanol [26]. However, due to a large number of polar moieties in the molecule, lignin tends to present self-interactions decreasing its solubility and compatibility with other polymers. According to the literature, the solubility of lignin in solvents increases in line with the hydrogen bonding capability of the solvent [27]. Miscibility or solubility of lignin into solvents is determined by competition between the self-interactions of lignin and the hydrogen bonds that can form with the other components. Additionally, lower molecular weight, reduced polydispersity and decrease in the length of aliphatic hydrocarbon side chains lead to a higher solubility of lignin [28].

Lignin is an amorphous polymer that exhibits thermoplastic behaviour, with a corresponding glass transition temperature T_g that depends upon factors such as molecular weight, the used recovery method, water content and thermal history [28]. Determining the T_g of isolated lignin becomes challenging due to the complexity and heterogeneity of its structure and molecular weight. However, T_g becomes higher with increasing average molar mass. Comparing the T_g values between native and technical Kraft lignin, the latter presents higher values. Thus, it is used in the production of lignin-containing materials since they will benefit from better thermal properties. Additionally, technical lignin is usually less reactive than native lignin when the β-O-4 are replaced by C-C bonds after acid or alkali treatment (Kraft process) [17]. Price of Kraft lignin is also affected by its recovery method; the pricing range is between 260 to 500 USD/ton (*Table 1*).

Table 1. Properties of technical Kraft lignin [22].

Sulfur content (%)	Molecular weight (g/mol)	Polydiversity	Purity	T_g (ºC)	Price (USD/ton)
1.0-3.0	<25000	2.5-4.0	High	108-165	260-500

Another property of interest would be the thermal degradation, which is particularly important in the context of application of lignin in synthetic polymeric materials, such as thermosets. Thermal degradation is further characterized with thermogravimetric techniques (TGA). According to *Figure 5*, a first slight mass loss occurs at low temperatures due to dehydration or release of CO and CO_2 [14] between 40 to 100 ºC [29] [30]. Weight remains constant until 180-200 ºC and a significant loss follows, taking place between 200-300 ºC until 400 ºC, this is related to the breakdown of aromatic bonds followed by the condensation and polymerization reactions of the aromatic compounds [29]. The TGA curves are in accordance with the exothermic behaviour detected in DSC with the biggest exothermic peak between 400-450 ºC.

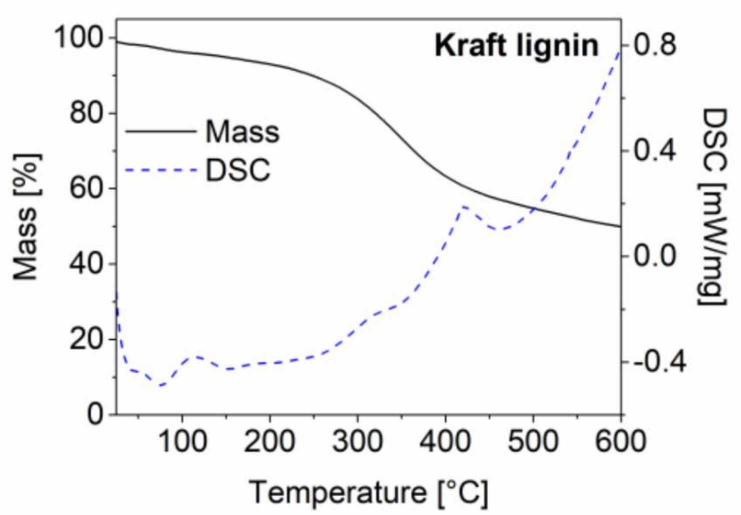


Figure 5. TGA and DSC curves for technical Kraft lignin [30].

2.5 Lignin-based epoxy resins

2.5.1 Epoxy resins

Epoxy resins are one of the most widely used thermosets available on the market. It is a crosslinked polymeric substance with at least two epoxy groups, which can be cured into thermosetting polymers. Chemical and corrosion resistance, thermal stability and mechanical performance are some of the desirable and notable properties that contribute to their popularity [31]. Epoxy resins are more costly than other polymers, but because of the ability to be combined with different curing agents, they may be tailored to a specific application, making them appropriate for a wide range of applications such as coatings, adhesives, composites, binder systems, stabilizers, packaging [32] [13].

The production of most Liquid Epoxy Resins (LER) requires the use of Bisphenol A (BPA) or Bisphenol F (BPF) along with epichlorohydrin (ECH). LER are manufactured via glycidation, or conventional epoxidation route of BPA or BPF and ECH in the presence of an alkali hydroxide (NaOH) and/or a phase transfer catalyst. Glycidation process consists in two steps. Firstly, a phase-transfer catalyst, normally a quaternary ammonium salt, is used to form the chlorohydrin, an intermediate that contains chlorine and hydroxyl group in adjacent carbons. This first step is known as coupling reaction. Thereafter, a strong base is added to induce the ring-closing reaction that results in the glycidation product and salt (*Figure 6*). The result of these reactions is the BPA-based epoxy resin, or also referred as diglycidyl ether of bisphenol A (DGEBA). Subsequent curing of the epoxy resin will form the thermosetting polymer network with a range of properties that suit the desired application. The most common curing agents are amine, that can range from aliphatic, cycloaliphatic, and aromatic amines. A three-dimensional network is formed upon the interaction between amine and the epoxy groups, developing the thermosetting network.

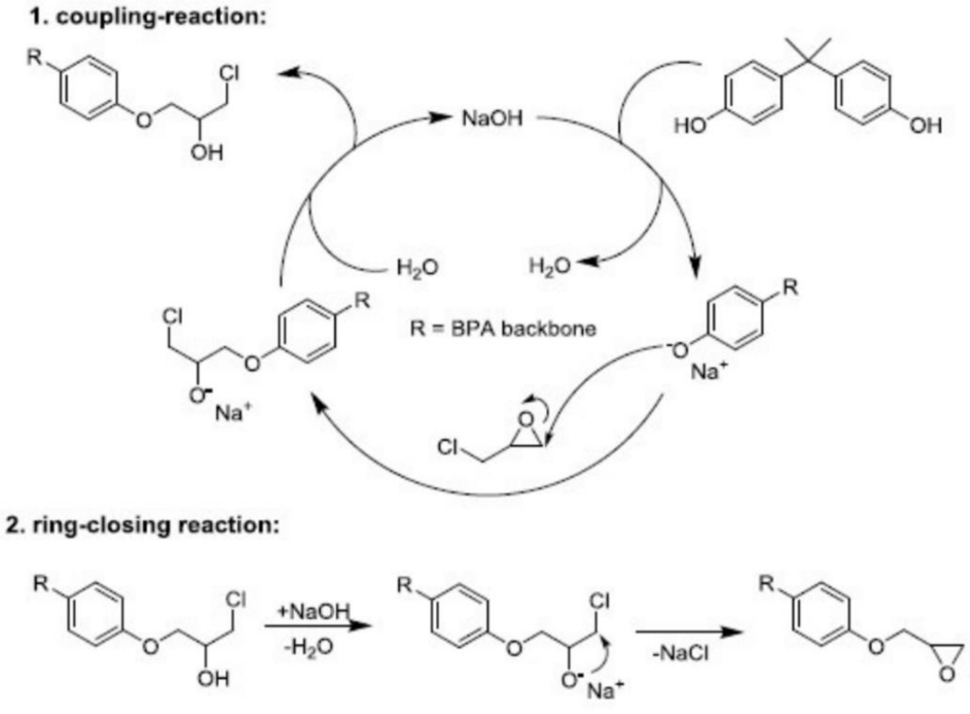


Figure 6. Two-step glycidation process for the production of epoxy resins.

Nevertheless, the petroleum-based BPA and BPF are associated with certain issues as a building block in the manufacture of epoxy resins. Firstly, BPA might come with possible health concerns like its suspected toxic endocrine-disrupting effect affecting the hormone system, which is the reason why its use in children's bottles or products and food contact materials is banned in many countries. Secondly, BPA is a petroleum derived compound which is affected by the depletion of fossil fuel resources and causing concern about future availability and arising environmental issues. Finally, the forecast of stricter measures on BPA imposed by governments in the past few years are encouraging the research for new alternatives such as from bio-based feedstock. Despite all of this, BPA remains the primary building block for about 85% of the world's production of epoxy resins [33]. Nevertheless, the transition towards more renewable products is already a trend within the industry for some years, and Westlake Epoxy is committed to add new bio-based epoxy resins to their portfolio.

2.5.2 Lignin as a building block for epoxy resins

Bio-based feedstock has gained relevance in the field over the last few years, becoming a competitor and promising alternative to the conventional petroleum-based feedstock. Bio-based feedstock present a variety of advantages, where the most remarkable ones are its lower ecotoxicity and CO_2 footprint [34]. Although some bio-based substrates can be widely available and inexpensive, others are limited by the uncertainty in price and availability. Different biobased alternatives to BPA have already been investigated, namely epoxidized cardanol, isosorbide, gallic acid, itaconic acid, rosins, vanillic acid, vanillin, eugenol, among others [14] [32]. However, emerging research initiatives are focused on lignin as a potential source of building block for epoxy resins. Moreover, lignin might exhibit certain advantages over the others biobased compounds that has been mentioned.

Chemical structure

When it comes to lignin, its chemical structure presents certain advantages. The aromaticity of lignin is probably the most noteworthy structural feature. The aromatic rings provide stiffness to the system which will shift the T_g of the resulting epoxy resin towards higher temperatures [9]. The structural stiffness will be advantageous in applications such as composites, since epoxy resins as used as matrices for fiber reinforcement, usually require high tensile modulus. Aromaticity will also influence the thermal stability of the epoxy resins; it is reported that aromatic epoxy resins exhibit better thermal performance than aliphatic ones [10]. Crosslink density is another factor that controls the thermal stability. Lignin structure is three dimensional and contains several hydroxyls which allows to stablish crosslinks between polymer chains, enhancing the crosslinked network of the thermosetting system. Thus, the aromatic structure of lignin is expected to enhance the stiffness and thermal stability of the epoxy resin. The existence of phenolic hydroxyl groups resembles the lignin chemical structure to that of BPA, which indicates its value as a possible substitute [11] [12]. The presence of different moieties in the lignin structure presents active sites that can be transformed to epoxy groups [58]. In general, the presence of both polar (OH groups) and non-polar (hydrocarbon and benzene rings) segments within the lignin structure can be used in the compatibilization of hydrophilic fibers into a hydrophobic matrix [10]. Additionally, the presence of the phenolic hydroxyl groups in lignin makes it suitable for synthesis of phenolic resins, epoxy resins, polyurethanes, and polyesters [10].

However, there are some challenges in substituting BPA with lignin which are related to its chemical structure. These are the polydispersity index, high molecular weight, different type of hydroxyl groups and limited solubility of lignin in organic solvents and water, which will decrease the reactivity of lignin towards ECH [14]. Its use in polymer systems is limited by the heterogeneity and complexity of lignin produced by the biosynthesis and extraction methods. One of the biggest obstacles to the up-scaling of lignin-based epoxy resins is the absence of structural characterisation techniques, together with the lack of control over the molecular structure after the synthesis and extraction methods [15]. Since companies need to be supplied with consistent and reproducible stream of lignin, it is essential to address the lignin heterogeneity before scale-up in production. However, depolymerisation techniques can mitigate these issues by generating lignin monomers that will have increased solubility and lower molecular weight, making it more suitable in for the synthesis of epoxy resins. At the same time, upgrading of modified lignin is limited by the changes introduced in its structure that make them differ significantly from native lignin [35].

Sustainability

The growing interest in utilization of lignin as a feedstock for the synthesis of polymeric materials is mainly due to sustainability driving factors. The material is sustainable and renewable and quite abundant as a by-product in pulp/paper industry and cellulosic ethanol industry. Moreover, due to lignin's inherent biodegradability, it is expected that polymers containing lignin will be more biodegradable than those made of petroleum [36]. The use of lignin into value-added chemicals can mitigate the sense of dependence towards fossil fuels [37]. Most of the lignin produced by the pulping and paper industry is landfilled or incinerated for energy recovery purposes, which brings detrimental effects to the environment. Revalorisation of this bio-based feedstock can ease the environmental impact of the current practices. This statement is supported by the environmental impact assessment carried out by Yadav *et al.*, in which the results showed 139 kg CO_2 eq./kg and 0.23 kg CO_2 eq./kg for scenarios 1 and 2 respectively. The environmental impact of organosolv products is increased to 2.14 kg CO_2 eq./kg when considering the co-production of tannin [38].

Economics

Lignin is produced on a large scale from paper and pulp industries and some biorefineries. Thus, it can provide a readily available and steady flow of feedstock to value-added products, such as epoxy resins. The use of lignin for epoxy resins enhances the economic benefits for the pulp and paper industry that generate this compound as a by-product [12]. Moreover, the cost of epoxy resins is considerable higher when compared to other type of polymers, using lignin as feedstock can make the production of these thermosetting systems more affordable. It is estimated that the production of lignin will grow from $732.7 million to $913.1 million by 2025 [38].

2.5.3 State-of-the-art on the synthesis of lignin-based epoxy resins

This section examines earlier reported attempts to synthesise lignin-based epoxy resins in literature. This is of particular significance from the synthesis perspective, when considering the scale-up of the production, parameters such as reaction duration, reaction temperature, lignin content, lignin type, and so on are critical. The growing interest in lignin’s potential has resulted in the development of numerous lignin synthesis and modification methods:

1. Blending technical lignin with epoxy resins
2. Direct epoxidation of unmodified technical lignin
3. Modification of technical lignin prior to epoxidation

Each of these synthesis methods produces distinct products with different physico-chemical properties which can be applied to different sectors of application. As mentioned in the previous section, there are several challenges in replacing BPA with lignin, mainly its lower reactivity that can be attributed to high molecular weight, polydispersity, low solubility, etc. Modification of technical lignin prior to epoxidation aims at enhancing the reactivity of the active sites of the lignin, however, they may cause additional side reactions introducing changes into the lignin molecule, affecting its final properties.

Direct epoxidation of unmodified technical lignin

Previously, Simionescu *et al.* reacted a calcium lignosulfonate with ECH under alkali conditions on a slow process at a temperature of about 70-75 °C for 4.5-7.5 hours. The best results, in terms of higher epoxy content, were obtained when using high concentrated NaOH and low molar ratio of ECH [39]. Over *et al.* synthesized a lignin-based epoxy resin from organosolv lignin. In this experiment, 25.0 g of lignin was mixed with 100 mL of ECH. Then, 9.5 g of TBAB was added to the mixture under ice cooling for 30 minutes. After this, 29.9 g of KOH were added over 2.5 hours and stirred for another 5 hours at room temperature. Extraction was performed by using dilution of dichloromethane (DCM) and water. The resulting lignin epoxy resin had an epoxy content of 3200 mmol/kg, which is a high value considering that the organosolv lignin did not undergo any depolymerisation process. In case a depolymerisation technique would have taken place, the phenolic hydroxyl groups would increase, thereby increasing the epoxy content of the product resin [40]. Another attempt at fully replacing BPA with technical or unmodified lignin was made by Nikafshar *et al.*. Various forms of technical lignin (Kraft, soda, and organosolv) from diverse sources were used in their study (softwood, hardwood, peanut shell, wheat straw). In the experiments, 5 g of the lignin was first dissolved in 20 g of N,N-dimethylformamide (DMF) to later add 0.4 g of TBAB and 40 g of ECH. This mixture was stirred for 3 hours at temperature of 60 °C and cooled down to room temperature before dropwise addition of 2 wt.% NaOH solution of 50 mL with 1.2 wt.% of TBAB. At room temperature, the reaction continued for 8 hours while stirring. The highest epoxy yield was obtained for samples of organosolv lignin from corn stover (4-O-CS) and Kraft lignin from hardwood resins (11-K-HW) [14].

Unmodified lignin has also been co-reacted with BPA as a way of partially replacing the petroleum-based building block in epoxy. Zhu *et al.* conducted research in which lignin from pulping black liquor was glycidated with BPA, and results reported that the content of lignin and reaction temperature had a significant impact in the yield of the resulting lignin-based epoxy resin. At a temperature of 90 °C, the optimal yield was achieved with a lignin content of 20 wt.%, and at this lignin content conditions, the yield was increased with increasing temperature reaching a maximum of 36.4% yield at 90 °C [37].

2.5.4 Characterisation of lignin epoxy resins

Different techniques have been used for the characterisation of lignin epoxy resins. This section details the most important methods that are employed.

Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical technique that measures the molar heat capacity of samples as a function of temperature [41]. The difference in the change in heat flow is measured by exposing both the sample and the reference to a temperature gradient at a constant rate in identical cells [31]. Compositional differences between sample and reference means that different energy uptake will be required, thus, the instrument measures this difference in the amount of heat flow needed to reach the temperature in the cell. The data obtained from this analysis can be correlated to certain thermodynamic properties of the sample, such as glass transition temperature (T_g), onset and completion of cure, heat of cure, percent of cure, etc.

Thermogravimetric Analysis (TGA)

This technique monitors the mass of a sample as a function of temperature or time when subjected to a controlled temperature in an inert atmosphere. Both physical and chemical changes are measured by monitoring the change in weight experimented by the sample as the temperature varies. In general, weight gain is attributed to phenomena such as adsorption or oxidation, whereas weight loss is mainly due to decomposition, desorption, dehydration, or volatilization [41]. It determines the thermal stability and degradation of the sample, moreover, it is one of the most used methods of polymers characterisation [31]. It is for its screening nature that TGA is an appropriate method for evaluating polymers such as lignin [42].

TGA will be used as a characterisation technique for the weight loss behaviour and thermal stability of both the lignin epoxy resins and the lignin substrates. It is expected that the TGA curves for the lignin substrates present two plateau regions, which indicates a two-step degradation mechanism and subsequent weight loss drop after each of them. The first degradation step is attributed to the release of light molecules such as CO, $CO_{2,}$ and water, while the second degradation step must involve the degradation of functional groups, aromatic groups, or oxidation of C-C bonds [14]. For both coatings and composites it is essential to determine the thermal stability of epoxy resins to assess the suitability in high-temperature applications.

Dynamic Mechanical Analysis

This analysis aids in measuring the response of a samples to a sinusoidal stress or strain. It provides information on the viscoelastic behaviour of polymers, determining several properties namely the stiffness, elasticity, and damping [31] as well as T_g values after curing. These can be expressed in terms of storage modulus (elastic modulus, E'), loss modulus (viscous modulus, E''), and tan δ (damping coefficient, E''/E') as a function of temperature, frequency, or time when applying the dynamic force [43]. This technique is more sensitive to the crystalline structure and to amorphous transitions than TGA and DSC, the reason is that there is a greater change in the polymer's mechanical properties during these transitions than there is in its specific heat [44].

Thermosets' properties are highly dependent on the crosslinking density, and the effect of crosslinking densities can be observed in different regions in the DMA curve. The glassy region is more independent of the crosslinking density but as the temperature increases, the effect of crosslinking is more visible in the transition and rubbery plateau region. Higher crosslinked thermosets present a higher T_g value and loss modulus peak at higher temperature in comparison with thermosets with a lower crosslinking density (*Figure* 7).

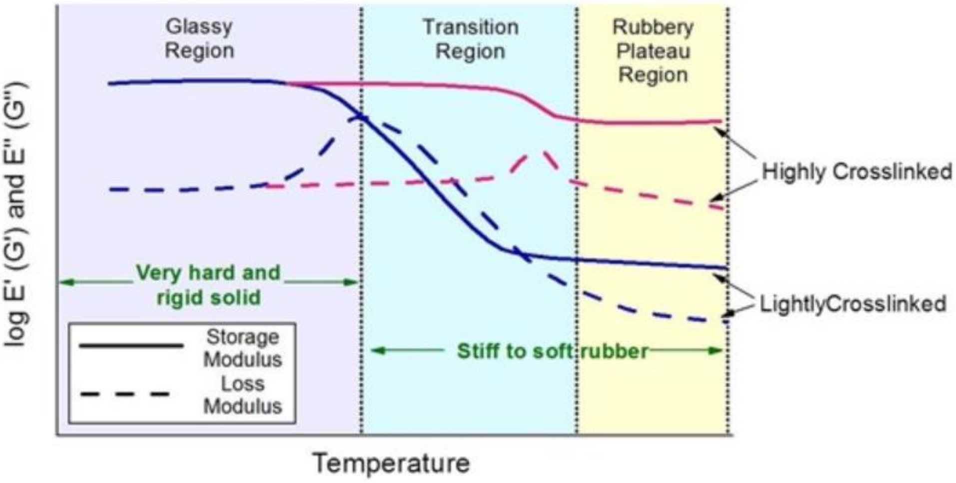


Figure 7. DMA curve for highly and lightly crosslinked thermoset [45].

Nuclear Magnetic Resonance (NMR)

It is an analytical tool for determination of molecular structure of organic compounds. This approach uses a magnetic field and radio frequency pulses to measure an atomic nucleus' resonance frequency in response to its chemical or environmental surroundings [46]. This characterisation technique is the most sensitive and efficient tool for the determination of polymer structures and the presence of moieties in polymer chains [47]. This technique is particularly beneficial for understanding the complex and heterogeneous structure of lignin. In this case, ^{31}P-NMR was the chosen technique for the molecular characterisation of lignin. This technique detects the compounds containing phosphorus, for this, a phosphorylating reagent reacts with hydroxyl groups present in the sample to obtain the subsequent phosphorylated products. This way, the aromatic, phenolic and carboxylic acids groups are detected. These are especially relevant for the reactivity of the substrates towards the glycidation.

Fourier-transform infrared spectroscopy (FT-IR)

It is an analytical technique that identifies the presence of functional groups in a sample by using a range of infrared (IR) radiation wavelengths. The generated infrared spectrum of transmission or absorption of the sample show peaks corresponding to the frequencies of vibration which are characteristic for each bond or set of bonds [48]. In this way, the molecular fingerprint of the samples can be obtained, since each functional groups presents unique and characteristic spectrum.

2.5.5 Properties of lignin epoxy resins

This section summarizes the results on the properties of the obtained lignin-based epoxy resins for some of the experiments mentioned in section 2.5.3 State-of-the-art on the synthesis of lignin-based epoxy resins above.

Structural properties

Nikafshar *et al.* used different sources of lignin to obtain epoxy resins, one of them being hard wood Kraft lignin (11-K-HW) and the other organosolv lignin from corn stover (4-O-CS). Chemical properties of these two technical lignin sources are presented in *Table 2*. Although Kraft lignin generally presents higher molecular weight than organosolv lignin [22], harsh conditions during the Kraft extraction process may have caused Kraft lignin to repolymerize, lowering its molecular weight [14]. Moreover, the T_g of Kraft lignin is usually higher than organosolv lignin, however, due to the high content of sinapyl alcohol in hardwood lignin (11-K-HW), the two methoxy groups in the monolignol (*Figure 2*) hinder intermolecular linkages leading to a more linear structure, explaining the low T_g value.

Table 2. Chemical properties of the selected technical lignin [14].

Sample	Ash content (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)
4-O-CS	0.50	1900	5380	2.8	174
11-K-HW	1.62	1400	3200	2.3	146

The total hydroxy content in Kraft lignin samples was determined using ^{31}P-NMR; this analysis revealed that the total OH content in Kraft lignin samples (6.09 mmolg^{-1}) is higher on average than in organosolv (3.24 mmolg^{-1}). This can be seen in *Figure 8*.

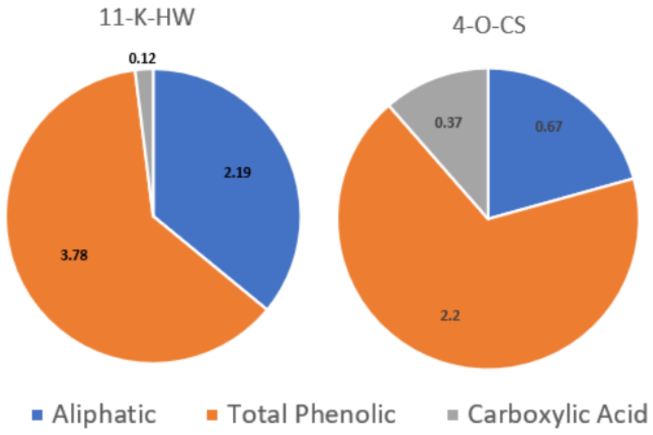


Figure 8. Hydroxyl group content in mmolg-1 for lignin samples.

The analytical techniques used for the quantification of the epoxy content in the epoxidized lignin samples were titration and ^{1}H-NMR. Although the total OH content in Kraft lignin is higher than in organosolv according to *Figure 8*, the epoxidation yield of the 4-O-CS samples is higher than that of the 11-K-HW sample (*Table 3*). This difference in epoxidation yield is caused by the different reactivity of the OH groups towards ECH that decreases in the order of phenolic OH, carboxylic acid and aliphatic OH [14]. Moreover, hard wood lignin is rich in sinapyl alcohol monolignol which contains two methoxy groups that can potentially sterically hinder the reactivity of OH group towards the ECH, explaining the lower epoxy content. The average number of epoxy groups in each molecule n (calculated as epoxy content (mmolg^{-1})·M_n) reflects the crosslinking density of the cured epoxy resin, which seems to be higher in the case of 4-O-CS. The epoxy content for the 4-O-CS sample is significantly higher than the 11-K-HW, this is in accordance with the yield obtained. Moreover, this can be caused by the higher content of phenolic OH groups in the 4-O-CS sample (almost 68%) in comparison to that of 11-K-HW (62%), according to *Figure 8* or simply due to more affinity of the organosolv lignin towards the glycidation process.

Table 3. Epoxy properties of the selected technical lignin [14].

Sample	EEW (titration)^1	EEW (^{1}H-NMR)^1	Yield (%)	n	Epoxy content^2
4-O-CS	347	343	90	5.6	2947
11-K-HW	354	359	46	3.7	1146

^{1} unit in g/eq ^{2} units in mmol/kg

Over *et al.* attempted to use organosolv lignin as a building block for epoxy resins. Organosolv lignin is glycidated and subsequently analyzed via different characterisation techniques. The epoxy content was analyzed by means of titration while the content of different types of OH groups was done via ^{31}P-NMR. Results can be found in the *Table 4* below. According to this data, all the phenolic OH reacted and the aliphatic OH groups were reduced from 2.70 to 1.92 mmol/g, this would add up to an epoxy content of 2.6 mmol/g [40]. However, these numbers are not in accordance with the one obtained by titration (3.2 mmol/g). This reduction in the epoxy content could be caused by some side reaction, such as the hydrolysis of the epoxy group.

Table 4. Chemical properties of organosolv lignin and epoxidized lignin [40].

Sample	Epoxy content	Aliphatic OH	Aromatic OH	Total OH
Organosolv lignin	0	2.70	1.83	4.53
Epoxidized organosolv lignin	3.2	1.92	0	1.92

Thermal and mechanical performance

First, the outcomes of the lignin-based epoxy resins by Nikafshar *et al.,* which are composed entirely of technical lignin, will be examined. The selected technical lignin to synthesize the epoxy were organosolv lignin from corn stover (4-O-CS) and hardwood Kraft lignin (11- K-HW). The thermosets are cured with the same agent (GX-3090), and its properties are measured and compared to those of the BPA-based one (DGEBA). DMA analysis is performed on the cured samples and the results are attained in *Figure 9*. At temperature of 25 ^{o}C, the DGEBA sample has a greater storage modulus (E’) than the 4-O-CS and 11-K-HW, which have moduli ranging from 1.3 to 1.4 GPa (*Table 5*). However, at temperatures above 100 ^{o}C, the storage modulus for the DGEBA sample decreases considerably in comparison to the moduli of the lignin-based ones, this is most probably a result of crosslinks weakening [14]. At temperatures above 100 ^{o}C, the loss moduli (E”) for 4-O-CS and 11-K-HW samples were also higher than that of the DGEBA one, which implies that the lignin-based systems are better at dissipating deformation energy at higher temperature. These two phenomena can be supported by the tan δ values; high tan δ correspond to viscous behaviour while low values indicate elastic behaviour in the material. The peak temperatures of the tan δ and E” are considered the glass transition temperature (T_g), which is higher for the cured lignin-based epoxy resins, and it explains the reduction in the storage modulus for the DGEBA sample. Additionally, Kraft lignin epoxy (11-K-HW) seems to present two T_g values. Larger area under the tan δ can be interpreted as the ability of the material to dissipate energy at a certain temperature, and the area for the lignin-based systems is considerably larger than that of the DGEBA one. The width of the tan δ represents homogeneity in the sample, broader peaks are related to greater heterogeneity, and these are present in the lignin-based samples as expected due to the complexity of the lignin structure.

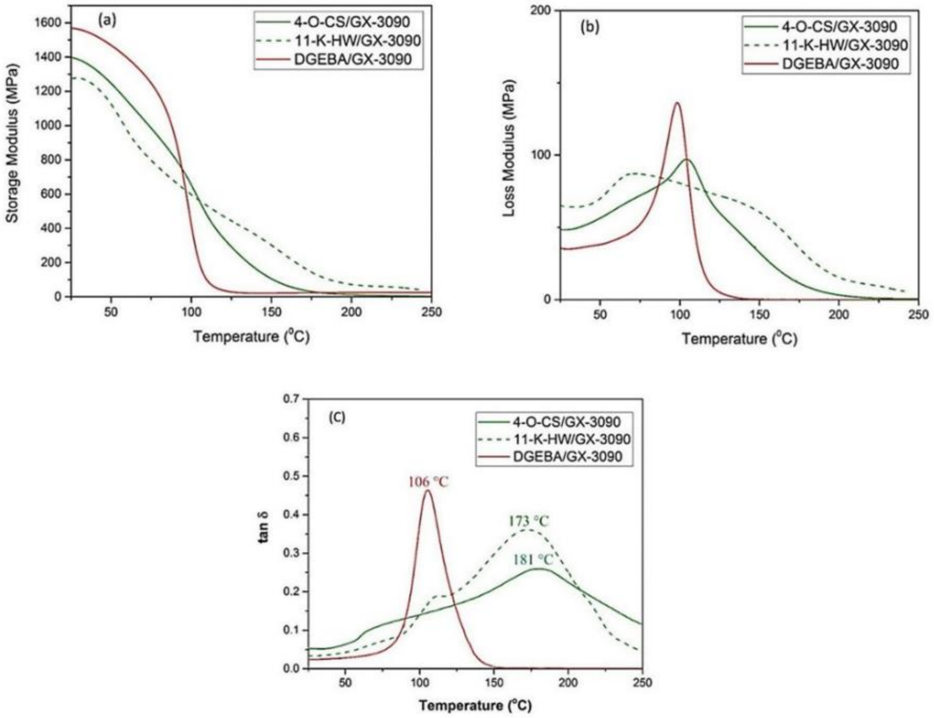


Figure 9. Storage modulus E’ (a), loss modulus E” (b) and tan δ [14].

Table 5. Storage modulus E’ and tan δ E”/E’ for the cured lignin-epoxy resins.

Sample	E’ [1]	E’ [2]	Tan δ (ºC) [3]
4-O-CS/GX-3090	1396	701	181
11-K-HW/GX-3090	1275	613	112 and 173
DGEBA/GX-3090	1557	331	106

[1] GPa at 25 ºC [2] GPa at 100 ºC 3 These values are the maximum of the peak in the tan δ curve

TGA analysis on these very same samples show their thermal stability (*Figure 10*). The curves present two plateau regions, which indicated two-steps degradation mechanism and subsequent weight loss drop after each of them, just as it was explained in section 2.4 Properties of Kraft lignin.

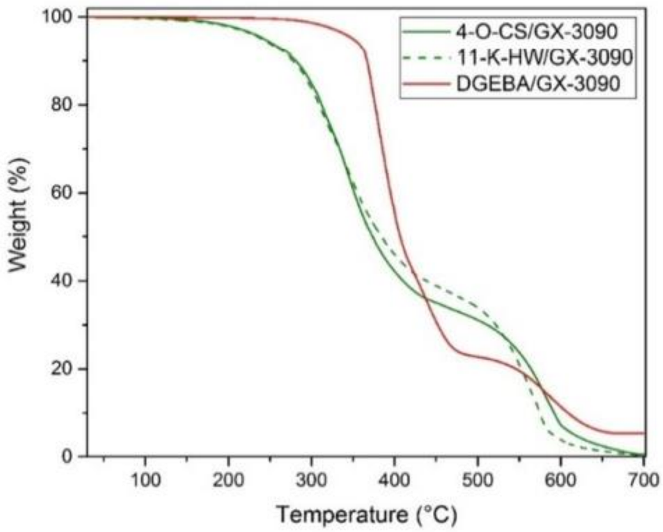


Figure 10. TGA curves for cured epoxy resin samples [14].

The decomposition temperature at 5% ($T_{d5\%}$) and 10% ($T_{d10\%}$) weight loss along with the static heat-resistant index (T_s) provide information on the thermal stability of the cured thermosetting (*Table 6*). T_s can be calculated with the following formula: $T_s = 0.49 \times (T_{d5\%} + 0.6 \times (T_{d30\%}-T_{d5\%}))$. Both the $T_{d5\%}$ and $T_{d10\%}$ of the lignin-based epoxy resins are lower than those of the DGEBA, as well as its thermal stability.

Table 6. Thermal stability of the cured lignin and BPA-based epoxy resins [14].

Sample	$T_{d5\%}$ (°C)	$T_{d30\%}$ (°C)	Ts (°C)
4-O-CS/GX-3090	241	345	149
11-K-HW/GX-3090	245	334	146
DGEBA/GX-3090	350	385	182

These findings suggest that thermosets made from unmodified technical lignin have similar thermomechanical capabilities to their BPA-based equivalents. However, the lignin-based epoxy resins present poorer thermal stability, indicating that they are not suitable for applications with high thermal demands.

2.6 Lignin epoxy resins as coatings and composites

2.6.1 Coatings application

The demand for paints and coatings and other durable products is predicted to rise in response to the rapid development in global manufacturing activities in the marine and automobile industry, flooring, white goods, food containers, etc. This is forecast to increase product demand around the world. Epoxy resins are widely used in the coatings industry, due to its high performance and adhesion to the surfaces of metal and non-metal structures for protection and/or decoration. Its remarkable properties, including adhesion, mechanical strength, chemical and heat resistance, protect the metal surface against corrosion, rust, oil, and a wide range of chemical reactions [49] [50]. Different layers are applied throughout the painting process of a vehicle's metallic frame, but the first layer (primer) is the most important. The primer has different purposes, which includes inhibiting corrosion of the metal substrate during application, protecting the paint system from mechanical damage and prevent it from spreading to the metal substrate, etc. [51]. As a result, coatings account for more than half of all epoxy resin manufacturing [52].

In the case of clear coating, a high-end colorless coating, the following properties are desired in the material:

- Transparent and glossy surface finishing, as well as a homogeneous and smooth surface is desired. A rough or uneven surface result in a decrease in gloss. For this, visual inspection is done on the coating surfaces.
- Good impact resistance is one of the most important properties. The coating must exhibit impact resistance to withstand a shock and avoid fracture by dissipating the energy from the impacts that it will be exposed to during service.
- Flexibility, defined as the material's ability to bend without undergoing any failure. Coatings are subjected to mechanical stresses such as deformation or changes in the substrate dimensions due to temperature or other factors, thus, the coating must exhibit flexibility to compensate for these changes. It is highly related to adhesion.

- Good adhesion to the surface of the material. Clear coatings are used as a primer; therefore, it requires a strong bond between the coating and the substrate during its service life. Adhesion failures will lead to exposure of the substrate to external environmental factors such as water, humidity, dust, or other contaminants.
- Fast drying time, this is especially important for the manufacturing process when multiple coating layers are required. In this way, the next coating layer can be applied at the right moment using knowledge on the drying time.

2.6.2 Composites application

Composite materials are made up of a variety of integrated materials that are combined to provide the desired qualities. In a composite, fibers (carbon, glass, or aramid) are embedded in a host polymer matrix (epoxy, phenolic, polyester, etc.). Among the different polymeric matrixes possible, epoxies are the most popular and is used in 80% of the total composite manufacturing [53], due to its remarkable properties. Because of their low cost, good mechanical properties, high specific strength, excellent adhesion and good heat and solvent resistance, epoxy-based composite materials are frequently used in load-bearing applications, such as those in the automotive, aerospace, construction, oil and gas, and marine industries [54].

The resin will often be used as a matrix in prepregs system. In the case of prepregs, the mechanical properties are mainly governed by the fibers, therefore, the adhesion between the fibers and the matrix is the most relevant parameter for the composite application of this novel lignin resin. Consequently, the manufacturing method of the prepreg must be adapted to the properties of the resin, in this case the viscosity and thermal stability being the main properties of interest.

3 Materials and methodology

This chapter provides an overview of the different materials that will be used during this project. Experimental methods and analytical techniques will also be described as the standards used for testing or analysing the different materials.

3.1 Materials

For this study, different sources of Kraft lignin from various suppliers will be used, properties of the substrates will be described in *Table 7* below. Softwood (gymnosperm) lignin, also referred to as type-G lignin, exhibit abundance of guaiacyl monolignol units which contain one methoxy group at position C3 in the aromatic ring [16].

Table 7. Properties of Kraft lignin sources.

Technical lignin	Molecular weight (g/mol)	pH	Solid content (%)	Source
Lignin #1	5500-7500	2.5–3.5	94 ± 3	Softwood pine and spruce
Lignin #2	-	6.5	95	Unknown softwood
Lignin #3	5000	2.5 - 4.5	65	Softwood pine

3.2 Synthesis of lignin epoxy resin

This section details the different experimental methods that have been conducted, they will be divided into three categories: experimental procedures, analytical and material testing techniques that have been conducted.

3.2.1 Confidential Fractionation of technical lignin

In accordance with *Table 7*, the lignin sources are technical, which means that high molecular weight (M_w) molecules are present in these substrates. These technical lignin sources are bulk feedstock with a highly crosslinking and functionalised structure (aliphatic hydroxyl, phenolic hydroxyl, carboxyl, carbonyl and methoxy groups). Reactivity of technical lignin is much lower compared to depolymerized lignin given that its reactive sites are restricted by its complex structure [55]. To improve the availability of these reactive sites, and thus the utilization of this substrate, some method must be applied. However, due to lack of in-house technology for treating technical lignin, a new process has to be developed at Westlake Epoxy. The most promising solution for Westlake Epoxy is the Confidential Fractionation of lignin, an invention from which fractionated lignin is obtained and used as a substrate for the novel epoxy resins (*Figure 11*).

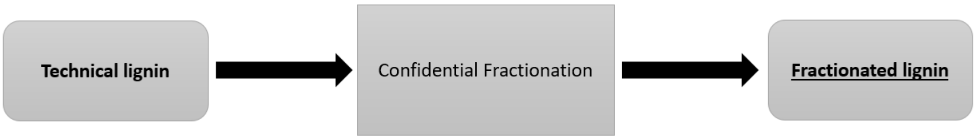


Figure 11. Confidential Fractionation of technical lignin.

In order to improve the fractionation yield of the technical lignin, an additional Confidential Treatment is included in the process. Therefore, *Figure 12* presents the solvent extraction of lignin with the acidification step.

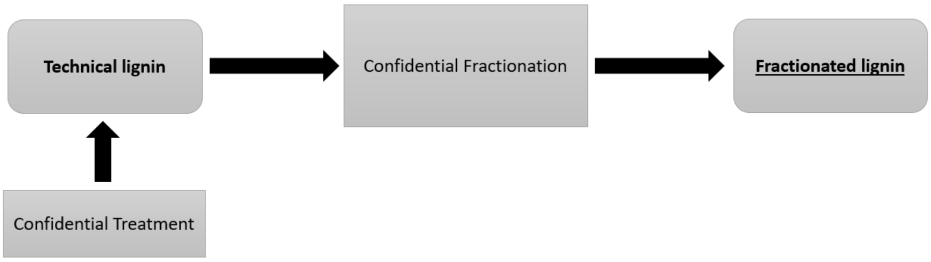


Figure 12. Confidential Fractionation of technical lignin using Confidential Treatment.

3.2.2 Glycidation of lignin epoxy resin

The synthesis of epoxy resins is carried out via glycidation. The initial goal was to synthesize a full bio-based lignin epoxy; however, only using technical lignin will create a solid product with considerable insoluble material making it unsuitable for further applications. A solid epoxy resin would be very difficult to handle both during the process and the subsequent application testing. This way a Confidential Epoxy Treatment was developed to decrease the viscosity of the lignin-based epoxy resins.

The glycidation reaction will be performed in small and large scale given the different needs for either coatings or composites application, therefore, this section will be divided in two parts. The material which is used for coating testing will be synthesized on a small-scale (250 g), whilst, for composites testing a higher amount of material is required (~500 g) and it will be performed in a 2-litre reactor. In this way also, a comparison between small and large-scale can be done.

It must be noted that since no NMR analysis was available at the start of the project, the phenolic OH groups was estimated to be 3400 mmol/kg. This number is in accordance with a rough average that was found in the literature, which gives a value of about 3230 mmol/kg [56] or between 3900 and 3200 mmol/kg [57].

- **Small-scale glycidation of lignin epoxy resins**

The unit employed to perform the glycidation on a small-scale is a multi-reaction block. This consists of 5 flasks of 100 or 250 ml each placed on a heating block (*Figure 13*). Hot oil is contained in one of the flasks for temperature control system with respect to measurement of the hot oil temperature. Based on this temperature (hot oil flask), the temperature of the system is adjusted manually on the heating block. For safety and operational purposes, condensers are attached to the other 4 flasks. This multi-reaction block is used to perform small-scale experiments with the advantage of allowing screening of the reaction and easy reproduction of the experimental conditions. Stirring magnet is added to all the flasks containing the reaction mixtures, the stirring speed can be controlled in the heating block as well. The magnetic stirrers are strong rare-earth metal magnets, which aids in stable stirring over the course of the reaction and especially when salts are formed during glycidation.

1. Water inlet
2. Condensers
3. Round-bottom flasks
4. Heating block

Figure 13. Multi-reaction block setup for glycidation.

The experimental conditions and steps in which the glycidation reaction is performed will be detailed in the flow diagram in the *Figure 14*. Note that the Confidential Epoxy Treatment is used in the depicted process below to yield a liquid epoxy resin, however, this is not indicated due to confidentiality.

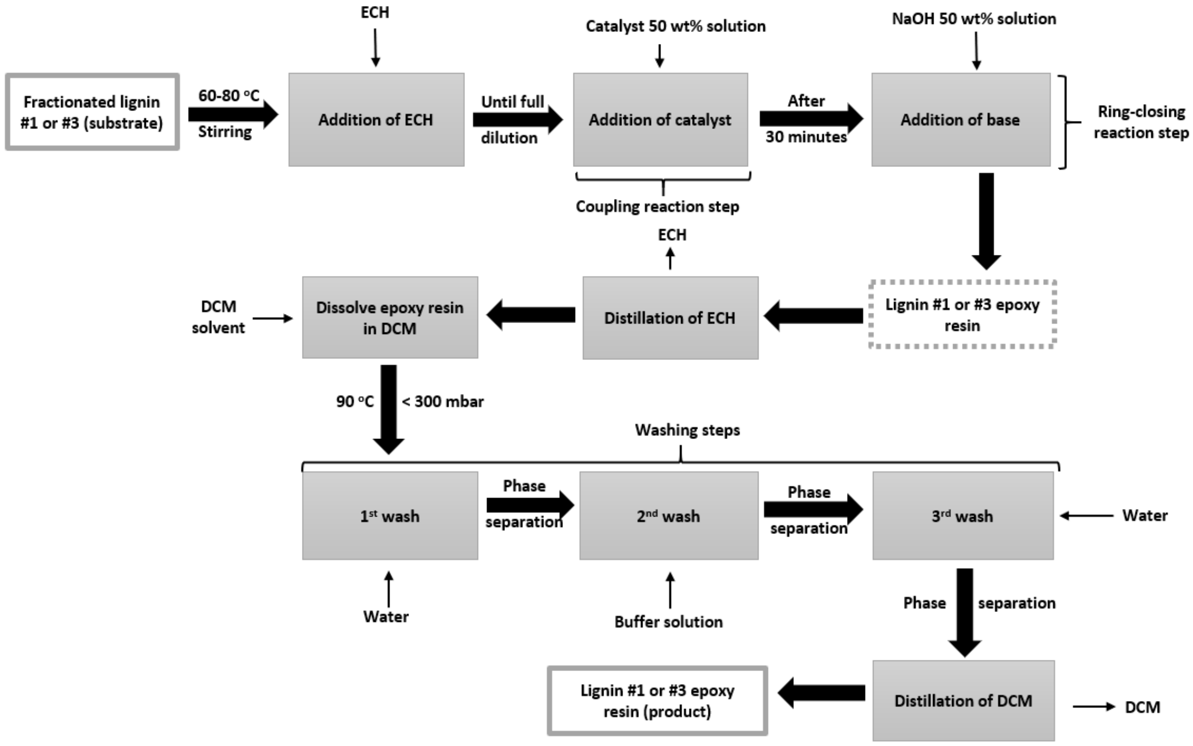


Figure 14. Diagram for the small-scale glycidation process.

This synthesis on small-scale was carried out to obtain the material for the coatings testing, since they require less amount of material in comparison to composites. The washes are performed in the following fashion: the resin dissolved in DCM is added to small bottles to later add the water or buffer for the wash. Subsequently, these bottles are put in the centrifuge to collapse the organic phase and later remove the water or buffer phase. During these washes it was observed that there was an interphase formed between the organic and water phase with a foamy consistency. This interphase is suspected to be some polymeric compounds that are not identified.

- **Large-scale glycidation on lignin epoxy resins**

The scale-up glycidation is carried out in a 2-liter jacket reactor (*Figure 15*), which will allow to obtain a larger amount of material. The vessel reactor is equipped with pump, overhead stirrer, thermoregulator and dosing device to achieve reproducibility and optimisation of a chemical process. Performing such reaction in a reactor present a few differences in comparison to the setup for small-scale:

- It allows for a more homogeneous stirring and temperature control compared to the reaction taking place in different round-bottom flasks. This makes it possible to make a better screening of the temperature throughout the course of the reaction.
- Presence of a dosing device which makes it easier to add a reagent over time. While using the multi-reaction block setup, the base would have to be added manually.
- Azeotropic distillation can be added to the synthesis, which will remove the water from the reacting system.
- All the steps in the synthesis can be carried out in the reactor, which will positively impact both the effort and the time invested in the reaction. In the small-scale glycidation, the washing steps would have to be carried out in small bottles which have to be put in the centrifuge and the removal of solvents is done in a rotary evaporator, which can be very time consuming, and a lot of material can be lost in the process of transferring the material.

1. Vessel reactor
2. Overhead stirrer
3. Dosing device

Figure 15. Reactor for large-scale glycidation reaction.

Not only a synthesis in a 2-liter reactor has the advantaged mentioned above, but it also opens the door to different routes and changes in the synthesis. This is the reason why different options are explored on a large-scale in comparison to the small-scale performed in the multi-reaction block setup. Here, the different routes or changes that can be applied to this new synthesis:

A) ”Wet” glycidation

This process is performed at 70 °C and no pressure, therefore, the water that is formed or added to the reaction stays in the reaction. The reaction conditions and the sampling will be presented in *Figure 16*. Note that the Confidential Epoxy Treatment is used in the depicted process below to yield a liquid epoxy resin, however, this is not indicated due to confidentiality.

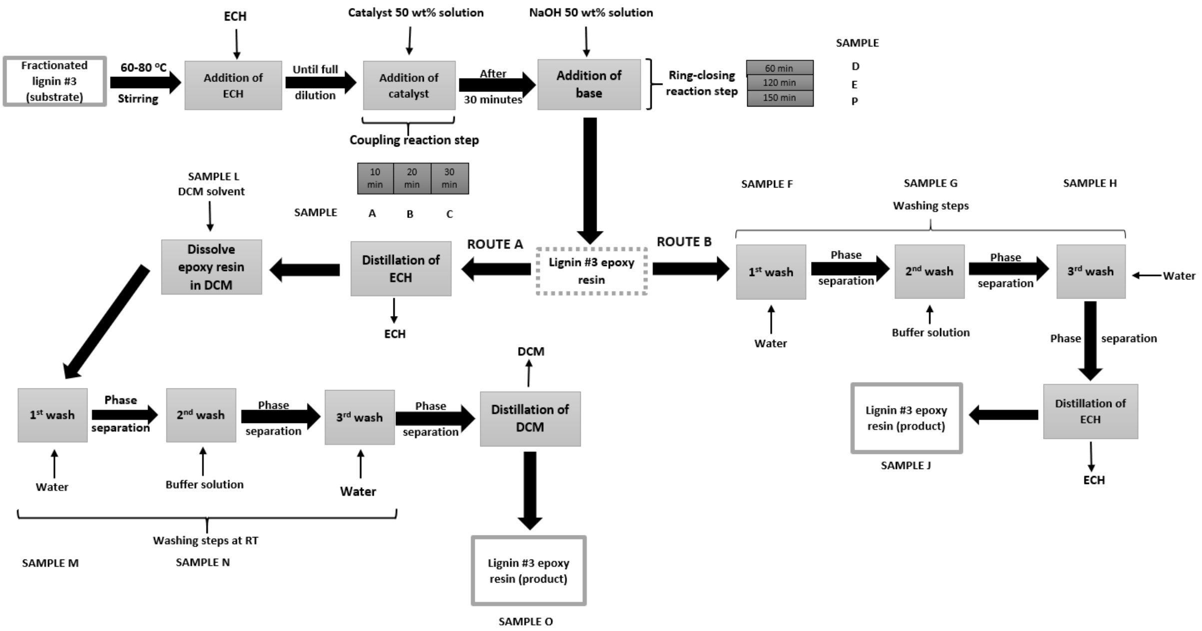


Figure 16. Scheme of large-scale glycidation under "wet" conditions.

It is important to remark that when the lignin epoxy resin was obtained, half of the content remained in the reactor to continue with route B, whilst the other half was transferred to another flask in which route A was followed. Some of the observations noted during the last wash in the route B was that no phase separation was taking place, therefore, the foam interphase was not removed and left with the organic phase leading to a product with foamy aspect. This was different for the final product from route A, in which the product resembled more to that obtained from the small-scale reaction.

B) ”Dry” glycidation

Azeotropic distillation of water is carried out during the synthesis, therefore, temperature ranges from 60 to 80 °C and low pressure is applied. *Figure 17* depicts the reaction steps and the sampling. It must be noted that during this synthesis, a smaller number of samples are taken because otherwise the pressure would have to be stopped for the sampling and this could affect the progress of the reaction. Moreover, there were some issues encountered during the washing steps. No phase separation was observed after the 1st wash; therefore, the system was left to separate overnight. Due to the long phase separation, it was decided that no more washes would be performed. The final product had a much different consistency in comparison to the other ones, this could have been caused by some molecular build-up that comes associated with the azeotropic distillation. Note that the Confidential Epoxy Treatment is used in the depicted process below to yield a liquid epoxy resin, however, this is not indicated due to confidentiality.

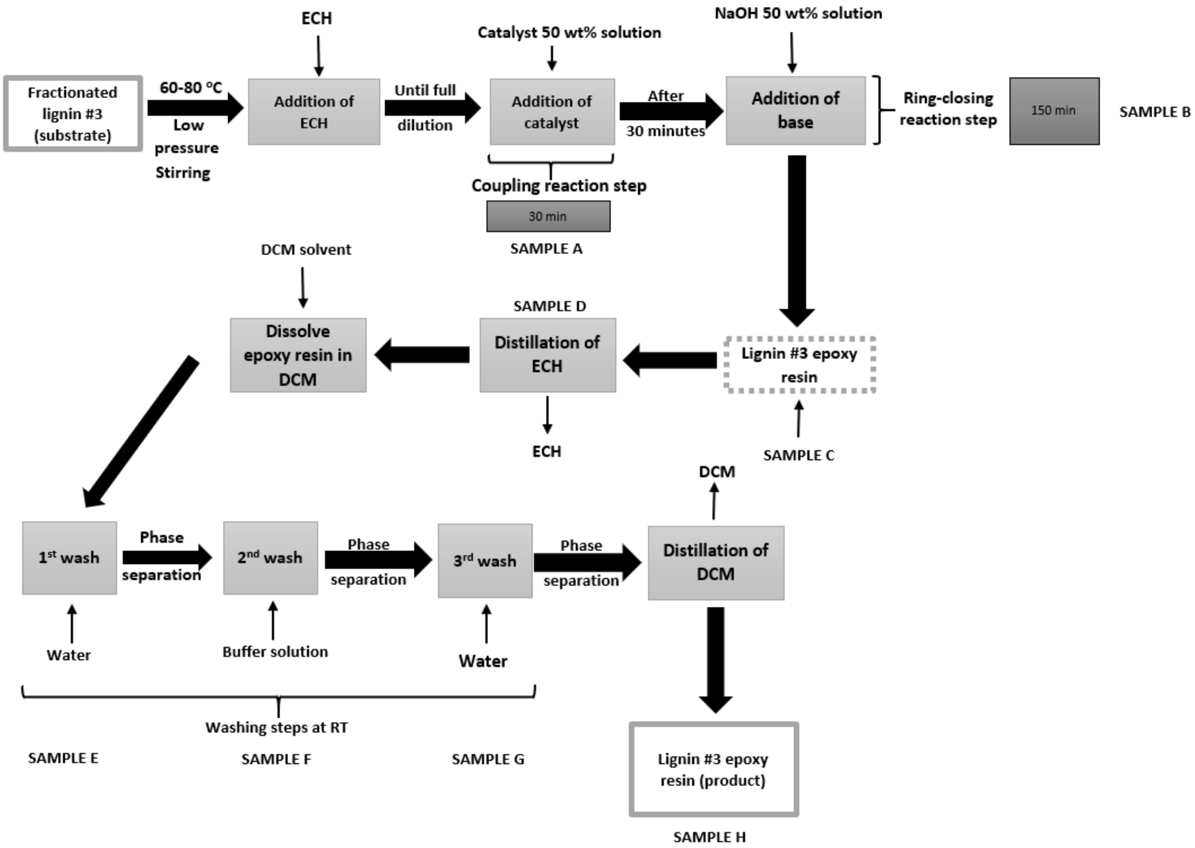


Figure 17. Scheme of large-scale glycidation under "dry" conditions.

C) "Wet" glycidation + Confidential Pre-treatment

This process was decided after looking at the "dry" and "wet" glycidation. In this case, apart from the Confidential Epoxy Treatment, another Confidential Pre-treatment is applied to the substrate. Reaction conditions and description of the process are found in and *Figure 18*. The distillation of ECH was done on two different days, and thus, the reason why two samples (J and K) were taken for the same step in the process.

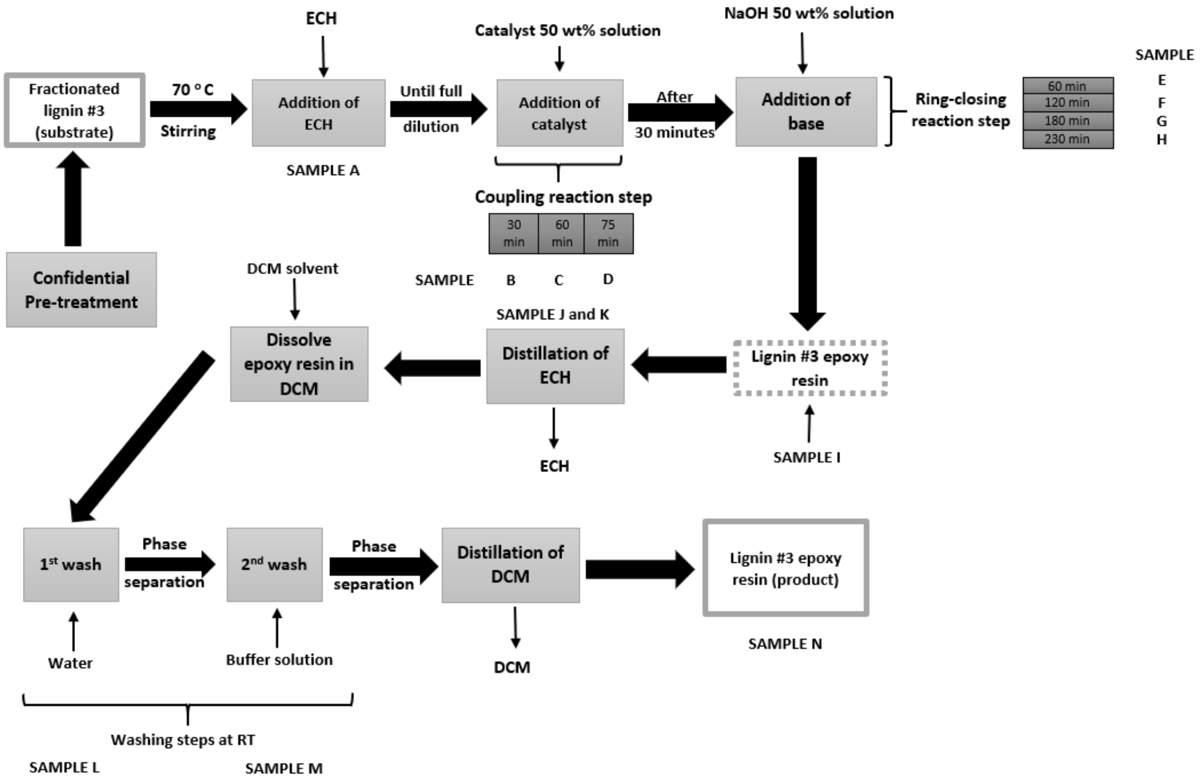


Figure 18. Scheme of large-scale glycidation under "wet" conditions + Confidential Pre-treatment.

3.3 Analytical methods for lignin epoxy resins

Analytical techniques aid in the separation, identification, characterisation, and quantification of a certain analyte. These methods, which range from classical to instrumental, can be qualitative or quantitative. The goal of these analytical techniques is to elucidate on the chemical structure and composition of a material, in this case epoxy resins. This section describes the different analytical techniques that have been employed for the development of these novel lignin-based epoxy resins. Each of these techniques has a distinct function in the characterisation of these materials.

3.3.1 Gas Chromatography (GC) for ECH determination

The synthesis of epoxy resins involves the reaction with an excess of ECH, which exhibits certain hazards, therefore, monitoring of residual ECH in epoxy resins is essential. Gas Chromatography (GC) is a key analytical technique for the determination of residual ECH present in the obtained product resins. An analytical method is developed to obtain the quantitative amount of these compound in the lignin-based epoxy resins. Quantitative analysis was possible by using an internal standard (n-butanol) which is a compound that aids in the quantification of an analyte, which in this case is ECH. *Figure 19* shows the GC unit that was used for the analysis.

Figure 19. Gas Chromatography (GC) equipment.

Preparation of the GC samples goes as follows: 0.5 g of the sample is measured with 0.65 µl of the internal standard (n-butanol) and dissolved in 10 ml of DCM solvent. An amount of 1 ml of this mixture is transferred to a GC vial that is later placed into the sample tray of the GC unit.

3.3.2 Titrations

Titration is a quantitative (volumetric) analysis to determine the concentration of an analyte. A titrant is employed as a reference solution that will react in a known volume or concentration with the solution of analyte [58]. Two different titration methods are used for these epoxy resins.

- ***EGC determination***

The epoxy group content (EGC) is a significant variable in determining the reactivity and properties of these epoxy resin in different applications such as coatings and composites. The EGC is determined by the standard test method ASTM D1652-11. This method allows to determine 1,2-epoxy group in epoxy resins in the range of 200 to 8000 mmol/kg. Perchloric acid is used as the titrant along with a quaternary ammonium halide, tetraethylammonium bromide (TEAB) was employed for these titrations. The reaction between the perchloric acid and the quaternary ammonium halide generated the hydrogen halide which reacts stoichiometrically with the epoxy groups via ring-opening to form bromohydrins. Thus, the amount of perchloric acid used in the titration is correlated to the epoxy group content (EGC). *Figure 20* depicts the ring-opening reaction mechanism for the formation of the bromohydrin.

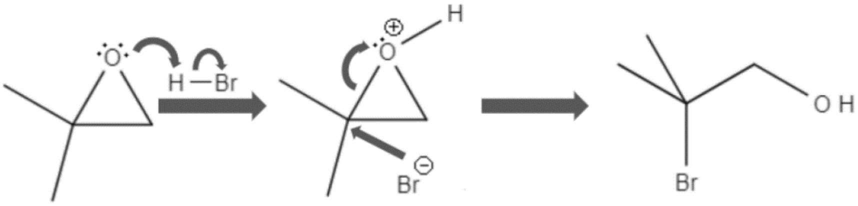


Figure 20. Ring-opening reaction of epoxy group with hydrogen bromide to obtain the bromohydrin.

For the EGC titrations, about 30 mg of the epoxy resin sample is dissolved in 30 ml of DCM and 10 ml of acetic acid with the addition of a spoon of TEAB. This mixture is mixed and once dissolved, it is put in the measurement station.

- ***Hydrolysable chloride determination***

Glycidation (epoxidation) process consist in two consecutive steps: coupling reaction and ring-closing reaction. During the coupling reaction, chlorohydrin intermediates are formed, and some difficulties can be encountered in the dehydrohalogenation process taking place on the second step. This conversion of the chlorohydrin moieties with NaOH is not complete due to competing reactions in the reaction mixture, often due to the presence of ECH in it. These 1,2-halohydrin intermediates molecules that have not been dehydrohalogenated are the main source of hydrolysable chloride in epoxy resins. High presence of hydrolysable chloride species indicated that the ring-closing step has not been effective, which would have an effect in the EGC and thus, the quality of the product epoxy resin.

In this titration, the sample is dissolved in 30 ml of dimethyl sulfoxide (DMSO) and 25 ml of potassium hydroxide (KOH) in ethanol solutions, this mixture is left to react for 15 minutes. After this time, 20 ml of acetic acid and 50 ml of methyl ethyl ketone (MEK) are added, to be followed by a titration used silver nitrate.

- ***Inorganic chlorine determination***

Inorganic chlorine content is a very important parameter for the quality of the epoxy resin. The presence of this inorganic chlorine can lead to undesirable side reactions that can finally affect the properties of the material. Chlorine impurities and other chlorine-containing compounds, especially in ionic form, can cause corrosion in the presence of moisture [59]. For this titration, silver nitrate is used as a titrant agent to determine the content of inorganic chlorine in the epoxy resin.

For this titration, the sample is added to a 50 ml of MEK. Once it is dissolved, 20 ml of acetic acid are added, and silver nitrate is used as a titrant in this determination.

3.3.3 Nuclear Magnetic Resonance (NMR)

In this case, ^{31}P-NMR was the chosen technique for the molecular characterisation of lignin. The phosphorylating reagent used in this case is (2-chloro-4,4,5,5-tetramethyl-1,3-2-dioxaphospholane (TMDP)) which will react with the hydroxyl groups as it is depicted in *Figure 21*. For the preparation of internal standard, cyclohexanol is mixed with pyridine as a base, deuterated chloroform ($CDCl_3$) and chromium (III) acetylacetone ($Cr(Acac)_3$).

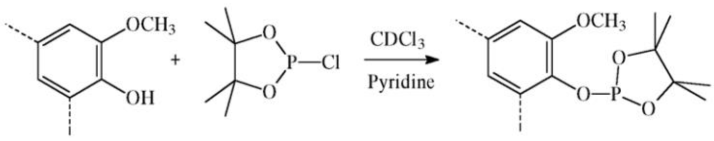


Figure 21. Reaction between phenolic structures and phosphorylating reagent TMDP [60].

3.3.4 Fourier-transform infrared spectroscopy (FT-IR)

This qualitative analysis is used for the identification of the different functional groups present in the lignin molecule. Before starting the analysis, a background measurement is done to make sure the Attenuated Total Reflection (ATR) crystal, where the sample will be placed, is clean. Otherwise, this will be cleaned with alcohol. No sample preparation is required, so the solids are directly placed in the ATR crystal place in a way that fully covers the crystal. To make sure there is a proper contact between the sample and the diamond, apply pressure on the solid using the swivel pressure tower that has a pointed tip (*Figure 22*).

1. ATR crystal plate
2. ATR crystal
3. Swivel pressure tower with pointed tip

Figure 22. FT-IR equipment.

3.3.5 Gel permeation chromatography (GPC)

This size-exclusion chromatography is based on molecular mass differences as it is widely used for polymer analysis. This very effective technique allows the determination of the molecular weight and weight distribution of polymers samples. The components in the samples are dissolved in a solvent (mobile phase) and travel through the stationary phase (crosslinked gel) with a specific pore size at different velocities depending on its molecular size and molar mass [61]. The column is packed with porous beads, while smaller molecules will permeate the pores and diffuse into the beads, larger molecules do not permeate the pores and have a shorter residence time. One important factor that determines lignin's reactivity and physical properties is its molar mass, therefore, its determination is crucial. This technique is used for the determination of molecular weight of the fractionated lignin substrates, as well as for the screening of glycidation reactions.

For the experiment, 0.1 g of the sample is dissolved in 10 ml of tetrahydrofuran (THF). Then 1 ml of this mixture is transferred to a vial that is later placed into the sample tray of the GPC unit.

3.4 Material characterisation methods for lignin epoxy resins

3.4.1 Differential Scanning Calorimetry (DSC)

The DSC measurements are obtained by heating an uncured or cured epoxy resin at a rate of 10 K/min from -20 ºC to 250 ºC. Curing of a thermosetting is an irreversible crosslinking reaction in which heat is involved, and this can be monitored using DSC measurement. The T_g can be detected as an endothermic stepwise increase in the heat flow (W/g) when the resin transitions from a glassy to a rubbery material. The integrated area under the exothermic peak is the heat of cure (ΔH_{cure} in J/g). This heat of cure can be used to determine the percentage of cured resin and gives an idea on what is the temperature required for the resin to cure. The more crosslinked the resin, the smaller the heat of cure, therefore, a fully cured resin presents an undetectable heat of curing. This way, the onset and the end of curing can be determined by DSC as well.

3.4.2 Dynamical Mechanical Analysis (DMA)

This analysis is performed on the cured prepreg laminates made of the lignin epoxy resin as a matrix. The laminate sample is subjected to a temperature range from 25 to 280 °C at a heating rate of 2.00 K/min and a frequency of 1 Hz. The mode of the analysis was 3-point bending and the samples were cut in standard dimensions of about 40 mm length, 8 mm width and 2 mm thickness.

3.4.3 Thermogravimetric analysis (TGA)

TGA is performed in both the substrates and the raw epoxy resins, to understand the thermal stability that they exhibit. In this case, the analysis is performed from 25 to 1000 °C at a heating rate of 10.00 K/min. TGA curves will give information about the degradation of the material upon time.

3.4.4 Thermomechanical Analysis (TMA)

TMA is performed on the cured resins to determine the expansion behaviour and softening temperature of materials. The samples are exposed to a range of temperature of -40 to 240 °C with a heating rate of 5.00 K/min.

3.4.5 Interlaminar Shear Strength (ILSS)

ILSS determines the ability of a composite to withstand delamination damage or the shear strength between the laminates in the composite. In this way, the strength of the matrix or the interaction between matrix-fiber can be determined. In this case, the analysis was performed on the cured prepreg laminates at 23 °C and relative humidity of 60.3% with an initial load of 10 N at a displacement rate of 1 mm/min. The specimens were cut in standard dimensions of about 10 mm width and 2 mm thickness.

3.4.6 Rheometer

The viscosity of the experimental samples is measured using an Anton Paar Rheometer MCR 92, equipped with a cone-plate measuring set. Viscosity of the material is one of the most important properties, especially for the application both for coatings and composites. For this, the rheometer will be used both in rotation and oscillation mode, and the isothermal and dynamical viscosity can be determined. In the rotation mode, the shear rate is 10 s^{-1} when measuring viscosity of the resin mixed with the other components (curing agents and catalyst) while it increases to 100 s^{-1} for the raw resin. In the case of oscillation mode, the frequency was 10 Hz with amplitude gamma of 1.25%. Additionally, from the oscillation viscosity it is possible to obtain the storage (G’) and loss modulus (G”) of the resin mixtures.

3.4.7 Impact testing

This standard method is commonly used in the coatings industry to forecast the performance of organic coatings in terms of their capacity to withstand cracking caused by fast deformation. According to the methods ASTM D2794-93, the impact resistance is defined as the number of inch-pounds required to produce cracking in the deformed coating under standard conditions. However, to comply with the SI units, the data will be presented in kilogram-meters. Impact resistance is one of the most important chemical properties of a coating, especially those use for protective purposes such as the clear coatings since they subjected to damaging impacts both during manufacturing and service.

The apparatus consists in a vertical tube with graduation marked in inch-pounds along it, the base allows for a flat panel specimen to be placed at 2 inches below the vertical tube. A metal cylinder acts as a weight that is placed in the guide tube which also has a steel hemispherical head indenter. The support panel has a cylindrical hole centered under the indenter. For the test, the panel is placed flat against the base support so that the indenter is in contact with the panel surface. Raise the weight at a certain height and release it so that it drops on the indenter. It is advised to start at a height where no failure is expected, after observing the impact area if not cracks are identified, increase the height every time. The impact failure point would be the inch-pound level at which the coating mainly exhibits failure, the test is repeated 4 times at that certain level.

3.4.8 Pendulum hardness testing

Hardness of an organic coating is measured by means of using König pendulum damping testers following the standard ASTM D 4366-95. Whilst hardness is the ability of a material to resist localized deformation [62], König hardness is defined as the time in seconds it takes to decrease the amplitude of the tester from 6 to 3°. The principle behind this test is based on the idea that the amplitude of oscillation of a pendulum touching a surface decrease more rapidly the softer the surface (*Figure 23 a*). Therefore, the shorter the damping time, the lower the hardness of the coating.

König Pendulum Apparatus is depicted in *Figure 23 b.* The cured uniform coating layer on a panel is placed on the panel table, subsequently, the pendulum is gently brought in contact with the panel surface. The pendulum is deflected 6° and then released, a timing device will time the number of oscillations it takes for the amplitude of swing to decrease from 6 to 3°. The König Hardness is calculated by multiplying the number of oscillations by the time it takes in each swing (1.4 seconds). It is recommended that the procedure is repeated in different areas (upper, middle, and lower) of the coating to obtain accurate results.

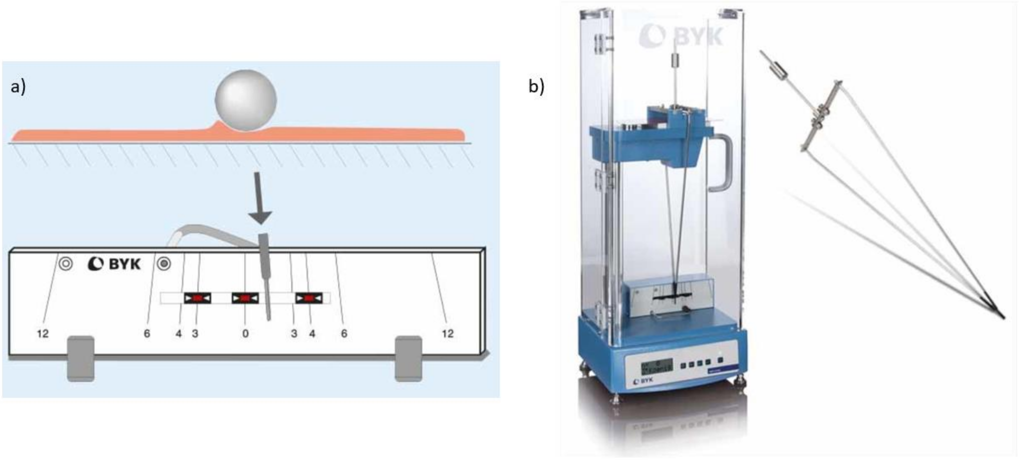


Figure 23. a) Principle of Pendulum Damping Testing and b) König Pendulum Hardness Apparatus. Photos retrieved from BYK Instruments.

3.4.9 Cupping testing

This method is used for assessing the resistance of a coating to crack or detachment from a metal substrate after when subjected to a gradual deformation by indentation under standard conditions, according to ISO 1520:2006. The Erichsen cupping test is a widely used method in the coatings industry for assessing the elongation and adhesion properties of coatings [63]. Determining these two properties of a coating is quite essential since they can give information on the applicability of a certain coating.

The Erichsen cupping device is equipped with a spherical-ended penetrator that can be used to push the specimen's center through the die creating a dome shape indentation until the test's end point is reached. The end point is reached when cracks or detachment occurs in the coating, this is the minimum depth of indentation which is the distance travelled by the indenter from the zero position. A microscope or magnifier is used to examine the coating during the test. Low results from this test may suggest that the coating cannot withstand elongation stresses, which would restrict its use in certain applications. The components of a standard Erichsen cupping test device are shown in *Figure 24* below.

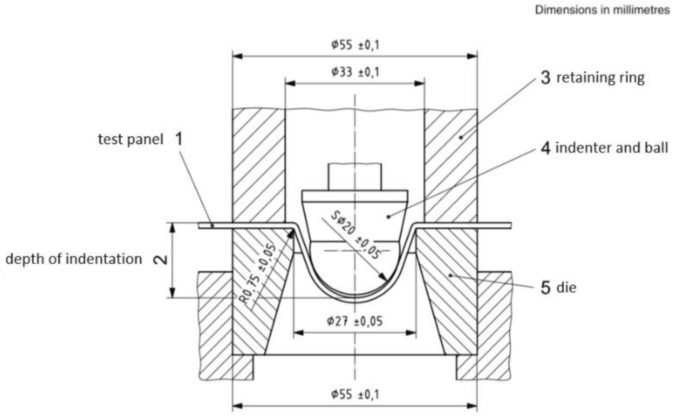


Figure 24. Components of a Erichsen cupping test apparatus. Adapted from ISO 1520:2006.

3.4.10 Becker drying test

This test is widely used in the coating industry to determine the rate of dry-film formation, and the different stages involved in this process. Once a coating is applied, it settles under the effects of gravity, and as it starts to harden leading to a thin and dry film produced on the surface. The coating then keeps drying until it is ultimately fully cured. This test method is in accordance with ASTM D 5895 – 01, in which a needle carrier travels through the length of test strip in which the organic coating is applied in 6, 12 or 24 hours. A straight-line recorder is used; thus, the drying time recorder is placed on the wet film and the stylus moved across the glass strip at the selected speed.

There are four stages associated with the dry-fil formation of organic coatings. Set-to-touch time is observed by the formation of a pear-shaped depression when the film stops flowing over the path of stylus and leaves a track in the film. The track-free time is reached when the where the stylus starts to tear the film leaving a discontinuous cutting in the film. Dry-hard time appears when the stylus stops tearing or cutting the film and leaving only a visible trace on the film. Finally, the dry-through time is reached when no visible track is observed in the film.

Figure 25 depicts the mentioned dry-film formation stages. The coating is applied to a crystal strip plates to later be placed on the sample holder. After that, make sure to mark on the crystal strip where the needle carries lie at the start of the test, since this will be the starting point.

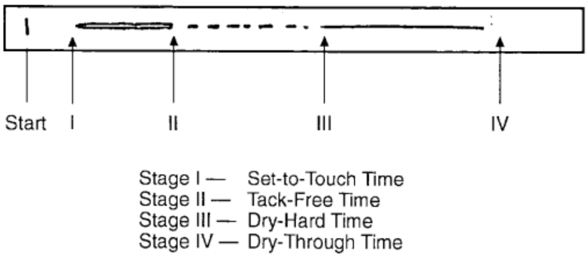


Figure 25. Stages of the dry-film formation on an organic coating using a straight-line drying time recorded. Retrieved from ASTM D 5895-01.

3.4.11 Cross-cut test

This method is in accordance with the standard ISO 2409:1992(E). This test includes the procedure for determining how well paint coatings resist pulling away from substrates when a right-angle lattice pattern is carved into the coating and penetrates all the way through to the base material. Moreover, the property measured with this test relies on the adhesion of the coating to the substrate. The test is performed on cured coatings that have been applied to a steel plate. The cutting tool is used at a constant pressure, and with the help of a spacing guide to ensure that the lattice pattern is formed.

4 Results and discussion

This chapter conveys the results obtained from the experiments performed and its corresponding discussion.

4.1 Confidential Fractionation of technical lignin

This section focuses on the development and analysis of the fractionation method that was carried out on the technical lignin substrates, to obtain a reactive system for the epoxy resin synthesis.

4.1.1 Confidential Fractionation yield

As mentioned in the previous section, three of the lignin sources are technical lignin which means that their reactivity is much lower if compared to further depolymerized form of lignin. Direct utilisation of technical lignin is limited due to the high polydispersity and complex structure [64]. However, fractionation methods allow to obtain narrow molecular weight distribution and high purity fractions, leading to the possibility of tailoring lignin structure to maximize its value [65]. *Table 8* below compiles the extraction yields obtained for the different technical lignin.

Table 8. Confidential Fractionation yield of the different lignin sources.

Source	Confidential Fractionation yield (%)
Lignin #1	50-60
Lignin #2	0-5
Lignin #3	20-30

As it is observed from the table above, about half of the *lignin #1* gets fractionated. On the other hand, significantly lower fraction is obtained in the case of *lignin #2* and *lignin #3*. The Confidential Fractionation yield for the latter two lignin is too low to even consider a potential scale-up process, therefore, it is necessary to find a way to enhance this yield. As mentioned before, a Confidential Treatment is chosen as a potential solution.

Table 9. Confidential Fractionation yield of lignin #2 and #3 after Confidential Treatment.

Source	Confidential Fractionation yield (%)
***Lignin #2* + Confidential Treatment**	50-60
***Lignin #3* + Confidential Treatment**	60-70

The Confidential Fractionation yield improves significantly in both cases as depicted in *Table 9*, indicating that Confidential Treatment is an effective method. However, when performing on a large scale the Confidential Fractionation of *lignin #2*, the process becomes very difficult. Thus, *lignin #2* was excluded from further use in the development of epoxy resins. After a fractionation method has been developed, it is important to characterise the material that is obtained. Therefore, the next sections will cover the use of different characterisation techniques on fractionated lignin substrates.

4.1.2 Thermal stability of fractionated lignin substrates

According to the findings of the previous section, there is a considerable variation in the Confidential Fractionation yield between technical lignin and with or without Confidential Treatment. Therefore, it is of interest to have an idea of the differences in composition of the fractionated lignin that has been obtained. Therefore, an initial TGA analysis was performed for the characterisation of these fractions. Thermal stability can give an initial idea on the difference in composition for the different fractionated lignin substrates. A rapid change in weight can be associated to a lower molecular weight lignin fraction, and thus, a lower thermal stability. *Figure 26* presents the results of the TGA analysis for the fractionated lignin.

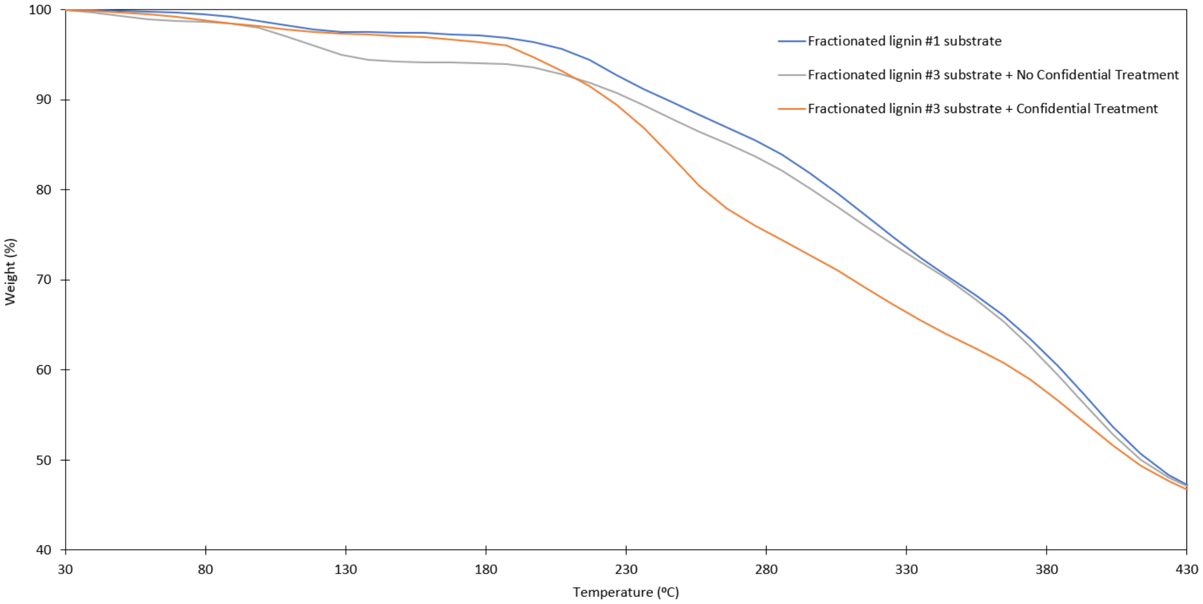


Figure 26. TGA curves for the fractionated lignin substrates.

A common finding that can be observed in all the three TGA curves is a two-step degradation mechanism due to the presence of two plateau regions, the first one between 40 to 100 ºC and the latter between 200 to 400 ºC. According to literature, the first degradation step can be associated to the release of light molecules such as CO, CO_2, and dehydration while the second is associated to the breakage of bonds between the aromatic compounds in the lignin molecule [14].

From the TGA curves, different parameters of thermal stability can be deducted such as the temperature at 5% weight loss ($T_{d5\%}$), at 30% weight loss ($T_{d30\%}$) and the statistic heat-resistance index temperature (T_s). These three parameters are interconnected with each other in the formula below:

$$T_s = 0.49 \times (T_{d5\%} + 0.6 \times (T_{d30\%} - T_{d5\%}))$$

These parameters are compiled and calculated in *Table 10.*

Table 10. Thermal stability parameter for the fractionated lignin substrates.

Source	Total weight loss (%)	$T_{d5\%}$ (ºC)	$T_{d30\%}$ (ºC)	T_s (ºC)
Fractionated lignin #1	67.72	212	344	143
Fractionated lignin #3 + No Confidential Treatment	67.19	128	346	127
Fractionated lignin #3 + Confidential Treatment	66.39	197	310	130

While no significant differences are found between the total weight loss for all the different samples, the other thermal parameters seem to deviate more from each other. The heat-resistance index, which is defined as ability of a certain material to withstand a heat flow [66], is higher for *fractionated lignin #1* compared to the other two lignin sources, same applies for the $T_{d5\%}$. However, the most interesting observation is the impact of the Confidential Treatment in the thermal stability of fractionated lignin #3 samples. The $T_{d5\%}$ for *fractionated lignin #3 + Confidential Treatment* is much larger than for *fractionated lignin #3 + No Confidential Treatment,* but the reverse scenario is encountered when considering the $T_{d30\%}$, meaning that the *fractionated lignin #3 + Confidential Treatment* presents a much rapid weight loss. The difference in the T_s is probably caused by dissimilarities in their chemical composition and molecular weight between the samples, especially considering that they come from different sources. According to *Table 7*, the *lignin #1* sources has higher molecular weight molecules in comparison with *lignin #3*, which explains its higher T_s values as well as for the other thermal parameters. The differences in $T_{d5\%}$ and $T_{d30\%}$ between the two fractionated lignin #3 samples is attributed to the Confidential Treatment. This one can cause the breaking down of high molecular lignin molecules, making them more soluble and thus, increasing the fractionation yield, which is reflexted in a higher $T_{d5\%}$ of the *fractionated lignin #3 + Confidential Treatment* sample. However, these smaller components are more volatile, and will induce a faster degradation upon heating which can be reflected in the rapid mass loss in the TGA for the same. It must be noted that *fractionated lignin #3 + Confidential Treatment* is the selected substrate. However, for the sake of simplicity it will be referred to as *fractionated lignin #3*.

4.1.3 Molecular weight of fractionated lignin substrates

For this GPC analysis will be used to study the molecular weight distribution of the substrates. The results from the GPC analysis (*Figure 27*) show similar molecular distribution curves for both *fractionated lignin #1 and #3* (latter one is using Confidential Treatment). The main difference is found in the presence of a small molecular weight peak at 32 minutes for the *fractionated lignin #3 substrate*. This is an indication that the latter contains lower molecular weight molecules in comparison to *fractionated lignin #1* substrate, which is in accordance with what is found in *Table 7.* The 3 downward peaks can be interpreted as water in the carrier solvent (THF), nitrogen and oxygen, respectively [67].

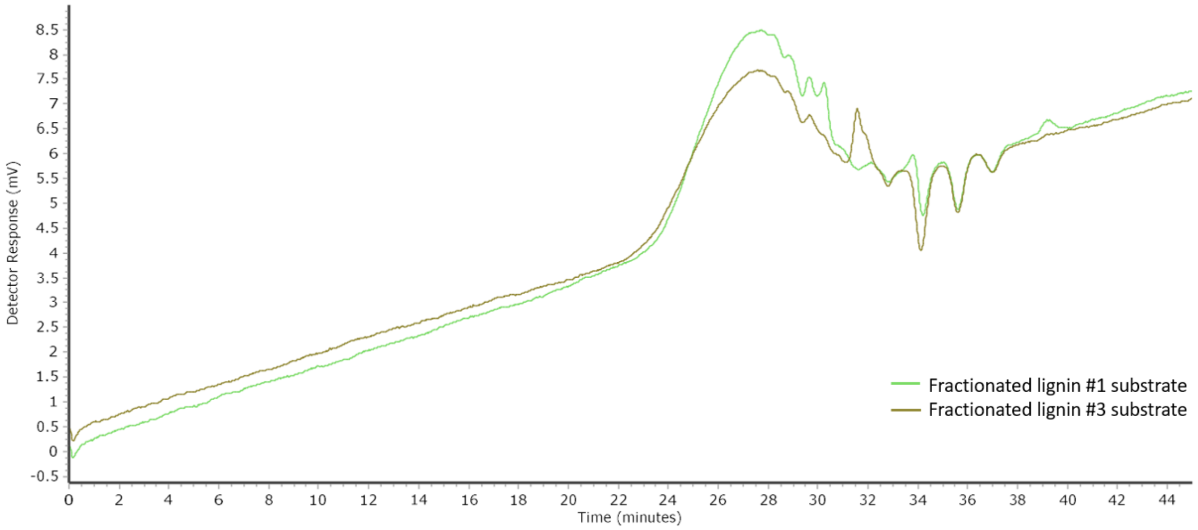


Figure 27. GPC curve of fractionated lignin #1 and #3 substrates.

4.1.4 Composition of the fractionated lignin substrates

Lastly, understanding the composition of the fractionated lignin is necessary since it will explain the reactivity of the substrate and will be related to the properties of the material. ^{31}P-NMR analysis is performed both on the technical and the fractionated lignin substrates to understand the difference between each one from an elemental composition perspective. *Figure 28* exhibits the NMR spectra of the technical and fractionated lignin sources. The hydroxyl groups are found between 150-130 ppm with aliphatic hydroxyl groups present between 149-146 ppm and carboxylic groups at 136-133 ppm. The phenolic OH groups are divided into three peaks according to the 3 monolignol units in lignin. Sinapyl OH (S unit) and condensed phenolic units corresponds to the peak at 144-140 ppm, guaiacyl OH (G unit) from 140-137 ppm and finally p-hydroxyphenyl OH (H unit) at 138-137 ppm [68]. The sharp peaks at 144 and 132 ppm are related to the internal standard and hydroxylated phosphorylating reagent, respectively [69]. After assigning the peaks, a few conclusions can be obtained from this data. Firstly, the Confidential Fractionation process has increased the number of moieties or functional groups in the lignin, as more peaks are detected in the spectra for fractionated lignin in comparison to the technical, especially in the aliphatic hydroxy region. Secondly, aliphatic OH groups are more abundant in *fractionated lignin #3* substrate in comparison to *fractionated lignin #1* substrate, as it is depicted in *Figure A 1.* Additionally, this same figure exhibits the region in the spectra where phenolic OH groups are, and it is observed that the peak corresponding to guaiacyl OH has more intensity in *fractionated lignin #1* substrate. These last two observation can be a prior indication on the different reactivity of the fractionated lignin substrates.

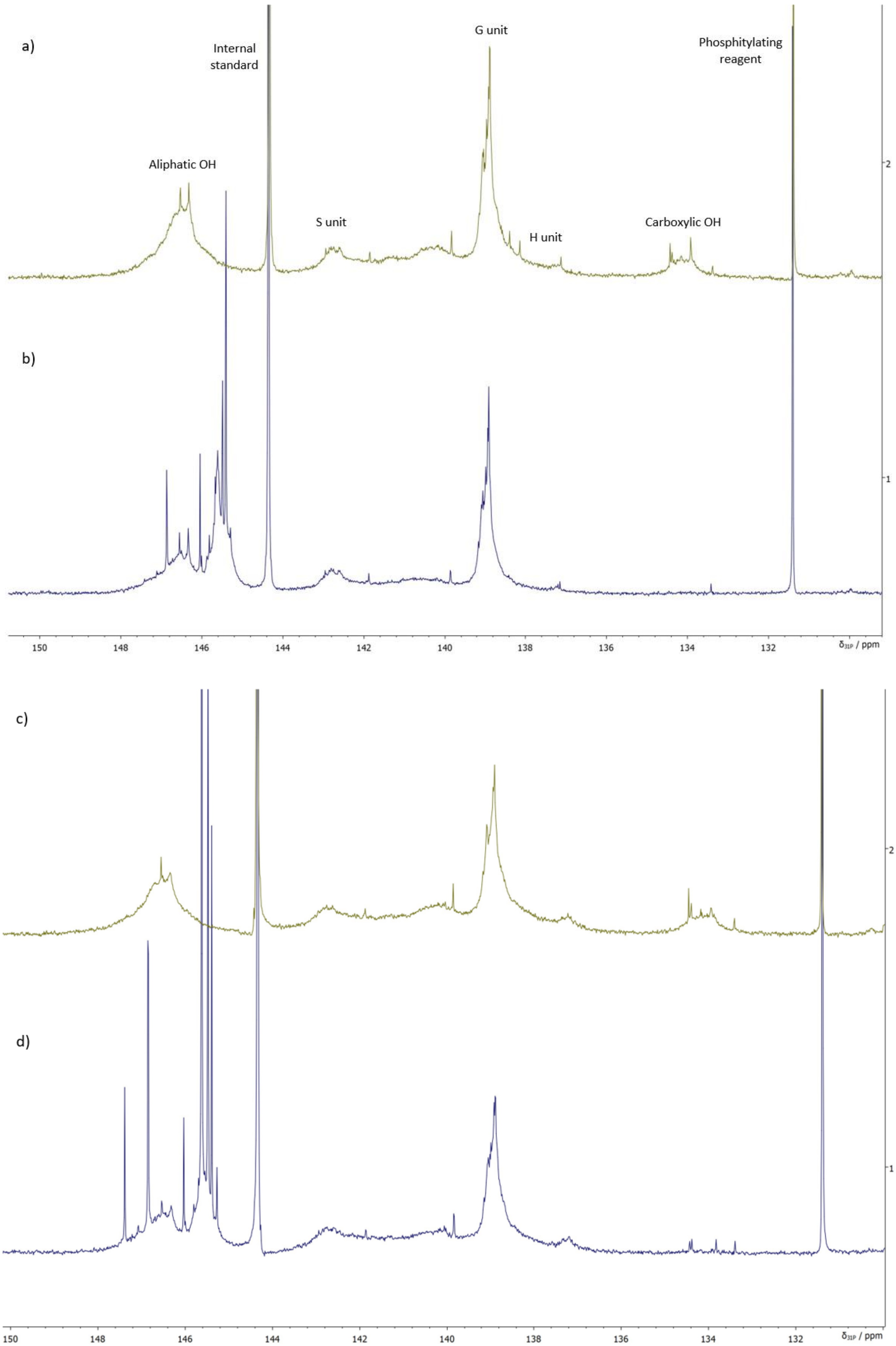


Figure 28. ^{31}P-NMR spectra of a) technical lignin #1 b) fractionated lignin #1 substrate c) technical lignin #3 and d) fractionated lignin #3 substrates.

Moreover, the FT-IR spectra of the fractionated lignin substrates was obtained (*Figure 29*). The band at 3370 cm^{-1} corresponds to O-H stretching vibration from hydroxyl groups in phenolic and aliphatic structures. The peak at 2935 cm^{-1} belongs to C-H stretching of aromatic methoxy groups and methyl and methylene groups present in the side chains [70]. The C=O stretching vibration corresponding to carboxyl/carbonyl groups can be found at 1720-1700 cm^{-1} [71]. The bands at about 1600, 1510 and 1425 cm^{-1} belong to aromatic skeleton vibration deformation along C-H deformation and aromatic ring vibrations at 1460 cm^{-1} [70]. The other peaks are a combination of different vibrations that are specific for each monolignol unit.

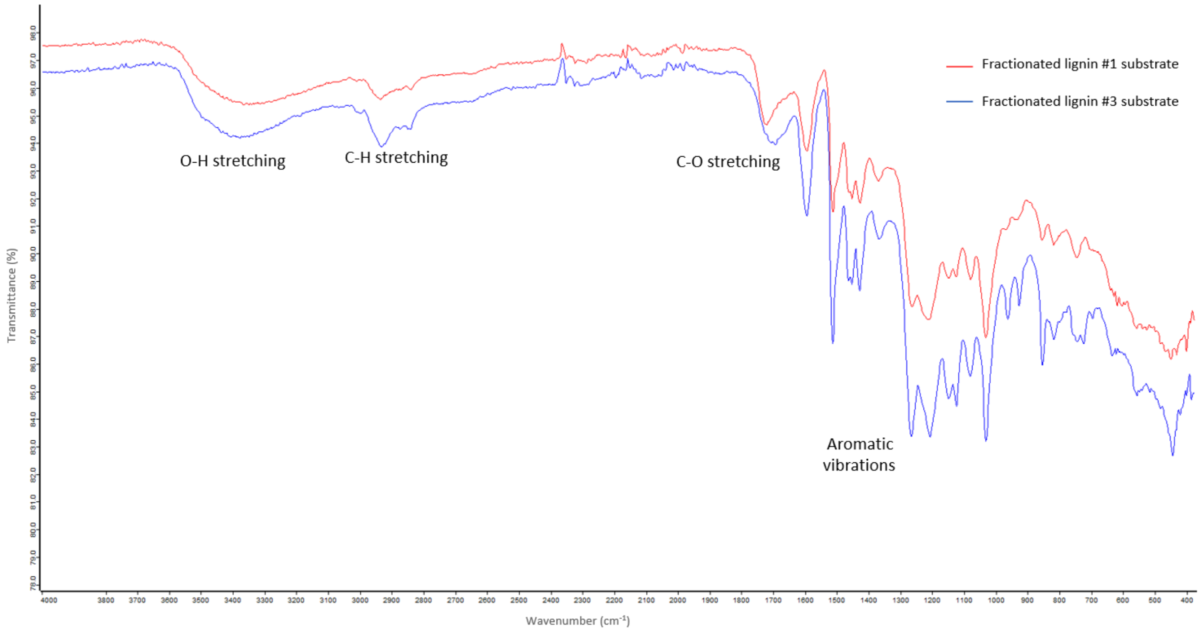


Figure 29. FT-IR spectra of fractionated lignin #1 and #3 substrates.

4.2 Glycidation reactions for synthesis of epoxy resins

4.2.1 Small-scale glycidation

Different batches for each resin were obtained, thus, the values compiled in *Table 11* correspond to the average of epoxy group content (EGC), hydrolysable chloride (HyCl) inorganic chlorine (Cl$^-$) and epichlorohydrin (ECH) content.

Table 11. EGC values and HyCl and water content for the resins obtained from the small-scale glycidation.

Resin	EGC (mmol/kg)	HyCl total(ppm)	Cl$^-$ (ppm)	HyCl content (ppm)	ECH (%)
Lignin #1 epoxy resin	4100	11100	150	10950	1.2
Lignin #3 epoxy resin	3750	29400	170	29230	3.1

Lignin #1 epoxy resin presents a higher EGC value and lower HyCl content, while the contrary is encountered for the *lignin #3 epoxy resin*. The HyCl content in *lignin #3 epoxy resin* is much higher, which indicates that the ECH has coupled with the lignin but has not proceeded to the ring-closing, leading to a lower EGC value. These differences can be attributed to the different reactivity between the substrates, implying that *fractionated lignin #1* substrate is more reactive in comparison to *fractionated lignin #3* substrate. In that case, this difference in reactivity is in accordance with the NMR observations above. *Fractionated lignin #3* substrate exhibits higher content in aliphatic hydroxy groups and lower for phenolic ones. Reactivity of hydroxy groups towards ECH decrease in order of carboxylic acid, phenolic and aliphatic. Therefore, the reactivity of *fractionated lignin #3* is much lower, which is reflected in a lower EGC value of the corresponding epoxy resin.

4.2.2 Large-scale glycidation

4.2.2.1 "Wet" glycidation

After that, the EGC and hydrolysable chloride (HyCl) and inorganic chlorine content is measured for both the products (samples O and J) as well as the water content (*Table 12*).

Table 12. EGC values, HyCl, Cl- and ECH and water content for the resins obtained from the large-scale "wet" glycidation.

Resin	EGC (mmol/kg)	HyCl total (ppm)	Cl^- (ppm)	HyCl final (ppm)	ECH cont. (%)
Sample O	3741	25000	6920	18080	2.20
Sample J	3582	56000	1096	54904	1.54

Lower content in HyCl means that the elimination step or ring-closing reaction proceeded successfully, and thus, a higher EGC can be expected. This is in accordance with the data obtained above obtained. The reason why the presence of HyCl in the sample J is because the phase separation was not as effective as in the sample O.

The 2-liter reactor is equipped with a thermostat that allows control and screening of the temperature during the reaction. Two temperatures are recorded, the interior and jacket temperature. The interior and jacket temperature are plotted as a function of time (*Figure 30* left) as well as the change in temperature between these two (*Figure 30* right). The coupling reaction is exothermic while the ring-closing step is endothermic. A drop of temperature is observed at 10 minutes during the coupling reaction; however, this drop is very slow and can be attributed to the addition of catalyst. As it can be seen, the temperature remains relatively constant during the reaction, this can be a prior indication on the low reactivity presented by the lignin substrate.

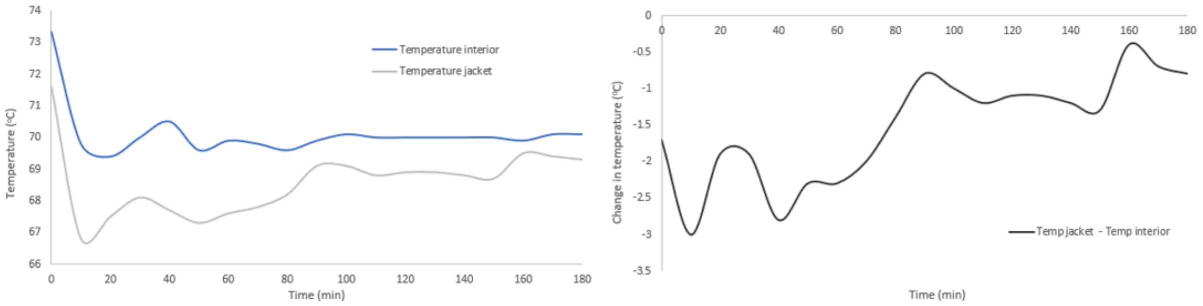


Figure 30. Screening of temperature in the interior and jacket of the reactor for the large-scale "wet" glycidation.

The GPC results from the samples taken during the reaction cannot be displayed due to Confidentiality.

4.2.2.2 *"Dry" glycidation*

According to the values from *Table 13*, the obtained resin has a higher EGC value and a lower HyCl content in comparison to the resin that was the product from the "wet" glycidation (*Table 12*).

Table 13. EGC values, HyCl and ECH and water content for the resins obtained from the large-scale "dry" glycidation.

Resin	EGC (mmol/kg)	HyCl total (ppm)	Cl^- (ppm)	HyCl content (ppm)	ECH content (%)
Sample E	4000	10600	4050	6550	2.07

Figure 31 shows the changes in temperature during the reaction, the change in temperature from 75 to 80 at 30 minutes is to allow the distillation of water once the ring-closing step starts. In this case, the endothermic peak during the coupling step is not very significant in comparison to the "wet" glycidation (*Figure 30*).

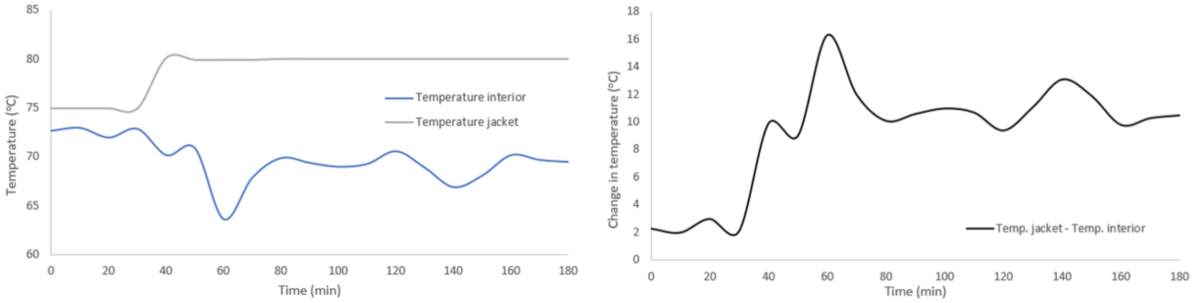


Figure 31. Screening of temperature in the interior and jacket of the reactor for the large-scale "dry" glycidation.

The GPC results from the samples taken during the reaction cannot be displayed due to Confidentiality. However, a conclusion can be drawn from them, analysis with GPC proved to be unsuccessful due to the monophenolic and small molecules of lignin which co-elute in the same peak which hinders the identification.

4.2.2.3 *"Wet" glycidation + Confidential Pre-treatment*

From the 400 grams of *fractionated lignin #3* substrate and 400 grams of *reference epoxy resin*, it was possible to produce 670 grams of the *lignin #3 epoxy resin*. The possible losses and lower yield of the reaction can be caused by undissolved or unreacted lignin, washing steps or the interphase layer that was formed during these washing steps. *Table 14* shows the properties that this resin presents.

Table 14. EGC values and HyCl and water content for the resins obtained from the large-scale ''wet" glycidation + Confidential Pre-treatment.

Resin	EGC (mmol/kg)	HyCl total (ppm)	Cl^- (ppm)	HyCl content (ppm)	ECH content (%)
Sample M	3509	38300	8027	30273	1.38

This resin will be employed for further attempts to make lignin-based composites for application testing. The EGC of the resin obtained from *fractionated lignin #3* on small and large-scale differs by 250 mmol/kg. However, the main difference in the viscosity of the resin, which is higher in the one obtained on large-scale. This could be due to the molecular build-up or any other complication during the process when performing on a larger scale.

4.3 Lignin epoxy resin as coatings

After performing the synthesis of the materials, these will be tested for different applications. The resins obtained from the small-scale glycidation are used for the development of clear coatings. This section will be divided in two parts. Firstly, a suitable coatings formulation must be developed for the *lignin #1* and *lignin #3 epoxy resins*. The formulation consists in three components: the epoxy resin, a solvent and the curing or crosslinking agent. The solvent is used to decrease the viscosity of the epoxy resin and allow workability, the curing agent will crosslink the epoxy to build up a network. Thus, the three components in the formulation must be compatible between each other. After that, the curing profile of the formulation must be determined to obtain a crosslinked network that can be later tested. Secondly, the performance of these coatings is tested according to the method presented in section 3.4 Material characterisation methods for lignin epoxy resins.

4.3.1 Coating formulation and curing profile

Viscosity is one of the most relevant properties of a material, thus, it is important to analyse it. In both *lignin #1* and *lignin #3 epoxy resin*, the viscosity at room temperature is too high to measure, therefore, dynamical viscosity will be measured in the range of 40 to 120 °C.

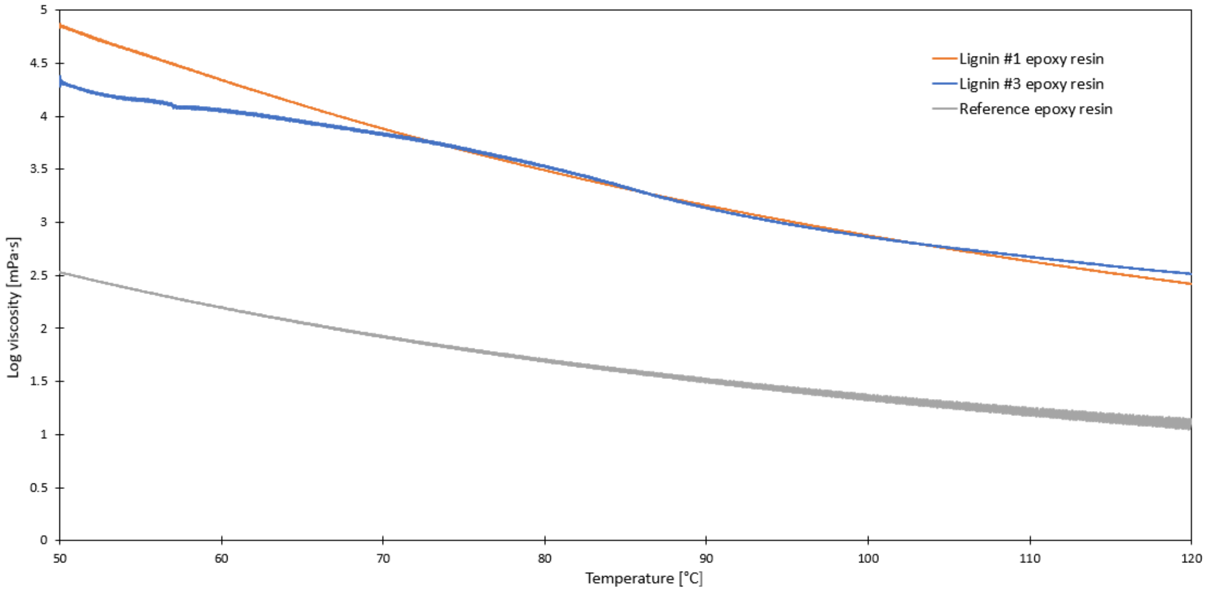


Figure 32. Dynamical viscosity of lignin epoxy resins in comparison to the reference epoxy resin.

As it is observed in *Figure 32*, the viscosity of both lignin epoxy resins is very high which indicates that a solvent is required to reduce the viscosity. The viscosity of the lignin epoxy resins is much higher in comparison to the *reference epoxy resin* at any temperature. Additionally, from the range of 50 to 70 °C, the viscosity of *lignin #3 epoxy resin* is significantly lower in comparison to *lignin #1 epoxy resin*, but these two become comparable at about 70 °C. The viscosity of the *reference epoxy resin* is lower because it presents a more defined and linear structure while lignin has a more heterogeneous and entangled structure. Lignin presents a complex structure, and it is prone to have strong self-interactions which lead to more entanglements and stiff aromatic structure [72]. This self-interactions among the lignin molecules are caused by the large number of polar groups in the lignin structure. The difference in viscosity between the two lignin-based epoxy resins can be explained based on its different molecular weight. *Lignin #1 epoxy resin* have a larger chain length, leading to stronger dispersion forces and a higher viscosity as the one displayed. The longer the chain becomes (higher M_w molecules), the chain mobility decreases and thus causing its viscosity to increase. This statement is in accordance with the M_w for the substrate technical *lignin #1* and *#3* in *Table 7* and GPC results, and the hypothesis that the Confidential Treatment (applied to lignin #3) breaks down of high molecular weight lignin molecules.

Since the viscosity of the lignin-based epoxy resins is very high, it is necessary to find a suitable solvent that decreases its solubility. Once the solvent is chosen (Confidential Solvent), it must be added to the lignin epoxy resin until their workability improves. The amount of solvent used in the case of *lignin #1* and *#3 epoxy resin* was 20 wt.%, since it was considered the adequate amount to provide a good workability of the resin in coatings. The resulting viscosity of the resins after addition of 20 wt.% Confidential Solvent is depicted in *Table 15*.

Table 15. Viscosity of lignin epoxy resin with 20 wt.% Confidential Solvent in comparison to reference epoxy resin.

Resin	Temperature (ºC)	Viscosity (Pa·s)
Reference epoxy resin	25	4.6 -4.7
Lignin #1 epoxy resin	25	10.1 - 10.3
Lignin #3 epoxy resin	25	8.4 – 8.7

Next step in the formulation is the selection of the curing agent. This one is going to react with the epoxy groups in the resin to create a crosslinked network. The curing agents used are amine which contain active hydrogens atoms that are transferred to transform the epoxy resin in a crosslinked network through polymerization [73]. The curing or crosslinking process is governed by the between the active hydrogen atom which can open one epoxy groups. Therefore, the stoichiometry between the curing agent and the epoxy resin is very important for the curing process. While the epoxy resins have the epoxy equivalent weight (EEW), the curing agents have the Active Hydrogen Epoxy Weight (AHEW). *Table 16* below presents the different curing agents that are using with the lignin epoxy resins and their corresponding properties.

Table 16. Properties of the used curing agents.

Curing agent	AHEW (g/eq)	Type of amine
Curing agent A	115	Modified cycloaliphatic amine
Curing agent B	109	Modified cycloaliphatic amine
Curing agent C	60	Polyetheramine
Isophorone diamine (IPDA)	82.5	Cycloaliphatic amine

It is important to note that Curing agent C is usually not used as a curing agent for coatings, but more like an additive, therefore, in this case it will be mixed with Curing agent B in a 50/50 molar ratio. Additionally, when Curing agent C is used as a curing agent for *reference epoxy resin*, a curing shrinkage in the coating film is observed when curing both at room and high temperature (*Figure A 2*). This situation was not encountered in the case of lignin epoxy resins, however, Curing agent C is excluded from being used alone as curing agent since it does not give good results on the reference, which is required for the comparison. The coatings will be applied to both glass and aluminium metal panels with a thickness of 200 µm.

The compatibility of *lignin #1 epoxy resin* with the different curing agents is done by visual inspection. *Figure 33* shows the result of the cured coatings using the curing agents specified above. As it is observed, the texture of the coating using Curing agent A is not flat but rather rough, which will affect the adhesion of the film, therefore, not providing a good compatibility between resin and curing agent. Similar situation occurs when using IPDA, the texture of the coating is matte and slightly coarse. For this reason, the selected curing agents for *lignin #1 epoxy resin* are Curing agent B and Curing agent B+C 50/50 molar ratio since the coating presents a more uniform surface. Moreover, Curing agent C is a very low viscosity curing agent which may also help in decreasing the viscosity of the overall resin. It is suspected that the compatibility with Curing agent B, and not with Curing agent A, might be due to the presence of an aromatic accelerator in it, more aromaticity in the system will lead to a better compatibility in the system.

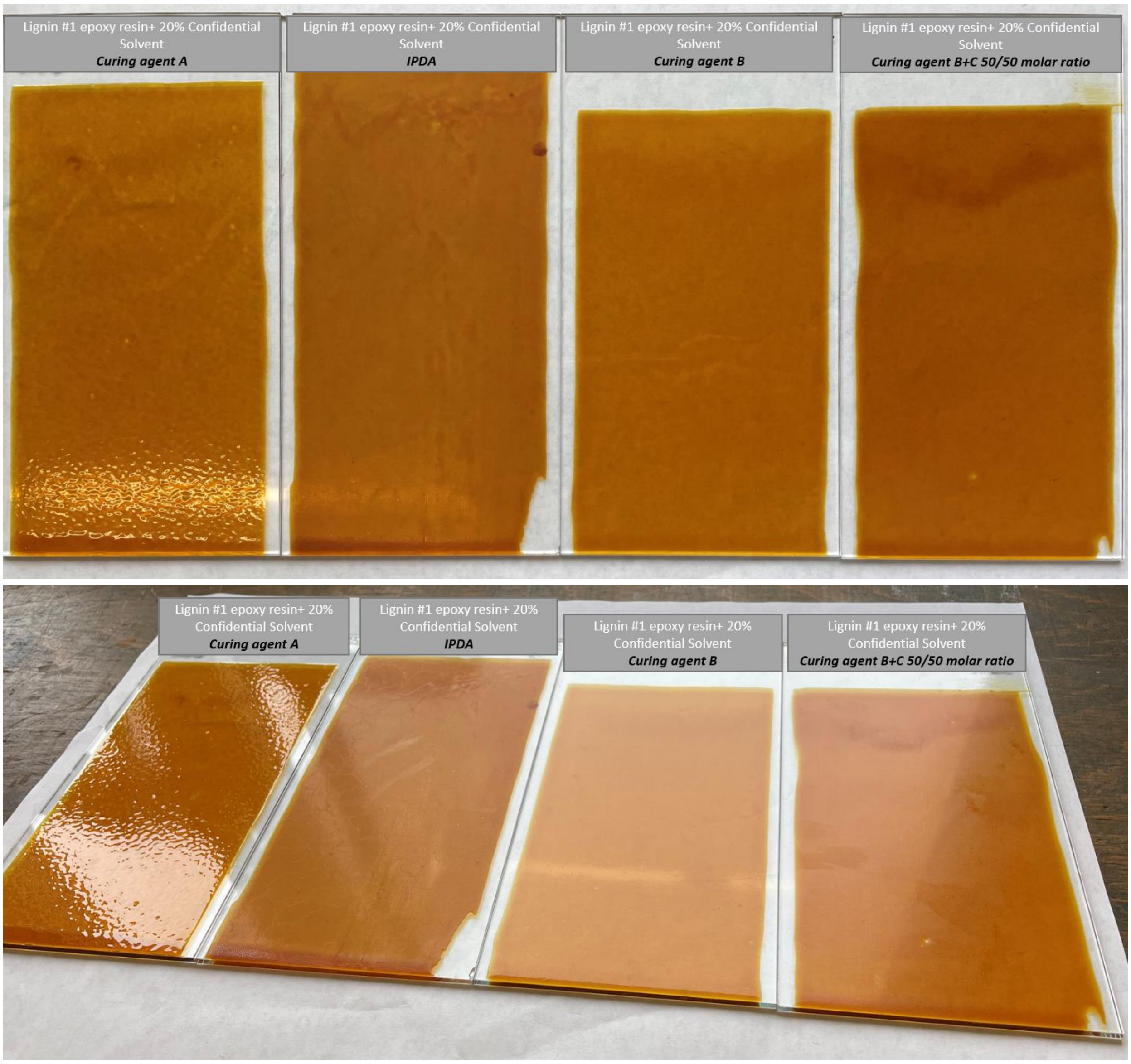


Figure 33. Cured lignin #1 epoxy resin coatings.

Secondly, the evaluation of curing agents on *lignin #3 epoxy resin* follows. In this case, Curing agent A and Curing agent B were used as curing agents and both seemed to be compatible with the resin, as it can be observed in *Figure 34*. Surprisingly, Curing agent A exhibits compatibility with *lignin #3 epoxy resin* resulting in a very uniform film, opposite to what was obtained from its combination with *lignin #1 epoxy resin*.

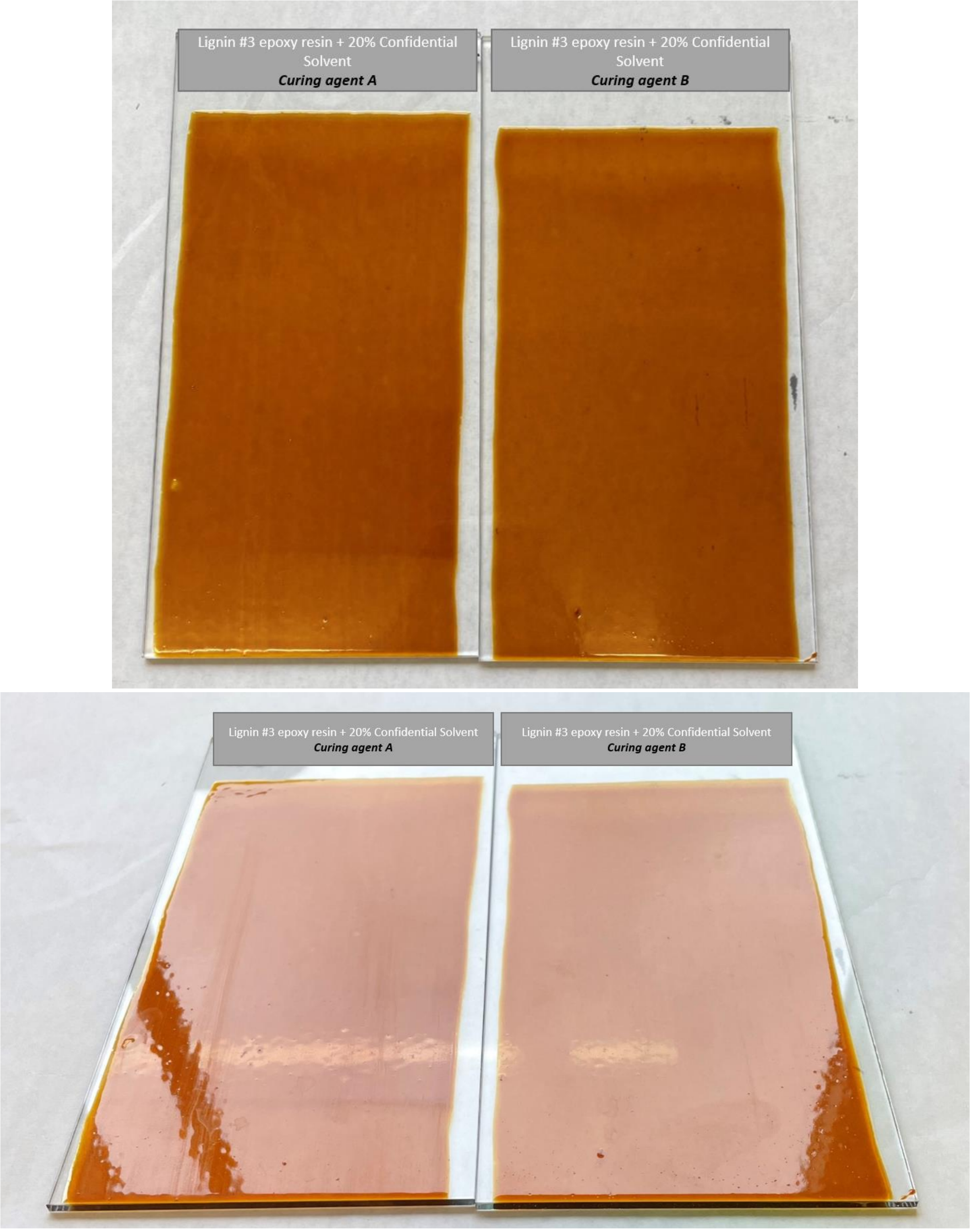


Figure 34. Cured lignin #3 epoxy resin coatings.

Thus, the different combination of epoxy resins with the curing agents are depicted in *Figure 35*. It must be remarked that the analogues combinations are prepared for the *reference epoxy resin* which will be used for benchmarking.

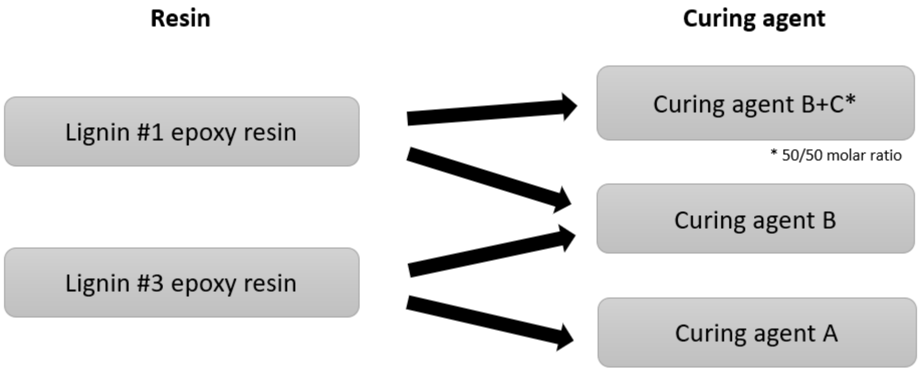


Figure 35. Combination of resin with selected curing agents.

Two curing profiles will be performed on the clear coatings, which are the following:

- Two weeks at room temperature (RT): this is a standard in the coating industry
- High temperature: it will be determined based on the DSC curves of the resin with the difference curing agent.

DSC analysis on the resins is performed to determine the curing profile and the glass transition temperature (T_g) of the samples. The DSC are performed from 20 to 250 °C at a heating rate of 10 K/min. The DSC results for the lignin epoxy resins and the reference resins can be found in the Appendix (*Figure A 3*, *Figure A 4* and *Figure A 5*). From the DSC curves of *lignin #1 epoxy resins*, two T_g values are detected, the first one between 40-50 °C and the second one between 80-90 °C. In the case of *lignin #3 epoxy resins*, the first transition is not present. The reason why two T_g values are observed in the DSC curves is that fractionated lignin consists of short and stiff molecules, thus, the flexibility of these varies to a very small extent that is detected as a slight change in the DSC curve as they go through the glass transition [72], in this case the first T_g. On the other hand, the absent of this first peak in the *lignin #3 epoxy resin* is again explained by its molecular weight. The lower M_w in *fractionated lignin #3* leads to an even more restricted mobility of its and this cannot be detected by the DSC, leading to the absence of this first transition at low temperature.

When analysis the heat of reaction, this appears to be significantly different between the reference resins in comparison to the lignin epoxy resins (*Table 17*). Less heat of reaction is observed when curing the lignin epoxy resins, compared to the reference epoxy resins. This can be partially caused by the lower EGC of the lignin epoxy resins, and due to the steric hindrance and adjacent groups in the lignin. Bulky moieties in the lignin can lead to lower flexibility and molecular mobility that can decrease the reactivity of its active sites. This steric hindrance and bulky moieties could also explain the higher viscosity of the lignin epoxy resins. This high functionality of the lignin can lead to some epoxide groups being unavailable and therefore, affecting the crosslinking density, reflected in a lower heat of reaction.

Table 17. Heat of reaction (J/g) of curing reaction of reference and lignin epoxy resins.

Resin + curing agent	Heat of reaction (J/g)
Lignin #1 epoxy resin + Curing Agent B	-182.60
Lignin #1 epoxy resin + Curing Agent B+C 50/50 molar ratio	-203.65
Lignin #3 epoxy resin + Curing Agent A	-113.11
Lignin #3 epoxy resin + Curing Agent B	-150.83
Reference epoxy resin + Curing agent A	-284.01
Reference epoxy resin + Curing agent B	-346.96
Reference epoxy resin + Curing agent B+C 50/50 molar ratio	-387.25

The exothermic peaks in the DSC curves for the lignin epoxy resins have a peak temperature of 100 °C. Therefore, it was decided that the high temperature curing for the lignin epoxy resins would be for 4 hours at 80 °C. There are several reasons why it was decided to not cure at temperature higher than 80 °C:

- Higher temperature can lead to overcuring of the thin coating films.
- Clear coatings have a thickness of 200 µm which might become too brittle when exposed to temperature higher than 80 °C.
- At a high heating rate (as the one in DSC), the temperature for the onset of curing, exothermic peak, and end of curing shift to higher values, this is because the resin has less time at a specific temperature leading to decreasing the degree of curing at that temperature. Therefore, if the heating rate is lower and stable, all the temperature (onset of curing, exothermic peak, and end of curing) will shift to lower values, thus, it is expected that 80 °C for 4 hours is enough to achieve full curing of the samples. Overcuring can lead to an increase in the brittleness of the coating whilst undercuring will ensure maintaining toughness.

The final curing profile of the combination of resins and curing agents are specified in *Table 18* below. Once the resins have been cured, the clear d coatings can be tested for application

Table 18. Curing profile for lignin epoxy resin and reference epoxy resins for clear coatings.

Resin	Curing agent	Curing profile
Lignin #1 epoxy resin	Curing agent B	• 2 weeks at RT • 4 hours at 80 °C
	Curing agent B+C	
Lignin #3 epoxy resin	Curing agent B	
	Curing agent A	
Reference epoxy resin	Curing agent B	• 2 weeks at RT • 2 hours at 80 °C
	Curing agent A	
	Curing agent B+C	

4.3.2 Clear coating application testing

The first testing method is pendulum hardness, which determines the hardness of the coating. In this case, a greater damping time is correlated to a higher hardness of the coating. From what it is observed in *Figure 36*, the first observation is that high temperature curing results in increasing in hardness. Moreover, coatings made from *reference epoxy resin* exhibit a better performance in comparison with the lignin epoxy resins. On the other side, *lignin #1 epoxy resin* coatings present a higher hardness compared to *lignin #3 epoxy resin* ones, especially if comparing when they are both cured using a common curing agent (Curing agent B). Nonetheless, the *lignin #1 epoxy resin* coatings exhibit a similar hardness compared to the analogue reference-based coatings. The complex structure of lignin can be linked to hardness; entanglements in the lignin molecule enhance the density of the polymer, which in turn affects the degree of crystallinity and results in high hardness. Higher molecular weight in of the *fractionated lignin #1*, results in a higher hardness in comparison to *lignin #3 epoxy resin*. Although the entangled lignin structure enhances the hardness of the polymer, it compromises the flexibility (as it will be seen later) as the stiffness is increased.

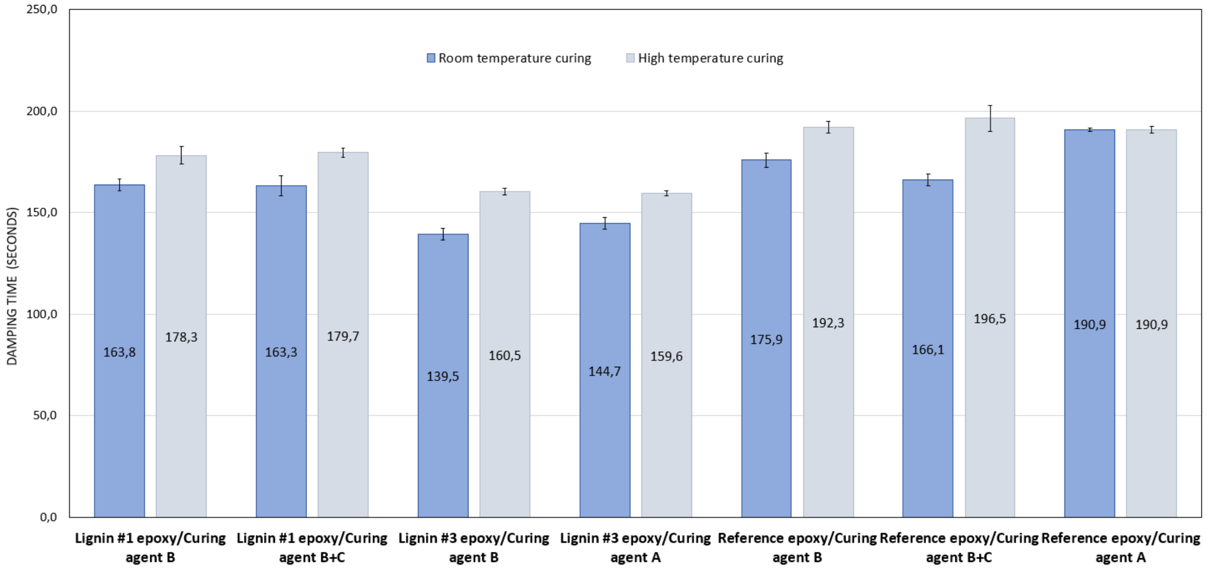


Figure 36. Pendulum hardness of lignin epoxy resins VS. reference epoxy resin.

Second testing is impact resistance. Firstly, the direct impact performance is assessed. *Figure 37* presents the results obtained from this test, and as it is observed, the performance of the lignin epoxy resins is poor in comparison to their analogue coatings made of *reference epoxy resin*. Again, in this case the better performance in the coating is obtained when curing at high temperature. According to standard method ASTM D 4366-95, coatings can be classified in 3 categories depending on the results obtained from direct impact test: brittle (< 0.07 kg-m), average (0.07-1.61 kg-m) or flexible (> 1.61 kg-m). Lignin-based coatings can be classified as brittle coatings when cured at room temperature while being average coatings when the curing is performed at high temperature. It seems that the lignin-based coatings do not present as much impact resistance in comparison to the reference resins. Although the impact resistance can benefit from high molecular weight and intermolecular entanglements, this can compromise the viscosity of the material. High viscous formulation will hinder dissipation of the energy absorbed from the shock, as the mobility of the molecules is impeded, resulting in a lower impact resistance. This is the case for the lignin epoxy resin coatings.

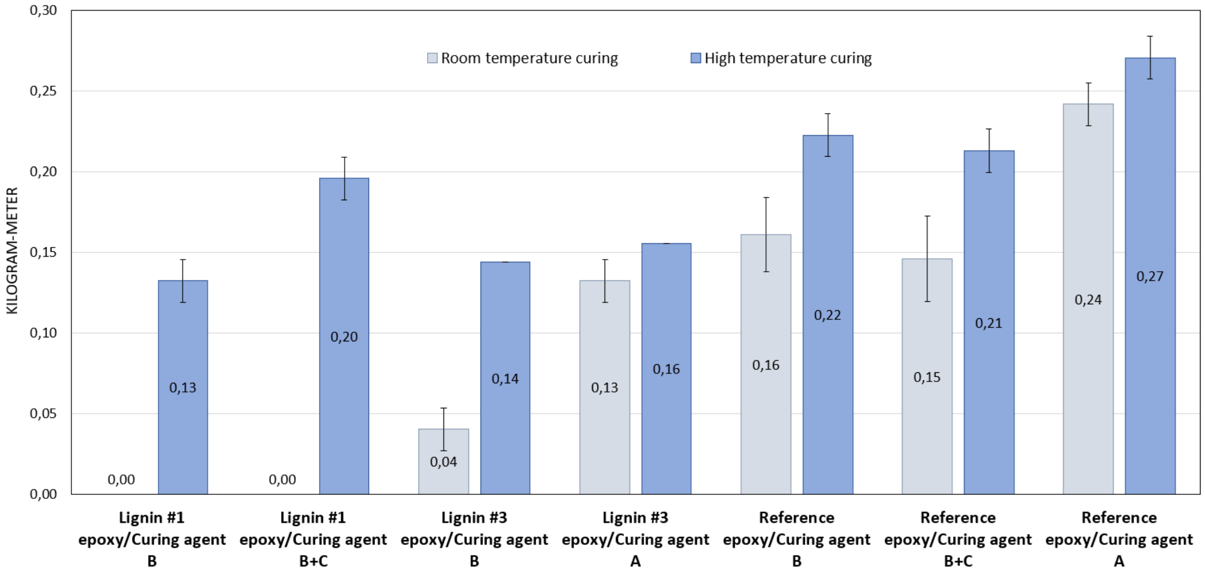


Figure 37. Direct impact results of lignin epoxy resins VS. reference epoxy resin.

Third and fourth testing are reverse impact and cupping testing, whose results are presented in *Figure 38* and *Figure 39*. In both cases, the performance of the lignin epoxy resins is null (for reverse impact) or much poorer (Cupping test) in comparison to the reference coatings. These can be caused by different factors. Firstly, the presence of impurities or small particles that can act as crack-initiating sites in the coating. This is the case for the lignin-based coatings since they present small pinholes over the coating surface. Secondly, the poor adhesion performance of the lignin coatings to the substrate. Adhesion of the lignin coatings is tested, and the performance was showing a very poor bond strength between the formulation and the substrate. Additionally, adhesion is highly influence by the cohesion of the components in the mixture, which in the case of the lignin epoxy resins might not be as optimal, considering the tendency to self-interactions. And finally, low flexibility caused by the very branched and stiff structure of the lignin molecules, which increase the stiffness of the material. Moreover, clear coatings present a very small thickness that leads to a reduction in the cohesive strength of the coating, that can easily result in cracking and delamination more easily.

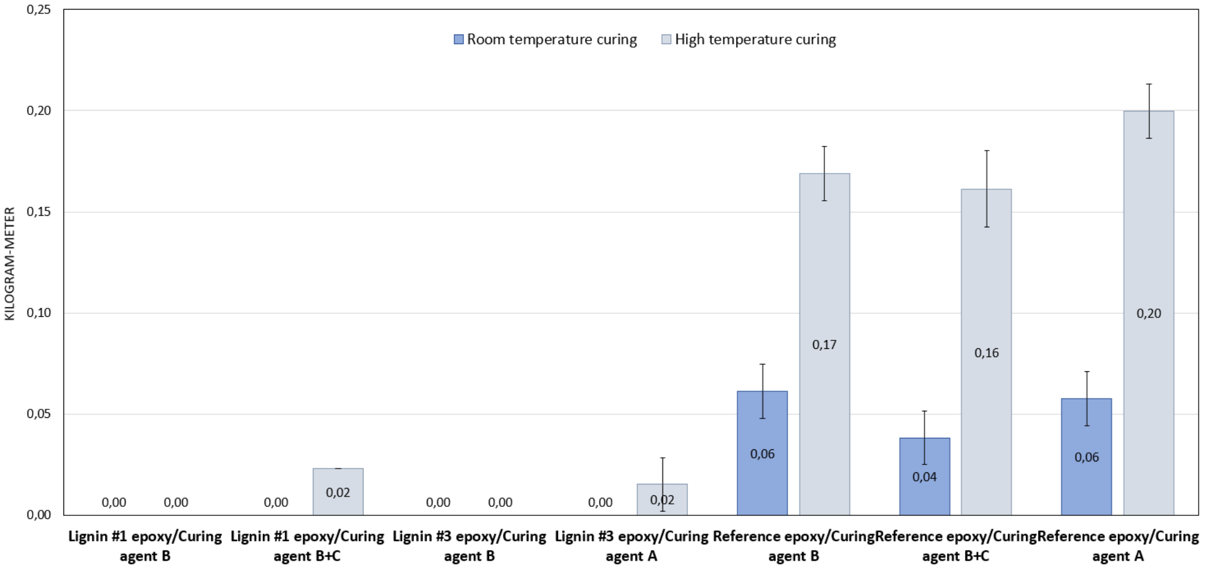


Figure 38. Reverse impact results of lignin epoxy resins VS. reference epoxy resin.

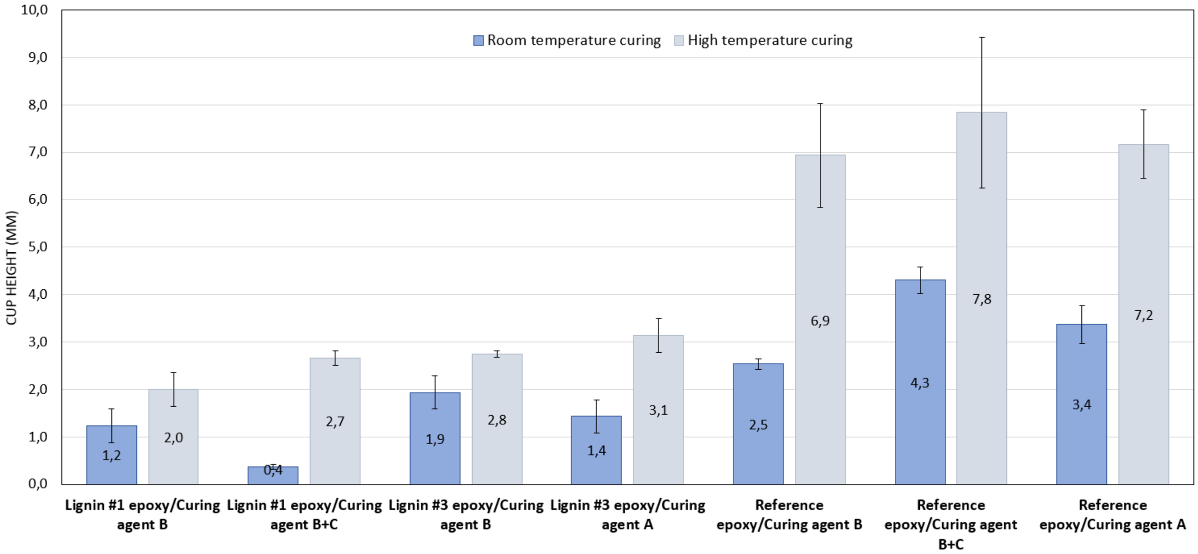


Figure 39. Cupping test results of lignin epoxy resins VS. reference epoxy resin.

Finally, the drying time of the resins is studied. According to the results obtained from *Figure 40*, the lignin epoxy resins tend to dry much faster in comparison to the reference resins. This can be linked to the higher viscosity of these resins; the mobility of the molecules is more limited leading to a faster drying time. However, a faster drying time can affect in the formation of the coating surface, leading to surface defects.

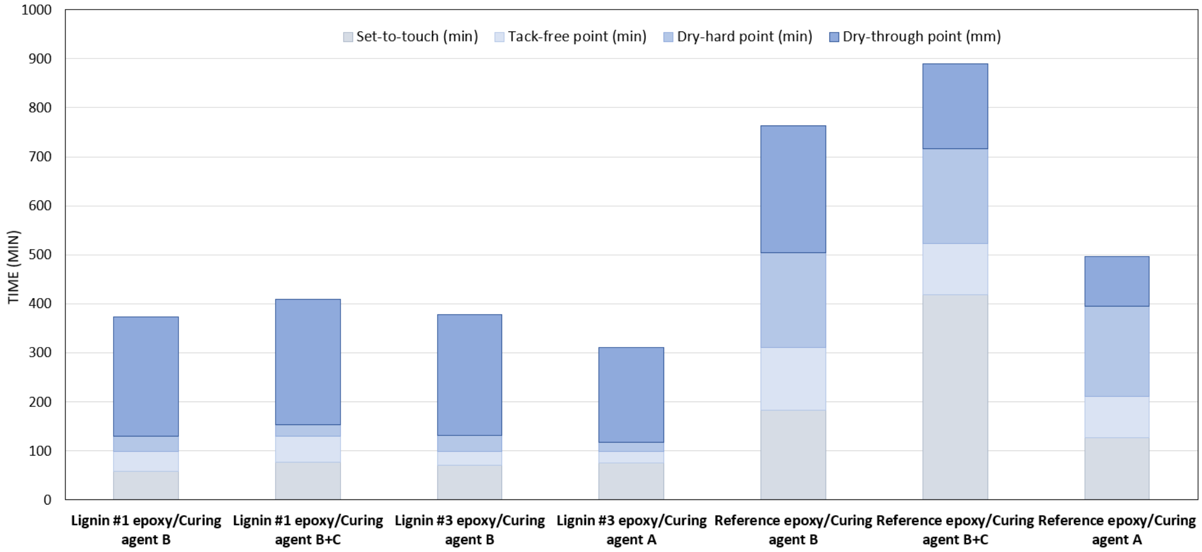


Figure 40. Drying test results of lignin epoxy resins VS. reference epoxy resin.

4.4 Lignin epoxy resin as composites

Second application that will be tested is composites. The resin obtained from the large-scale glycidation is used for the development of composites. For the composite formulation, a hardener or curing agent and a catalyst are used. Curing agent D is a pasty material which contains a powder curing agent having four or more active hydrogen sites depending on the curing temperature. Thus, this curing agent is typically used in under stoichiometric levels when cured at elevated temperatures. Moreover, due to its latency, it requires a catalyst to accelerate the reaction and reduce the activation energy and thus a third component is added – Catalyst A. The term ”mixture” refers to the combination of the resin with the hardener and catalyst, this will be used to tell the difference with the neat resin which contains only the resin.

Compression molding is the most suitable option, the prepregs are obtained by manually impregnating the resin in the fibers to later be treated in a press where the resin will flow through the fibers and curing in the final stage to obtain the prepreg laminate. Since the viscosity of the material is very high, the chosen reinforcement is glass fibers since they are easier to impregnate in comparison to carbon fibers.

4.4.1 Viscosity and thermal stability

As mentioned above, viscosity of the material is one of the critical parameters to study for the manufacturing of composites for two main reasons. First, the resin must flow enough so that it can adequately impregnate the fibers during the preparation of the prepreg layers. Second, the resin must flow in between the layers easily when it is pressed in the compression molding step, otherwise it might lead to fiber displacement. Low viscosity before curing is desired because it can help in the wetting and saturation of the fibers, which in the end helps in minimizing the air voids and maximizing the adhesion between the matrix and the reinforcement fibers. Therefore, it is very important to assess firstly the viscosity of the resin and its dependency with time (isothermal) and temperature (dynamical). The reason why no solvents was used for the composites its use is restricted to China and the equipment was not adequately equipped for working with solvent-containing composites. Additionally, from a market perspective, the use of solvents is not desired.

For composites, 100 Pa·s is generally the maximum accepted viscosity for a resin from a manufacturing perspective. In case of the *reference epoxy resin* mixture, this applies until 135 ºC; whilst for *lignin #3 epoxy resin* mixture viscosity values lower than 100 Pa·s are achieved between 65 to 140 ºC (*Figure 41*).

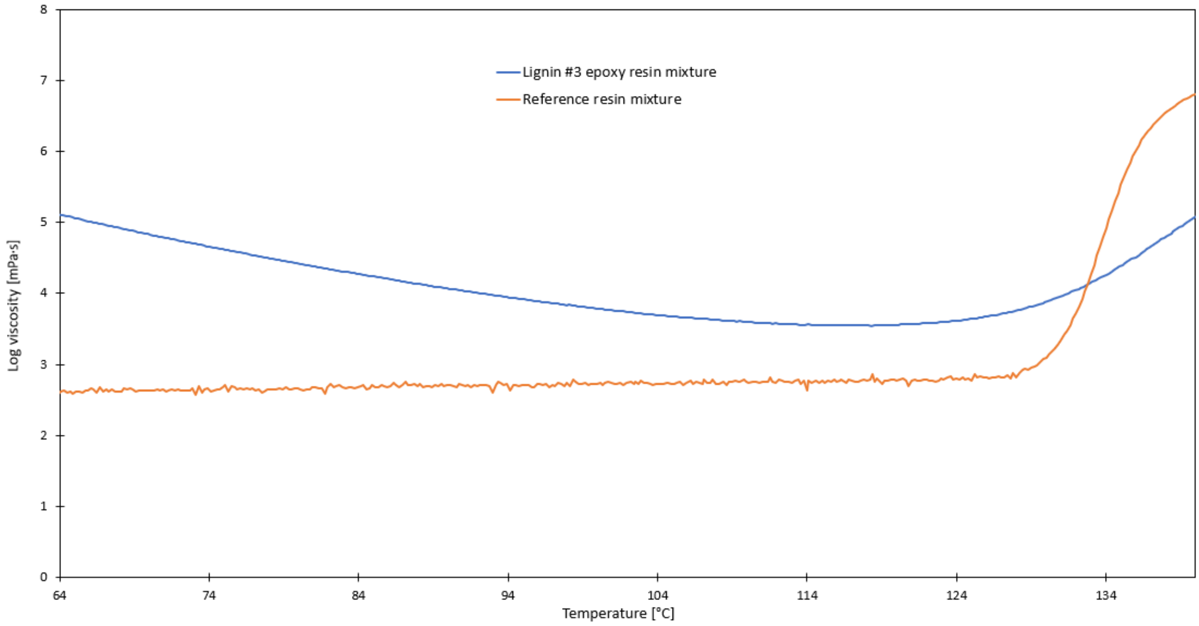


Figure 41. Oscillation dynamical viscosity of lignin #3 epoxy resin and reference epoxy resin mixture comparison.

The gel point is defined as the point in which the storage modulus is larger than the loss modulus, transforming into an elastic gel and the average value of molecular weight becomes infinite [74]. When plotting the storage and loss modulus dependency against the temperature (*Figure 42*), the gel point is the intersection between the storage and loss modulus. The gel point for the *lignin #3 epoxy resin* mixture is reached at 134 °C and at 129 °C for the *reference epoxy resin* mixture.

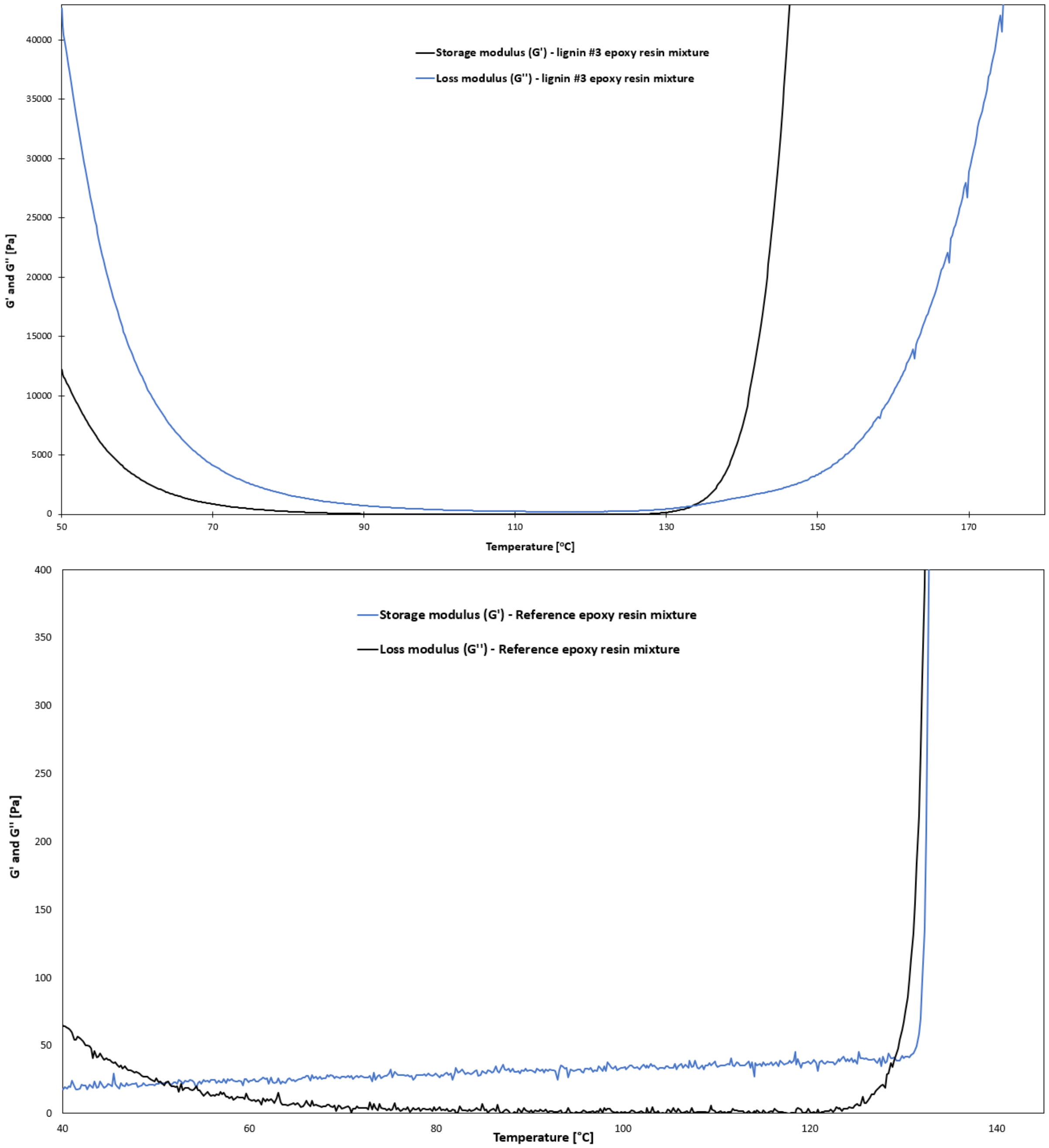


Figure 42. Storage and loss modulus of lignin #3 epoxy resin and reference epoxy resin mixture comparison.

Once the gel point temperature is known, it is important to stablish at what time it is reached. If the gel point is achieved at the beginning of the compression, then the resin will stop flowing due to increase in viscosity and the reinforcement fibers will not be properly impregnated in the matrix. Moreover, when the resin reaches the gel point then residual stresses will build up causing detrimental performance or induce deformation in the material [75]. Therefore, the isothermal viscosity of the material is studied at 120 °C and 140 °C, which are temperature values between the gel point obtained for the resin mixtures (134 °C and at 129 °C). According to *Figure A 6,* viscosity increase very rapidly at 140 °C, surpassing the 100 Pa·s after less than 300 second. However, viscosities higher than the maximum permitted are reached after 1400 second for the *lignin #3 epoxy resin* mixture and after 800 second for the *reference epoxy resin* mixture at a temperature of 120 °C. A significant difference can be observed from the way the viscosity increases over time in the two-epoxy resin mixture. In contrast to the reference mixture, which has a faster and nearly exponential increase in viscosity, the *lignin #3 epoxy resin* mixture experiences a more gradual and slower increase. These differences are due to the curing kinetics, which are faster for the reference epoxy mixtures. At the same time the curing kinetics differ due to the homogeneity of the resin. *Reference epoxy resin* consists of only one monomer, it is more homogeneous, and it has same spacing between the monomers that causes a higher curing kinetics in the system. Moreover, the slower curing kinetics in the *lignin #3 epoxy resin* can be caused by bulky and complex structure of the lignin that hinders the formation of the crosslinking network. The presence of lignin in the system might have an impact in the reactivity of the epoxy resin towards the curing reaction caused by the steric hindrance and high functionality.

The thermal stability of the neat resin is investigated by TGA. According to *Figure 43*, the thermal degradation of *lignin #3 epoxy resin* is much faster in comparison to the *reference epoxy resin*, a more rapid weight loss is observed at any temperature. For the *lignin #3 epoxy resin*, some weight loss is already detected at 100 °C which could be attributed to possible impurities (H_2O, CO_2, or CO) or other volatile small molecules present in the sample.

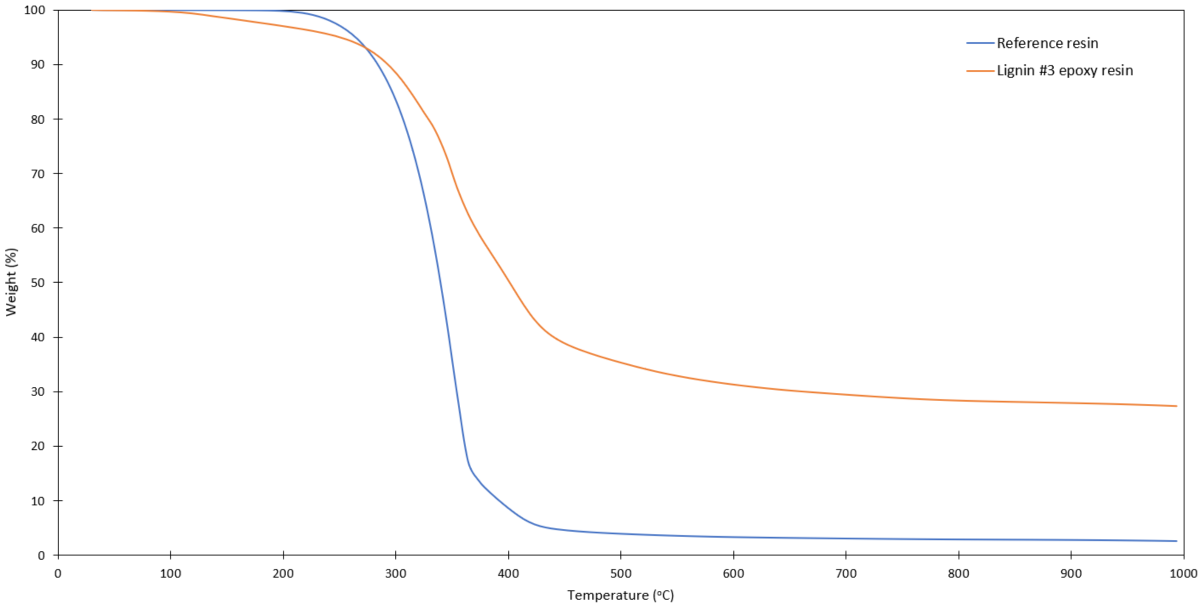


Figure 43. TGA curves of reference and lignin #3 epoxy neat resin.

The total weight loss of the *lignin #3 epoxy resin* is lower in comparison to the *reference epoxy resin*. Moreover, the calculated heat-resistance index temperature of the lignin-based resin is greater as well, as it can be seen in *Table 19*. Addition of lignin in the resin has notably increased the thermal stability of the system. This is caused by an increased in aromaticity which is introduced by the lignin molecules, as it was already predicted on literature [10]. The *reference epoxy resin* presents a much linear and homogeneous structure compared to that of *lignin #3 epoxy resin*, which also affects in the thermal stability of the material.

Table 19. Thermal stability parameter for reference and lignin #3 epoxy resin.

Source	Total weight loss (%)	$T_{d5\%}$ (ºC)	$T_{d30\%}$ (ºC)	T_s (ºC)
Reference epoxy resin	97.41	262	320	145
Lignin #3 epoxy resin	72.65	250	351	152

Thermal analysis can provide information on the crosslinking density and free volume of the neat epoxy resins. From the data presented in *Table 20*, it is observed a big difference in the T_g in the second and third run and that the *reference epoxy resin* exhibits a lower coefficient of thermal expansion (CTE) in the glassy region. Difference in the T_g over the runs are caused by relaxation effects or post-curing phenomena, this difference is larger for the *lignin #3 epoxy resin*. *Reference epoxy resin* exhibits a lower CTE due to a higher crosslinking density and less free volume since the polymer chains are more linear.

Table 20. TMA data for reference and lignin #3 epoxy neat resin.

	Unit	*Reference epoxy resin*	*Lignin #3 epoxy resin*
T_g (second run)	[ºC]	124	105
α_{glassy} (second run)	[10^{-6}/ ºC]	38.64	47.13
$\alpha_{rubbery}$ (second run)	[10^{-6}/ ºC]	172.20	163.07
T_g (third run)	[ºC]	123	112
α_{glassy} (third run)	[10^{-6}/ ºC]	37.47	45.15
$\alpha_{rubbery}$ (third run)	[10^{-6}/ ºC]	174.29	173.06

4.4.2 Curing profile and kinetics

Understanding the curing kinetics of the material is essential for the further processing of the composites. The epoxy resin after curing becomes a crosslinked polymer matrix that binds the reinforcement together and transfer the load to and between the reinforcement fiber, apart from other goals. Therefore, knowing the curing kinetics of the resin can help in defining a curing profile that can guarantee the full curing of the resin. DSC analysis is going to be a key technique in investigating this.

Firstly, dynamical DSC is performed on the uncured resins to stablish the enthalpy of the curing reaction. *Figure A 7* shows that the heat of reaction of the curing of *reference epoxy resin* (-389.54 J/g) is much higher than for the *lignin #3 epoxy resin* (-245.11 J/g), which is also in line with what was observed for the coatings and supports the CTE results obtained from the TMA analysis, the *reference epoxy resin* has a higher crosslinking density.

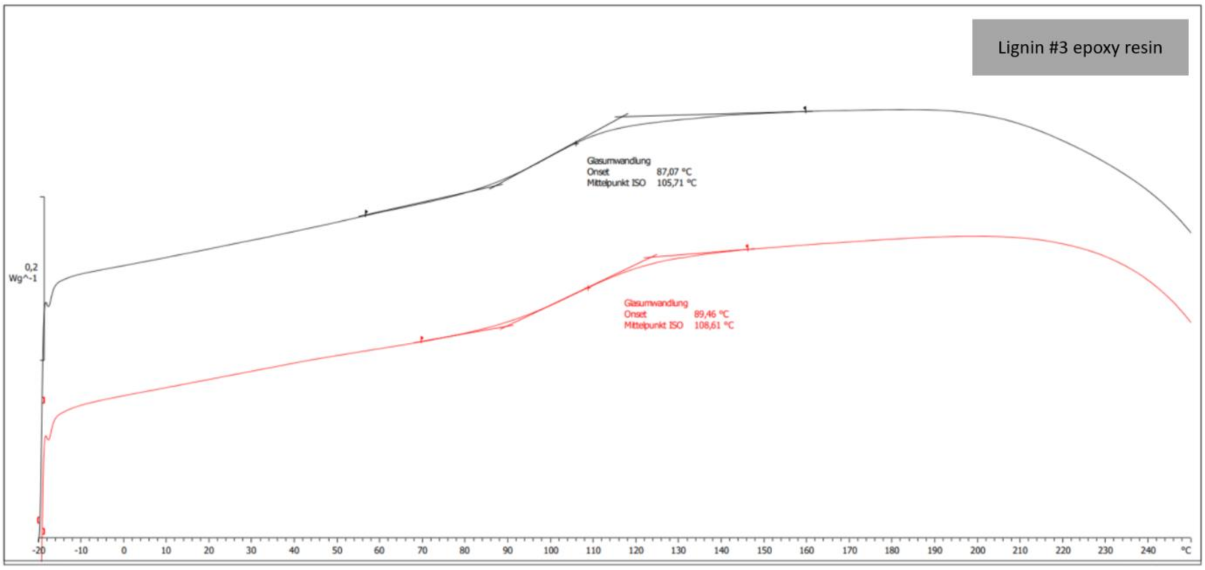
Secondly, isothermal DSC at 160 ºC is investigated for the curing kinetics of the resin at this temperature. Therefore, the samples are cured at this temperature for two hours at a heating rate of 10 K/min. *Figure A 8* and *Figure A 9* present the isothermal DSC curves for the *lignin #3 epoxy resin* and *reference epoxy resin*, respectively. The data obtained from the analysis is presented in

Table 21, and shows that 95% curing is reached faster for the *reference epoxy resin* than for the *lignin #3 epoxy resin*. Moreover, little differences in the T_g after the second (blue) and third (green) run indicate full curing of the samples, slight changes in the value are caused by some exothermics left. Slower curing kinetics for the *lignin #3 epoxy resin* support the hypothesis that the structure of lignin is hindering the curing process due to its structure.

Table 21. DSC data of reference and lignin #3 epoxy neat resin after curing for 2 hours at 160 °C.

Sample	Heat of reaction (J/g)	95% curing (min)	T_g 2nd run (°C)	T_g 3rd run (°C)
Lignin #3 epoxy resin	-375.41	46	106	112
Reference epoxy resin	-570.54	30	133	120

Finally, the T_g of the resin must be determined, and DSC analysis is performed on the samples cured at 80 °C 2 hours + 160 °C 2 hours. Temperature of 80°C ensures the removal of some exothermics before starting the actual curing process at high temperature. As reflected in *Figure 44*, after curing for 80 °C 2 hours + 160 °C 2 hours, the T_g does not change as much in both cases due to total curing achieved. The DSC curve for the *reference epoxy resin* seems to show to T_g values, however, the first one can be associated to water or any other volatile substance present as an impurity in the sample. An important observation is the difference between the onset and the midpoint temperature in the glass transition. In the case of *reference epoxy resin*, the difference is of about 10 °C, it consists of only one unit or monomer, thus, the network is very homogeneous and due to the same spacing in the chains, the network density is very high and constant. Therefore, there is a nice transition in the T_g and the difference between the onset and the middle point the glass transition is not very high. The difference is about 20 °C in the case of the *lignin #3 epoxy resin* which is caused by the complex structure of lignin.



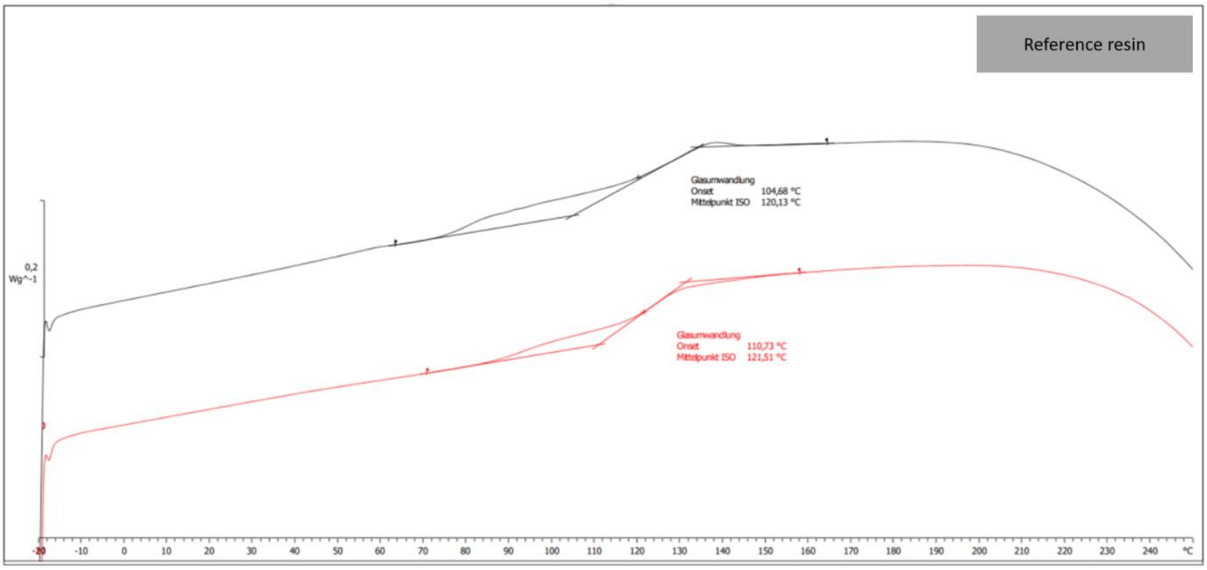


Figure 44. Dynamical DSC analysis of cured lignin #3 epoxy resin (above) and reference epoxy resin (below) cured at 80 ºC 2 hours + 160 ºC 2 hours.

4.4.3 Processing and mechanical testing of the prepreg laminate

After this, the resin was processed to obtain the prepregs laminates. For this, glass fibers are impregnated in the resin to later being pressed in the mold at 120 ºC, after that the laminated are placed in an over for 160 ºC to make sure that they are properly cured. The resulting laminates are presented in the *Figure 45,* the laminates have a thickness of 4 mm and are made of 4 prepreg layers of 0/90 º orientation of the fibers. It is observed that the resin has not fully impregnated the fibers, since a few yellow spots are observed, as well as the fibers are not completely aligned. The reason why one side of the laminates seem more impregnated is because during the manual impregnation, the resin was placed on that side. *Figure 46* presents the resulting prepreg laminate using *reference epoxy resin* as matrix, it is observed how the matrix has fully impregnated the fibers and these ones are completely aligned and have not been displaced.

Figure 45. Prepreg laminates made of lignin #3 epoxy resin.

Figure 46. Prepreg laminates made of reference epoxy resin.

To further check if the resin has flowed correctly through the fibers, microscopy is done on the laminates after cutting a small segment of them (*Figure 47*). The black spots that appear in the section of the fibers orientated at 0º correspond to air trapped in between the fibers. Large air bubbles are also trapped in the resin as it is presented in *Figure 47* on the right. These voids present in the laminate will act as crack-initiating sites that can lead to failure. Additionally, the resin has not fully impregnated or passed through the fibers. These values will have an effect on the mechanical testing of the lignin laminates.

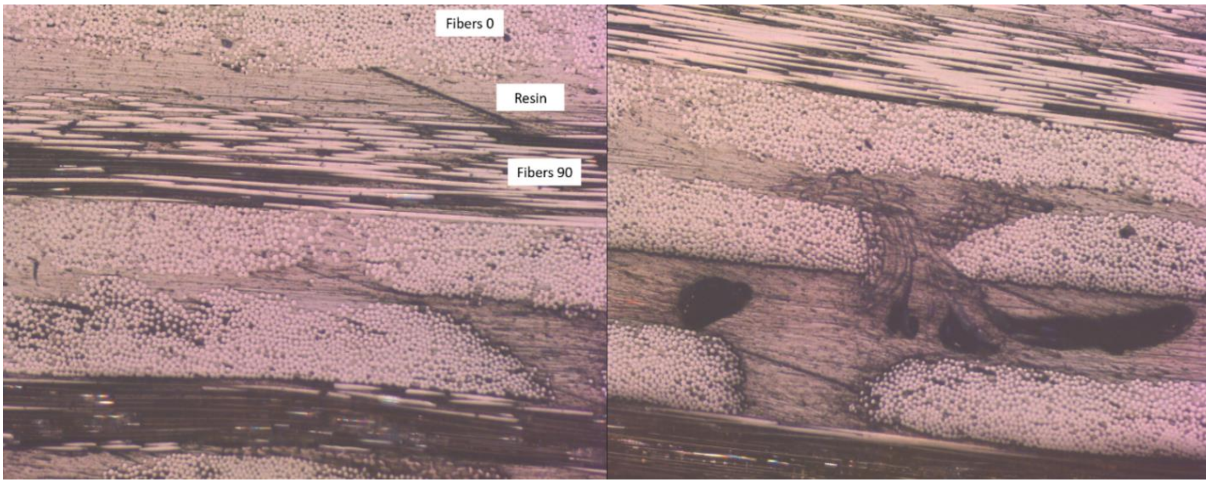


Figure 47. Microscope image of lignin #3 resin prepreg laminate.

DMA analysis was performed on the samples (*Figure 48*). The crosslinking density of the system is reflected in the transition and rubbery region in the curves. Low crosslinking thermosets present a decrease in the storage modulus (E’) at a lower temperature, the onset for this decrease is always at lower temperature in the case of *lignin #3 epoxy resin* laminates. Moreover, the lower storage modulus for the *lignin #3 epoxy resin* laminates in the rubbery region also supports the lower crosslinking density for the material, and thus, the incorporation of lignin does not reinforce the epoxy matrix. These results are in accordance with the lower heat of reaction for the *lignin #3 epoxy resin* caused by the complex structure of lignin. The loss factor (tan δ) is also lower for the *lignin #3 epoxy resin* laminate, meaning that is not as effective for energy dissipation. The mechanical losses in the *lignin #3 epoxy resin* laminate are caused by less energy required for the motion of the molecular of molecular chains as the glass transition approaches. Additionally, lower loss factor is highly influenced by a poorer interaction between the matrix and the fibers, as it is expected according to the micrographs presented in *Figure 47*.

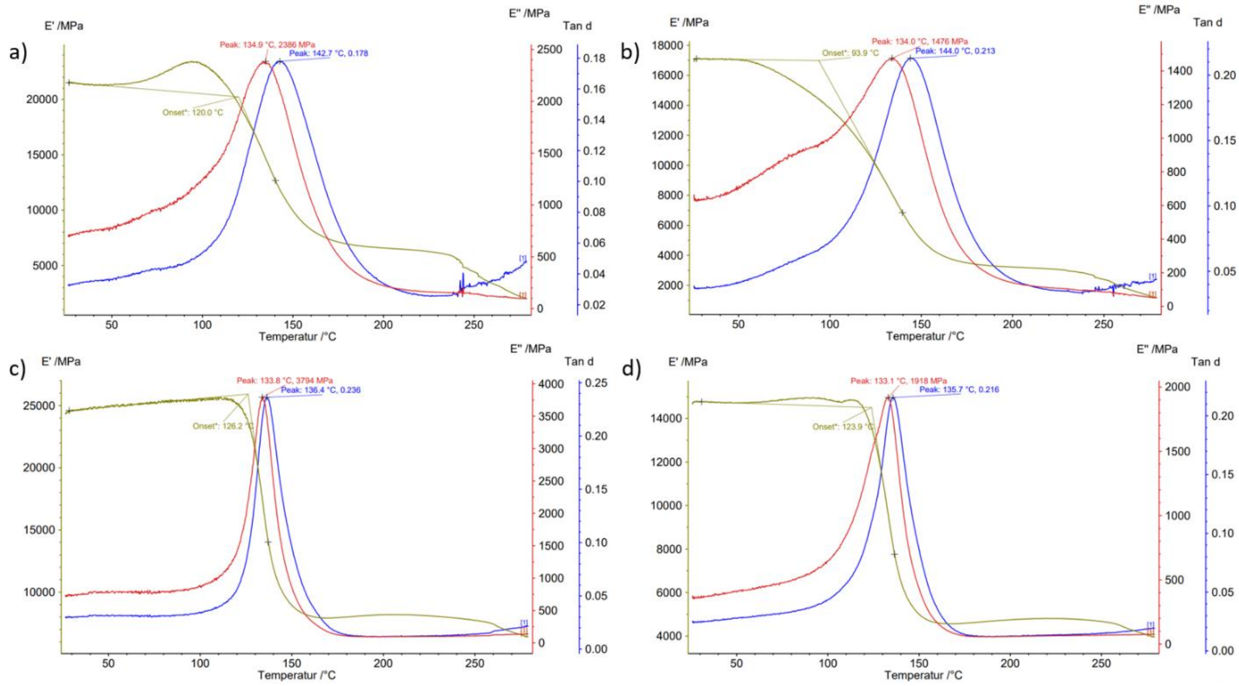


Figure 48. DMA curves for a) lignin #3 epoxy resin laminates 1st measurement b) lignin #3 epoxy resin laminate 2nd measurement c) reference epoxy resin laminates 1st measurement and d) reference epoxy resin laminates 2nd measurement.

The glass transition temperature is detected as a sudden decrease in the storage modulus in DMA (*Figure 48*) or can be obtained from the DSC analysis (*Figure 44*). Below in *Figure 49*, it is observed that the T_g for the *reference epoxy resin* composite is higher in comparison to the lignin-based composite, and especially the data obtained from the DMA, indicates that the incorporation of lignin to the matrix decreases its crosslinking density. Higher T_g value detected from the DMA analysis for the *lignin #3 epoxy resin* composite on the 1st measurement can be caused by the irregularities present in the obtained composite.

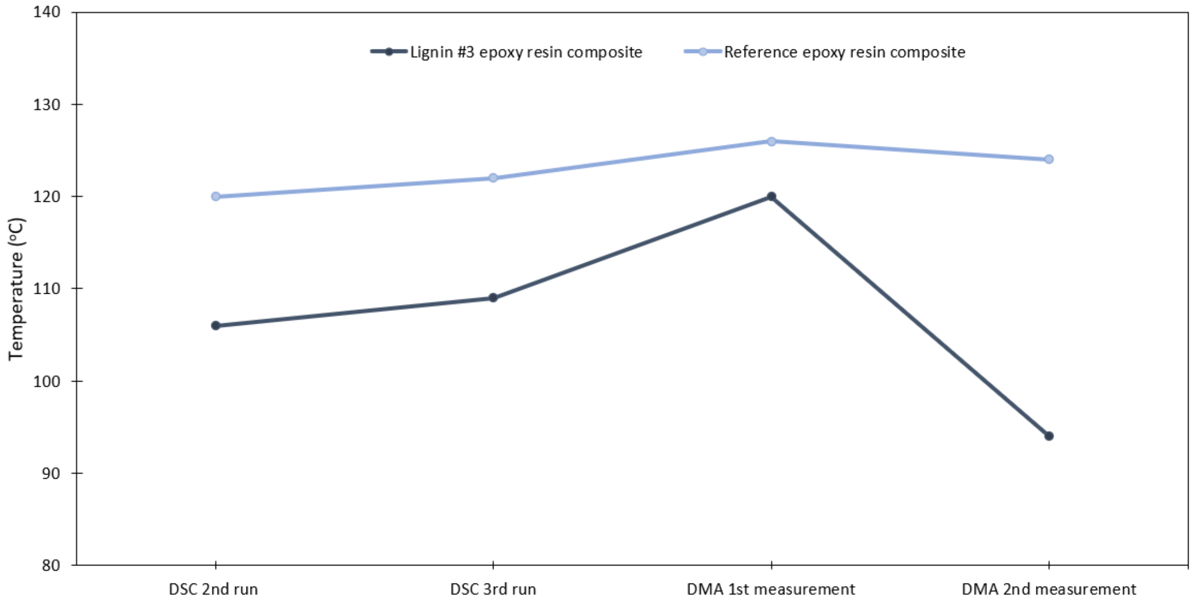


Figure 49. Comparison of T_g obtained from DSC and DMA of lignin #3 epoxy resin and reference epoxy resin composites.

Lastly, ILSS analysis will give some information on the interphase between the matrix and the fibers. *Figure 50* shows a lower shear strength value for the *lignin #3 epoxy resin* prepreg laminate, in comparison to the reference one. This is because the lignin resin was not able to properly wet the fibers, leading to a poor contact between the two components.

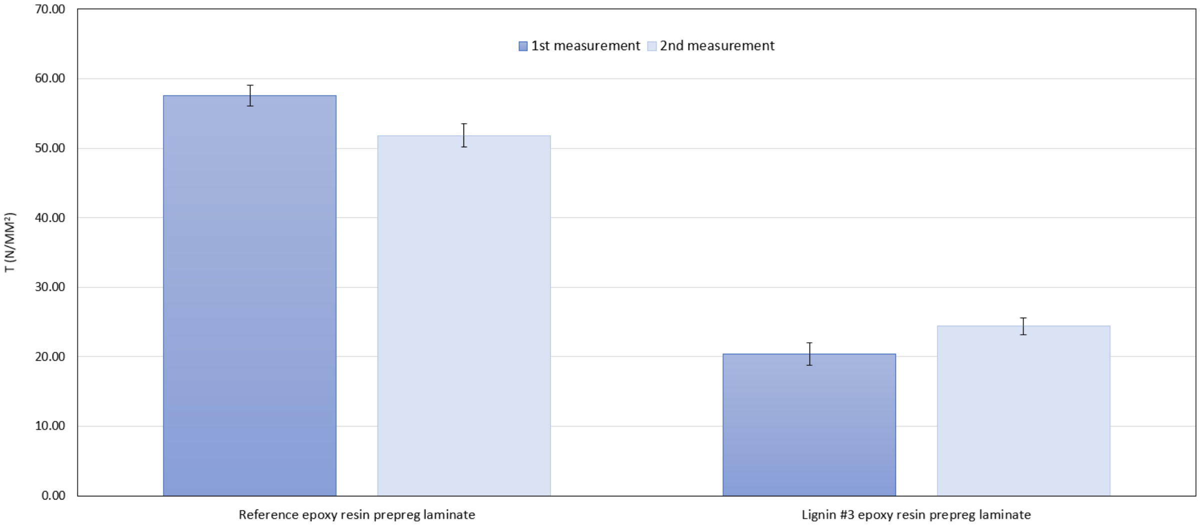


Figure 50. Shear strength comparison of prepregs from reference and lignin #3 epoxy resin.

Additionally, the *lignin #3 epoxy resin* prepreg laminates are much more brittle, with half the elongation at break value compared to the reference-based laminates (*Figure 51*).

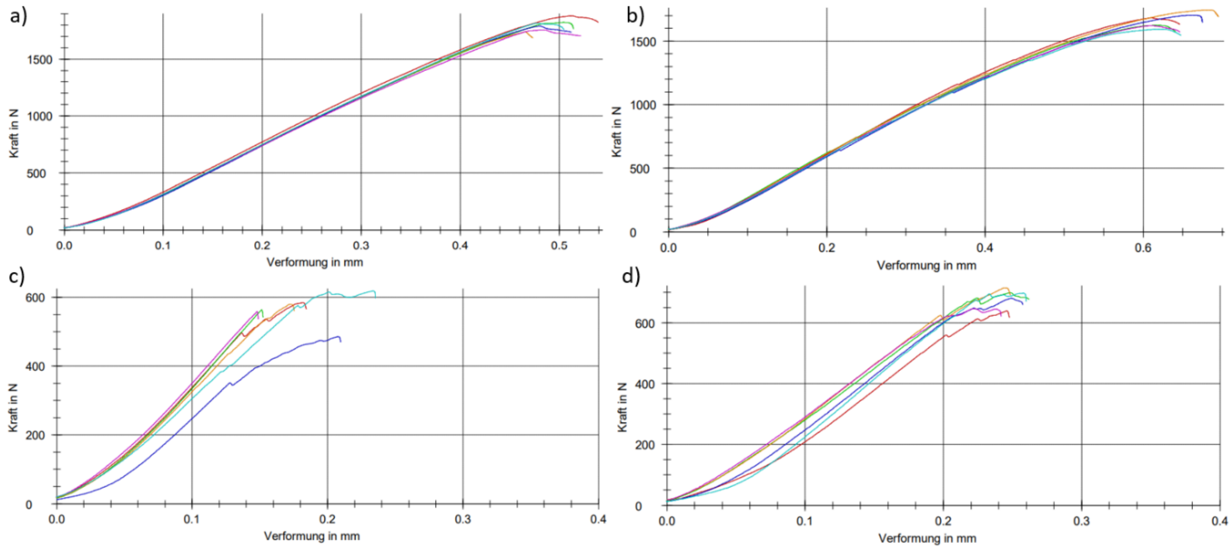


Figure 51. Load versus length curves for a) reference epoxy resin prepreg laminate 1st measurement b) reference epoxy resin prepreg laminate 2nd measurement. C) lignin #3 epoxy resin prepreg laminate 1st measurement and d) lignin epoxy #3 prepreg laminate 2nd measurement.

5 Conclusions

This study set out to determine how to incorporate lignin to epoxy resins and determine its applicability as a coating and composite. Based on the set research objectives and following conclusions can be made:

1. *Technical sources of lignin are used for the synthesis. Can a depolymerisation method be developed to have a reactive system for synthesizing epoxy resins? If so, it is essential to understand the yield of this process as well as characterising the substrate obtained from it.*

The Confidential Fractionation process has proved to be successful in aiming at obtaining a fractionated lignin substrate with an average yield of 50-60% for both the lignin sources. In the case of *lignin #3*, a Confidential Treatment was applied to improve the fractionation yield. TGA analysis on the fractionated substrates revealed a rapid weight loss in the case of *fractionated lignin #3* which can be caused by the breaking down of molecules caused by the Confidential Treatment. GPC analysis supported the idea that *fractionated lignin #1* exhibits a higher molecular weight than *fractionated lignin #3*, which supports previous statement. Finally, NMR analysis allowed us insight into the technical and fractionated lignin's composition. Firstly, it was observed how the Confidential Fractionation increased the number of aliphatic groups in the lignin, indicating the possibility of breaking down of the lignin substrates after the process. Changes in reactivity are expected between the *fractionated lignin #1* and *#3* due to a higher amount of aliphatic OH and lower content of G units in the latter.

2. *So far, the lignin-based epoxies have been synthesized on a small scale; however, translating this process to a larger scale is still challenging. What are the reaction conditions and process to follow to produce a realistic epoxy resin from lignin derivative? Different process conditions will be tested, and the obtained products will be characterised to choose the most suitable reaction conditions.*

Fractionated lignin #1 and *#3* were used to synthesize epoxy resins on a small scale, while the latter was the chosen substrate for the scale-up. "Dry" and "wet" glycidation processes were performed, as well as changes in the washing steps and it seems that the "wet" process is the most suitable one. The EGC of *lignin #1 epoxy resin* was higher than that of *lignin #3 epoxy resin*, suggesting that *fractionated lignin #1* is more reactive, which is in line with the obtained NMR data. The EGC of the *lignin #3 epoxy resin* when synthesized via small or large-scale was comparable, however, there seems to be a significant difference in the appearance of the resin (viscosity). This can be caused by some molecular build-up in the large-scale. The first trials of scale-up in the lab were successful in synthesizing a resin, however, further optimisation must be done. The EGC of the lignin-based epoxy resins is much lower than the *reference epoxy resins*. This can be attributed to bulky moieties in the lignin, which can lead to lower flexibility and molecular mobility that can decrease the reactivity of its active sites.

3. *How can lignin epoxy resins be implemented in the field of coatings and composites? What is the mechanical and thermal performances of the synthesized lignin epoxy resins? What is the performance of these lignin epoxy resins compared to reference epoxy resins?*

The lignin-based epoxy resins have been successfully used in both coatings and composites. Lignin-based coatings present comparable results in hardness and at least reach 50% of the performance of the *reference epoxy resin* coating exhibits in impact resistance. However, these lignin-based coatings have very low flexibility, increasing the material's stiffness. Additionally, the presence of small particles or irregularities in the coating act as crack-initiating sites, mainly caused by the high viscosity exhibited by the resin. In the case of composites application, the high viscosity of the lignin epoxy resins makes it difficult to process the prepreg laminates. On the other hand, the lignin epoxy resin presents a higher thermal stability than the *reference epoxy resin*. The T_g values of the lignin-based resins do not differ significantly from that of the reference. However, due to the poor adhesion of the fibers and matrix, the shear strength and elongation at break are much lower for the lignin prepreg laminates.

4. *Understand the relationship between the chemical structure of the lignin and its epoxy resin and the performance they exhibit as coatings and composites.*

The lignin structure can explain the properties displayed by the coatings and composites made of lignin resin. High molecular weight, entangled structure and the tendency self-interact are the reason why lignin-based resin exhibit such high viscosity, affecting both the composites and coatings application. While the presence of entanglements in the lignin molecule benefits its hardness, it hinders the dissipation of the energy absorbed from the shock, as the mobility of the molecules is impeded, resulting in lower impact resistance. Flexibility is low due to the very branched, stiff structure and bulky moieties of the lignin molecules. The viscosity of the lignin resin in composites is the main reason the properties exhibited by the prepreg laminates are poor. Additionally, the lignin-based epoxy resin presents a lower heat of reaction during curing compared to the *reference epoxy resin*. This is caused by the lower EGC of the lignin epoxy resins, and bulky moieties in the lignin can lead to lower flexibility and molecular mobility that can decrease the reactivity of its active sites. This steric hindrance and bulky moieties could also explain the higher viscosity of the lignin epoxy resins.

6 Recommendations

During this research project, some limitations and difficulties were encountered, however, they can be suggestions for further research.

1. In this research, non-depolymerised technical Kraft lignin was used as a substrate. No other type of lignin is used, therefore, for further research it might be interesting to consider the use of other lignin such as organosolv, soda or lignosulfonate. As mentioned in the literature section, the properties of the lignin vary significantly depending on the extraction process. Analogue research can be performed considering another type of lignin and comparing it with the ones used for this project.

2. During the glycidation reaction, different samples were taken as a method for screening, however, only GPC was used as an analytical technique. To further understand the glycidation of lignin, it would be important to use other methods for the screening of the reactions, for example UHPLC which might potentially give more insight into the process.

3. After the glycidation reactions, washing steps are performed on the product in order to remove the other impurities present. In this case, DCM was used for the organic phase, however, most of the issues were encountered in the phase separation, probably due to very similar density between the water and DCM. For a better phase separation, which will make the washing steps quicker, the use of other solvent would be benefitial.

4. Optimisation of the large-scale glycidation is required, there are some differences between the resin obtained from the large and small-scale, therefore, further improvement in the process can lead to reproducibility in the results obtained.

5. The expectation is also that the lignin epoxies are substantially cheaper from a raw material perspective. Therefore, it would be interesting to analyse what is the minimum performance that is needed on the resin so that the price is significantly lower to a standard epoxy resin.

6. In order to understand the mechanical properties of the lignin epoxy resins, the testing should be done on the neat resin. In this case, prepreg laminates using lignin epoxy resins were tested, however, the mechanical properties are mainly govered by the fibers. Therefore, to further understand and study the properties of the resin itself, the same mechanical testing can be performed on neat resin panels.

7. The lignin-based epoxy resins exhibit high brittleness, which affects both the performance as a coating and composite. It would be interesting to consider adding plasticiser to both the coating and composite formulation and study the effect that these would have in the performance of the material.

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Appendix

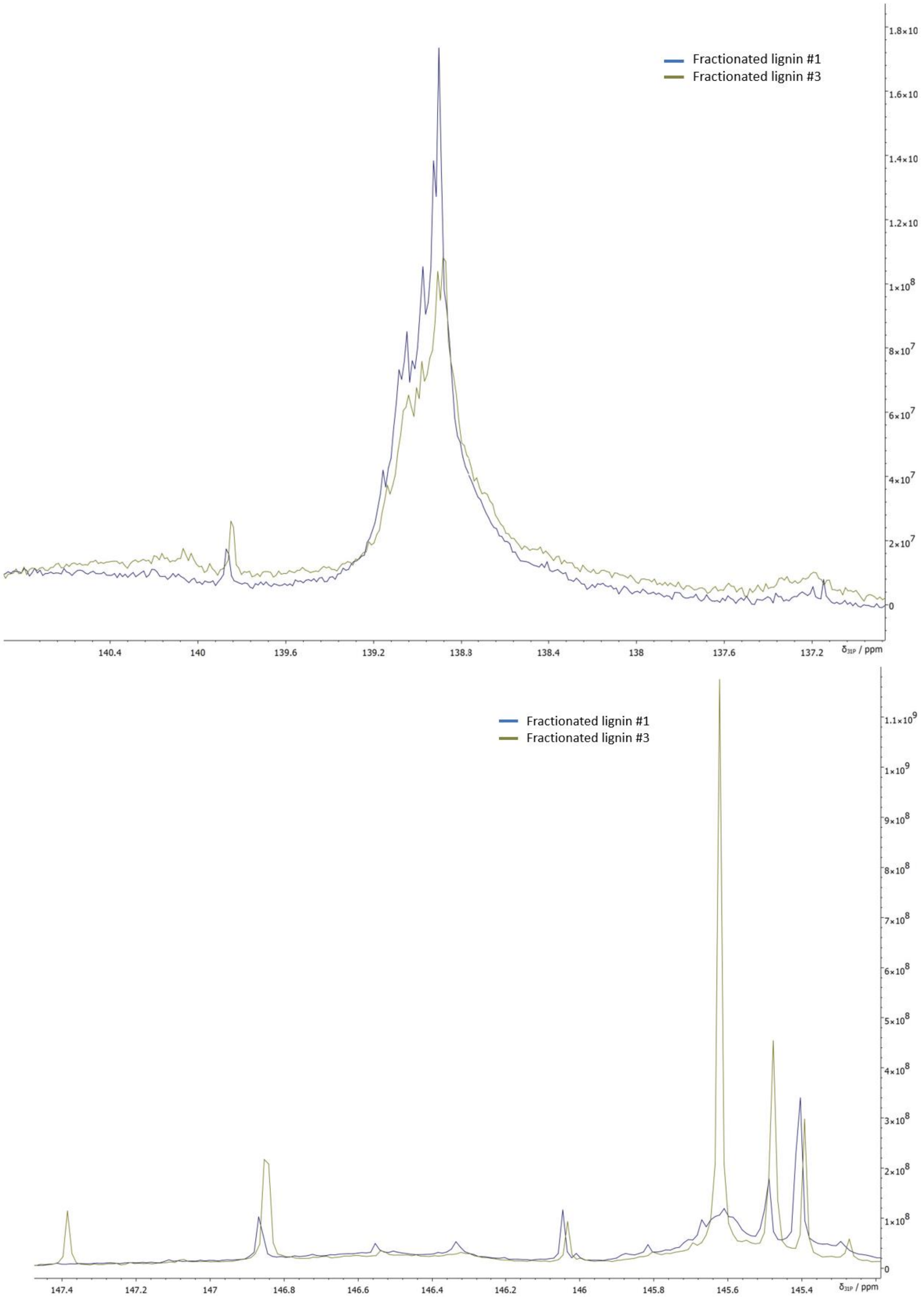


Figure A 1. Overlay of ^{31}P-NMR of fractionated lignin #1 and fractionated lignin #3.

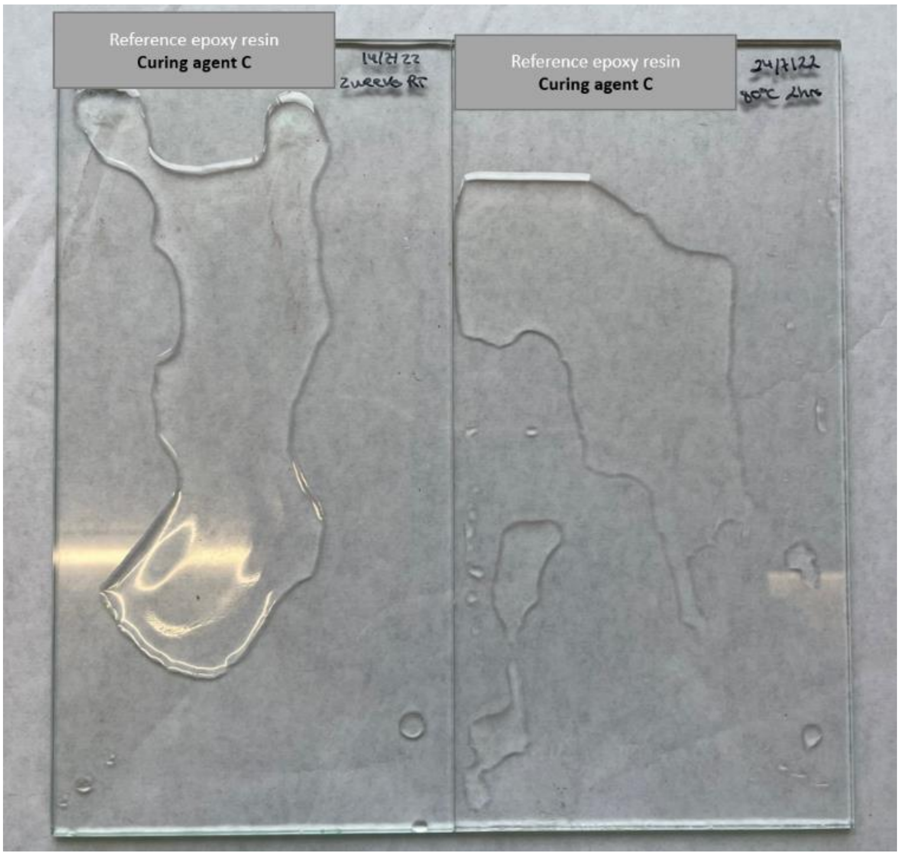
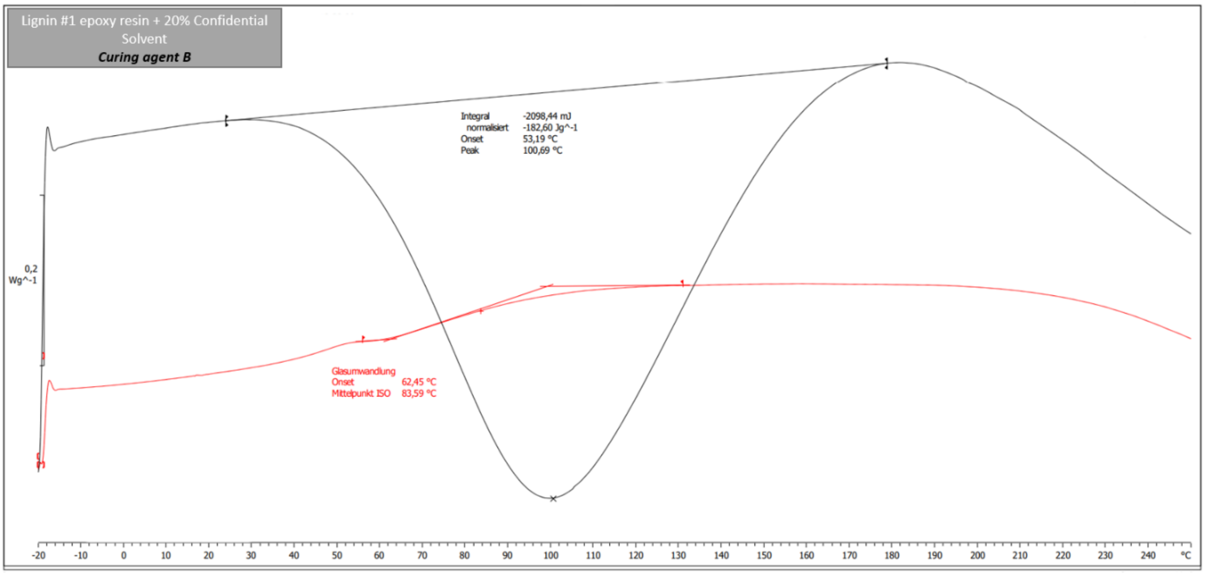


Figure A 2. Coating film of reference resin with Curing agent C cured at room and high temperature.



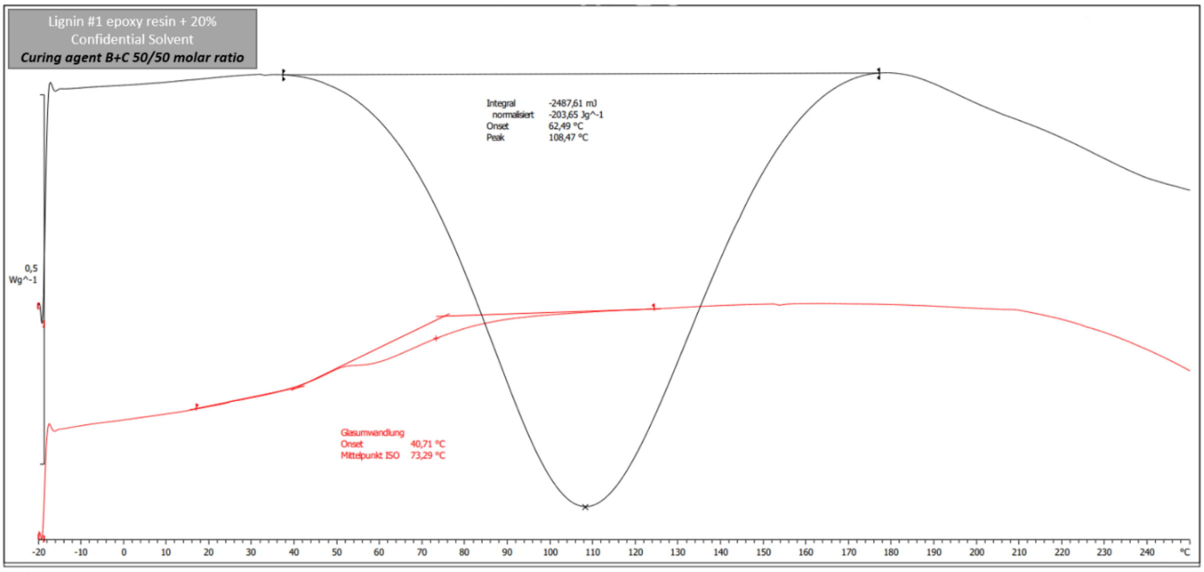


Figure A 3. DSC curves of lignin #1 epoxy resin with Curing agent B and Curing agent B+C 50/50 molar ratio.

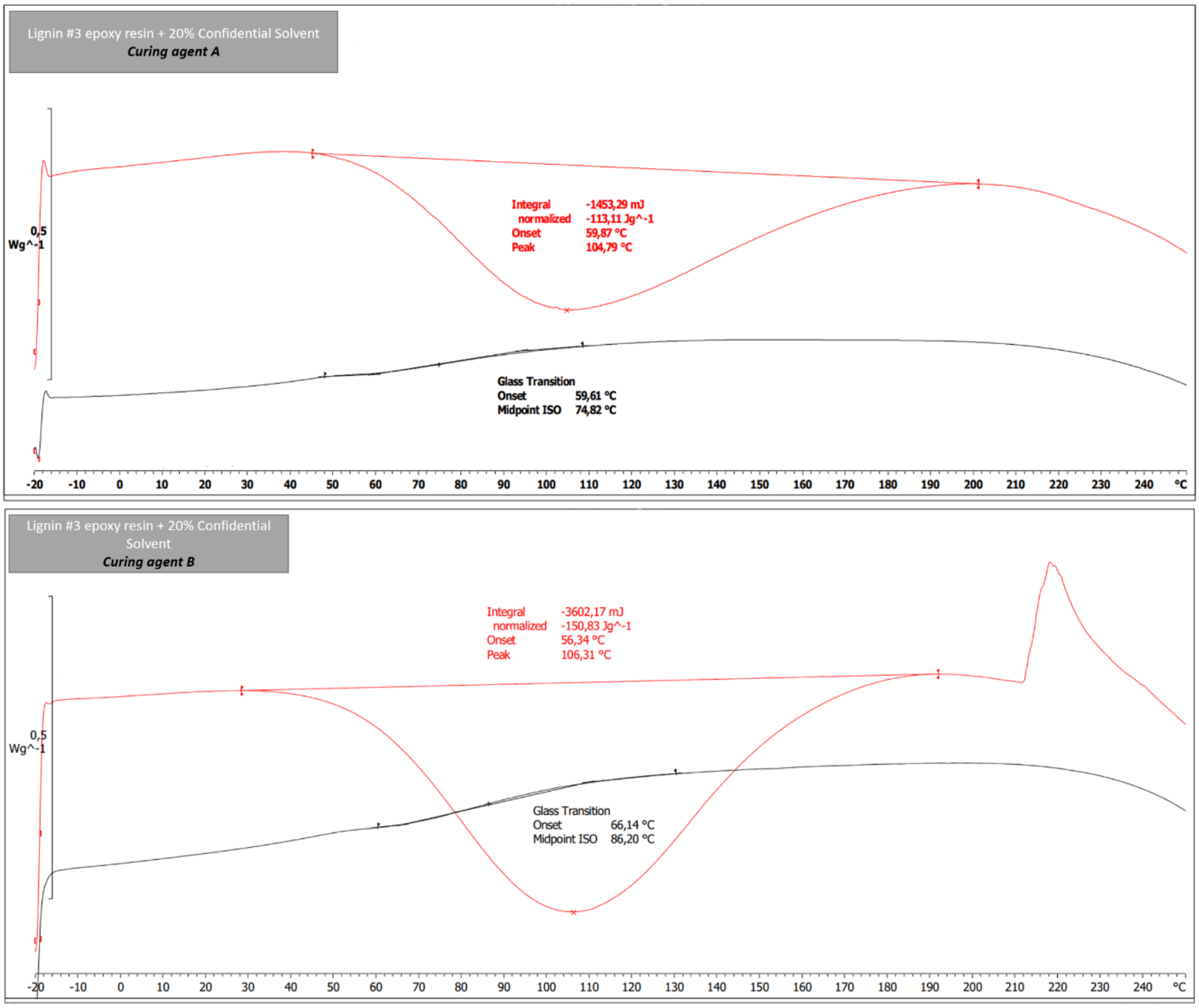


Figure A 4. DSC curves for lignin #3 epoxy resin with Curing agent A and Curing agent B.

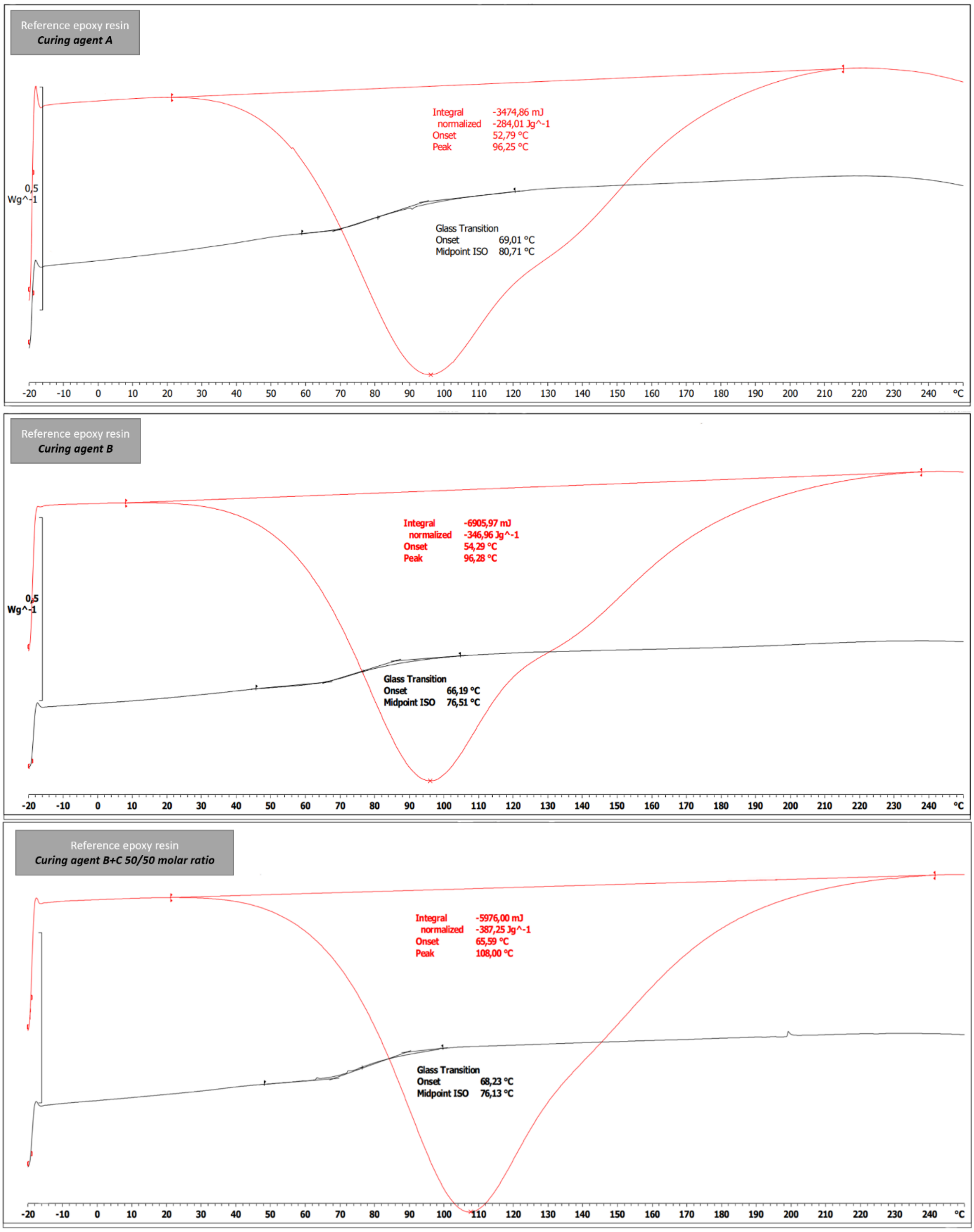


Figure A 5. DSC curves of reference epoxy resin with Curing agent A, Curing agent B and Curing agent B+C 50/50 molar ratio.

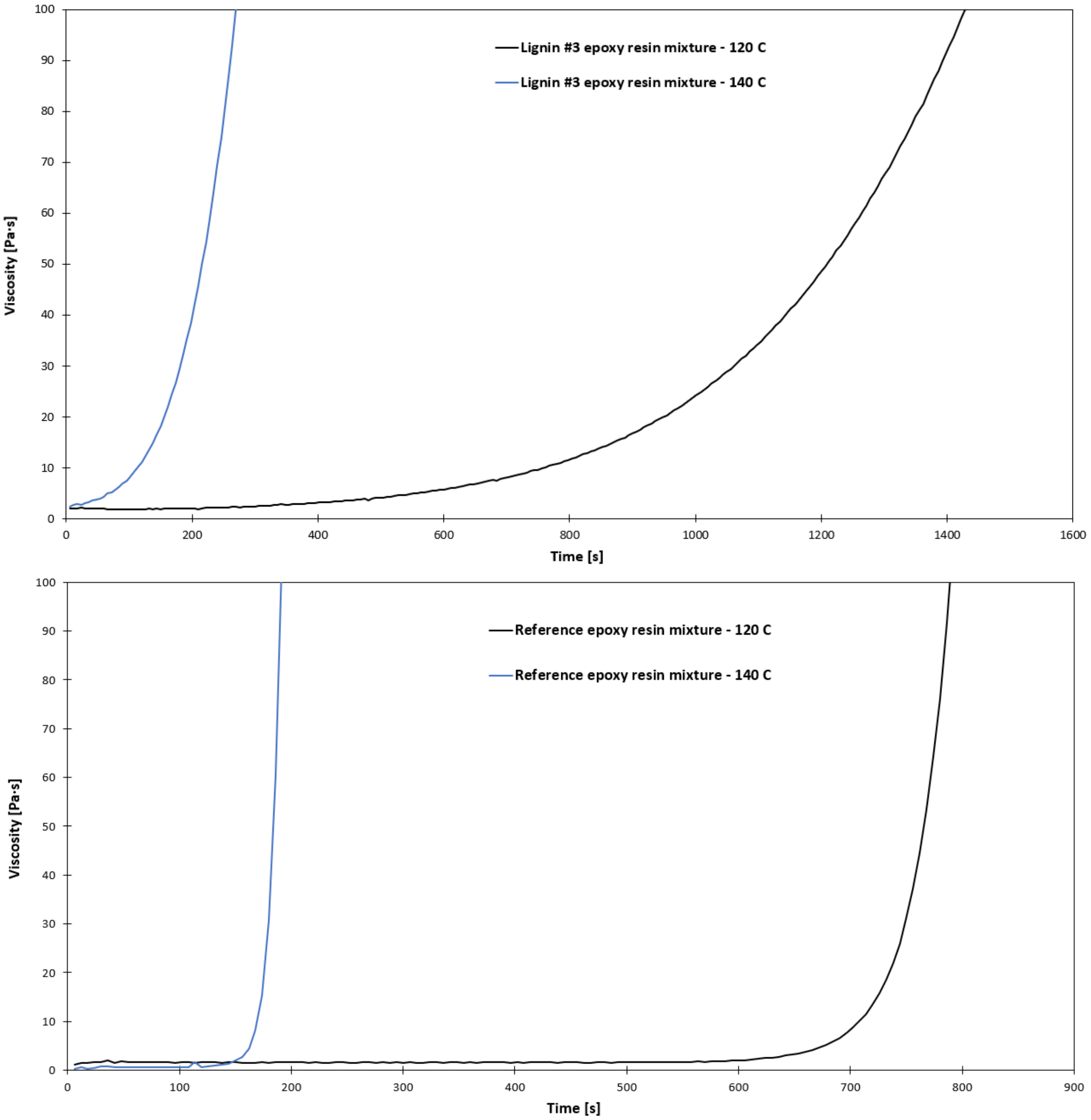


Figure A 6. Oscillation isothermal viscosity of lignin #3 epoxy resin and reference epoxy resin mixtures.

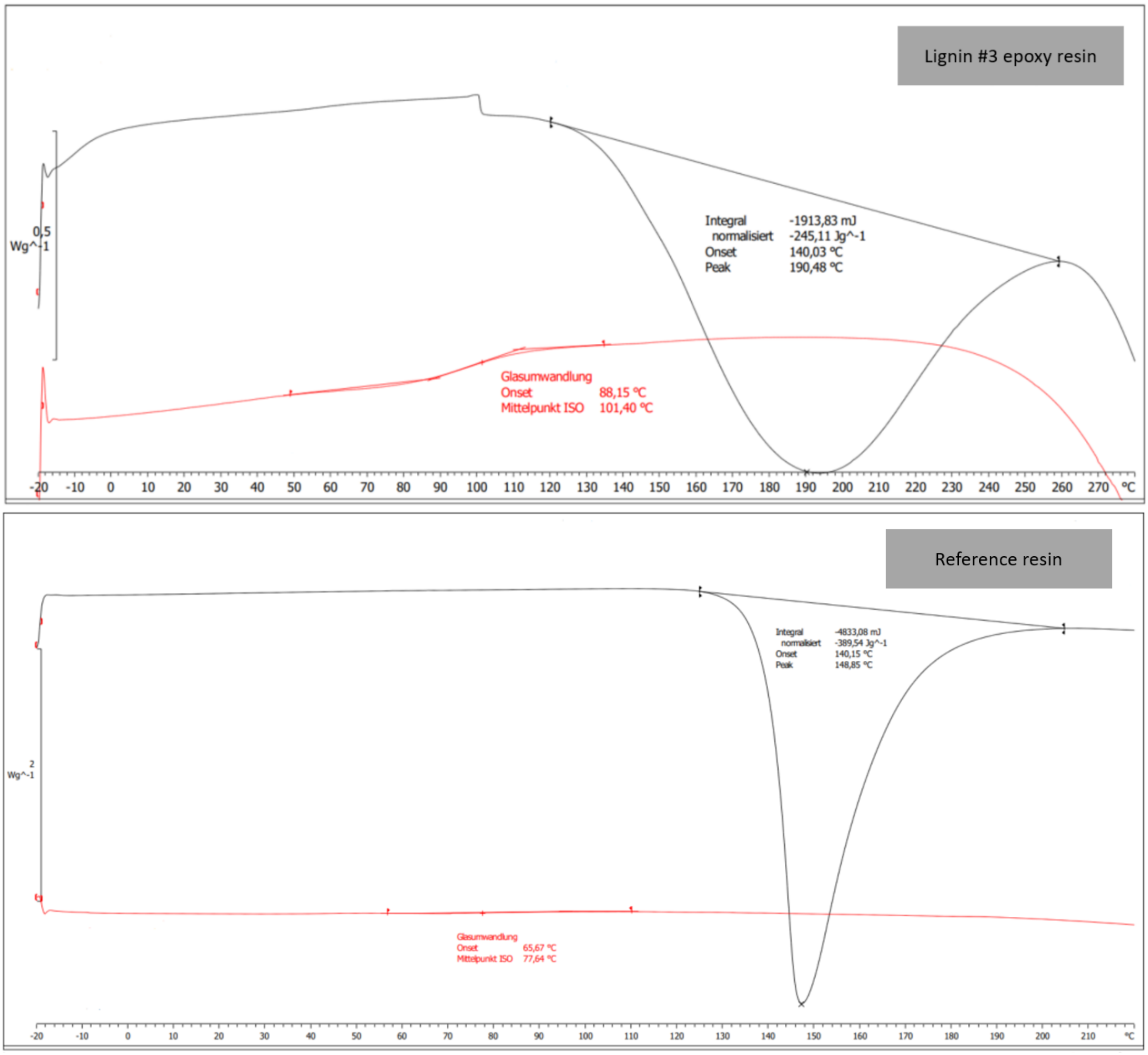


Figure A 7. Dynamical DSC analysis for uncured lignin #3 epoxy resin and reference resin.

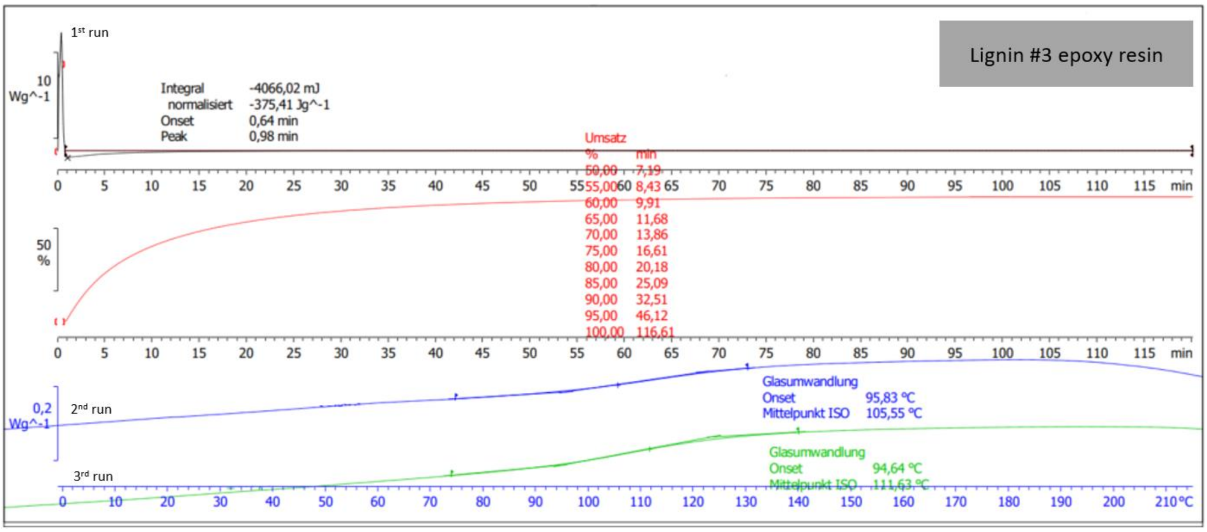


Figure A 8. Isothermal DSC analysis of uncured lignin #3 epoxy resin at and 160 °C for 2 hours.

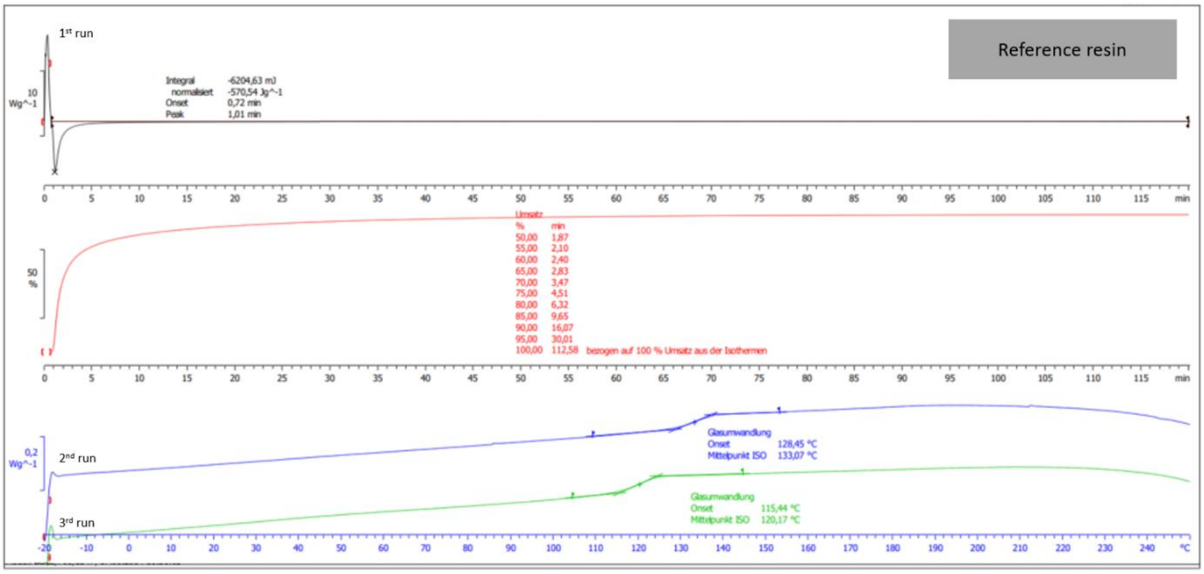


Figure A 9. Isothermal DSC analysis of uncured reference resin at 160 ºC for 2 hours.