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Design and Development of Advanced Thermosetting and Vitrimeric Materials Based on Sustainable Polymers

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List of abbreviations

°C	Celsius degree
ΔH_m	Melting enthalpy
ArG	Arabic Gum
C	Cellulose
CA	Citric acid
CANs	Covalent Adaptable Networks
$\bar{D}$	Dispersity index
DBU	1,5-diazabicyclo(5.4.0)undec-7-ene
DCP	Dicumyl peroxide
DGEIs	Isosorbide diglycidyl ether
DEM	Diethyl malonate
DMA	Dynamic Mechanical Analysis
DMAP	4-(Dimethylamino)pyridine
DMC	Dimethyl carbonate
Dipety	Dipentaerythritol
DSC	Differential Scanning Calorimetry
E_a	Activation energy
EBC	Erythritol bis(carbonate)
FT-IR	Fourier-Transform Infrared Spectroscopy
Gly	Glycerol
GPC	Gel Permeation Chromatography
GuG	Guar Gum
HDPE	High-performance polyethylene
L-LA	L-lactide
M_n	Number of average molecular weight
NIPU	Non-isocyanate polyurethane
NMR	Nuclear Magnetic Resonance
Pety	Pentaerythritol
PLA	Poly(lactic) acid
p-TSA	<i>p</i> -Toluenesulfonic acid
ROP	Ring-Opening Polymerization
SEM	Scanning Electron Microscopy

Sn(Oct) ₂	Sn(2-ethylexanoate) ₂
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TEA	Triethylamine
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMSS	Tetrakis(trimethylsilyl)silane
T _v	Topology Freezing Transition Temperature
WCA	Water Contact Angle
X _c	Cristallinity
XaG	Xanthan Gum
Xyl	Xylitol
Zn(OAc) ₂	Zinc acetate

Abstract

The growing accumulation of fossil-derived plastic waste represents one of the major environmental challenges of nowadays.

Although thermoplastics can be recycled with relative ease, thermosets remain difficult to reprocess due to their permanent cross-linked networks, despite offering excellent mechanical and chemical performance.

This limitation underscores the need to redesign such materials to better align with circular economy principles.

This PhD work focuses on these issues by developing new sustainable dynamic polymer systems based on aliphatic polyesters, incorporating dynamic covalent bonds to try to obtain reprocessability, repairability, and extended material lifetimes while maintaining comparable mechanical and thermal performances to commercial systems.

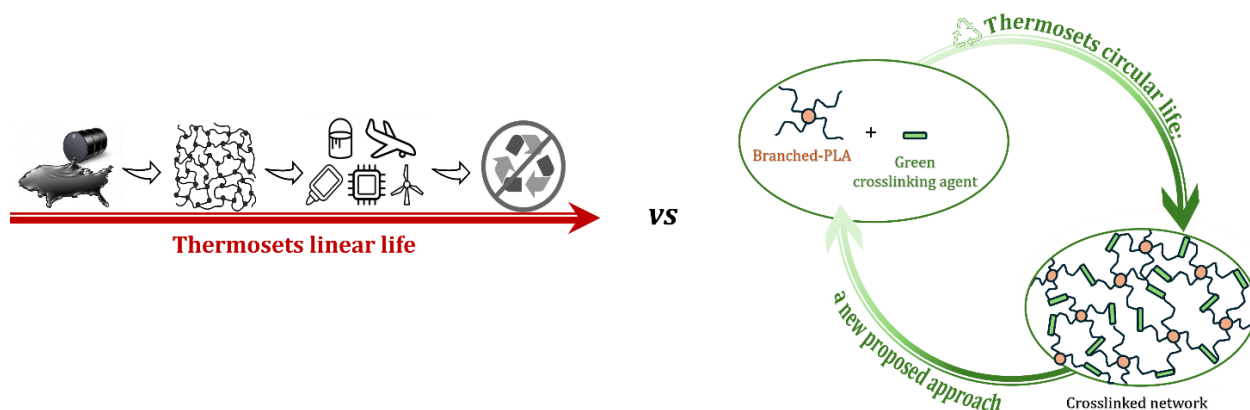


Figure – Thermosets circular life: a new proposed approach

Branched poly lactic acid (PLA) prepolymers were chosen for this work precisely because of their renewable origin, established scalability, and intrinsic recyclability. They were synthesized by ring-opening polymerization of L-lactide using multifunctional bio-derived polyols as initiators and extensively characterized by NMR and GPC.

Their potential for nontoxic, bio-based crosslinking was investigated using a set of bifunctional reagents, including diethyl malonate, citric acid, erythritol biscarbonate, and isosorbide diglycidyl ether, under various catalytic and thermal conditions.

To address their limited reactivity, the PLA prepolymers were then functionalized with carboxylic acid end groups and successfully crosslinked with isosorbide diglycidyl ether.

The optimized formulations yielded highly crosslinked, insoluble materials with high gel fractions, which were analyzed by DSC, TGA, rheological and mechanical testing, SEM, and water contact angle measurements.

These analyses confirmed the formation of a crosslinked network exhibiting vitrimer-like behavior.

To explore their potential in a circular economy, preliminary depolymerization tests were carried out in mildly basic aqueous conditions, giving early insights into how these materials might be recycled at the end of their life.

Complementary research carried out at *École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris* (ESPCI Paris) focused on incorporating various bio-based fillers into high-density polyethylene (HDPE) to make conventional thermoplastics more sustainable.

By using reactive extrusion with both established and newly developed grafting agents, the compatibility between the fillers and the polymer was improved, leading to better mechanical performance.

These improvements were confirmed through DMA, tensile testing and DSC, highlighting the potential of bio-based additives to enhance traditional plastics.

Overall, this work represents an advance in more sustainable polymeric materials by combining renewable feedstocks, dynamic covalent chemistry, and compatibilization strategies.

The resulting materials contribute to the development of high-performance thermosets and thermoplastics with improved circularity, reduced environmental impact, and viable pathways toward recyclable and responsible polymer networks.

CHAPTER 1

State of the Art

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1.1 The “Plastic Age”

The increasing volume of plastic waste and its harmful effects on the environment pose a significant challenge to the sustainability of the polymer industry.

Global annual plastic production has surpassed 359 million tons¹ and has surged dramatically in recent decades, leading us into what is now commonly known as the "Plastic Age."²

The material's properties, such as durability, flexibility, and low cost, have made it ubiquitous and indispensable in daily life, resulting in its global distribution.

However, growing evidence shows that the current use and disposal of plastic are causing substantial pollution in both terrestrial and aquatic ecosystems, with plastic waste now being seen as a new planetary boundary threat.³

The European Green Deal, launched by the European Commission in 2019, acknowledges this issue and promotes a transition to a circular economy, where plastic is designed to be reused, recycled, and minimized.

Part of this transition involves adopting sustainable practices across the entire plastic value chain, from production to waste management, through measures that encourage the use of recycled materials, reduce single-use plastics, and improve recycling infrastructure.

The Green Deal not only aims to tackle plastic pollution but also seeks to create an economic system that values plastic as a circular material, while reducing its negative environmental impacts and promoting a more responsible and sustainable use of natural resources.⁴ **Figure 1.1** offers a schematic overview of the main points addressed in the Green Deal and their implementation.

According to data from the European Parliament, a total of 16.13 million tons of plastic waste were produced in the EU in 2021, of which only 6.56 million tons were recycled.⁵

The difficulty in recycling plastics primarily lies in their complex chemical structure, which makes it challenging to break them down and repurpose them efficiently.

Plastics are typically categorized based on their physical and chemical properties and applications, with two main types being thermoplastics and thermosetting plastics.

While integrating thermoplastics into a circular economy is becoming increasingly feasible, the task is far more challenging when it comes to thermosets. These plastics, which not only originate from fossil fuels but also feature a crosslinked structure, are much harder to recycle, making their inclusion in sustainable systems a significant hurdle.⁶

Thermosets are valued for their superior mechanical and chemical properties, making them ideal for a wide range of applications such as coatings, tires, contact lenses, elastomers, adhesives, and foams. As a result, integrating thermosets into a circular economy is crucial.

In the last decade, a promising research approach has emerged, based on synthesizing polymer networks cross-linked with dynamic covalent bonds (defined in the literature as "covalent adaptable networks" or "CANs," "dynamic polymer networks," or, in some cases, "vitrimers").⁷

These materials are designed to perform like traditional thermosets under normal conditions. However, due to the presence of weaker bonds in the cross-links, they can flow and be reprocessed like thermoplastics when exposed to specific stimuli. In principle, they are also capable of being chemically recycled at the end of their lifecycle.

To enhance sustainability, the building blocks used to create these polymers can be sourced from renewable resources.

Following this line, the research project seeks to develop new thermoset materials with a reduced environmental impact, maintaining performance comparable to existing commercial options.

The project will also systematically explore sustainable alternatives for the materials' individual components.

Aliphatic polyesters are being studied as sustainable alternatives due to their ester linkages, which are prone to hydrolysis, making them biodegradable. Furthermore, they are derived from renewable biological sources.

The project focuses on synthesizing prepolymers based on branched PLA to produce cross-linkable and biodegradable thermosetting resins.⁸

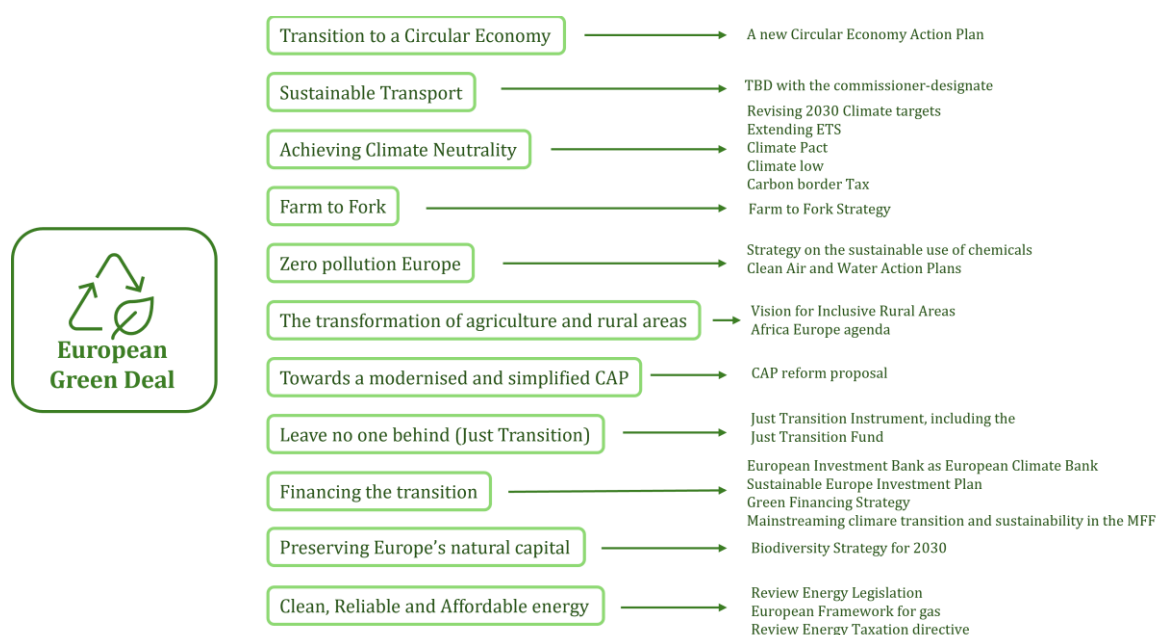


Figure 1.1 – Schematic outline of the key components of the European Green Deal and their corresponding policy actions

1.2 An Overview of Plastic Materials

Thermoplastic and thermosetting materials are two primary types of polymers, each with unique characteristics that make them suitable for different applications.⁹

Thermoplastics are soft, flexible, and moldable polymers that can be recycled and reshaped multiple times.

They are composed of linear or slightly branched polymer chains held together by weak intermolecular forces; as a result, they soften upon heating and harden upon cooling. This reversible behavior allows thermoplastics to be remolded and reprocessed repeatedly, making them particularly suitable for recycling and reuse.^{10,11}

Many thermoplastics exhibit a microstructure consisting of flexible, rubbery amorphous regions and more rigid, crystalline regions, which together provide a favorable balance of impact resistance, flexibility, and toughness.

In addition, thermoplastics have a melting or softening temperature lower than their thermal degradation temperature, allowing for processing without chemical decomposition. They

generally exhibit good chemical resistance and, depending on their chemical structure and degree of crystallinity, may be soluble in specific organic solvents.¹²

Because of these properties, they are used everywhere in industries. A few of the most widely used ones include polyethylene, polystyrene, and nylon, which are incorporated into consumer goods used daily, such as packaging materials, car parts, and household utensils.¹³

Thermosetting materials, in contrast, are a little more rigid and permanent due to their composition.

They consist of polymers that form a strong, continuous network. They are locked into a fixed shape by the three-dimensional structure that is produced. The polymer chains in thermosets undergo a curing process that results in crosslinking and hardening when they are heated or exposed to UV light. They cannot be reshaped like thermoplastics once this occurs because it is irreversible.¹⁴ When heated, thermosets do not melt because of their higher melting point. Rather, they become rigid and brittle.

Their crosslinked structure gives them strength and durability, but it also prevents them from being recyclable. Due to their exceptional resistance to heat and chemicals, thermosets are ideal for items that must withstand harsh environments.

Figure 1.2 outlines the main differences between the two polymer classes.



Property	Thermoplastics	Thermosets
Molecular Structure	Composed of linear polymers with weak bonds	Composed of network polymers with strong bonds
Melting Point	Melting point lower than degradation temperature	Melting point higher than degradation temperature
Microstructure	Comprise elastic amorphous and hard crystalline regions	Consist of solid resins and reinforcing fibers
Mechanical	Flexible, elastic and impact resistant; strenght from crystallinity	Brittle and inelastic; strenght from crosslinking
Recyclability	Recycalble and reusable	Not recyclable
Chemical Resistance	Highly resistant to chemicals	Resistant to chemicals and heat
Solubility	Can dissolve in organic solvent	Insoluble in organic solvent

Figure 1.2 - Thermoplastic vs Thermosets: key differences in terms of structure, properties, and recyclability

1.3 Thermosetting Polymers and Composites

1.3.1 Structure

Thermosetting polymers, or thermosets, are a category of polymers that undergo a chemical transformation when cured, transforming from a pliable or liquid state into a solid, rigid structure.¹⁵

This curing process, which involves heat, irradiation, or chemical reactions with a hardener or catalyst, forms a network of interconnected polymer chains.

Polymer networks, also known as crosslinked networks, are molecular structures that rely on covalent bonds or physical intermolecular interactions between macromolecules. When the connections between junction points are created through chemical bonds, they are called *chemical crosslinks*. In contrast, crosslinks that result from the entanglement of long polymer chains are known as *physical crosslinks* (**Figure 1.3**).¹⁶

In thermoset polymers, crosslinks are specifically of the chemical type.

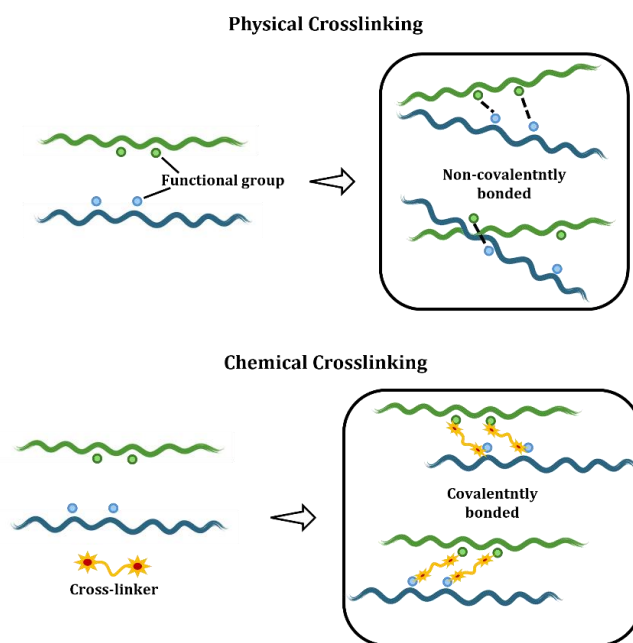


Figure 1.3 – Representation of physical crosslink (top) and chemical crosslink (bottom)

This curing process leads to non-reversible chemical reactions, causing the polymer chains to become crosslinked. As a result, the polymers do not melt at high temperatures and exhibit

superior mechanical strength. Additionally, they retain their shape and do not deform when exposed to cold temperatures, making them suitable for use in extreme and fluctuating temperatures.¹⁷

Thermosetting materials play a crucial role as the matrix in the development of composite materials.

A composite material is defined as a combination of two or more materials that, when combined, produce a final structure with properties that exceed those of the individual components (**Figure 1.4**).

Composites typically include reinforcement elements, commonly known as fillers, which are embedded within a matrix.¹⁸

The matrix is essential for maintaining cohesion and properly orienting the load, ensuring the composite's enhanced strength and durability. By binding the reinforcing fibers together, the matrix transfers the applied loads between them, contributing to the overall structural integrity of the composite material. Additionally, the matrix protects the fibers from environmental factors and physical damage, thereby increasing the lifespan and performance of the composite. This interaction between the matrix and the reinforcement is crucial in optimizing the material's properties, enabling its application in various demanding environments.

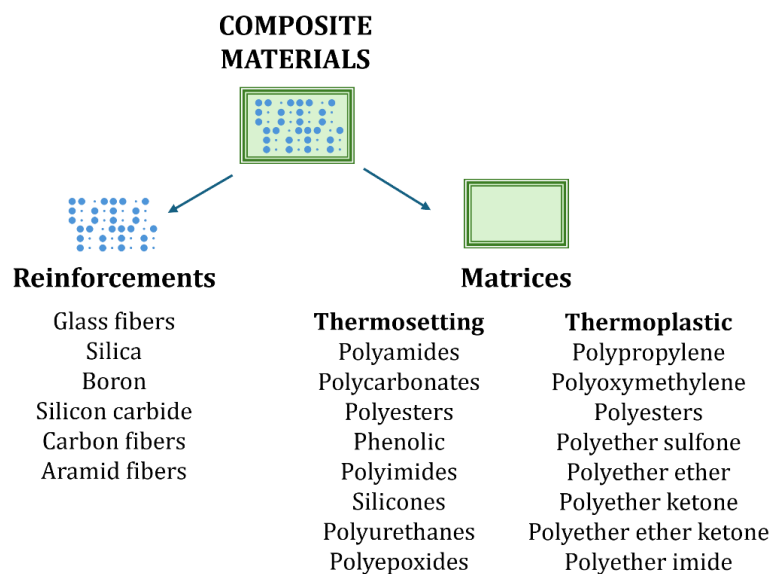


Figure 1.4 - Illustration of the main component of a composite material. Examples of reinforcements and matrices (thermoplastic or thermosetting) that can be used

1.3.2 Type and Applications

Thermosetting materials represent 15%-20% of the annual global plastic production, with forecasts indicating an increase in the coming years.¹⁹

This category includes several polymer classes, all derived from fossil sources:

- *Epoxy resins* – they are pre-polymers with a low molecular weight, characterized by the presence of multiple epoxide groups. The most widely used are derived from bisphenol A and epichlorohydrin. Cross-linking occurs when amines react with the epoxide rings, initiating the curing process. These resins are commonly used in engineering composites, adhesives, coatings, and electrical insulation.
- *Phenol formaldehyde resins* – they are strong, heat-resistant materials made by combining phenol with formaldehyde. There are two main types: novolac, which requires a hardener to cure, and resol, which can harden on its own. These resins are known for their durability, stability, and excellent resistance to heat and chemicals, making them ideal for a range of applications like automotive parts, adhesives, coatings, and electrical components. Their strength and insulating properties make them particularly useful in demanding environments.²⁰
- *Polyester resins* – Unsaturated polyester (UP) resins are affordable and adaptable materials made from a mix of unsaturated and saturated acids, along with diols and oxides. Depending on their composition, they can be thick liquids or brittle solids, and when combined with vinyl monomers, they form a strong, durable network. These resins have been in use since the early 1940s and are now a staple in many industries, particularly in construction, transportation, and electronics, often reinforced with glass fibers. Their ability to cure at room temperature makes them perfect for creating large structures like boat hulls, car bodies, and airplane parts. The construction industry is the biggest user of these versatile resins.²¹
- *Polyurethanes* - These polymers contain urethane groups within their chains, formed by the reaction between isocyanates and alcohols. Due to their durability and flexibility, polyurethanes are widely used in a variety of applications, including insulation foams, chemical-resistant coatings, automotive, construction, medical industries, sealants, and in the production of furniture and packaging materials.²²

- *Silicones* - consisting of an inorganic silicon-oxygen backbone, with organic functional groups attached to the silicon atoms. By varying the length of the siloxane chain, its branching, and the functional groups, a wide range of materials with different properties can be synthesized. Known for their high flexibility and resistance to heat, chemicals, sunlight, and aging, silicones are commonly used in applications such as gaskets, heat insulation, and soft-touch surfaces. Additionally, they serve as lubricants and anti-foaming agents.²³

1.3.3 Thermosets' Life Cycle

Thermosetting polymers have long been regarded as thermally unprocessable due to their covalent intermolecular cross-links.

Consequently, most thermosets are either landfilled or incinerated at the end of their life cycle, making these the least desirable waste management methods.²⁴

While some recycling solutions for thermosets are now available, there remains a strong need for further research into processes that are both environmentally sustainable and economically viable. More efforts are required to build a sustainable market for recycled thermoset materials.

The successful recycling of thermosets and thermoset-based composites depends on a variety of social, economic, and cultural factors, all of which play a critical role in supporting the shift from a linear (**Figure 1.5**) to a circular economy.¹⁷

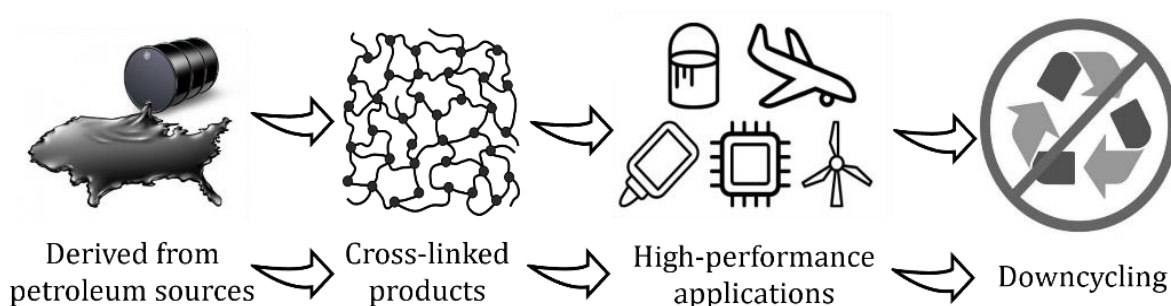


Figure 1.5 – Thermoset linear life: from its fossil-based production to the recycling difficulties

Currently, there are three possible recycling routes for thermosets: thermal, mechanical or chemical recycling (summarized in **Figure 1.6**).

- *Thermal recycling techniques*

Thermal recycling techniques, which involve high-temperature processing, can primarily be categorized into combustion or incineration for energy recovery,²⁵ fluidized-bed combustion for the recovery of reinforcement fibers,²⁶ and anaerobic combustion, such as pyrolysis, to obtain simpler molecules that can serve as raw materials for new chemical processes.²⁷

These methods offer advantages such as the recovery of energy, oils, and fillers without the need for solvents or catalysts.

However, they also present drawbacks, including the reduction in the dimensions and properties of the recovered materials and the production of emissions and CO₂, which raises concerns regarding their environmental impact.

Moreover, these recycling techniques cannot be effectively applied to glass fiber-reinforced composites, which are one of the most widely used materials. This comes mostly from the properties of glass fiber, which provide high tensile strength, low density, good chemical resistance, and a relatively low cost compared to carbon or aramid fibers. However, when thermal recycling is applied, the high-temperature treatment involved causes severe degradation or even combustion of the glass fibers themselves.^{28,29}

- *Mechanical treatment*

Mechanical recycling is a well-explored and cost-effective technique due to its simplicity.

It involves reducing waste materials to smaller sizes, which can then be repurposed as powdered fillers or partially reinforced fibers to produce new composites or added to asphalt and cement.

This method allows for the recovery of fillers and matrix, which can be used as additives to create second-life materials.³⁰

However, it has some limitations, such as the long pre-treatment times required to recover the materials, the lower mechanical performance of the recycled materials, and the inability to re-manufacture the materials to their original form.

These challenges highlight the need for further improvements in mechanical recycling processes to enhance their efficiency and material quality.

- *Chemical recycling*

Chemical recycling of thermosetting polymers provides an effective method for recovering mono-oligomers and fillers, maintaining their original shape, size, composition, and mechanical properties.

This process involves breaking the 3D cross-links between the polymer chains, which allows for the recovery of these materials in composite products.³¹

However, it comes with some drawbacks, including the use of solvents and catalysts, which could present both environmental and economic challenges. Additionally, implementing the process on a larger scale is difficult due to its complexity and the need for precise control over the degradation process.

Various techniques, such as solvent-based degradation, catalytic systems, and irradiation-assisted methods, have been explored to break the cross-links and enable recycling, but scalability and efficiency remain key concerns for broader adoption.

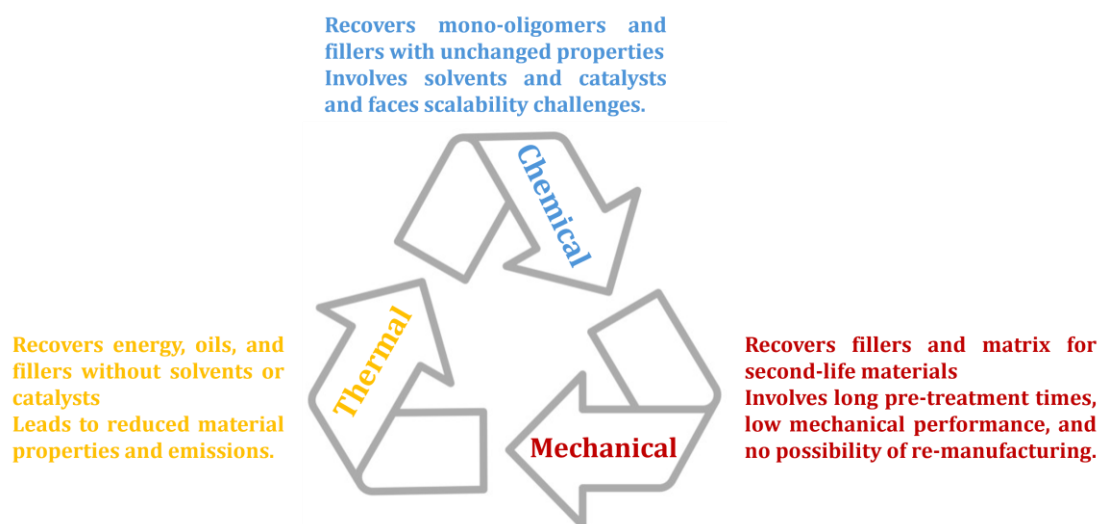


Figure 1.6 – Advantages and disadvantages of the possible recycling routes for thermosets: in yellow, the thermal recycling techniques; in blue, the chemical recycling; in red, the mechanical treatment

1.4 Covalent Adaptable Networks (CANs) and Vitrimers

One of the most straightforward ways to make cross-linked polymer networks more recyclable is by introducing dynamic covalent bonds: chemical bonds that can break and reform under certain conditions. When enough of these reversible, responsive bonds are included, the new materials are categorized as Covalent Adaptable Networks (CANs).

This concept was first introduced in the polymer field by *Bowman* and his team.

CANs represent a significant advancement in the design of thermosetting polymers. They have covalent cross-links that can be activated again by external factors like heat, light, changes in pH, or specific catalysts.³²

These dynamic networks maintain many benefits of traditional thermosets. They offer high mechanical strength, dimensional stability, and long-lasting durability. However, thanks to their reversible bonding structure, CANs also provide extra and valuable features, like recyclability, malleability, shape memory, and self-healing.

Their flexibility comes from the wide variety of chemistries that can be used for dynamic cross-linking. They also adapt well across different polymer systems and uses.

CANs are usually grouped into two main types based on how bond exchange happens: dissociative and associative.

In dissociative CANs, cross-linking bonds break before new bonds form, which temporarily lowers the cross-link density. A common example of a dissociative system is the reversible Diels–Alder reaction between maleimides and furans (**Figure 1.7**). When heated, this reaction becomes reversible, which speeds up bond breaking and reformation. As the temperature rises, the equilibrium shifts toward bond dissociation, allowing for dynamic rearrangement within the network structure. A similar dynamic is observed in systems based on alkoxyamine bonds, where heating promotes radical dissociation and shifts the equilibrium toward a more mobile, dissociated state, which then returns to its original configuration as the system cools (**Figure 1.7**).³³

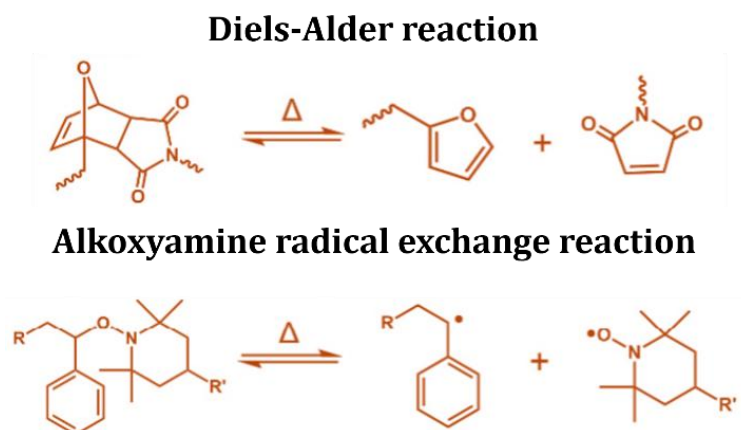


Figure 1.7 - Dissociative dynamic covalent bonds examples: Diels-Alder reaction and alkoxyamine radical exchange reaction

The discovery of vitrimers by Leibler *et al.* in 2011 marked a major turning point in the development of dynamic polymer materials.³⁴

Vitrimers are a subclass of CANs, in which covalent bond exchange occurs through an associative mechanism: when exposed to heat, bond exchange takes place only concurrently with, or as a consequence of, the formation of a new bond (**Figure 1.8**).³⁵ In the most extreme cases, vitrimers theoretically experience no bond breaking at all, yet they can still be reshaped and recycled through rapid interchain addition- and elimination-type exchanges.³⁶

This bond exchange strategy preserves the network's structural integrity, keeping the cross-link density essentially constant.^{37,38} Thanks to this mechanism, vitrimers are much more resistant to dissolution and plastic deformation than their dissociative counterparts.^{39,40} The name vitrimer reflects the material's viscous and temperature-dependent behaviour, exhibiting an Arrhenius-like dependence, similar to that of vitreous silica.

This gives them a special ability: they remain solid and strong at lower temperatures, but become malleable and reprocessable when heated, all without melting or losing their internal structure.

Since their introduction, researchers have developed many different types of vitrimeric materials, exploring various polymer backbones and dynamic bond exchange chemistries, such as transesterification, transamination, disulfide exchange, transcarbamylation, transacetylation, olefin metathesis, boronic ester exchange and many others.

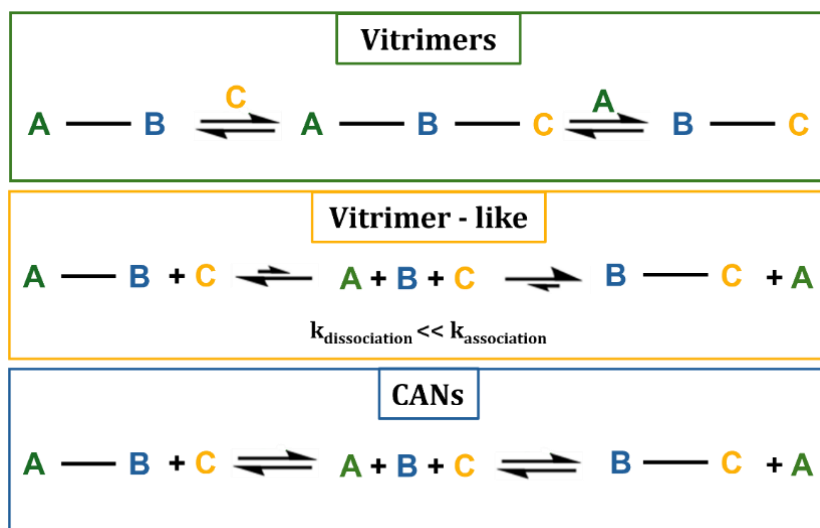


Figure 1.8 - Vitrimers and CANs dynamic mechanism

The ability to remake covalent bonds in polymer networks is at the basis of dynamic material design. Among the numerous mechanisms enabling this process, transesterification has been one of the most highly investigated (**Figure 1.9**).⁴¹

A classic example is the early work by *Leibler* of a polyester system end-functionalized with side-chain carboxylic acids. These reactive groups can respond with an epoxy-based cross-linker, producing hydroxyl functionalities and thereby creating a network that is capable of rearranging its structure over time. Above a certain temperature limit, this dynamic behavior was expressed, where the transesterification reactions were initiated and further catalyzed by zinc acetate as well.³²

Transesterification reaction

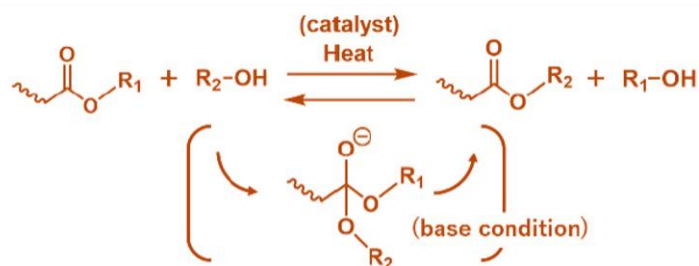


Figure 1.9 - Associative dynamic covalent bonds examples: transesterification reaction

More recently, the spotlight has shifted toward boronic esters, which have proven to be particularly promising in the context of vitrimeric materials thanks to their rapid exchange kinetics and chemical versatility (**Figure 1.10**). As described by *Gosecki* and colleagues, these compounds can undergo fast and reversible metathesis reactions, making them excellent candidates for designing adaptable and reprocessable polymer networks.⁴²

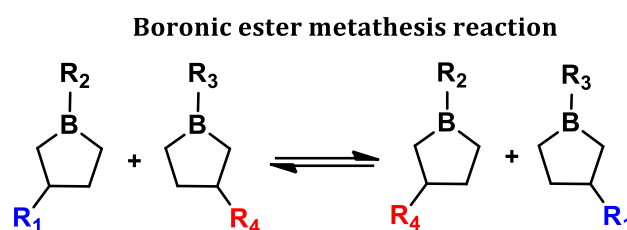


Figure 1.10 - Boronic ester methatesis reaction

The behavior of vitrimers depends on an Arrhenius-type relationship between temperature and viscosity. In addition to the usual glass transition temperature (T_g), vitrimers have a second important temperature known as the topology freezing transition temperature (T_v). Below this temperature, the dynamic bonds in the material are essentially "frozen," meaning the network structure stays locked in place and the material behaves like a flexible rubber within the T_g – T_v range. When the temperature rises above T_v , bond exchange reactions become fast enough to enable permanent network rearrangement, and the material shifts into a viscoelastic flow state with lower viscosity (**Figure 1.11**).⁴³

T_v can be experimentally determined through stress–strain relaxation tests, where a notable reduction in the imposed stress is observed over time under constant deformation.

By plotting the relaxation times vs the reciprocal of test temperatures, the Arrhenius-type behavior is observed from which the activation energy of the dynamic process is approximately estimated using the slope of the curve.

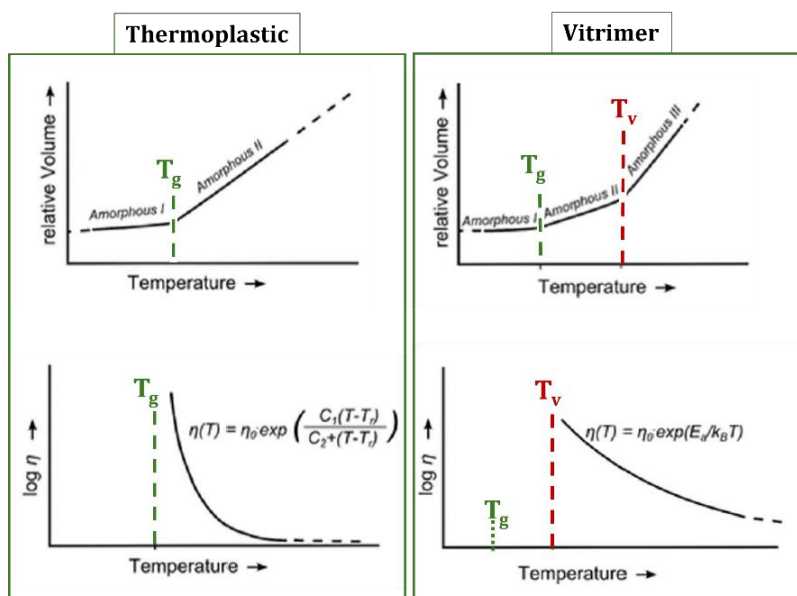


Figure 1.11 - Thermoplastics (left) and vitrimers' (right) dynamic behavior

1.5 Poly(Lactic) Acid

As reported before, a potential solution for recycling thermosetting materials at the end of their life could be the introduction of labile bonds within the polymer chain.²⁹

Aliphatic polyesters, such as polylactic acid (PLA), are considered sustainable alternatives.

PLA is particularly promising because its ester linkages are susceptible to hydrolysis, allowing it to break down naturally and biodegrade, making it an environmentally friendly option (**Figure 1.12**).^{44,45,46}

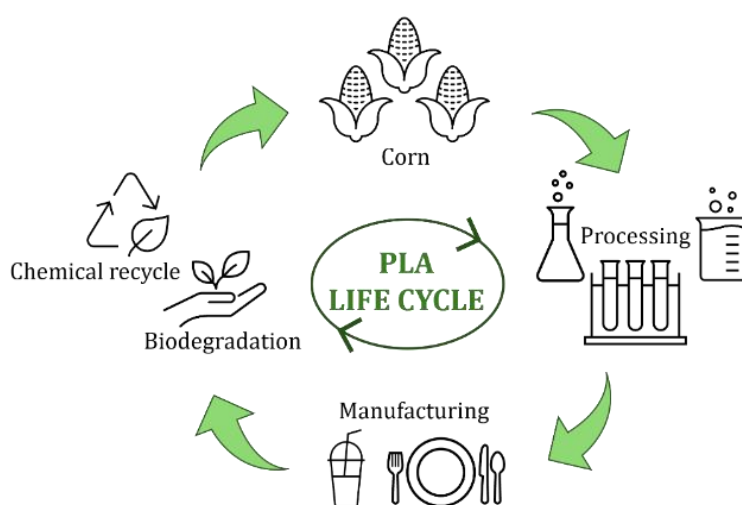


Figure 1.12 - PLA life cycle: from biobased resources to chemical recycle and biodegradation

Poly(lactic acid) (PLA) is a biodegradable plastic made from renewable resources like corn, sugarcane, or even waste biomass.⁴⁷

It's produced through two main methods: polycondensation of lactic acid or ring-opening polymerization (ROP) (preferred for industrial production) of lactide, a cyclic form of lactic acid.

The production begins with extracting starch from crops like corn, which is then converted into glucose through enzymatic or acidic hydrolysis. This glucose is fermented by bacteria or fungi to produce lactic acid, which is then purified, concentrated, and polymerized into PLA.⁴⁸

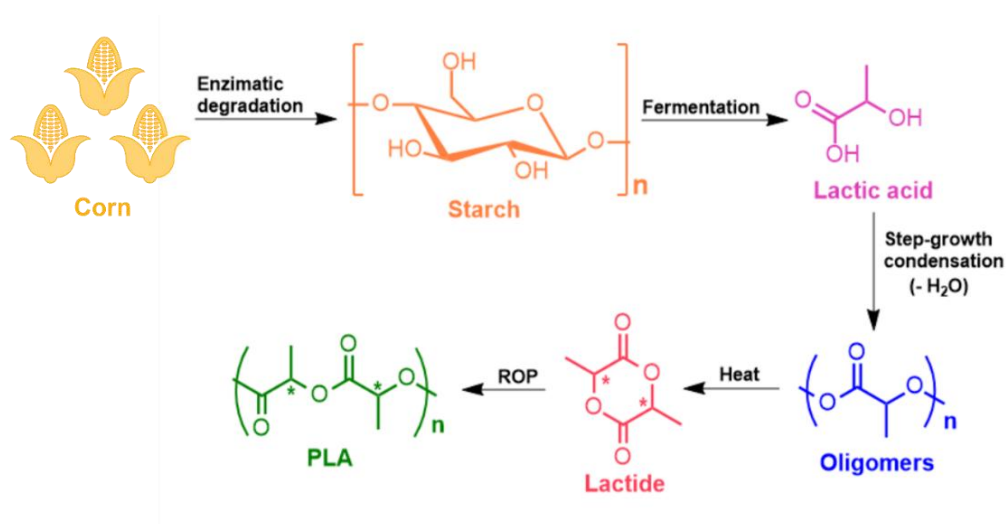


Figure 1.13 - PLA production from biomass

In reality, the monomer can be made through both biological and chemical methods, but the biological process (reported in **Figure 1.13**) using biomass is generally preferred in industry.

Most lactic acid used commercially comes from bacterial fermentation, which produces 99.5% L-isomer and just 0.5% D-isomer. On the other hand, the chemical method creates a racemic mixture.^{49,50}

Lactic acid has two asymmetric carbon atoms, which means it can form different types of lactide: D-lactide, L-lactide (either as pure enantiomers or in a racemic mixture), and meso-lactide (which is made through chemical processes like enolization of a PLLA monomeric unit or by thermal degradation of PLLA⁵¹) (**Figure 1.14**).

Due to the different stereochemistry of the starting monomer and the catalytic system used, it is possible to obtain polymers with varying microstructures⁵², which in turn results in products with different degrees of crystallinity and distinct chemical and physical properties. These variations can significantly impact the performance and applicability of the resulting polymers.

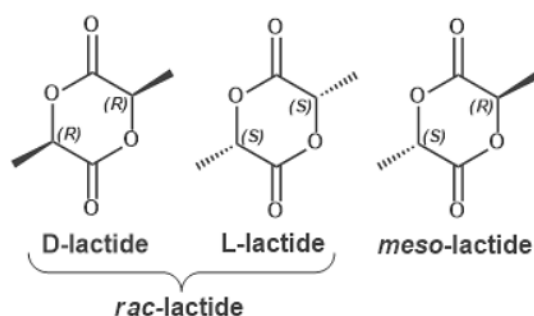


Figure 1.14 - Lactide isomers

In industrial settings, PLA is typically synthesized through the ROP reaction of L-LA using metal-based catalysts (**Figure 1.15**). One common catalyst used is Tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$), also known as stannous octoate.^{53,54}

This catalyst offers good control over the polymer chain length, resulting in PLA with a defined molecular weight. Alcohol is used as a co-catalyst to form the metal-alkoxide species, boosting the polymerization rate. $\text{Sn}(\text{Oct})_2$ is cost-effective and works well under tough conditions, such as temperatures above 180°C, without solvents, and with high monomer-to-catalyst ratios.

While $\text{Sn}(\text{Oct})_2$ may not exhibit enantioselectivity for rac-LA, it's still great for industrial processes using enantiopure monomers because it doesn't cause much racemization under harsh conditions.⁵⁵ Despite its toxicity, the majority of catalyst residues are effectively eliminated during processing, ensuring that the final product remains well below the 20 ppm limit considered safe by the Food and Drug Administration for food products.⁵⁶

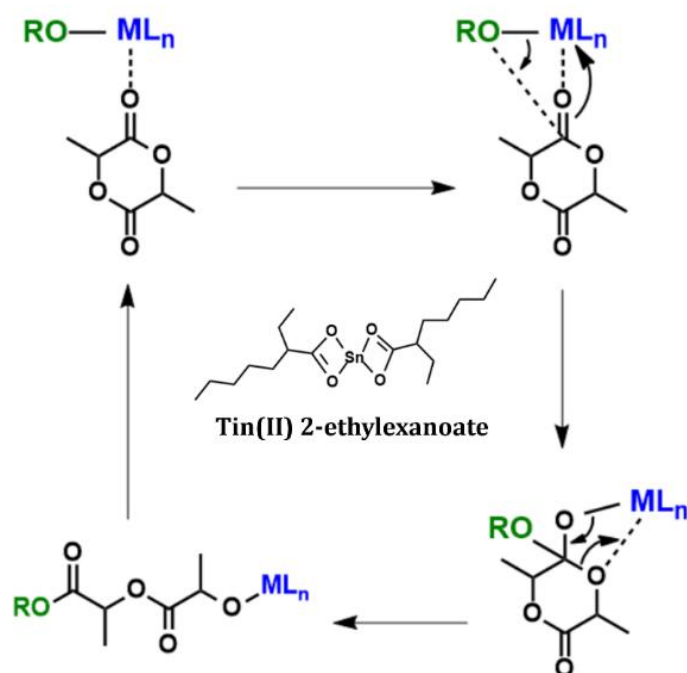


Figure 1.15 - ROP mechanism of LA catalyzed by $Sn(Oct)_2$

PLA is a widely used biodegradable plastic. By 2024, it is projected to represent approximately 37% of global production capacity, with annual output exceeding 300,000 tons.^{57,58}

Initially, its high cost and low molecular weight limited its use to medical and pharmaceutical applications, like internal sutures and drug delivery.

However, recent advances in production techniques have made PLA more cost-effective and allowed for stronger polymers with better control over their structure, expanding its use into other areas, especially packaging (due to its resistance to oils, fats, and its ability to block aromas and oxygen).

Additionally, it can be composted in industrial facilities.

With growing demand for sustainable materials, PLA is increasingly being used in industries like automotive and electronics, where there's a need for bio-based plastics that can perform similarly to traditional petroleum-based ones.⁵⁹

1.5.1 Branched PLA

As previously mentioned, PLA is the most widely used biopolymer on the market. Despite this, its mechanical properties limit its use in certain applications. With an elastic modulus ranging from 2.7 to 16 GPa and a tensile strength of 15.5 to 150 MPa, PLA is relatively strong, but its elongation at break is less than 10%⁶⁰, making it a brittle material with low impact resistance (2-6 kJ/m²).

To enhance the performance of PLA, additives like short carbon fibers (SCF) and glass fibers are incorporated, which significantly improve tensile strength, flexibility, and fracture toughness, while also offering better structural support.⁶¹

However, despite considerable research efforts, PLA continues to face challenges such as low melt strength, limited toughness, and an insufficient number of functional groups.

For PLA to function effectively as a matrix in composites, it is essential to further enhance these properties.

A promising approach to achieve these improvements is by introducing branching into the polymer's structure.

Branching can be done in several ways, leading to PLA with various structures, from star-shaped to long-chain-branched forms.

This adjustment improves PLA's rheological and mechanical properties, such as reducing viscosity and boosting strength.

By changing the molecular structure, PLA can take on shapes like star, comb, dendritic/hyperbranched, H-shaped, long-chain branched, or even dumbbell-shaped (**Figure 1.16**).⁶²

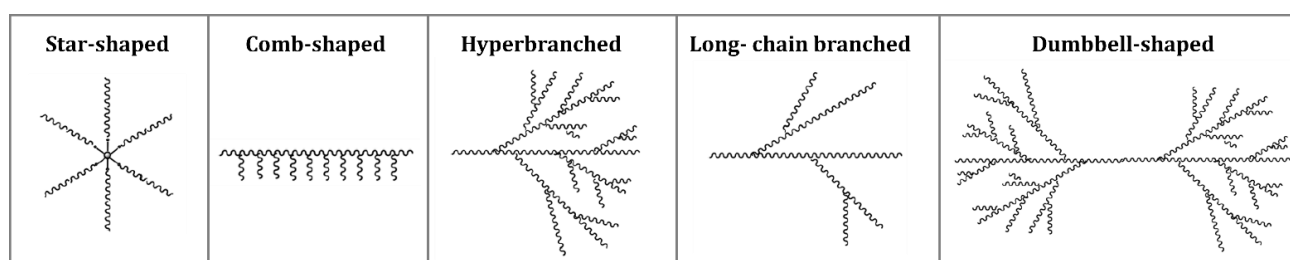


Figure 1.16 - Possible branched structures

Different polyol cores can be used to create star-shaped PLA, depending on the desired properties. Some examples are shown in **Figure 1.17**.

Flexible polyol cores, such as glycerol, pentaerythritol, di(trimethylolpropane), and xylitol, are often used to create three-, four-, or five-arm PLA stars. Pentaerythritol ethoxylate is another flexible core often used for creating four-arm PLA stars.

For PLA stars with a more rigid structure, cores such as tetrahydroxyperylene and hexakis[p-(hydroxymethyl)phenoxy]cyclotriphosphazene are used to form four- and six-arm stars. Typically, PLA stars with rigid cores tend to exhibit higher melting temperatures in comparison to those made with flexible cores.

There are three main ways to make star-shaped polymers:

- Core-first method → polymer chains are grown directly on a reactive core using living polymerization with a multi-functional initiator.
- Arm-first method → involves attaching linear polymer chains to a reactive core, either by using a multi-functional reagent or by taking advantage of the reactivity of telechelic polymers to bond the arms to the core.⁶³

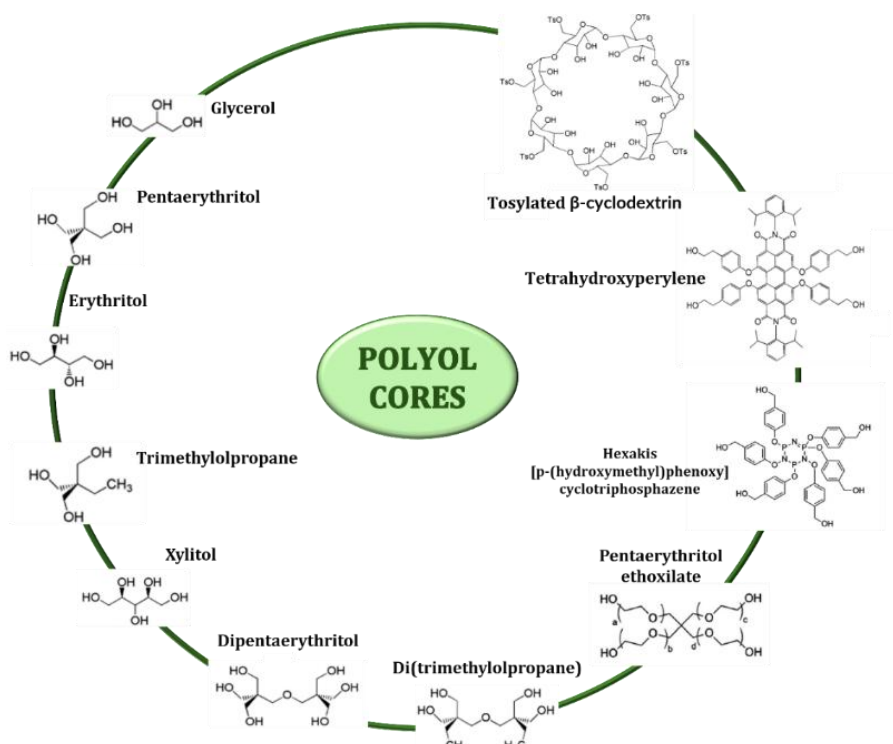


Figure 1.17 – Examples of polyol cores

Star-polymers offer several advantages over linear polymers of the same molecular weight. With a higher concentration of functional end groups, they are particularly effective when reacting with crosslinkers to form thermoset 3D networks. They also benefit from improved solubility and different hydrodynamic volumes, as well as lower melt viscosities and distinct thermal properties.

1.5.2 Cross-Linked PLA

To be effectively used as a matrix in composite materials, PLA needs to be cross-linked to improve the thermal stability and the tensile and impact strength.

In the literature, examples of chemical cross-linking of PLA through the reaction of the polymer chain with cross-linking agents, mainly based on isocyanates, are reported. These include triallyl isocyanurate, 2-methacryloyloxyethyl isocyanate (MOI), and methylenediphenyl diisocyanate (MDI).

Regarding the use of TAIC, the authors report that cross-linking occurs through dicumyl peroxide (DCP) initiation with a small amount of cross-linking agent (**Figure 1.18**). As a result, thermal and mechanical properties are improved. However, in this case, a highly cross-linked structure increases the material's brittleness.⁶⁴

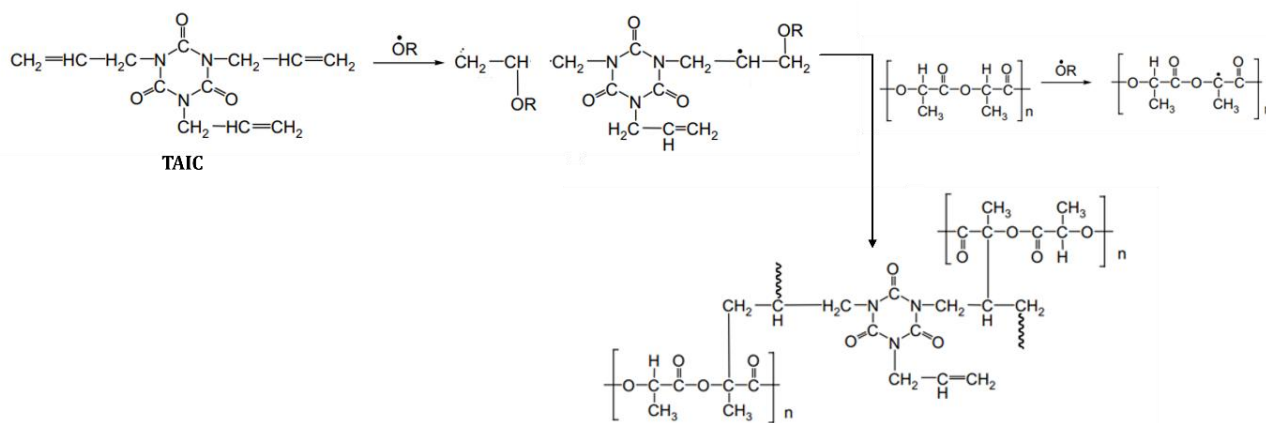


Figure 1.18 - Yang et al.

2-methacryloyloxyethyl isocyanate (MOI) was used by Chen et al. to enhance the physico-mechanical properties of PLA for biomedical applications (**Figure 1.19**). The result was the creation of a new, more ductile material with impact resistance twice as high as pure PLA,

achieved with just a 5% addition of isocyanate, without altering the inherent thermal properties of PLA.⁶⁵

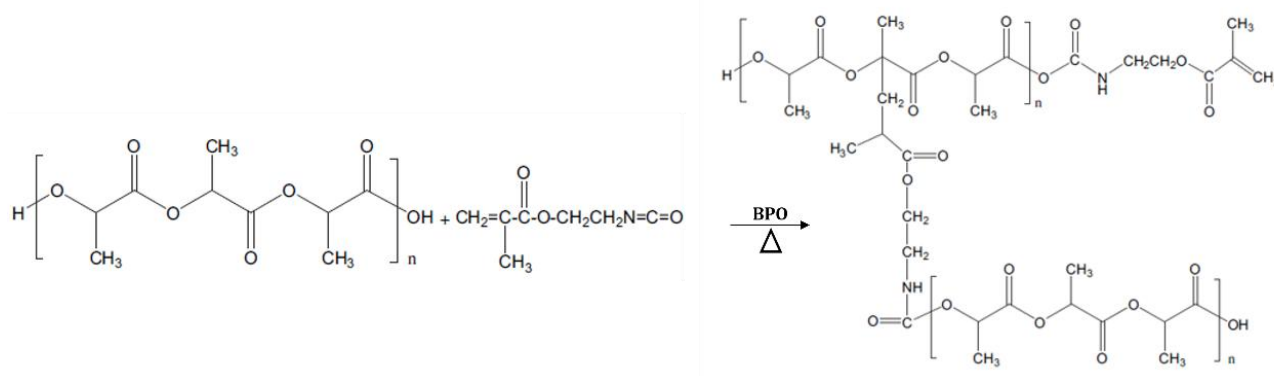


Figure 1.19 - Chen et al.

Recent studies focus on the synthesis of new cross-linked biopolymers with healing properties. In 2014, Hillmyer and colleagues reported the synthesis of PLA-based vitrimers, which can be easily processed, reprocessed, or healed after use or damage. They synthesized these "vitrimeric" polyurethanes from 4-arms-star-shaped oligomeric polylactide (PLA) with hydroxyl end groups, methylene diphenyl diisocyanate (MDI) (lacking OH groups), and tin(II) 2-ethylhexanoate (Sn(Oct)₂) as catalyst (**Figure 1.20**).⁸

The materials obtained exhibited very short relaxation times (50s at 140°C), as determined by stress-relaxation tests. When fractured, they could be effectively healed using compression molding, recovering up to 67% of their ultimate elongation, 133% of their tensile modulus, and 102% of their tensile strength values.

But, this behavior, initially attributed to easier transesterification reactions due to the high concentration of ester groups in the network, was later attributed by the same authors to the reversal reactions of the urethane groups.⁶⁶

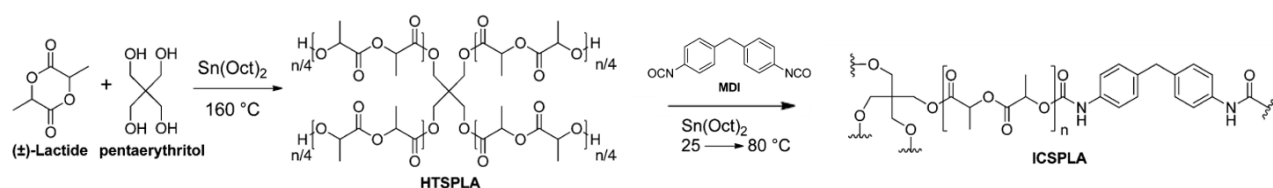


Figure 1.20 – Hillmyer *et al.*

The most common method for obtaining cross-linked PLA is the reaction between hydroxyl end groups and isocyanates. However, a major issue with using these substances is that isocyanates, along with their precursors, are toxic. They are produced through the reaction between an amine and phosgene, which is a highly dangerous poison. Phosgene is particularly insidious, as its odor may go unnoticed, and symptoms of poisoning can be slow to appear.⁶⁷

1.6 Non-Toxic Crosslinking Agents

Transesterification is a very promising way to add dynamic, adaptable behavior to polyester-based materials.⁶⁸ To help with this, we're looking at several bio-based molecules, like diethyl malonate, citric acid, erythritol bis-carbonate, and isosorbide diglycidyl ether, that can be used as crosslinking agents. These compounds are not only rich in reactive sites, which makes them great for building strong networks, but they're also sourced from renewable materials, making them perfect candidates for creating more sustainable thermosetting polymers.

1.6.1 Diethyl Malonate

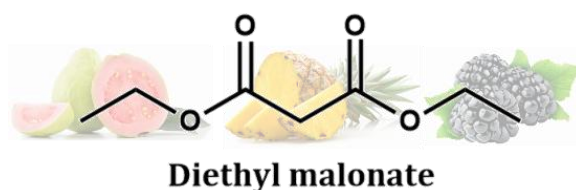


Figure 1.21 – DEM structure

Diethyl malonate (DEM) is an affordable β,β' -diester that occurs naturally in several fruit juices, including guava, pineapple, and blackberry (**Figure 1.21**). Its structure contains β -activated ester groups, which make it particularly reactive and useful in polyester synthesis, as already reported in the literature.^{69,70} More recently, Ojha *et al.* explored the potential of DEM in the development of vitrimers, using poly(hydroxyethyl methacrylate) (PHEMA) as the

hydroxyl-containing component.⁷¹ The materials they created showed promising mechanical properties, with tensile strengths between 11.3 and 33.0 MPa and elongations ranging from 80% to 290%, along with good resilience. Notably, these vitrimers could self-heal and be reprocessed with heat, without losing their mechanical integrity. These encouraging results suggest that DEM-based vitrimers could be a valuable, more sustainable option for applications such as coatings, hydrogels, biomaterials, adhesives, and everyday plastics.

1.6.2 Erythritol Bis-Carbonate

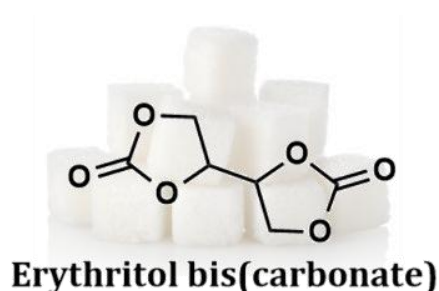


Figure 1.22 – EBC structure

Biscarbonates have been explored in the literature as crosslinking agents for a variety of polymers, including polylactic acid (PLA) and elastomers.⁷² For instance, compounds like spiro-bis-dimethylene carbonate have been used to create crosslinked PLA networks.⁷³ Among the molecules in this category, erythritol biscarbonate (EBC) stands out as a particularly interesting option. It's currently used as a monomer in the production of non-isocyanate polyurethanes (NIPUs), offering a safer and more sustainable alternative to traditional isocyanate-based systems. EBC is derived from erythritol, a sugar alcohol naturally found in fruits and vegetables, and can be synthesized in several ways. One of the most efficient and environmentally friendly methods, developed by Meier et al., uses dimethyl carbonate (DMC) both as a solvent and reagent, with 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst.⁷⁴ The reaction is highly selective, the product can be easily recovered by filtration, and the catalyst system can be reused up to eight times without losing activity. This makes the process not only practical but also economically and environmentally attractive.

1.6.3 Citric Acid

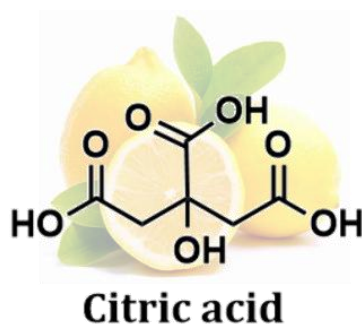


Figure 1.23 – CA structure

Citric acid ($C_6H_8O_7$) is a remarkably versatile organic acid, widely used in the food, pharmaceutical, and cosmetic industries as an acidulant, preservative, emulsifier, and buffering agent. Originally isolated from lemon juice in 1784, its large-scale production shifted in the early 20th century from citrus extraction to microbial fermentation using *Aspergillus niger*, a method still commonly used today, especially due to its efficiency and use of low-cost raw materials like molasses.⁷⁵ Thanks to its non-toxic, biodegradable, and renewable nature, citric acid has gained attention as a key building block in the bioeconomy. A notable example is a 2013 study by *Halpern et al.*, where citric acid and glycerol, two safe and inexpensive monomers, were used to create a degradable thermoset polymer through a simple, catalyst-free melt polymerization process.⁷⁶

1.6.4 Isosorbide Diglycidyl Ether

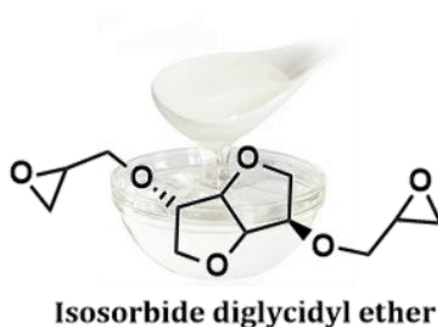


Figure 1.24 - DGEIs structure

Thanks to their strength, durability, and resistance to chemicals, epoxy resins are among the most commonly used materials in industries. Of the different epoxy precursors, diglycidyl

ether of bisphenol A (DGEBA) remains the most widely used monomer, accounting for about 75% of global epoxy resin production. However, it is derived from petroleum-based sources (BPA and epichlorohydrin) and raises health concerns due to BPA's endocrine-disrupting properties.⁷⁷ As industries shift toward safer and more sustainable materials, isosorbide has emerged as a promising alternative. It is a plant-based compound derived from glucose, recognized as safe by the Food and Drug Administration (FDA),⁷⁸ and valued for its rigid structure and non-toxic nature. One of the most exciting isosorbide-based epoxies is Isosorbide diglycidyl ether (DGEIs). It provides the same beneficial properties as traditional epoxies, such as strong bonding and chemical resistance, but with the added advantages of being renewable, non-toxic, and aligned with green chemistry principles.⁷⁹

1.7 Aim of the thesis

This research project aims to develop innovative thermosetting materials with a reduced environmental impact, while maintaining chemical and physical properties comparable to those of commercially available resins.

A key focus of the study is to rethink both the polymer matrix and the crosslinking agents, looking for sustainable alternatives that can reduce the environmental footprint of traditional thermosets.

Aliphatic polyesters have been identified as promising candidates due to their biodegradable nature, resulting from the presence of hydrolysable ester linkages, and their derivation from renewable biological sources.

To create biodegradable and cross-linkable thermosetting resins, the project involves the synthesis of branched PLA-based prepolymers, using multifunctional alcohols like glycerol, pentaerythritol and dipentaerythritol as initiators.

In addition, we have been exploring several bio-based molecules, such as diethyl malonate, erythritol bis-carbonate, citric acid, and diglycidyl isosorbide ester, as potential crosslinking agents.

A central goal of this work involves the development and optimization of a crosslinking protocol that can achieve an efficient, stable, yet reprocessable dynamic polymer network. We

plan to achieve this using transesterification reactions, a reliable and versatile method that can be carried out with commercially available monomers and catalysts.

In fact, among various cross-linking methods to prepare vitrimers, transesterification is one of the most studied and industrially feasible techniques.⁸⁰

This approach was first demonstrated by *Leibler* and colleagues, who showed that compounds containing epoxy and carboxylic acid groups can undergo associative dynamic bond exchanges, leading to materials with remarkable recyclability and self-healing capabilities.⁸¹

Our resulting materials will then undergo thorough chemical, physical, and mechanical characterization to better understand their properties and explore their potential applications in sustainable industrial sectors.

During the final year of my PhD, I had the opportunity to spend six months at *École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI Paris)*, where I worked on a different but complementary topic: vitrimeric systems based on high-density polyethylene (HDPE), compatibilized with biopolymers.

To achieve this, I formulated and tested several blends, using two different grafting agents, one already known in the literature (azidotriazine system ⁸²) and another, based on maleimide, that I developed as part of the project.

I processed these systems via reactive extrusion and analyzed them using a combination of mechanical (DMA, tensile testing) and thermal (DSC) techniques to evaluate the effect of compatibilization.

This approach not only valorizes waste plastics but can also enhance the mechanical properties of recycled polymers, contributing to a more circular and sustainable materials life cycle.

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CHAPTER 2

Results and Discussion

*Synthesis, Characterization and Cross-Linking
Reaction of Hydroxyl-Terminated Star-
Shaped Poly(L-Lactic Acid) Oligomers*

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Introduction

Star-shaped polymers are a versatile class of materials whose branched molecular architecture enables fine-tuning of their physical and chemical properties compared to their linear counterparts. Typical characteristics, such as viscosity, crystallinity, glass transition temperature (T_g), and degradation rate, can be varied by altering the number of arms, core functionality, and arm length.^{1,2}

From the materials design perspective, this offers a high density of terminal groups with reactive handles for further chemical modification, crosslinking, or functionalization with bioactive molecules. These terminal groups can participate in esterification, urethane, or carbonate-forming reactions, which enable the synthesis of tailored networks, vitrimers, or thermoset materials with tunable mechanical and dynamic properties.

In particular, in the case of branched PLA-based polymers, several advantages derive from using poly(L-lactic acid) synthesized from L-lactide, a renewable-resource-based cyclic diester obtained either from corn or sugarcane.^{3,4}

Moreover, due to ester linkage, PLA also offers the remarkable advantage of several end-of-life management options: it is biodegradable under specific composting conditions and chemically recyclable through depolymerization to its monomeric form.⁵⁻⁷

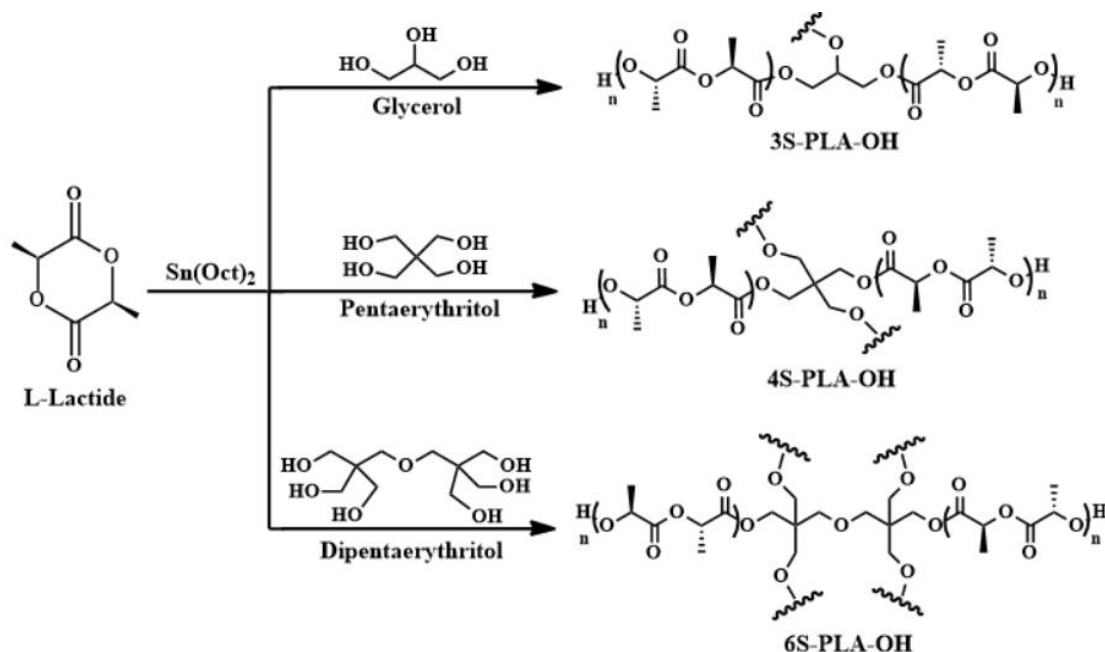
This property combination supports a sustainable and circular material lifecycle and makes PLA a platform for the design of branched, crosslinkable, next-generation biodegradable polymer systems.

In this chapter, hydroxy-terminated branched oligomers were synthesized through the ROP of L-LA initiated by multifunctional alcohols in both bulk and solution conditions. The resulting star-shaped poly(L-lactic acid) oligomers were characterized by a series of complementary analyses, which provided comprehensive information on their molecular weight distribution, average arm length, and branching efficiency.

Consequently, this work explores the crosslinking of PLA branched oligomers prepared under different conditions using three bio-based crosslinking agents: diethyl malonate (DEM), erythritol bis(carbonate) (EBC), and citric acid (CA). Each compound was chosen for its

renewable origin and peculiar chemical reactivity, giving a chance to evaluate different transesterification routes in the process of network formation.

2.1 Hydroxyl-Terminated 3-Arm, 4-Arm and 6-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers Synthesis



Scheme 2.1 - Branched PLA synthesis pathways: top, formation of 3S-PLA-OH; middle, 4S-PLA-OH; bottom, 6S-PLA-OH.

The hydroxy-terminated branched oligomers were synthesized using the core-first method in which polymer chains grow directly from a multifunctional alcohol initiator.⁸

Glycerol, pentaerythritol, and dipentaerythritol were used as the cores to produce three-arm (3S-PLA-OH), four-arm (4S-PLA-OH), and six-arm (6S-PLA-OH) oligomers, respectively (**Scheme 2.1**).

In each case, the polymer arms were kept relatively short, with an average length of about three lactide units, resulting in oligomers of similar overall size despite their different degrees of branching.

To optimize the synthetic procedure, the ring-opening polymerization (ROP) of L-lactide (L-LA) using pentaerythritol, a polyfunctional initiator, is considered, using a 12:1 monomer-to-initiator ratio and $\text{Sn}(\text{Oct})_2$ (0.004 eq) as catalyst.

The reaction was tested under two different sets of conditions: one designed to reflect industrial processes (solvent-free at 160 °C), and a milder alternative carried out in toluene at 100 °C. The bulk reaction proved to be significantly faster, reaching completion in just 4 hours, compared to the 24 hours required under solution conditions.

Since both approaches produced polymers with similar molar mass distributions, the bulk method was chosen for further work due to its clear advantages in speed and scalability.

It was subsequently used to synthesize 3S-PLA-OH, using a 9:1 monomer-to-initiator ratio, and 6S-PLA-OH, with an 18:1 monomer-to-initiator ratio.

2.2 Hydroxyl-Terminated 3-Arm, 4-Arm and 6-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers Characterization

The synthesized polymers were comprehensively characterized using a combination of nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) to understand the molecular structure and molecular weight distribution of the product materials (*Figure 2.14-2.19*).

The results demonstrated the successful synthesis of star-shaped PLA oligomers with 3-, 4-, and 6-arm architectures. The M_n were between ca. 1–3 kDa with an average arm length equivalent to about 3 lactide units for branch.

By analyzing the proton NMR spectrum and integrating the characteristic signals of the product, it is possible to estimate the average arm length of the polymer.

Specifically, for the 4S-PLA-OH oligomer, starting from the integration of the multiplet at 5.17 ppm, which corresponds to the methine protons of the oligomeric chain, the quartet at 4.35 ppm ($J = 6.91$ Hz) related to the terminal methine protons and the broad signal at 4.17 ppm attributed to the protons of the pentaerythritol initiator, it is possible to calculate an average arm length of about 3.2 lactic acid units per arm. This corresponds to an NMR-derived molecular weight of about 1975 Da, which is in reasonable agreement with the theoretical molecular weight calculated from the stoichiometric data (1864 Da) and with the value obtained by GPC analysis (2233 Da). These discrepancies in values could be attributed to experimental error and transesterification reactions occurring during bulk polymerization,

which is generally less controlled and prone to side reactions compared to solution polymerization.

The same type of analysis was carried out for 6S-PLA-OH and 3S-PLA-OH oligomers.

For the 6S-PLA-OH sample, the ^1H -NMR spectrum gives an average arm length of approximately 3.3 lactide units corresponding to an NMR-derived molecular weight of 2998 Da. It is in good agreement with the theoretical value derived from the stoichiometric feed (2592 Da) and also corresponds to the GPC-determined molecular weight (3178 Da).

In the case of 3S-PLA-OH, the calculated arm length is about 3.2 lactide units, giving an NMR molecular weight of 1522 Da, which compares reasonably well with the theoretical value of 1296 Da and the GPC value of 1763 Da.

The calculated, theoretical, and experimental molecular weights are summarised and compared in the table below (**Table 2.1**).

Oligomers^a	$M_{n\text{ theo}} \text{ (Da)}$	$M_{n\text{ NMR}} \text{ (Da)}$	$M_{n\text{ GPC}} \text{ (Da)}$	$\bar{D}$
3S-PLA-OH	1389	1522	1763	1.4
4S-PLA-OH	1864	1975	2233	1.3
6S-PLA-OH	2846	2998	3178	1.3

Table 2.1 - Oligomers' molecular mass calculated by stochiometric ratio ($M_{n\text{ theo}}$), by ^1H -NMR ($M_{n\text{ NMR}}$) and GPC ($M_{n\text{ GPC}}$) in THF. ^aOligomers synthesized by the ROP of L-LA: 3S-PLA-OH by using using a 9:1 monomer-to-initiator ratio, 4S-PLA-OH with a 12:1 monomer-to-initiator ratio, 6S-PLA-OH, with a 18:1 monomer-to-initiator ratio; 0.004 eq of $\text{Sn}(\text{Oct})_2$ 160 °C, 4h

2.3 Crosslinking Tests with Diethyl Malonate

In recent years, several studies have indicated the potential offered by vitrimers based on ester linkages, in particular β -activated esters, through their ability to be reprocessed thermally with similar structural and mechanical characteristics as thermoset materials.^{9,10}

In this context, *Ojha et al.* (2020) reported the synthesis of a series of β -activated ester vitrimers that were thermally reprocessable at 150 °C without any catalysts, while the relaxation temperature decreased to 110 °C after adding $\text{Sn}(\text{Oct})_2$.¹¹

The DEM precursor is an available low-cost ester molecule found in various fruit juices.

In their work, poly(hydroxyethyl methacrylate) (PHEMA) was used as the hydroxyl precursor for the synthesis of vitrimers and the materials obtained possessed good mechanical properties (tensile strength 11.3-33.0 MPa, elongation 80-290%) and excellent self-healing and reprocessability with no loss of mechanical properties.

Based on these findings, we hypothesize that the transesterification reaction of DEM can be used as an efficient cross-linking method for branched polymer systems. Specifically, DEM can serve as a bifunctional cross-linker to connect two branched prepolymer chains and create the three-dimensional network typical of dynamic thermosets.

Following Ojha's approach, which studied the transesterification of DEM with a primary alcohol (hexanol), our study focuses on the analysis of the reactivity of DEM with our systems, starting from the 4S-PLA-OH, to assess whether the reaction proceeds similarly and with comparable efficiency (**Scheme 2.2**). This research is a starting point for understanding the potential of DEM-based vitrimer chemistry in more complex and sustainable polymer systems.

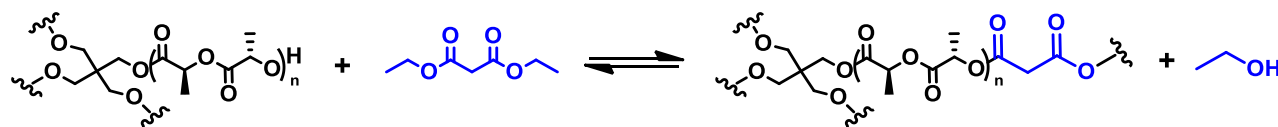
2.3.1 DEM and 4S-PLA-OH

The reactivity of DEM with 4S-PLA-OH was monitored by ^1H -NMR with a kinetic study in an NMR tube (**Figure 2.1**). Tetrakis(trimethylsilyl)silane (TMSS) was used as an internal standard, and the reaction progress was evaluated by comparing the relative integral of the singlet of the TMSS (around 0 ppm) with that of the DEM methyl triplet at 1.17 ppm ($J = 7.29$ MHz). Changes in the intensity or chemical shift of this triplet were expected, reflecting the formation and release of ethanol as a byproduct during the reaction.

DEM and 4S-PLA-OH were solubilized in TCDE and mixed in a 1:1 molar ratio [DEM]:[OH] in a vial. $\text{Sn}(\text{Oct})_2$ was added, as a catalyst, in an amount equivalent to 5 mol% relative to the diester. The mixture was transferred to an NMR tube with TMSS.

The reaction was monitored after 30 minutes at lower temperatures, such as 50 °C and 80 °C. Since no significant changes were observed in the NMR spectra, and considering that transesterification reactions typically occur at higher temperatures, the reaction was then examined after 20 and 40 minutes at 100 °C, after 20, 40, 60, and 80 minutes at 120 °C, and after 20 and 80 minutes at 130 °C.

Unfortunately, even under these conditions, the reaction did not proceed as expected. The relative ratio of the DEM signal to the TMSS reference was still high, around 98%, indicating no or a very minimal conversion. The mixture was therefore left to react overnight at 130 °C; however, no noticeable changes were detected, confirming that the reaction did not progress.



Scheme 2.2 - 4S-PLA-OH and DEM, general reaction scheme

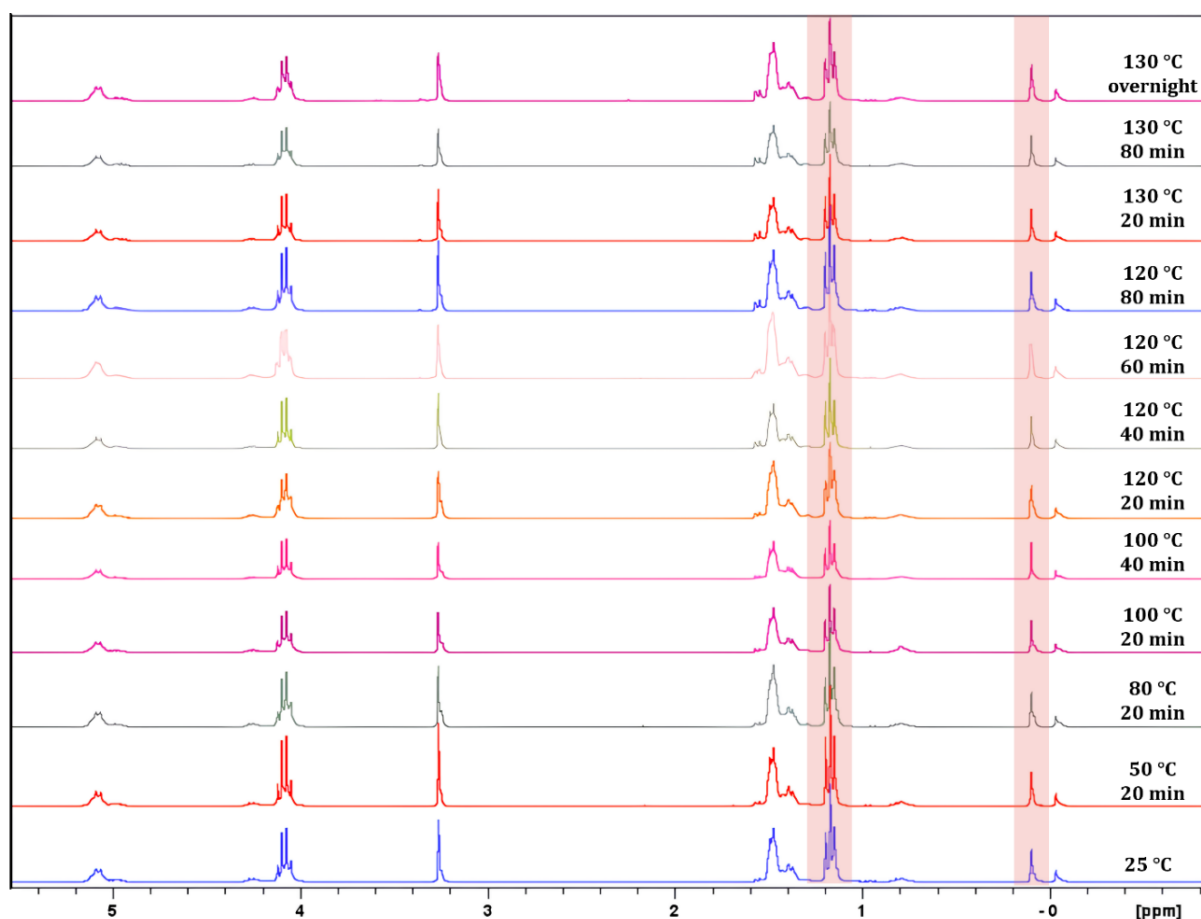


Figure 2.1 - ^1H -NMR kinetic experiment at different temperatures and times with standard, 300 MHz, TCDE, 298 K, 5 mol% of $\text{Sn}(\text{Oct})_2$ relative to the diester as catalyst. Highlighted the singlet of the TMSS (around 0 ppm) and that of the DEM methyl triplet at 1.17 ppm ($J = 7.29$ MHz)

The same kinetic experiment was carried out using a different catalyst. In this test, an organic nucleophilic catalyst, 4-(dimethylamino)pyridine (DMAP), was used while maintaining the same molar ratios, reaction times, and temperatures as applied in the previous experiments.

To further promote the transesterification process, the reaction temperature was increased to 145 °C, and the reaction mixture was monitored for up to 140 minutes.

Figure 2.2 below shows the ^1H -NMR spectrum of the sample at 140 minutes and at time 0. Once more, no striking differences were found between the relative integration ratio of the TMSS singlet and the DEM methyl triplet. This indicates that even in the presence of DMAP, no detectable conversion or product formation occurred under the tested conditions.

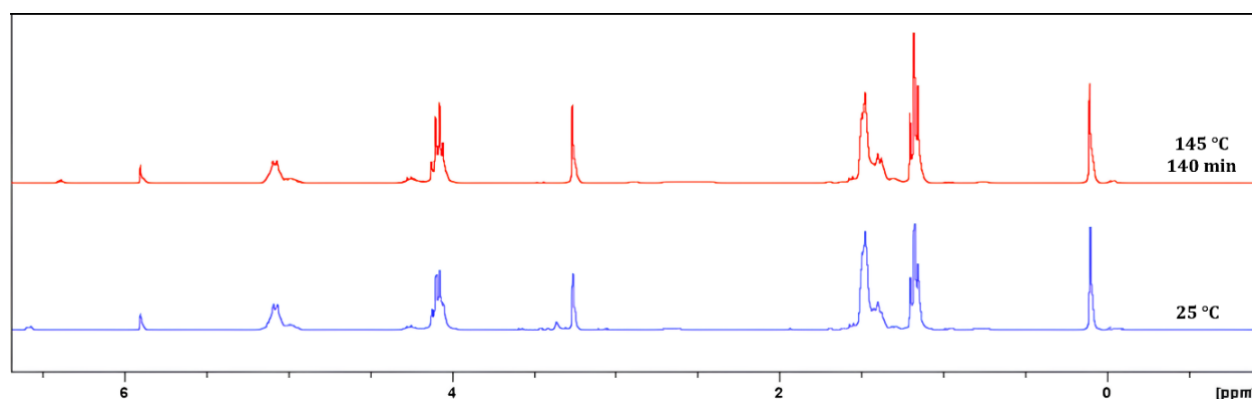


Figure 2.2 - ^1H -NMR kinetic experiment with standard, 300 MHz, TCDE, 5 mol% of DMAP relative to the diester as catalyst. ^1H -NMR at the starting time in blue and at the end in red)

A one-pot reaction striving to accomplish both the ROP of L-LA and its crosslinking in a single synthetic step was investigated.

All reagents were charged into a 50 mL round-bottom flask in an L-LA: pentaerythritol molar ratio of 12: 1, an L-LA: $\text{Sn}(\text{Oct})_2$ ratio of 100: 1, and a pentaerythritol: DEM ratio of 1: 4. A few drops of toluene were added to homogenize the mixture. Reaction was carried out for 6 hours at 130 °C.

The reaction yielded two fractions: one soluble and one insoluble in chloroform. The two phases were separated by centrifugation and analyzed by ^1H -NMR spectroscopy.

The spectra showed that the insoluble fraction was pure pentaerythritol and the soluble fraction was the star-shaped polymer obtained from the ROP of L-LA initiated by $\text{Sn}(\text{Oct})_2$, with the unreacted DEM (**Figure 2.3**).

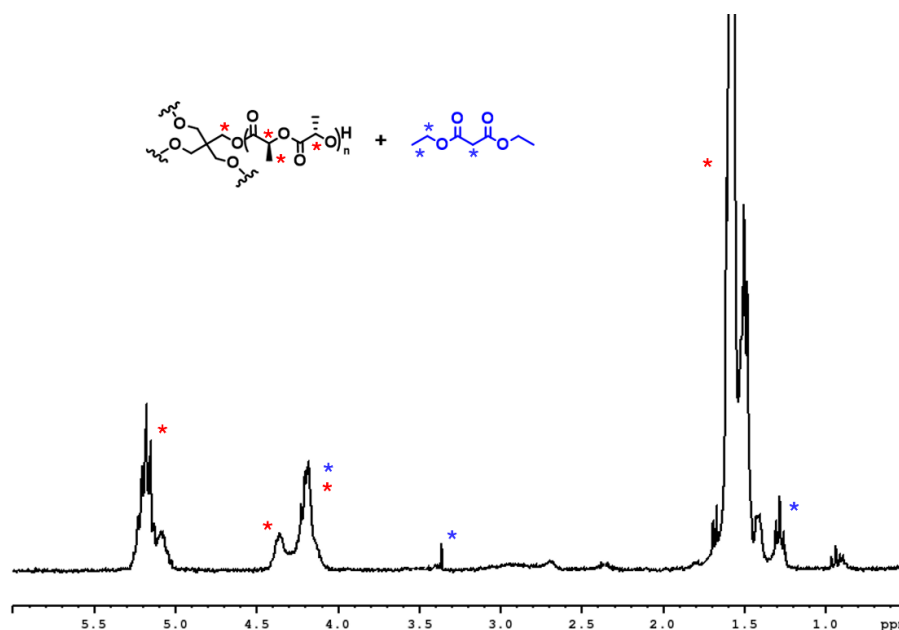


Figure 2.3 - One-pot polymerization-crosslinking test, $[\text{L-LA}]: [\text{pety}] = 12:1$, $[\text{L-LA}]: [\text{Sn}(\text{Oct})_2] = 100:1$, and $[\text{pety}]: [\text{DEM}] = 1:4$. ^1H -NMR spectra of soluble fraction with signal assignment (300 MHz, CDCl_3 , 298 K)

2.3.2 DEM and other systems

To determine whether the low reactivity observed was due to steric hindrance from the branched structure, a linear polymer was synthesized using ethylene glycol as an initiator.

The polymerization was carried out under solvent-free conditions, with a molar ratio of L-LA: ethylene glycol: $\text{Sn}(\text{Oct})_2 = 20: 1: 0.005$, at 160 °C for 4 hours.

This approach was designed to minimize steric effects and see whether the absence of branching could permit subsequent transesterification or end-group exchange reactions.

The resulting polymer was then analyzed by ^1H -NMR to confirm the formation of the linear PLA chain and the absence of side reactions (**Figure 2.4**)

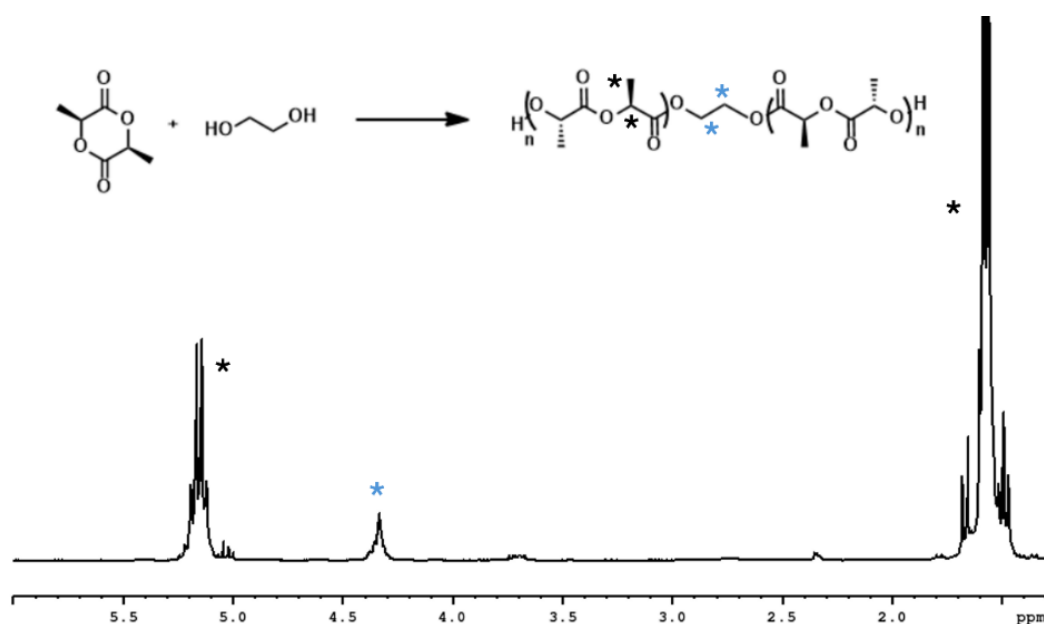


Figure 2.4 -Synthesis of linear di-hydroxy-terminated PLA, L-LA: ethylene glycol: $\text{Sn}(\text{Oct})_2 = 20: 1: 0.005$, at 160°C for 4 h. ^1H -NMR spectra (300 MHz, CDCl_3 , 298 K)

Using DEM in a 1:1 molar ratio with the hydroxyl end groups of the linear polymer and adding 5 mol% $\text{Sn}(\text{Oct})_2$ relative to DEM, the reaction was carried out at 110°C for 24 hours.

Under such conditions, no recognizable changes were observed in the ^1H -NMR spectrum, indicating no transesterification or ester exchange reactions.

Even after 56 hours of reaction, NMR signals for DEM remained unaffected, and no evidence of the formation of ethanol, as a side product expected, was detected.

These results align with the observation that the reaction does not proceed under the conditions explored, showing that greater activation energy or a different catalytic system may be required to enable the desired conversion (**Figure 2.5**).

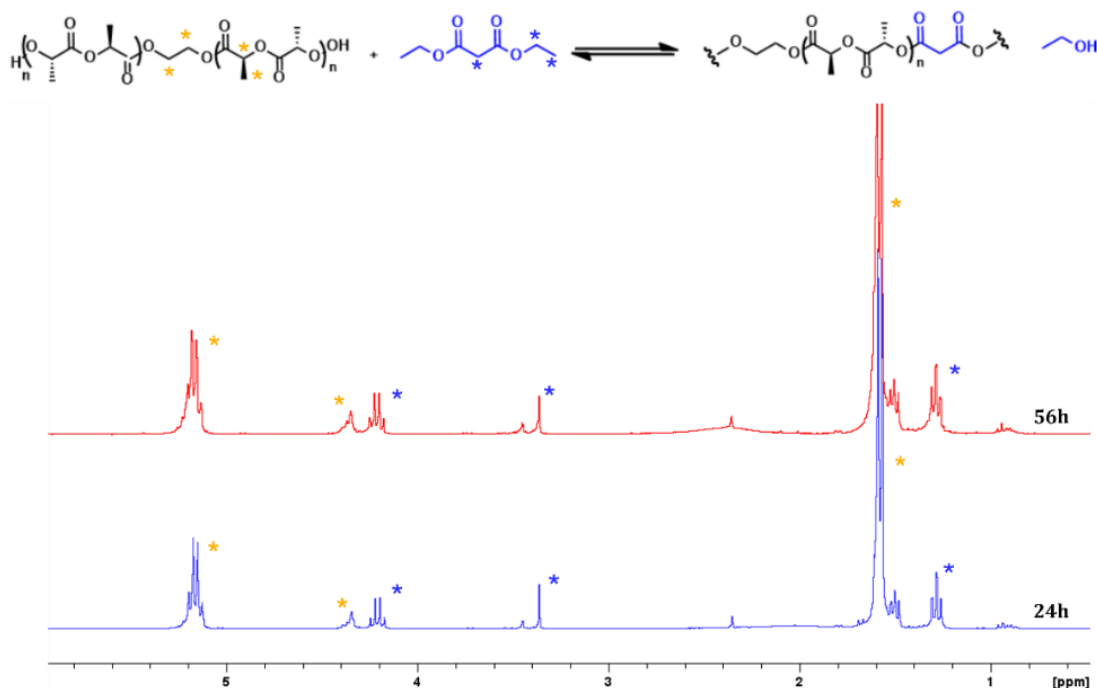


Figure 2.5 – ^1H -NMR (300 MHz, CDCl_3) of a crosslinking test between $[\text{DEM}]:[\text{hydroxyl end groups}] = 1:1$, 5 mol% $\text{Sn}(\text{Oct})_2$ relative to DEM, in blue after 24h and in red after 56h at 110 °C.

Following the system mentioned above, a further comb-like branched polymer system, called EB27, was investigated, which contained a higher molecular weight of approximately 59 kDa. The system was previously synthesized by our research group starting from L-lactide (1000 eq) and polyglycerol-10 (23 eq) and $\text{Sn}(\text{Oct})_2$ (1 eq) as a catalyst (**Figure 2.6**).

Based on the experimental data, this polymer's molecular structure can be described as consisting of a main chain with a molecular mass of about 10 kDa, bearing ten side chains, each with an average molecular mass of approximately 5 kDa.

This system was studied to assess whether variations in chain linearity, branch length, concentration of OH terminal functionalities, and consequently in molecular weight could lead to changes in reactivity.

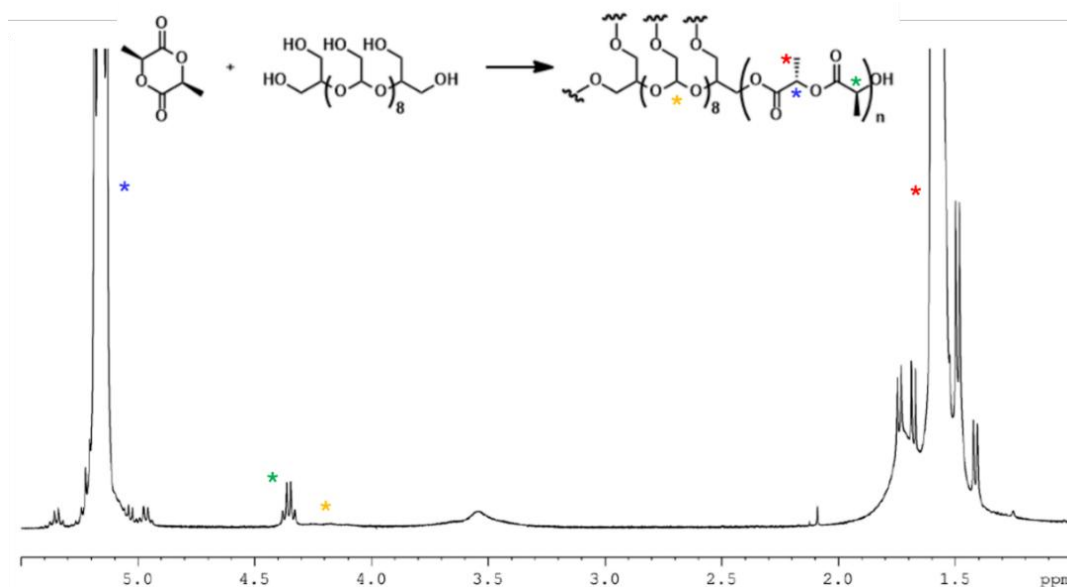


Figure 2.6 - Synthesis of EB27, L-lactide (1000 eq) and polyglycerol-10 (23 eq) and $\text{Sn}(\text{Oct})_2$ (1 eq)

In this case, several experiments were conducted:

- *Entry 1*: an equimolar ratio of DEM to hydroxyl functionalities was employed, and 5 mol% of $\text{Sn}(\text{Oct})_2$ with respect to DEM. The reaction was carried out at 145 °C for 24 hours in a closed vial under nitrogen atmosphere, under conditions essentially identical to those already described. Only a very minimal amount of anhydrous dichloromethane was added to obtain a more homogeneous reaction mixture.
- *Entry 2*: the ratio of DEM to hydroxyl functionalities was increased to 10:1, and 10 mol% of $\text{Sn}(\text{Oct})_2$ with respect to DEM. These increased ratios were employed to maximize the transesterification reaction as much as possible. The reaction was again conducted at 145 °C for 24 hours, in a vial under a nitrogen flow, using the minimum amount of dry dichloromethane to maximize reaction homogeneity.
- *Entry 3*: maintained the same stoichiometric ratios (DEM:OH = 10:1, $\text{Sn}(\text{Oct})_2$ = 10 mol% relative to DEM), but lowered the temperature to 110 °C, to study the influence of milder thermal conditions on the extent of the transesterification. The reaction setup and solvent usage were identical to those in the preceding cases.
- In the final experiment, *Entry 4*, the reaction was again performed at 110 °C with an excess of DEM (DEM:OH = 10:1) and 5 mol% of $\text{Sn}(\text{Oct})_2$ (relative to DEM), this time in a 25 mL round-bottom flask equipped with a reflux condenser and a thermometer at the top of the condenser. This setup allowed monitoring of the temperature of the

vapor to identify the nature of the evaporating substances (ethanol or DEM). The reaction was kept at 110 °C for 24 hours, without solvent, under an inert atmosphere with periodic monitoring. No change was observed during the reaction, and no gas was evolved.

Unfortunately, in the first two experiments, the high temperature and the nitrogen flow led to the loss of DEM. Although this compound has a relatively high boiling point, under these conditions, its removal from the system appears to be favored.

Upon decreasing the temperature to 110 °C and in a closed system, no variations were observed in the ^1H -NMR spectra, which showed the same signals as those of the polymer and DEM.

This finding attests that there was no crosslinking or transesterification for any of the conditions investigated.

The comparison of the ^1H -NMR spectra from the four tests clearly shows the absence of DEM in tests *Entry 1* and 2, while spectra from *Entry 3* and 4 reveal the lack of any reaction between the polymer and DEM (**Figure 2.7**).

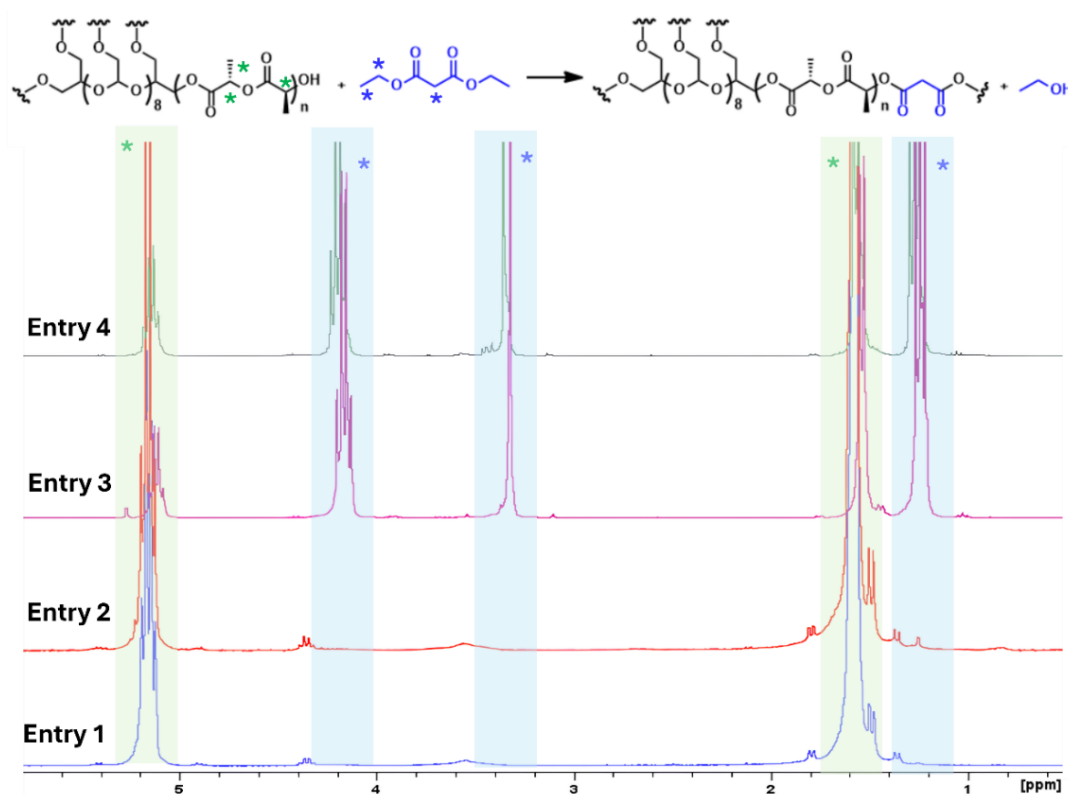
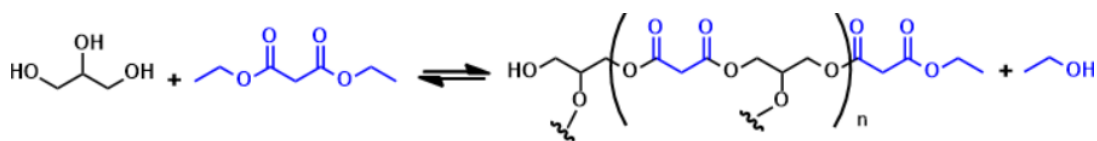


Figure 2.7 - Comparison of the ^1H -NMR spectra (300 MHz, CDCl_3 , 298 K) from the four tests

2.3.2 DEM and Glycerol

**Scheme 2.3** - General reaction between glycerol and DEM

Entry	[OH]:[DEM]	Catalyst	Temperature (°C)	Time (h)
5	1:1	/	150	3
6 ^a	1:1	/	150	3
7	1:1	Ti(OiPr) ₂ (5 mol%)	100	6
8	1:1	Sn(Oct) ₂ (5 mol%)	100	72
9	2:1	Sn(Oct) ₂ (5 mol%)	100	8
10	2:1	Sn(Oct) ₂ (5 mol%)	130	9
11	3:1	DBU (5 mol%)	100	12
12	3:1	ZnCl ₂ /p-TSA (1 mol%)	130	16

Table 2.2 – Glycerol and DEM test in different ratios, temperature, and time conditions, with the use of both inorganic and organic catalysts, ^a in methanol solution

A final series of experiments, reported in **Table 2.2**, was conducted using a structurally simple yet slightly more complex substrate relative to 1-hexanol reported earlier by Ojha et al. Herein, glycerol was selected as the model compound, a triol comprising two primary and one secondary hydroxyl functionality (**Scheme 2.3**).

The first attempt was made to reproduce the conditions already utilized with 1-hexanol to verify whether a similar reactivity trend could be observed. The reaction, therefore, was carried out using an equimolar ratio between hydroxyl functionalities and diethyl malonate (DEM), under standard conditions of 150 °C for 3 hours (*Entry 5*). After completion, the crude mixture was analyzed by ¹H-NMR spectroscopy. Unfortunately, no detectable changes were observed in the chemical shifts, and the spectra showed well-resolved and distinct signals related to the two unreacted starting materials, confirming the absence of any conversion.

A second experiment involved the addition of a minimum quantity of anhydrous methanol to improve the miscibility and homogeneity of the reaction mixture. Again, the reaction had to

be performed under the same conditions in terms of temperature and time; however, the subsequent NMR analysis showed no major differences, hence proving once more that the system was completely inert under such conditions (*Entry 6*).

In an attempt to promote the transesterification process, several catalytic systems were tried to favor the transesterification process. Thus, at first, titanium isopropoxide $[\text{Ti}(\text{OiPr})_4]$ was tested at 5 mol% loading with respect to DEM, at 100 °C (to minimize the evaporation of DEM) for a longer reaction time (*Entry 7*); then, at the same molar loading, $\text{Sn}(\text{Oct})_2$ was tried.

Reactions were carried out under different stoichiometric and thermal conditions: $[\text{OH}]:[\text{DEM}]=1:1$ at 100 °C for 72 h (*Entry 8*), monitored by NMR; $[\text{OH}]:[\text{DEM}]=2:1$ at 100 °C for 8 h (*Entry 9*) or at 130 °C for 9 h (*Entry 10*).

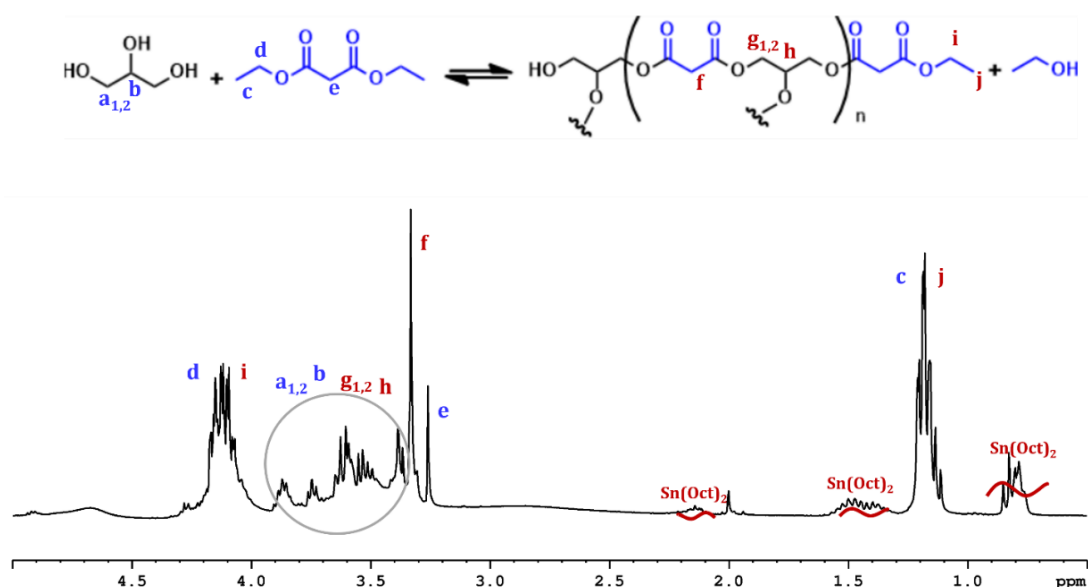


Figure 2.8 - ^1H -NMR spectrum (300 MHz, CDCl_3 , 298 K) of glycerol and DEM reaction of *Entry 10*, $[\text{OH}]:[\text{DEM}]=1:1$, $\text{Sn}(\text{Oct})_2$ (5 mol%) after 9 hours at 130 °C

In this case, by analyzing more in detail *Entry 9* and *10* at ^1H -NMR, clear variations in several signals suggest that the two species did react with each other, although the reaction did not reach full conversion (**Figure 2.8**).

In particular, comparing the spectra recorded at the initial check of *Entry 8* (reaction at 100 °C for 4 hours) with those collected at the final check of *Entry 9* (after 9 hours at 130 °C), and referencing them against the spectra of the pure reagents, noticeable differences appeared in the multiplicity of DEM signals at 4.22 and 1.28 ppm (**Figure 2.9**).

These signals, originally appearing as a quartet (4.22 ppm, $J = 7.0$ MHz) and a triplet (1.28 ppm, $J = 7.2$ MHz), evolve into multiplets, consistent with the formation of new chemical environments. The singlet at 3.35 ppm, corresponding to the CH_2 group of DEM, also shifts slightly to 3.42 ppm. By integrating these singlets, it is possible to estimate the amount of DEM, used as the limiting reagent, that has reacted after 9 hours at 130 °C, which is roughly 70%.

Assigning the signals related to glycerol proved considerably more challenging. This difficulty, probably, arises from the formation of an ill-defined mixture of products, which leads to extensive signal overlap and prevents reliable proton assignment.

Several attempts were made to separate the reaction products using different eluent systems, including chloroform and mixtures such as hexane: ethyl acetate (8:2 and 1:1) and hexane: acetone (1:1). However, none of these approaches proved effective. The various species in the mixture appeared to have very similar polarities and behaved almost identically on the stationary phase, making it impossible to achieve a clean separation under the conditions tested.

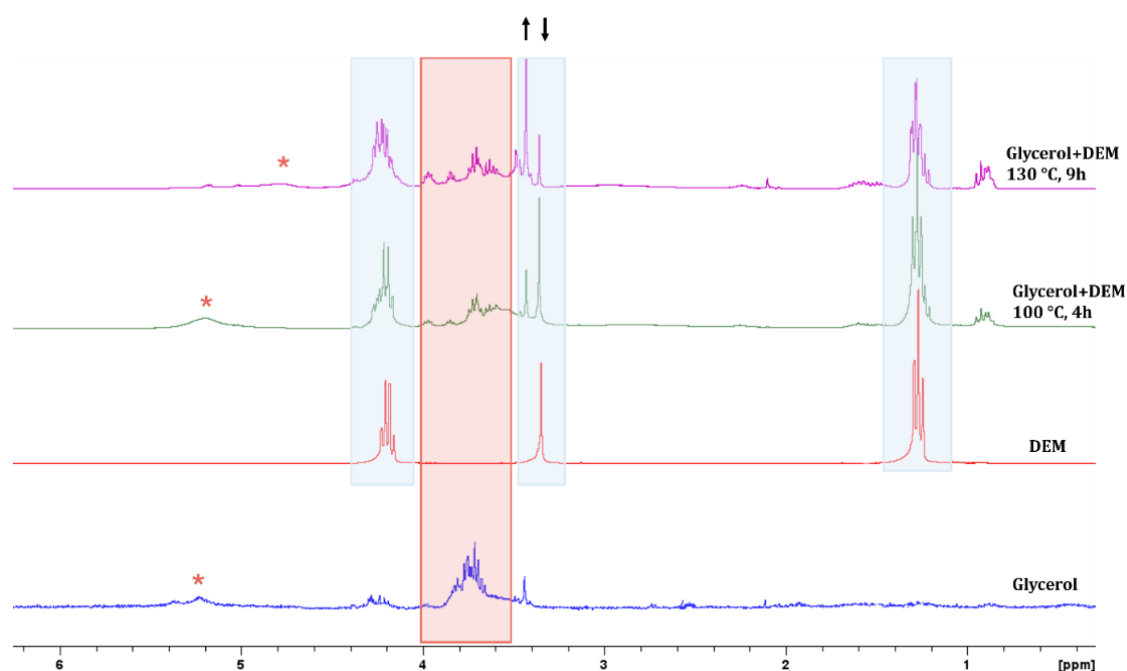


Figure 2.9 – Comparison of ^1H -NMR spectra (300 MHz, CDCl_3 , 298 K) recorded at the initial check of Entry 8 (green) with those collected at the final check of Entry 9 (purple), and referencing them against the spectra of the pure reagents (blue and red)

Other catalytic attempts were performed with zinc chloride (ZnCl_2) associated with p-toluenesulfonic acid (p-TSA) as a co-catalyst, both added at 1 mol% with respect to DEM. The

reaction was kept with a ratio OH:DEM=3:1 and it was performed at 130 °C for 16 hours (*Entry 12*).

At the end, an organic base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), was tested at 5 mol% with respect to DEM, and the reaction was conducted at 100 °C for 12 hours (*Entry 11*), with a ratio OH:DEM=3:1.

Despite these extensive investigations, none of the tested catalytic systems resulted in the appreciable formation of the desired transesterification product. All samples remained completely soluble, while ¹H-NMR analyses invariably confirmed the presence of only unreacted starting materials. These findings, therefore, suggest that, under the conditions examined, the transesterification reaction occurred only to a negligible degree.

2.4 Crosslinking Tests with Erythritol Bis-Carbonate

In the last several years, renewable polyol-based cyclic carbonates have attracted increasing interest as sustainable and multifunctional building blocks in polymer and materials chemistry.

They can find application as reactive crosslinkers, monomers, or functional intermediates for the synthesis of biodegradable polyesters and non-isocyanate polyurethanes (NIPUs), as an environmentally friendly and sustainable alternative to traditional phosgene- or isocyanate-based systems.^{12,13}

They have high functionality and chemical reactivity, enabling the introduction of carbonate bonds under relatively mild reaction conditions, and their bio-based character falls within the context of green chemistry and circular materials design.

Other than their well-known reactivity with amines for NIPU synthesis, cyclic carbonates can also be ring-opened by polyols or hydroxyl-terminated polyesters to give transesterification or transcarboxylation, depending on the catalyst system and reaction conditions.

In the reaction between a cyclic carbonate such as erythritol bis(carbonate) (EBC) and a hydroxyl-terminated polyester such as 4S-PLA-OH, the hydroxyl end groups of the polymer can attack the electrophilic carbonyl carbon in the carbonate ring. The nucleophilic attack

promotes ring opening and the formation of new ester linkages via a transesterification process.

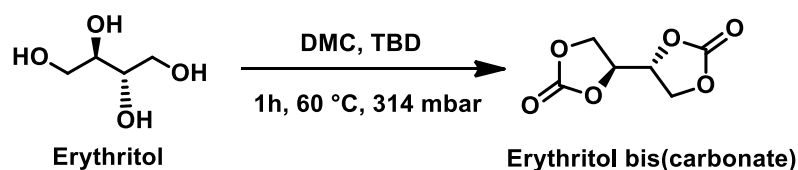
For the case of PLA and other aliphatic polyesters, this transesterification (often initiated by $\text{Sn}(\text{Oct})_2$, ZnCl_2 , or p-TSA) may result in chain-extended or branched morphology, and, when a multifunctional carbonate like EBC is utilized, possibly to the creation of a crosslinked polymer network.

2.4.1 Erythritol Bis-Carbonate Synthesis and Characterization

For the synthesis of erythritol bis-carbonate, we followed the procedure established by *Meier et al.*, in which a more environmentally friendly approach was used.¹⁴

The process has several advantages in terms of solvent choice, carbonyl source, reaction temperature, reaction time, lower pressure, simplified workup, and recycling of the reagent. In this reaction, dimethyl carbonate (DMC) serves as both a carbonylating agent and solvent, while 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is a good catalyst that improves the selective production of the desired cyclic carbonate (**Scheme 2.4**).

In our case, 1.0 eq of erythritol and 0.05 eq of TBD were dispersed in DMC (20.5 mL) in a 100 mL round-bottom flask and heated to 60 °C under reduced pressure (314 mbar) using a rotary evaporator for 1 hour. During the reaction, erythritol fully dissolved within approximately 30 minutes, and a white precipitate formed after about 35 minutes. The product, recovered by filtration, is a white powder in 80% yield.



Scheme 2.4 - Erythritol bis-carbonate reaction synthesis scheme

From the ^1H -NMR spectrum, the successful formation of the product can be confirmed, showing signals consistent with those reported in the literature (**Figure 2.10**). The multiplet at 5.25 ppm corresponds to the two protons on the carbon connecting the two cyclic carbonate

groups, while the multiplets at 4.69 and 4.47 ppm are attributed to the diastereotopic protons of the CH₂ groups.

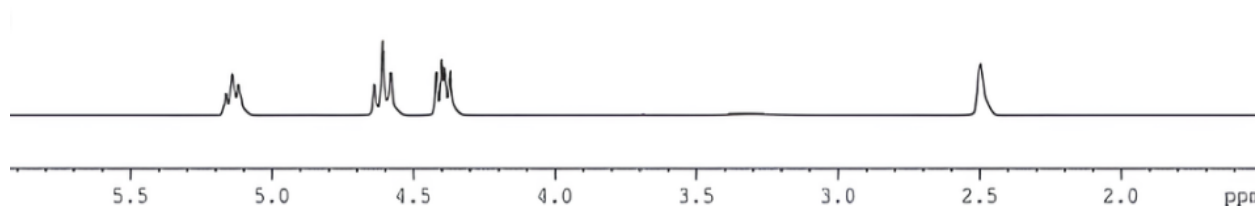
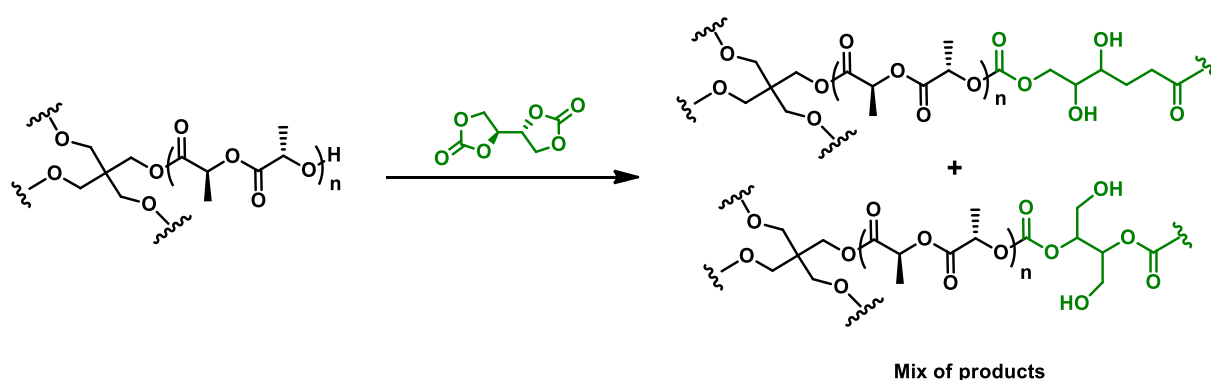


Figure 2.10 – ¹H-NMR of erythritol bis-carbonate (300 MHz, DMSO, 298 K)

2.4.2 Crosslinking Reaction

In the crosslinking reaction between the 4S-PLA-OH star-shaped prepolymer and EBC, the terminal hydroxyl groups of the prepolymer react with the carbonate rings of EBC, leading to ring opening and the formation of new ester linkages. Since the carbonate ring can open through two different pathways and the crosslinker contains stereogenic centers, a mixture of crosslinked structures is formed (**Scheme 2.5**). These structures vary in both the chemical nature of the junctions and the local stereochemistry at the connection sites between the polymer chains.



Scheme 2.5 - General scheme of crosslinking reaction between EBC and 4S-PLA-OH

Crosslinking tests using EBC as a crosslinking agent were carried out at a 1:1 molar ratio between EBC and –OH groups, to ensure an excess of carbonate functionalities and thus

increase the extent of reaction, with $\text{Sn}(\text{Oct})_2$ used as a transesterification catalyst at 5 mol% relative to EBC.

The reaction was carried out in a vial containing 100 mg prepolymer, which was immersed in a preheated oil bath at 110 °C for 4 hours.

The resulting product was fully soluble, indicating the absence of a cross-link network. This was also observed from the ^1H -NMR spectrum, where there was no variation in multiplicity and chemical shift for the unmodified signals of both the reactants, suggesting there was no visible interaction or transesterification between the reagents under such conditions (**Figure 2.11**).

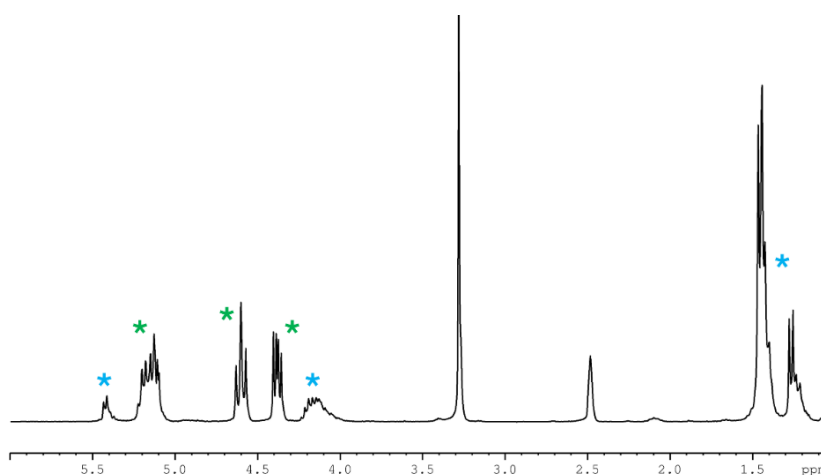


Figure 2.11 – ^1H -NMR spectra (300 MHz, DMSO-d_6 , 298 K) of unreacted product from the reaction between 4S-PLA-OH and EBC; (*) prepolymer, (*) EBC.

The same study was also conducted under a one-pot reaction to accomplish both the polymerization of L-LA and its subsequent crosslinking in a single synthetic step.

As no observable reaction was noticed under the previous test, the temperature was increased from 110 °C to 150 °C, and the reaction time was extended from 4 h to 24 h (monitoring the reaction during the time) to increase the conversion and achieve crosslinking.

All the reagents were placed in a 50 mL round-bottom flask with an L-LA: Pentaerythritol molar ratio of 12:1, an L-LA: $\text{Sn}(\text{Oct})_2$ ratio of 100:1, and an EBC: hydroxyl functionalities ratio of 1:1.

The reaction product consisted of two fractions of different nature: one insoluble in chloroform and the other soluble in chloroform. The two phases were separated by centrifugation.

Both fractions were analyzed by ^1H -NMR spectroscopy.

The spectra revealed that the solid part was pure EBC (**Figure 2.12**, spectrum b), while the liquid part was the star-shaped polymer with a residual amount of EBC (**Figure 2.12**, spectrum a).

This result suggests that under the one-pot conditions investigated, the crosslinking reaction was not effective, either due to the inefficiency of activation of the EBC functionalities or steric hindrance within the reaction medium.

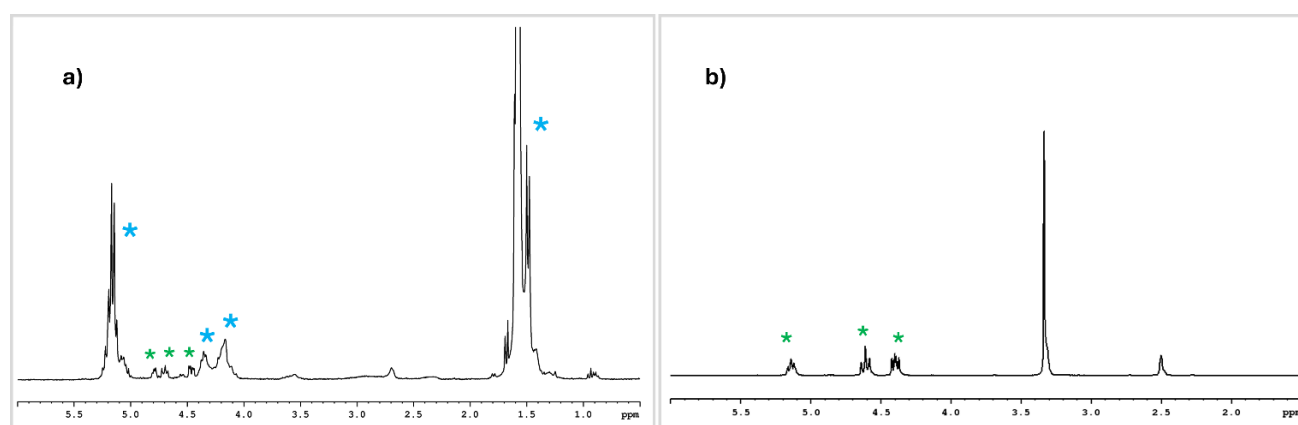


Figure 2.12 - ^1H -NMR spectra (300 MHz, $\text{DMSO}-d_6$, 298 K) of the liquid fraction (spectrum a) and the solid fraction (spectrum b); (*) prepolymer, (*) EBC.

2.5 Crosslinking Tests with Citric Acid

The biocompatibility, bio-based origin, and multifunctional chemical structure of citric acid (CA) have garnered significant interest across various scientific and engineering fields. Because it contains three carboxylic acid ($-\text{COOH}$) groups and one hydroxyl ($-\text{OH}$) group, CA can form extensive hydrogen bonds with polymer networks, improving their physicochemical properties.¹⁵

As a result of these reactive functional groups, CA has been widely utilized as a general polyfunctional modifier to convert hydroxyl-containing polymers to reactive materials

through cross-linking reactions, resulting in a family of materials known as citrate-based biomaterials (CBBs).¹⁶

CA is the ideal monomer for this purpose: non-toxic, available in large quantities commercially, cost-effective, and stable covalent linkages are established.

Several examples in the literature demonstrate using CA as an efficient cross-linking agent. CA, for example, can cross-link cellulose through esterification reactions where the carboxylic groups of CA react with the hydroxyl groups of cellulose.¹⁷

Inspired by the work of *Halpern et al.*,¹⁸ who developed a novel degradable thermoset biomaterial derived from simple, cost-effective, biocompatible, and renewable monomers like glycerol and citric acid, without the use of catalysts, we considered redesigning this system using star-shaped polymers with hydroxyl end groups.

So, the reaction was set up starting from 1 g of 4S-PLA-OH with a 1:1 molar ratio with citric acid. The reaction was carried out in the presence of 3 mol% or 5 mol% ZnCl₂ and p-TSA catalysts, and maintained at 130 °C for 16 hours. The progress of the reaction was monitored by ¹H-NMR spectroscopy.

After this time, chloroform was added to the reaction mixture to assess whether a crosslinked, insoluble product had formed.

Two phases were obtained: a liquid phase and a solid phase, which were separated from one another by centrifugation.

¹H-NMR analysis revealed that the solid phase was mostly unreacted citric acid (chloroform-insoluble), while the liquid phase contained the soluble polymer with a trace amount of citric acid (~2.06 ppm) dissolved in the organic phase (**Figure 2.13**).

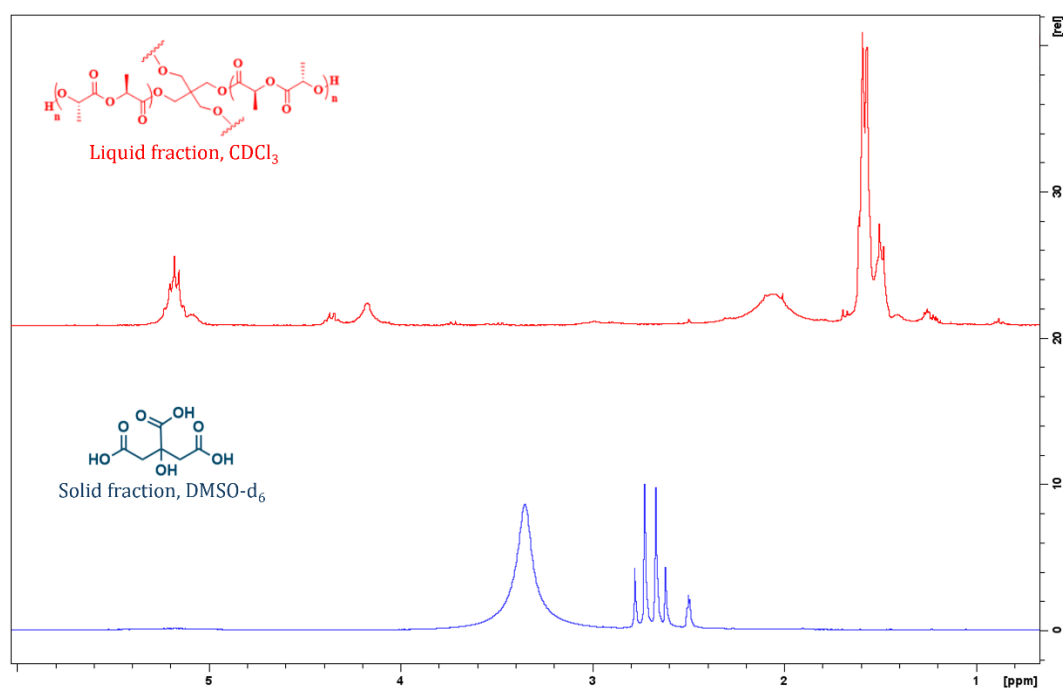


Figure 2.13 ^1H -NMR spectrum of solid fraction (blue) and liquid fraction (red), (300 MHz, $\text{DMSO}-d_6$, 298 K) of reaction test between $[4\text{S-PLA-OH}]:[\text{CA}] = 1:1$, 5 mol% ZnCl_2 and $p\text{-TSA}$ catalysts, at 130 °C for 16 hours

Conclusion

In this chapter, 3, 4, and 6-arm hydroxy-terminated star-shaped PLA oligomers were successfully synthesized by the core-first strategy using glycerol, pentaerythritol, and dipentaerythritol as multifunctional initiators. The polymerization process was optimized, indicating that ring-opening polymerization in bulk conditions at 160 °C provides shorter reaction times and analogous molecular weight distributions compared to milder solution-based processes. Characterization using ^1H -NMR and GPC confirmed the desired star-shaped structures with mean arm lengths of 3 lactide units and M_n values between ca. 1–3 kDa.

Subsequent crosslinking experiments using diethyl malonate, erythritol bis-carbonate, and citric acid highlighted the challenges encountered in forming three-dimensional networks from the low-molecular-weight star-shaped PLA oligomers synthesized.

Although glycerol, in the presence of 5 mol% $\text{Sn}(\text{Oct})_2$ and at a 2:1 ratio with DEM, appears to promote a DEM conversion of approximately 70%, none of the conditions we tested, including changes in catalyst type, temperature, stoichiometry, or one-pot polymerization/crosslinking setups, led to any clear signs of transesterification or crosslinking for the newly synthesized branched prepolymers.

Even comb-like and linear PLA systems were found to be extremely weakly reactive with these crosslinkers, which illustrates that steric hindrance, low functionality density, or absence of activation of the crosslinkers most likely inhibits network formation.

In conclusion, while synthesis and structural characterization of low-molecular-weight star-shaped PLA oligomers were successfully achieved, their direct crosslinking into covalent networks using the investigated reagents failed. These findings suggest that alternative crosslinking methods, additional molecular weight precursors, or more reactive coupling chemistries may be required in order to be able to achieve the potential of star-shaped PLA for vitrimer or thermoset applications.

2.6 Experimental Part

2.6.1 Materials and Methods

Reactions involving air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere, either inside a Braun Labmaster glovebox or using Schlenk techniques, depending on the setup required. To ensure anhydrous conditions, glassware was first dried in an oven at 120 °C overnight and then purged with nitrogen through several vacuum/nitrogen cycles.

Deuterated solvents were obtained from Aldrich, and methanol was dried over sodium and distilled under nitrogen before use.

The L-lactide used (technical grade, Lumilact® L supplied by Total-Corbion) contained no more than 0.03% w/w water and was pre-dried overnight with phosphorus pentoxide (P₂O₅). The same drying procedure was utilized to dry the polyalcohols before use.

All other reagents, except where otherwise stated, were purchased from commercial suppliers and used without further purification.

2.6.2 Instruments and Measurements

NMR spectra were recorded using Bruker Avance instruments operating at 300, 400, or 600 MHz (Ascend 3 HD), depending on availability and the resolution required. Chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (J) in hertz (Hz). For ¹H NMR, the residual CHCl₃ signal at δ 7.26 ppm in CDCl₃ was used as the reference, while for ¹³C NMR, the CDCl₃ peak at δ 77.22 ppm served as the reference point.

Gel permeation chromatography (GPC) was used to analyze the molecular weight distribution of the samples. The measurements were carried out on an Agilent 1260 Infinity Series system, equipped with a ResiPore column (3 μ m, 300 $\times$ 7.5 mm), and operated at a flow rate of 1.0 mL/min. Both UV detection (at 250 nm) and a refractive index (RI) detector (PLGPC 220) were used to monitor the elution. The analyses were performed at a constant temperature of 35 °C, using either THF or CHCl₃ as the eluent. Calibration was done using monodisperse polystyrene standards to ensure reliable molecular weight estimation. Instrument calibration

for temperature and enthalpy was carried out using high-purity indium (melting point: 156.60 °C; enthalpy: 28.45 J/g).

Molecular weight values were also confirmed by MALDI-TOF mass spectrometry. The spectra were recorded using a Bruker solariX XR FT-ICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany), which operates with a 7 Tesla actively shielded superconducting magnet, allowing for high-resolution mass analysis.

2.6.3 Synthesis of Hydroxyl-Terminated 3-Arm, 4-Arm and 6-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers

The polymerization process was conducted using an MBraun glovebox in a nitrogen environment. The proper amount of technical-grade L-lactide previously dried overnight over phosphorus pentoxide (P_2O_5) was weighed out based on the intended architecture (9 eq for 3S (5-15g), 12 eq for 4S (5-15g), and 18 eq for 6S (5-15g)). The monomer was transferred to a 100 mL two-neck round-bottom flask containing a magnetic stirring bar. Then the initiator (1 eq, glycerol or pentaerythritol) and catalyst (0.004 eq of tin(II) octanoate, $Sn(Oct)_2$) were added.

Once closed, the flask was removed from the glovebox and heated in an oil bath at 160 °C. The mixture was stirred and left to react for 4 hours. When the reaction time was complete, the system was opened to air and stopped by adding chloroform with trace water.

The crude mixture was dissolved in a minimal volume of chloroform and precipitated by adding hexane while shaking the flask thoroughly. A white precipitate formed, which was recovered by decantation. The solid polymer was then dried, first using a rotary evaporator and finally under vacuum at 100 °C to ensure complete removal of residual solvents.

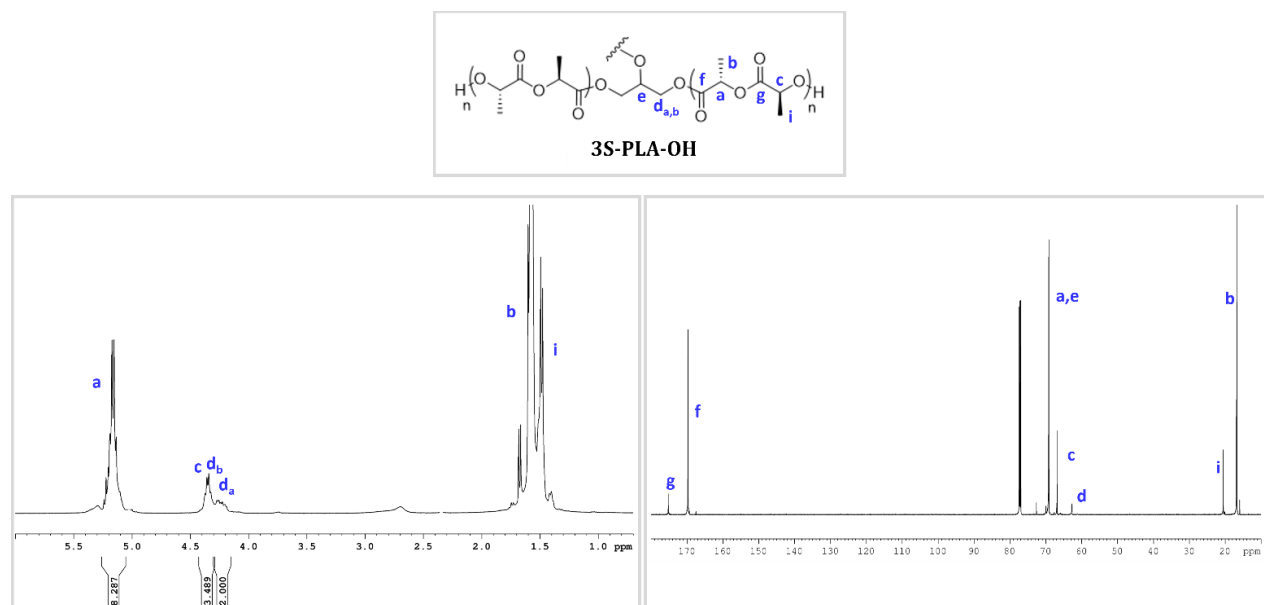


Figure 2.14 – ^1H -NMR spectrum of 3S-PLA-OH (left), ^{13}C -NMR spectrum of 3S-PLA-OH (right), (300 MHz, CDCl_3 , 298 K)

^1H -NMR (300 MHz, CDCl_3 , 298 K) δ : 5.17 (m, n1H), 4.34 (q, $J = 6.4$ MHz, n2H), 4.23 (m, n1H), 1.57 (d, $J = 7.0$ MHz, n3H), 1.48 (d, $J = 7.0$, n3H)

^{13}C -NMR (75 MHz, CDCl_3 , 298 K) δ : 175.23 (g), 169.69 (f), 69.15 (a, e), 66.87 (c), 62.69 (d), 20.62 (i), 16.77 (b)

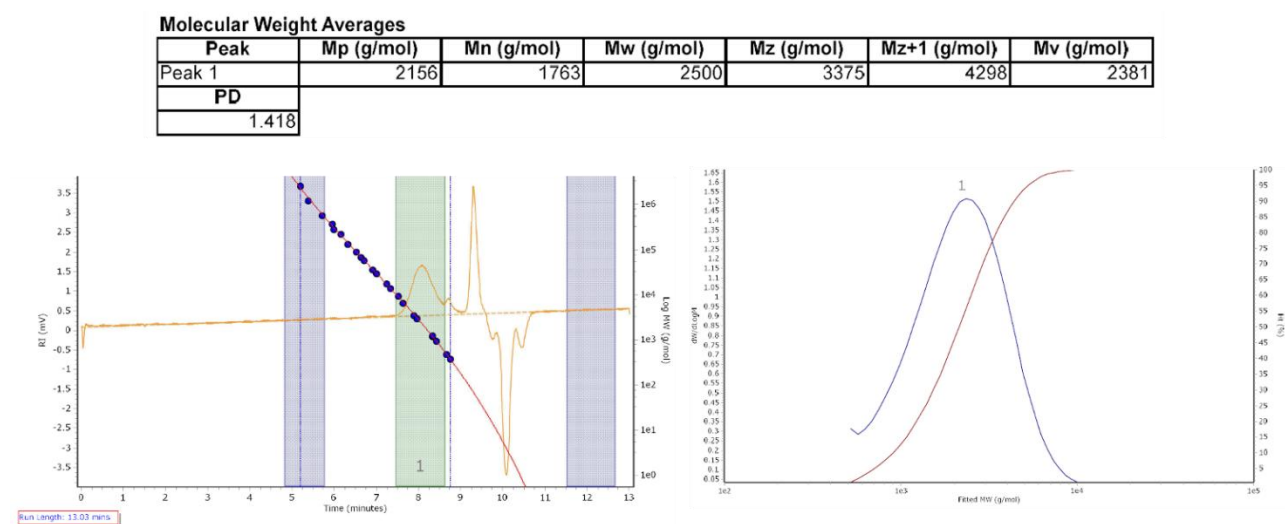


Figure 2.15 - GPC analysis of 3S-PLA-OH in THF using polystyrene standards, molecular weight averages, chromatogram plot, distribution plot

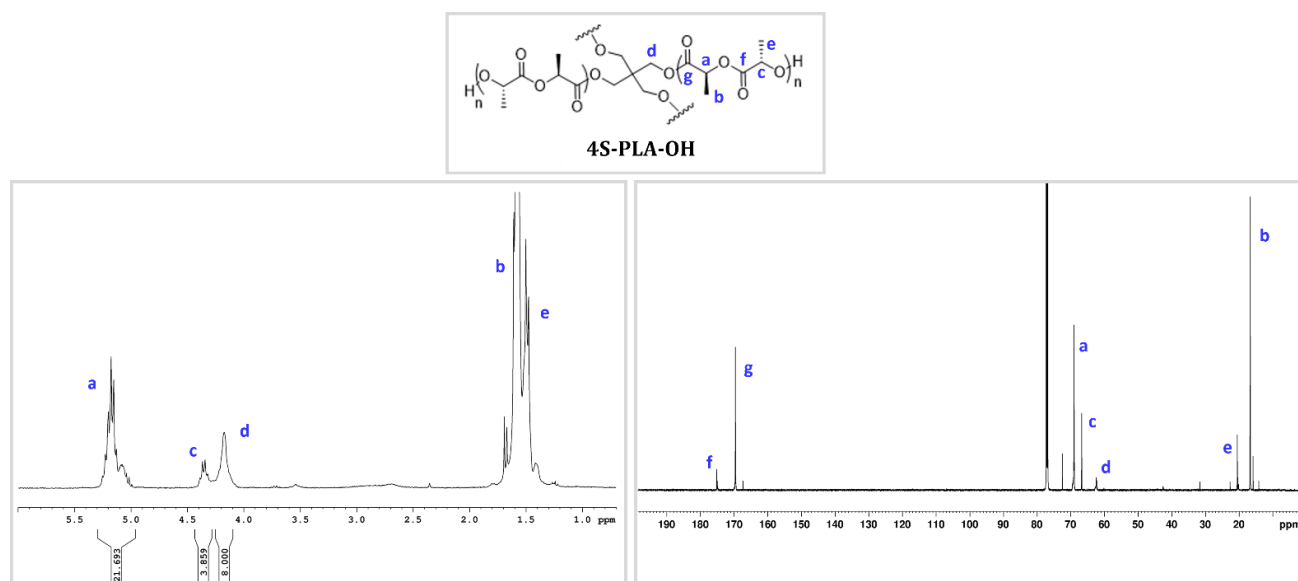


Figure 2.16 - ^1H -NMR spectrum of 4S-PLA-OH (left), ^{13}C -NMR spectrum of 6S-PLA-OH (right), (300 MHz, CDCl_3 , 298 K)

^1H -NMR (300 MHz, CDCl_3 , 298 K) δ : 5.17 ppm (m, n1H), 4.35 (q, $J = 6.9$ MHz, n1H), 4.17 (br, n2H), 1.57 (d, $J = 5.2$, n3H), 1.48 (d, $J = 7.4$, n3H)

^{13}C -NMR (75 MHz, CDCl_3 , 298 K) δ : 175.27(f), 169.74 (g), 69.14 (a), 66.85 (c), 62.53 (d), 20.64 (e), 16.78 (b)

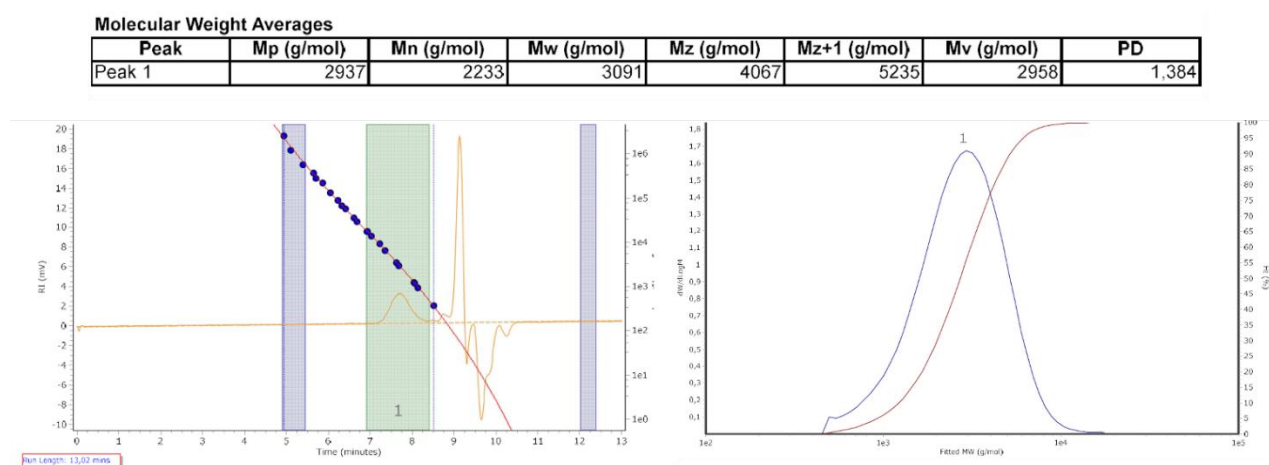


Figure 2.17 - GPC analysis of 4S-PLA-OH in THF using polystyrene standards, molecular weight averages, chromatogram plot, distribution plot

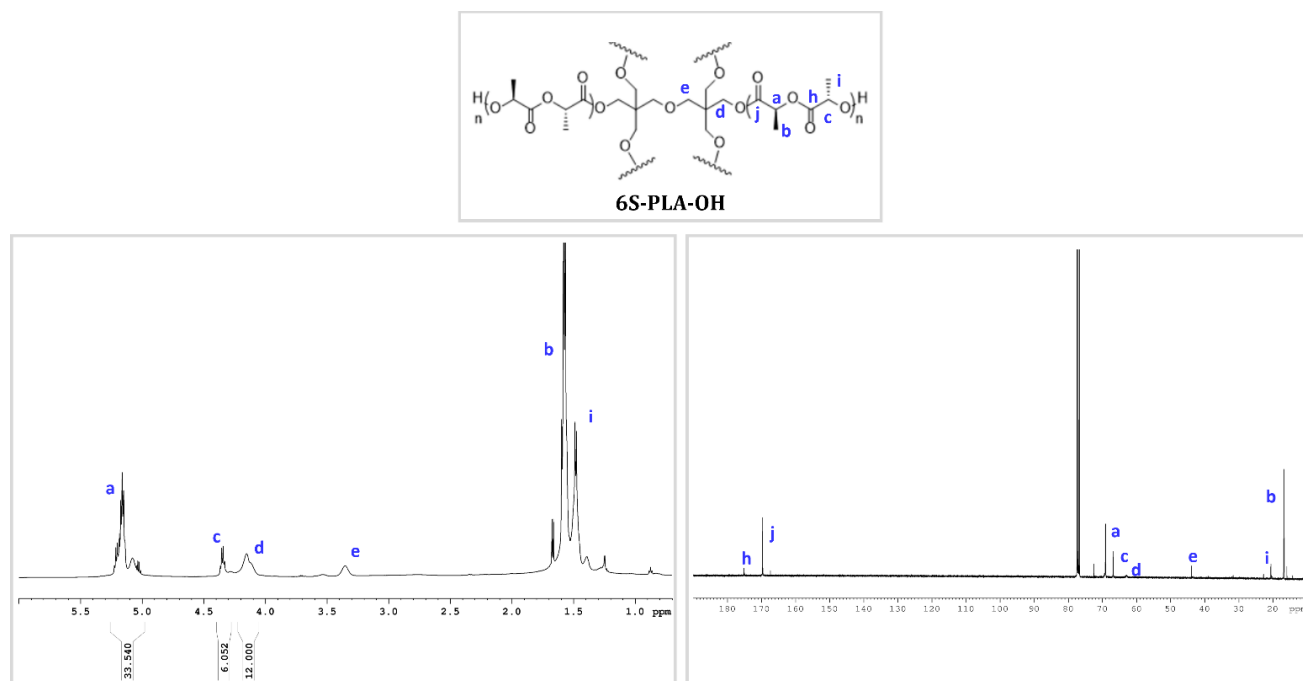


Figure 2.18 - ^1H -NMR spectrum of 6S-PLA-OH (left), ^{13}C -NMR spectrum of 6S-PLA-OH (right), (300 MHz, CDCl_3 , 298 K)

^1H -NMR (600 MHz, CDCl_3 , 298 K) δ : 5.16 (m, n1H), 4.34 (q, $J = 7.4$ MHz, n1H), 4.15 (br, n2H), 3.37 (br, n2H), 1.57 (d, $J = 7.37$, n3H), 1.48 (d, $J = 7.37$, n3H)

^{13}C -NMR (75 MHz, CDCl_3 , 298 K) δ : 174.69 (h), 169.15 (j), 68.56 (a), 66.27 (c), 62.43 (d), 43.34 (e), 20.06 (i), 15.37 (b)

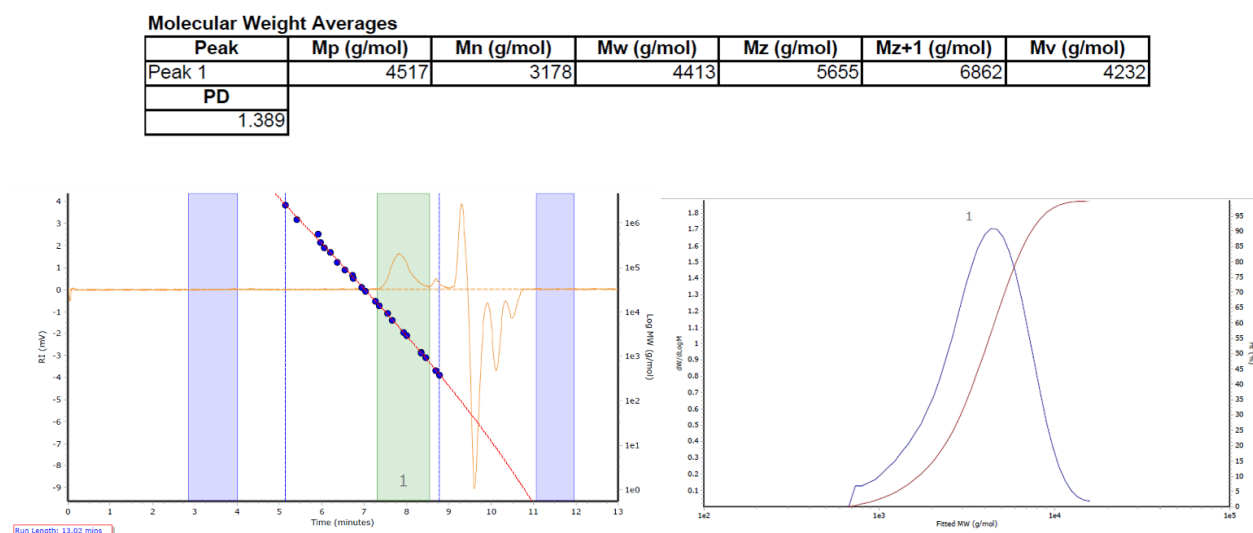


Figure 2.19 - GPC analysis of 6S-PLA-OH in THF using polystyrene standards, molecular weight averages, chromatogram plot, distribution plot

2.6.4 Crosslinking Reaction 4S-PLA-OH and DEM

– Kinetic study in NMR tube

DEM (8.6 mg, 5.42×10^{-5} mol, 8 μ L) and 4S-PLA-OH (15 mg, 1.35×10^{-5} mol) were dissolved in 0.4 mL of TCDE and mixed in a 1:1 molar ratio [DEM]:[OH] in a vial. Sn(Oct)₂ as catalyst was added in quantity equal to 5 mol% by the diester (1 mg, 2.5×10^{-6} mol, 0.2 mL of a 0.01 M solution in TCDE). The product mixture formed was poured into an NMR tube containing 0.4 mg of TMSS.

For DMAP-catalyzed experiments, 2.7×10^{-6} mol (0.3 mg, 0.1 mL of 0.03 M in TCDE) was added with the same conditions.

The NMR tube was subsequently inserted into a preheated oil bath with no cap.

Reaction progress was monitored by NMR spectroscopy after 30 minutes at 50 °C and 80 °C. Since no drastic spectral changes were observed at these temperatures, further reaction progress was monitored after 20 and 40 minutes at 100 °C, after 20, 40, 60, and 80 minutes at 120 °C, and after 20 and 80 minutes at 130 °C, and after 140 min at 145 °C, in the case of the DMAP-catalyzed system.

– One-pot polymerization-crosslinking reaction

All of the reagents were charged into a 50 mL round-bottom flask, with magnetic stirrer, in the following molar proportions: L-LA:pentaerythritol=12:1, L-LA:Sn(Oct)₂=100:1, and pentaerythritol:DEM=1:4. Specifically, L-LA (0.200 g, 1.2×10^{-3} mol), pentaerythritol (20 mg, 1.5×10^{-4} mol), DEM (0.010 g, 0.010 mL, 6.3×10^{-5} mol), and Sn(Oct)₂ (0.5 mg, 1.2×10^{-6} mol) were charged into the flask. A few drops of toluene were added to homogenize the mixture.

The reaction was run at 130 °C for 6 hours. Upon completion, the crude product was separated into two fractions: a chloroform-soluble and an insoluble fraction. The two layers were centrifuged and separated, with characterization via ¹H NMR spectroscopy.

The ¹H NMR spectra showed that the insoluble portion was caused by residual pentaerythritol that did not react, and the soluble portion had the star-shaped polymer resulting from ring-opening polymerization (ROP) of L-LA by Sn(Oct)₂ initiator and unreacted DEM.

2.6.5 Linear Di-Hydroxy-Terminated PLA

– Synthesis

In a 100 mL round-bottom flask equipped with a magnetic stirrer, 1.5 g of L-LA, 31 mg ethylene glycol, and 0.5 mL of a 0.005 M solution of Sn(Oct)₂ in toluene were introduced. The reaction was carried out under a nitrogen atmosphere at 160 °C for 4 hours in an oil bath.

¹H-NMR (300 MHz, CDCl₃, 298 K) δ: 5.15 (q, J= 7.2 MHz, n1H), 4.3 (s, 4H), 1.5 (d, J= 6.5, n3H)

– Crosslinking reaction of a linear di-hydroxy-terminated PLA and DEM

In a 20 mL vial, the dihydroxy-terminated prepolymer (0.300 g), DEM (45 μL, corresponding to a DEM:prepolymer molar ratio of 1:2), and 0.15 mL of a 0.1 M solution of Sn(Oct)₂ in toluene (corresponding to 5 mol% relative to DEM) were added. The vial was introduced into a preheated oil bath at 110 °C, and the reaction progress was monitored by ¹H NMR spectroscopy for up to 56 hours.

2.6.6 Synthesis and Crosslinking of EB27

– Synthesis

In a glove box, a 250 mL round-bottom flask with a magnetic stirrer was charged with L-LA (25 g, technical grade), polyglycerol-10 (304 mg), and Sn(Oct)₂ (9 mg), with an L-LA:alcohol molar ratio of 432:1. The flask was then taken outside the glove box and put in a preheated oil bath at 190 °C for 3 h 30 min. For the recovery, the resulting polymer was dissolved in dichloromethane and precipitated in methanol.

¹H-NMR (300 MHz, CDCl₃, 298 K) δ: 5.15 (q, J= 7.19 MHz, n1H), 4.37 (q, J= 7.34 MHz, n1H), 1.57 (d, J= 7.70 MHz, n3H)

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		102136	144826	123100	203779	275483	1,417982	1,407054	1,902156

Figure 2.20 - GPC analysis of EB27 in THF using polystyrene standards, molecular weight averages

– Crosslinking Reaction of EB27 and DEM

- 1) In *Entry 1*, an equimolar amount of DEM and hydroxyl groups was used. More specifically, EB27 (0.100 g, 1.7×10^{-6} mol) and DEM (2.7 mg, 1.7×10^{-5} mol) were blended with Sn(Oct)₂ (5 mol% relative to DEM, 17 µL from a 0.05 M dichloromethane solution). The reaction proceeded for 24 h at 145 °C in a sealed vial under nitrogen. A few drops of anhydrous dichloromethane were added to allow for better homogeneity of the reaction mixture.
- 2) In *Entry 2*, the DEM/hydroxyl ratio was increased to 10:1. EB27 (0.100 g, 1.7×10^{-6} mol), DEM (27 mg, 1.7×10^{-4} mol), and Sn(Oct)₂ (10 mol% based on DEM, 0.17 mL of 0.05 M solution in dichloromethane) were used. Reaction was again conducted at 145 °C for 24 h in a vial under nitrogen flow, a trace amount of anhydrous dichloromethane being added for improved mixture homogeneity.
- 3) In *Entry 3*, the same stoichiometric composition (DEM:OH = 10:1; Sn(Oct)₂ = 10 mol% of DEM) was employed but with decreased temperature to 110 °C to examine the effect of milder thermal conditions on transesterification progress. The same apparatus for the reaction as well as solvent conditions were utilized as described under the previous experiments.

- 4) In *Entry 4*, the reaction was carried out at 110 °C with excess DEM (10:1 DEM:OH) and 5 mol% Sn(Oct)₂ (with respect to DEM). The reaction was carried out in a 25 mL round-bottom flask with a reflux condenser and a thermometer at the top of the condenser. This arrangement allowed for vapor temperature to be tracked to ascertain the nature of evaporating species (DEM or ethanol). The reaction was carried out at 110 °C for 24 h in an inert atmosphere and without a solvent and with periodic monitoring.

All the experiments were monitored by ¹H-NMR.

2.6.7 DEM and Glycerol

- *Entry 5*: in a vial containing 0.6 mL of DEM (4.2 mmol), 0.130 g (1.4 mmol) of glycerol was added at a DEM:OH ratio of 1:1. After heating in the preheated oil bath at 150 °C for 3 h,
- *Entry 6*: 1.0 g of glycerol (0.01 mol) was dissolved in the minimum amount of methanol and added to a vial containing 1.0 mL of DEM (6.3 mmol) (DEM:OH ratio = 1:1). The methanol was allowed to evaporate overnight under a fume hood, and the vial was then placed into a preheated oil bath at 150 °C for 3 h.
- *Entry 7*: 0.300 g (3.3 mmol) of glycerol were introduced into a vial with 1.5 mL of DEM (9.8 mmol) (DEM:OH ratio = 1:1) and 0.139 g of Ti(OiPr)₂ (4.9×10^{-4} mol, 5 mol% relative to DEM). The mixture was heated in an oil bath at 100 °C for 6 h.
- *Entry 8*: Glycerol (0.500 g, 5.4 mmol) was added to a vial containing 2.5 mL of DEM (0.015 mol) (DEM:glycerol = 1:1) and 0.330 g of Sn(Oct)₂ (7.4×10^{-4} mol, 5 mol% with respect to DEM). The reaction mixture was heated at 100 °C in an oil bath for 72 h.
- *Entries 9-10*: 1.0 g of glycerol (0.01 mol) was added to a vial containing 1.2 mL of DEM (8.2 mmol) (DEM:OH ratio = 1:2) and 0.166 g of Sn(Oct)₂ (4.1×10^{-4} mol, 5 mol% relative to DEM). The vial was inserted oil bath at 100 °C for 8 h (*Entry 5*) and 130 °C for 8 h (*Entry 6*).
- *Entry 11*: 0.87 mL of DEM (5.4 mmol), 0.04 mL of DBU (2.7×10^{-4} mol, 5 mol% relative to DEM) and 0.500 g (5.4 mmol) of glycerol were added to a vial. The mixture was heated in a preheated oil bath at 100 °C for 12 h.

- *Entry 12*: 1.0 g (0.01 mol) of glycerol was added to a vial containing 1.7 mL of DEM (0.01 mol) (DEM:OH ratio = 1:3), 14.6 mg of ZnCl₂, and 19 mg of p-TSA (1.1×10^{-4} mol, 1 mol% relative to DEM). The mixture was heated in an oil bath at 130 °C for 16 h.

All the reactions were monitored by ¹H-NMR.

2.6.8 Erythritol Bis-Carbonate

– Synthesis

Erythritol (1.00 g, 8.2 mmol, 1.0 eq) and TBD (57 mg, 0.41 mmol, 0.05 eq) were dispersed in 20.5 mL of DMC in a 100 mL round-bottom flask. The mixture was heated to 60 °C under reduced pressure (314 mbar) using a rotary evaporator and maintained for 1 hour. Complete dissolution of erythritol occurred after approximately 30 minutes, followed by the formation of a white precipitate after about 35 minutes. Upon cooling to room temperature, the solid product was collected by filtration and washed with DMC, affording erythritol bis(carbonate) as a white powder (1.12 g, 80% yield).

¹H-NMR (300 MHz, DMSO-d₆, 298 K) δ : 5.25–5.07 (m, 2H), 4.69–4.52 (m, 2H), 4.47–4.31 (m, 2H)

¹³C-NMR (75 MHz, DMSO-d₆, 298 K) δ : 158.2, 74.9, 64.7.

– Crosslinking Reaction with Erythritol Bis-Carbonate

Crosslinking reaction with erythritol bis(carbonate) (EBC) was carried out in a closed vial with 0.117 g of 4S-PLA-OH (0.11 mmol) in a 1:1 molar ratio of EBC (77 mg, 0.43 mmol) to hydroxyl end groups. Sn(Oct)₂, 8.7 mg (0.021 mmol) was added, corresponding to 5 mol% relative to EBC. The vial, closed with a rubber septum pierced with a fine needle to allow the release of volatile by-products (ethanol), was put in a preheated oil bath and the reaction was conducted at 110 °C for 4 hours.

– Crosslinking Reaction with Erythritol Bis-Carbonate (one-pot reaction)

0.200 g of L-lactide (1.4 mmol), 20 mg of pentaerythritol (0.12 mmol), 83 mg of EBC (0.48 mmol), and 5.7 mg of Sn(Oct)₂ (0.014 mmol) were charged in a 50 mL round-bottom flask. The respective molar ratios were therefore: L-LA: Sn(Oct)₂ = 100: 1, Pentaerythritol: L-LA = 1: 12, and EBC: Pentaerythritol = 4: 1.

The reaction was performed in solvent-free conditions at 150 °C for 24 hours and monitored by using ^1H -NMR spectroscopy. The reaction mixture after completion was subjected to chloroform, which resulted in two distinct phases: a solid fraction that was identified as unreacted EBC and a liquid fraction that comprised the star-shaped polymer and excess EBC. The two phases were separated by centrifugation.

2.6.9 Crosslinking Reaction with Citric Acid

The reaction was carried out using 1.00 g (9.3×10^{-4} mol) of 4S-PLA-OH and citric acid (0.173 g, 9.0×10^{-4} mol) in a mole ratio of 1:1. The reaction was performed in the presence of either 3 mol% catalysts (ZnCl_2 : 4 mg, 2.7×10^{-5} mol; p-TSA: 5 mg, 2.9×10^{-5} mol) or 5 mol% catalysts (ZnCl_2 : 6.6 mg, 4.8×10^{-5} mol; p-TSA: 8.3 mg, 4.8×10^{-5} mol). The mixture was maintained at 130 °C for 16 hours, and the reaction was monitored by ^1H NMR spectroscopy.

After 16 hours, the reaction mixture was charged with chloroform to examine the formation of an insoluble crosslinked product. Two phases were separated: a solid phase and a liquid phase, and these two phases were separated by centrifugation and then ^1H NMR-analyzed.

The ^1H -NMR analysis revealed that the solid phase was predominantly unreacted citric acid (chloroform-insoluble), while the liquid phase was a star-shaped polymer dissolved with residues of citric acid in the organic phase.

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CHAPTER 3

Results and Discussion

*Synthesis, Characterization and Cross-Linking
Reaction of Carboxyl-Terminated Star-Shaped
Poly(L-Lactic Acid) Oligomers*

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Introduction

Epoxy resins are among the most adaptable and widely used thermosetting polymers, playing a key role in a broad range of industries, from composite materials and electronics to adhesives, coatings, construction, aerospace, and automotive manufacturing. Their popularity stems from a unique combination of properties, including customizable mechanical strength, excellent electrical insulation, strong adhesion, dimensional stability, and ease of processing.^{1,2}

Despite these advantages, the vast majority, over 98%, of epoxy resins on the market today are still produced from petroleum-based sources.³

This reliance has raised growing concerns due to the environmental impact and potential health risks associated with these materials.⁴ In particular, more than 90% of epoxy resins are based on diglycidyl ether of bisphenol A (DGEBA), which is synthesized from bisphenol A (BPA) and epichlorohydrin (ECH). Both BPA and ECH are recognized as substances of very high concern because of their carcinogenic, mutagenic, and reprotoxic (CMR) properties.^{5,6}

Even though awareness of the risks linked to these substances is increasing, BPA production continues to rise in response to the ongoing demand for high-performance epoxy materials. BPA is also suspected of being an endocrine-disrupting chemical (EDC), capable of interfering with hormonal systems in both humans and wildlife.^{7,8}

These concerns have prompted further scrutiny from the scientific and regulatory communities. For instance, the International Agency for Research on Cancer (IARC) has classified DGEBA as a Group 3 carcinogen, meaning there isn't enough evidence to determine whether it causes cancer in humans.⁴

In response to these environmental and health challenges, a growing body of research is now focused on finding safer and more sustainable alternatives to conventional epoxy resins. The goal is to develop bio-based, non-toxic epoxy systems that can match the performance of BPA-based resins without the associated risks. One promising approach involves sourcing renewable raw materials that mimic the structure of DGEBA, especially those that include aromatic rings, which are essential for achieving the thermal and mechanical strength required in demanding applications.⁹

Several bio-based epoxy resins derived from vegetable oils, such as soybean, linseed, and castor oil, have already been explored.² However, these materials often contain long aliphatic chains, which limit their ability to form strong, high-performance networks comparable to those made with DGEBA.

To overcome this, researchers have turned to natural polysaccharides as building blocks for new epoxy monomers. Compounds like sorbitol and maltitol have been successfully transformed into multifunctional epoxy molecules.¹⁰ Among the most promising is isosorbide diglycidyl ether (DGEIs), a fully bio-based, non-toxic crosslinker with considerable potential.

Isosorbide is derived from sorbitol through a double cyclodehydration process, typically carried out with acid catalysts under heat, pressure, or vacuum.¹¹ There are several ways to synthesize DGEI starting from isosorbide, including, for example, epoxidation of isosorbide diallyl ether, acid-catalyzed reaction of ECH with isosorbide, NaOH-catalyzed addition of ECH to isosorbide, and reaction of isosorbide sodium alkoxide with ECH.¹²

In the current chapter, the crosslinking action of DGEIs will be investigated in branched PLA-based systems, which were prepared and analyzed in the previous chapter.

Since the terminal hydroxyl groups of the star-shaped PLA chains tend to be relatively unreactive, an initial modification was necessary.

To address this, the end groups were converted to carboxylic acid functionalities, which offer better reactivity toward epoxide groups and facilitate crosslinking.

Despite this adjustment, carboxylic acids are relatively less reactive, and reactions with epoxides usually need activation. Suitable organic or inorganic catalysts are typically used to promote the crosslinking reaction. These catalysts help overcome the kinetic inertia of the carboxylic acid-epoxy reaction and enable the formation of a wide range of ester-based polymer networks.¹³

The reaction between epoxide groups and carboxylic acids is particularly important in industrial applications, especially in the formulation of coatings and advanced polymer systems.

This chemistry is widely used in commercial carboxyl-terminated polyester resins, like Uralac® and Crylcoat® (both from Allnex), which are popular choices for epoxy–polyester powder coatings.¹⁴

Unlike other pathways, this ring-opening condensation reaction doesn't produce any volatile by-products, which makes it more environmentally friendly and cleaner from a processing standpoint. Moreover, the resulting crosslinks tend to be highly stable, offering excellent resistance to chemical and thermal degradation, qualities that are crucial for developing durable, high-performance, and sustainable materials.¹⁵

In this chapter, rheological properties were carried out in collaboration with Prof. *Di Maio's* group at the *Department of Industrial Engineering* at the *University of Salerno* (UNISA, DIIN), while mechanical, SEM and WCA analyses were carried out in collaboration with Prof. *Scaffaro's* group at the *Department of Chemical Engineering* at the *University of Palermo* (UNIPA).

3.1 Hydroxyl End-Capped 4-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers Crosslinking Reaction with DGEIs

The prepolymer 4S-PLA-OH was evaluated in a crosslinking reaction with isosorbide diglycidyl ether (DGEIs).

For this purpose, zinc acetate ($\text{Zn}(\text{OAc})_2$) was selected as the catalyst because it's widely recognized for being practical and environmentally friendly. It's especially effective in transesterification reactions and is favored due to its low toxicity and ready availability.

Unlike more hazardous metal catalysts, such as those containing tin, zinc acetate offers a safer, greener alternative without compromising on performance. This makes it an excellent choice for sustainable and efficient chemical processes.^{16–18}

The catalyst was used at a loading of 10 mol% relative to the hydroxyl functionalities of the prepolymer. The reaction mixture was prepared by dissolving the prepolymer and the DGEIs in dichloromethane, maintaining a 1:1 molar ratio between hydroxyl and epoxy functionalities.

A separate methanolic solution of $\text{Zn}(\text{OAc})_2$ was then introduced into the mixture, and the entire solution was sonicated to achieve uniform dispersion of all components. The resulting homogeneous solution was poured into a Teflon Petri dish. After allowing the solvents to fully evaporate, the sample was placed in an oven under a nitrogen atmosphere and heated to 180 °C.

This temperature was selected to facilitate the transesterification reaction, which typically requires elevated temperatures. However, under these conditions, the material showed clear signs of thermal degradation, indicating that 180 °C was too high for the system to remain stable.

The study was continued using the same molar ratios of reagents, but with a lower reaction temperature of 160 °C in an effort to avoid thermal degradation. After 3 hours of heating, the material remained completely soluble, and the ^1H -NMR analysis revealed distinct, unaltered signals from both the prepolymer and the crosslinker, suggesting that no reaction had taken place (**Figure 3.1**).

Even after extending the reaction time to 8 hours, there was still no significant evidence of crosslinking, indicating that the lower temperature was insufficient to drive the process forward.

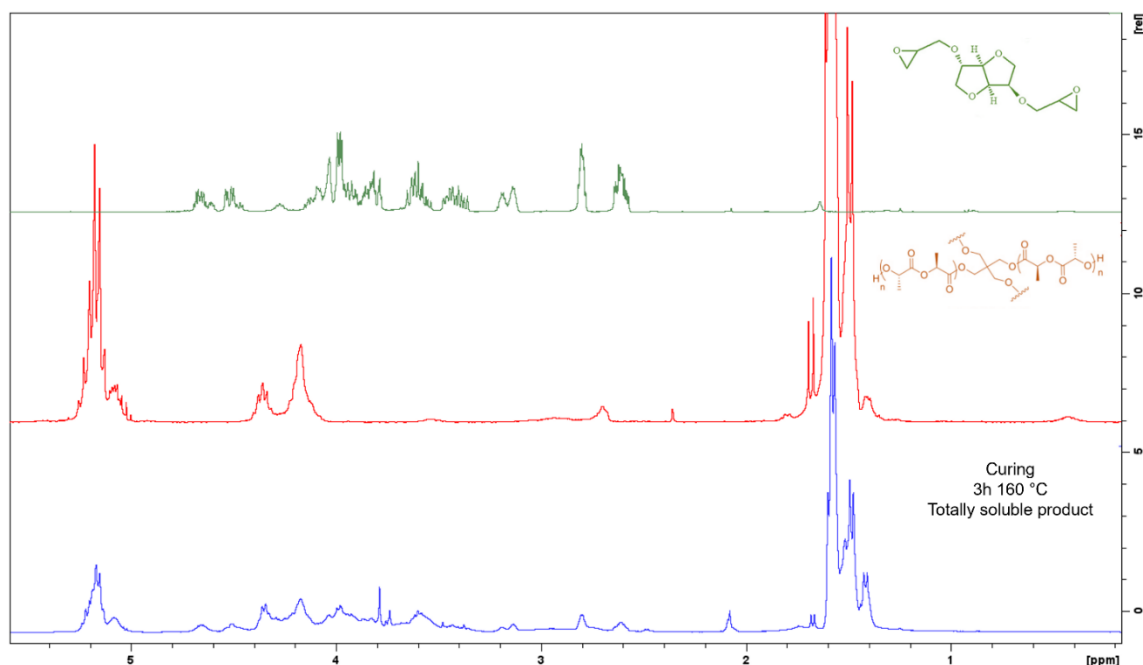
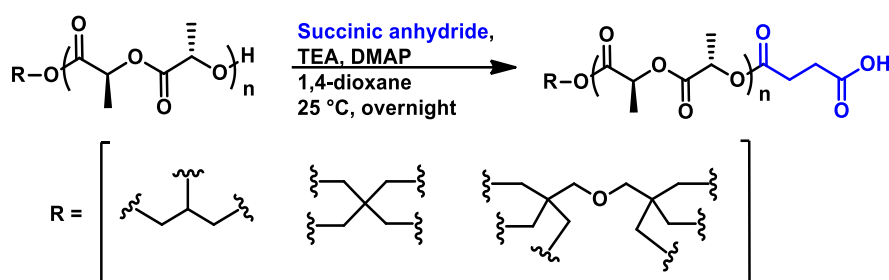


Figure 3.1 – Comparison of ^1H -NMR (400 MHz, CDCl_3 , 298 K) spectra: DGEIs, green; 4S-PLA-OH, red; evidence of unreacted product, blue.

3.2 Carboxyl End-Capped 3-Arm, 4-Arm and 6-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers Synthesis



Scheme 3.1 - acidification reaction scheme of $n\text{S-PLA-OH}$

Based on the results of the cross-linking reactions of the 4S-PLA-OH, it was apparent that the limited reactivity observed was likely a consequence of the inherent low nucleophilic character of the terminal $-\text{OH}$ groups toward the selected cross-linkers.

To overcome this limitation, carboxylic acid groups were introduced at the terminal positions of the polymer chains. This modification was intended to increase the nucleophilicity of the end groups, thereby improving their reactivity in cross-linking reactions.

Carboxylation of the terminal hydroxyl groups in the nS-PLA-OH samples was performed by reacting them with succinic anhydride at a 1:1 molar ratio to the hydroxyl groups (**Scheme 3.1**). The reaction was carried out in 1,4-dioxane at 25 °C, using TEA and DMAP as catalysts at 0.5 wt% relative to the prepolymer, following the procedure described by *Kim et al.*¹⁹

3.3 Carboxyl End-Capped 3-Arm, 4-Arm and 6-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers Characterization

Evidence of successful carboxylation of star-shaped PLA (nS-PLA-COOH) was obtained by ¹H-NMR analysis (**Figure 3.2** reports the comparison between the 4S-PLA-OH and 4S-PLA-COOH), which showed the characteristic signals of the methylene groups of the incorporated succinic acid (peak “e” at 2.7 ppm) and the absence of the terminal methin proton signal (peak at 4.2 ppm).

¹H and ¹³C NMR spectra of all the synthesized star-shaped PLAs are shown in **Figures 3.26**, **3.28**, and **3.30** of the Experimental Part of this chapter.

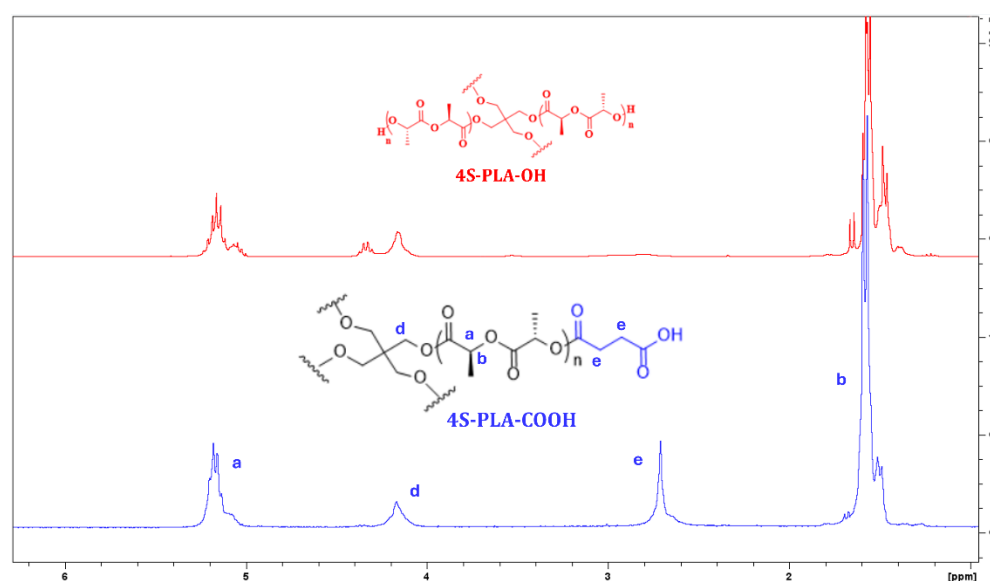


Figure 3.2 - Comparison between the proton NMR spectra of 4S-PLA-OH (red) and 4S-PLA-COOH (blue) (400 MHz, CDCl₃, 298 K)

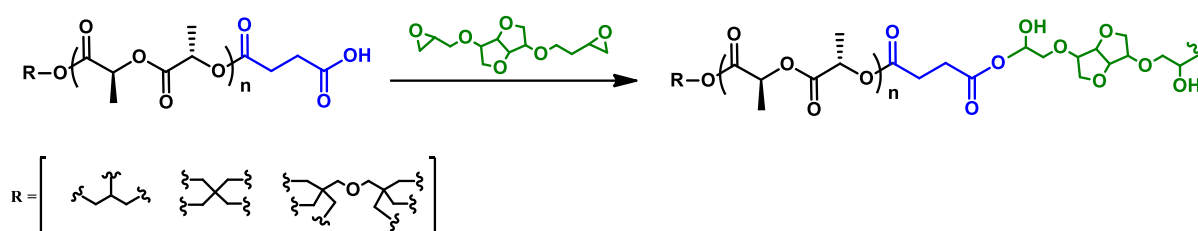
GPC analysis was used to determine the molecular weights of the carboxylated prepolymers, and the results aligned well with the theoretical values expected based on their design. The measured molecular weights were around 1715 Da for 3S-PLA-COOH, 2111 Da for 4S-PLA-COOH, and 3513 Da for 6S-PLA-COOH, showing a consistent increase with the number of branches.

A titration was performed using a 0.1 M KOH solution in methanol to assess the extent of functionalization. The comparison between theoretical and experimental acid values reported in **Table 3.1** shows close agreement and indicates that the introduction of carboxylic groups can be considered complete.

	$M_{n\text{ theo}}$ (Da)	$M_{n\text{ nmr}}$ (Da)	$M_{n\text{ GPC}}$ (Da) ^a	PD	Acid (mmol/g) _{Theo}	Acid (mmol/g) _{Sper}
3S-PLA-COOH	1686	1660	1715	1.5	1.8	1.7
4S-PLA-COOH	2264	2048	2111	1.4	1.8	1.8
6S-PLA-COOH	3446	3428	3513	1.9	1.7	2.0

Table 3.1 - Characterization of *n*S-PLA-COOH. Values of $M_{n\text{ theo}}$ calculated by NMR, ^aexperimental M_n and M_w/M_n ($\bar{D}$) values were determined by GPC analysis in CHCl_3 vs. polystyrene standards. Quantification of $[\text{COOH}]$ calculated by stoichiometry (*theo*) and by titration (*sper*)

3.4 Star-PLA-COOH Crosslinking Reaction with DGEIs



Scheme 3.2 - Crosslinking reaction scheme between *n*S-PLA-COOH and DGEIs

For the crosslinking reaction between *n*S-PLA-COOH and isosorbide diglycidyl ether, $\text{Zn}(\text{OAc})_2$ was selected as the catalyst (**Scheme 3.2**).

To optimize the crosslinking process, we focused solely on 4S-PLA-COOH.

For the procedure, the prepolymer was first mixed with the appropriate amount of DGEIs in dichloromethane. $\text{Zn}(\text{OAc})_2$ was added as a catalyst, dissolved in dry methanol. The mixtures were poured into Teflon Petri dishes, allowed to cast at room temperature overnight, and then cured in an oven under a nitrogen atmosphere.

The study began by varying the molar ratio between epoxy and carboxylic acid functional groups ([epoxy]:[acid]) (**Table 3.2, Entries 4 and 5**). Two different [epoxy]:[acid] molar ratios were tested, 1:1 and 2:1, while keeping the reaction temperature fixed at 180 °C for 3 hours, and using 10 mol% $\text{Zn}(\text{OAc})_2$ with respect to the total acid functionalities.

To evaluate the extent of crosslinking, the gel fraction was measured using the following formula:^{20,21}

$$\% \text{Gel Fraction} = \frac{M_f}{M_i} \times 100$$

M_i = initial sample mass; M_f = final mass

This test was carried out in both boiling chloroform and boiling o-dichlorobenzene.

The gel fraction refers to the portion of the material that remains insoluble after extraction, due to the presence of permanent covalent bonds between polymer chains. A higher gel fraction typically indicates a more densely crosslinked structure.

In addition to this, a swelling test was also performed in boiling chloroform. In this case, the wet sample was weighed after extraction, and the swelling degree was calculated using a specific formula:^{20,21}

$$\% \text{Swelling} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

The extent of swelling provides complementary information to the gel fraction as it indicates the network's ability to swell up without dissolving. Highly crosslinked networks, in general, swell less by virtue of the low mobility of the chains.

The two analyses together provide a complete assessment of the crosslink density as well as the structure of the polymer network.

The 1:1 ratio consistently produced the highest gel content, with values exceeding 90% in both solvents. This suggests that a balanced stoichiometry between epoxy and acid groups favors more efficient network formation. Based on these results, the [epoxy]:[acid] ratio was fixed at 1:1 to study the influence of catalyst concentration.

Reactions were repeated under the same thermal conditions (180 °C, 3 h) using 2, 5, and 10 mol% of Zn(OAc)₂ (**Table 3.2, Entries 1-3**). As expected, the highest gel fraction was observed with 10 mol% catalyst (>90%), followed by 5 mol% (ranging between 78% and 88%). The lowest values were recorded with 2 mol%, where the gel fraction dropped to just over 50%. These findings highlight the crucial role of catalyst concentration in driving the system's crosslinking efficiency.

As a final step, the effect of temperature on the crosslinking reaction was assessed while keeping all other parameters constant (**Table 3.2, Entries 5-7**). Results indicated that a reaction temperature of 180 °C is key for effective network formation, reaching a gel fraction of approximately 60% within just one hour. Lower temperatures (165 °C and 140 °C) resulted in significantly lower gel content in 1 hour, confirming that higher temperatures are necessary to effectively initiate and maintain the crosslinking process.

Entry	[F _x E _{epox}]:[F _z COOH] ratio	Zn(OAc) ₂ (mol-% vs [COOH])	T (°C)	Time (h)	Gel Fraction	%Swelling ^d
1 ^a	1:1	2	180	3	58% ^b /52% ^c	/
2 ^a	1:1	5	180	3	88% ^b /78% ^c	/
3 ^a	1:1	10	180	3	93% ^b /96% ^c	1204
4 ^a	2:1	10	180	3	60% ^b /58% ^c	520
5 ^a	1:1	10	140	1	14% ^b	/
6 ^a	1:1	10	165	1	26% ^b	/
7 ^a	1:1	10	180	1	67% ^b	/

Table 3.2 - Crosslinking tests of ^a4S-PLA-COOH, ^bGel Fraction in boiling CHCl₃, ^cGel Fraction at 150 °C in *o*-dichlorobenzene, under variable process conditions; ^d Swelling in boiling CHCl₃

Overall, the screening results clearly showed that the most reliable curing conditions involve a 1:1:0.1 molar ratio of epoxide, carboxylic acid, and Zn(OAc)₂, respectively, a reaction temperature of 180 °C, and 3 hours in an oven under a nitrogen flow.

At this point, the same curing process was applied to 3S-PLA-COOH and 6S-PLA-COOH to evaluate their behavior. Both samples showed good gel fraction values, although slightly lower than those obtained with 4S-PLA-COOH (**Table 3.3**).

Unfortunately, unlike the films successfully produced from 4S-PLA-COOH and 6S-PLA-COOH, obtaining homogeneous films using 3S-PLA-COOH proved to be quite difficult. The resulting films are not uniform, likely due to the structural characteristics of the starting prepolymer. Therefore, the analysis moving forward will concentrate on the more consistent and reliable results obtained from 4S-PLA-COOH and 6S-PLA-COOH.

Entry	[Fz _{Epoxy}]:[Fz _{COOH}] ratio	Zn(OAc) ₂ (mol-% vs [COOH])	T (°C)	Time (h)	Gel Fraction	%Swelling
3 ^a	1:1	10	180	3	93% ^b /96% ^c	1204
8 ^d	1:1	10	180	3	86% ^b /82% ^c	1017
9 ^e	1:1	10	180	3	75% ^b /84% ^c	1080

Table 3.3 - Crosslinking tests of ^a4S-PLA-COOH, ^d 6S-PLA-COOH, ^e 3S-PLA-COOH, at [Fz_{Epoxy}]:[Fz_{COOH}]=1:1, Zn(OAc)₂ mol% vs [COOH], 180 °C, 3h process conditions, ^bGel Fraction in boiling CHCl₃, ^cGel Fraction at 150 °C in *o*-dichlorobenzene

3.4.1 DSC

Differential Scanning Calorimetry is a thermal analysis technique that measures heat flow into or out of a sample in relation to an inert reference as a function of time or temperature while heating or cooling under controlled conditions. In a crosslinking reaction induced by heat, the process is exothermic because it involves the formation of chemical bonds with the evolution of heat.

When analyzing the pre-curing formulation of 4S-PLA-COOH, the DSC thermogram typically shows a broad exothermic peak, indicating that the crosslinking reaction is taking place during the heating scan (**Figure 3.3, Panel a**). However, this exothermic signal disappears from the DSC trace once the material has been fully cured through thermal treatment (**Figure 3.3, Panel b**). This absence confirms that the reactive groups have already been consumed, and no further crosslinking occurs within the measured temperature range.

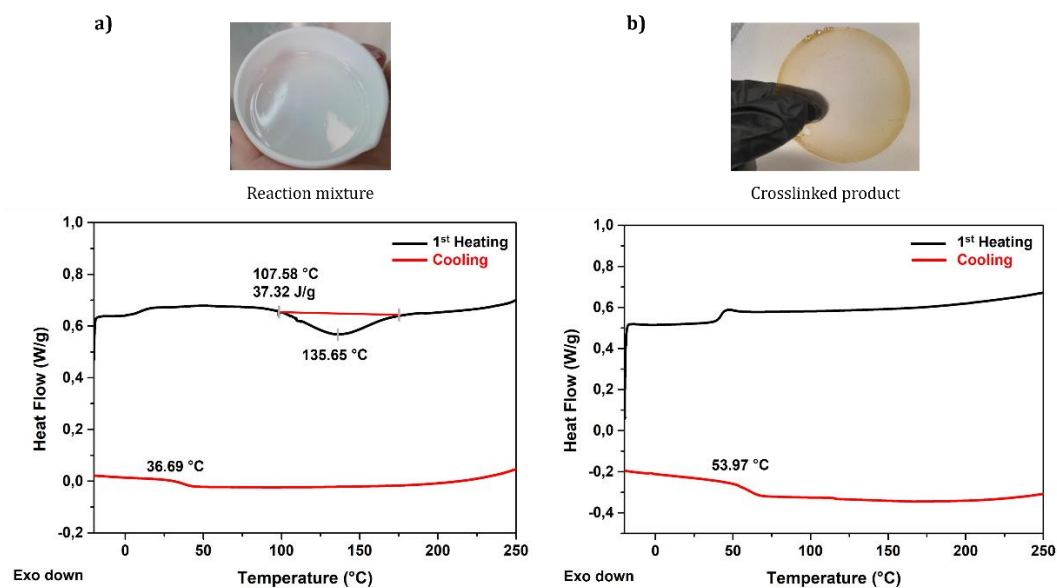


Figure 3.3 - DSC thermograms of 4S-PLA-COOH system: Panel a) uncured reaction mixture DSC, Panel b) cured product DSC (Entry 3)

The DSC results provide further evidence that using 10 mol% of the catalyst leads to the most effective formulation.

Even after curing at 180 °C for 3 hours, samples containing only 2 or 5 mol% of $\text{Zn}(\text{OAc})_2$ still show a residual exothermic peak, suggesting that the crosslinking reaction hasn't fully completed under those conditions (**Figure 3.4**). On the other hand, when 10 mol% of the catalyst is used, this exothermic signal disappears, indicating that the reaction has reached completion.

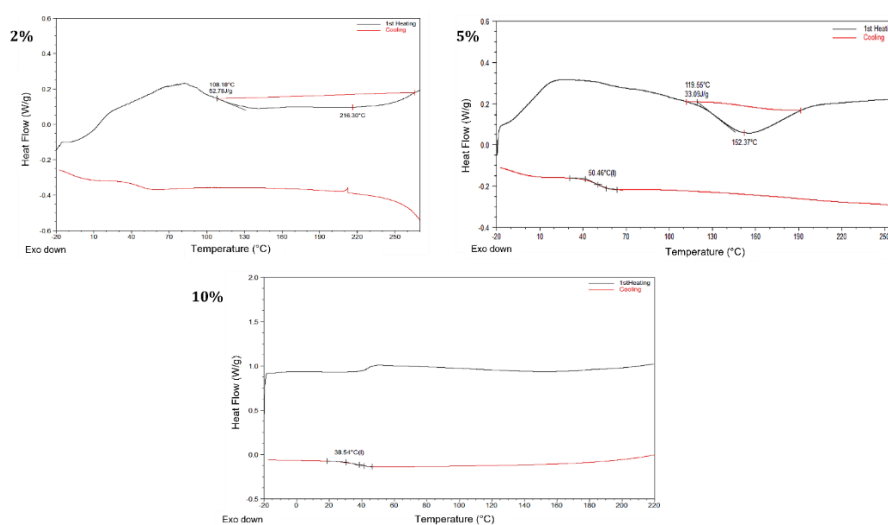


Figure 3.4 - DSC thermograms. Top left: product cured using 2 mol% of $\text{Zn}(\text{OAc})_2$ (Entry 1); Top right: with 5 mol% (Entry 2); Bottom 10 mol% (Entry 3)

The influence of reaction time suggests that a 3-hour curing step may be needed.

This is confirmed by the complete disappearance of the exothermic peak in the DSC thermogram, indicating that the crosslinking reaction has fully completed.

When applying the same curing conditions, using a 1:1 molar ratio of epoxy to carboxylic acid groups, 10 mol% of catalyst (relative to the acid groups), and heating at 180 °C for 3 hours, but this time starting with 6S-PLA-COOH as the prepolymer, a clear exothermic peak appears in the thermogram of the pre-curing mixture (**Figure 3.5, Panel a**). Also, in this case, after thermal treatment, this peak disappears, indicating that the curing reaction has taken place (**Figure 3.5, Panel b**).

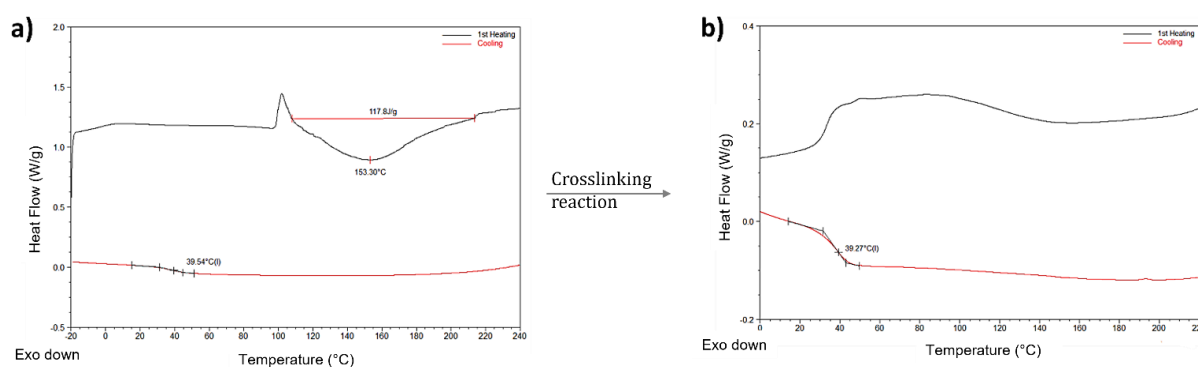


Figure 3.5 - DSC thermograms of 6S-PLA-COOH system: Panel a) uncured reaction mixture DSC, Panel b) cured product DSC (Entry 8)

3.4.2 Rheology Tests

To better define the curing conditions, crosslinking kinetics of the sample were determined using transient-mode rotational rheological measurements.

Particularly, the *Temperature Sweep* and *Time Sweep tests* were conducted using a rotational rheometer, which measures shear stresses as a function of the applied dynamic oscillatory deformation of the sample.

The measurement conditions were optimized based on literature data reported for vitrimer systems.^{22,23}

In the *Temperature Sweep tests*, the sample, initially in a fluid state, was subjected to a constant oscillation frequency of 1 rad/s and a 1% strain while the temperature was steadily increased.

During the test, the evolution of shear stress is followed. With the progression of the crosslinking reaction, stress increases as the polymer matrix solidifies in a gradual manner.

In the *Time Sweep tests*, however, the temperature is maintained constant, and the time evolution of the viscoelastic properties is monitored to analyze the kinetics of the curing process.

The *Temperature Sweep tests* were performed on the pre-cure reaction mixture prepared from 4S-PLA-OH as the prepolymer and following the conditions reported in *Entry 3* of **Table 3.3**.

For simplicity, this will be referred to as the *4S reaction mixture* throughout this paragraph.

The results of the temperature sweep test for the *4S reaction mixture* are presented below (**Figure 3.6**).

The evolution of the storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) is plotted as functions of temperature. These data provide insights into the formation of the internal polymer structure during heating.

As illustrated in **Figure 3.6**, the complex viscosity shows a sharp, exponential rise at around 172 °C, clearly indicating the onset of the crosslinking reaction. This change reflects the thermal activation of chemical bonds that drive the transformation from a fluid material into a solid-like, three-dimensional polymer network.

Time Sweep tests at 140 °C, 165 °C, and 180 °C were performed to investigate the isothermal curing of the *4S reaction mixture* (**Figure 3.7, Panel a**). These measurements allow identifying the main phases of the curing process: initiation, propagation, and stabilization, as the polymer network develops over time. The tests were performed with a constant oscillation frequency of 1 rad/s and a 5% strain.

At 140 °C, the storage (G') and loss (G'') moduli, as well as the complex viscosity (η^*), remain practically constant throughout the test (around 1 Pa·s). This indicates an absence of significant crosslinking, and the resin remains in a liquid-like, precursor state. A steady rheological state is reached by the system, and this can serve as a reference for non-reactive behavior (**Figure 3.7, Panel b**).

At 165 °C, there is a gradual increase of both G' and G'' with time, ranging from approximately 10 Pa to over 1000 Pa. This marks the beginning of active network formation, during which

the material transforms from viscous to more elastic, solid-like behavior. The increase in viscosity confirms the start of the propagation stage, where crosslinking takes place at a moderate rate (**Figure 3.7, Panel c**).

At 180 °C, the rheological response is much more intense. A pronounced rise in both G' and η^* is observed, pointing to a highly efficient crosslinking process, with η^* surpassing 10,000 Pa·s before the end of the test. The system quickly evolves into a stiff elastic network with minimal relaxation, typical of irreversible curing. These results show that 180 °C is the most effective thermal activation to achieve full crosslinking within a short time (**Figure 3.7, Panel d**).

Gel fraction tests were conducted to measure the amount of insoluble gel remaining after 1 hour of treatment at various temperatures (see **Table 3.2**). When combined with rheological data, it becomes clear that temperature has a significant influence on the speed and extent of network formation.

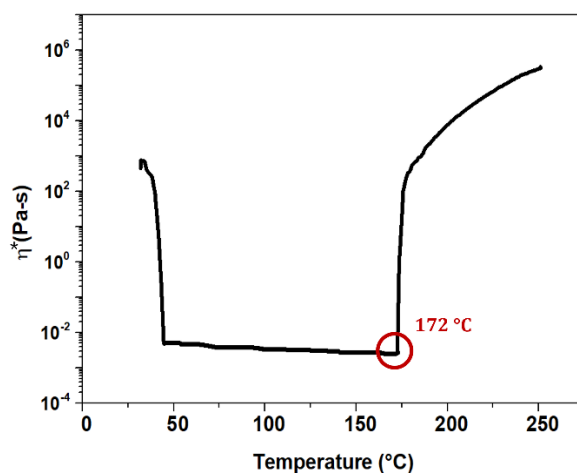


Figure 3.6 - Temperature Sweep Test of 4S reaction mixture (30-250 °C); frequency of 1 rad/s and a 1% strain

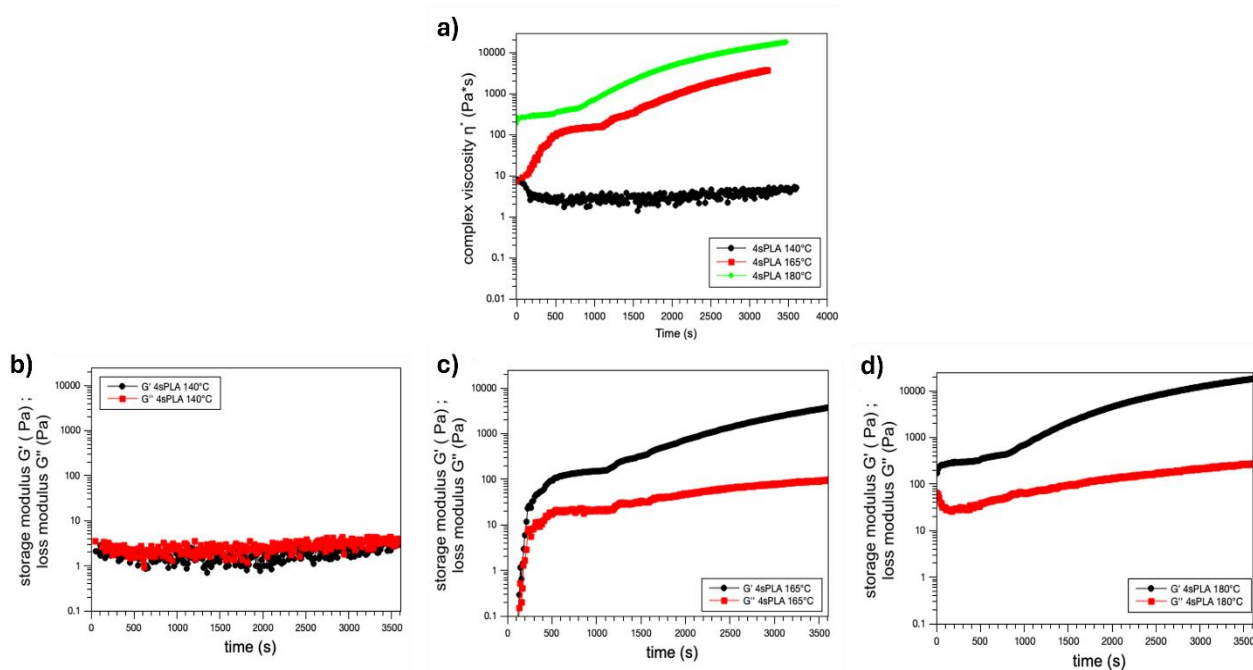


Figure 3.7 - Time sweep test showing the curing kinetics of 4S reaction mixture : (Panel a) complex viscosity vs. time at the three investigated temperatures; (Panel b): G' - G'' vs time at 140 °C for 1 hour; (Panel c): G' - G'' vs time at 165 °C for 1 hour; (Panel d): G' - G'' vs time at 180 °C for 1 hour.

The temperature sweep tests on the 6S-PLA-COOH pre-cured system (6S reaction mixture), conducted under the conditions listed in Entry 8 of **Table 3.3** with a 1% strain and a frequency of 1 rad/s, reveal an activation temperature around 132 °C (**Figure 3.8**). Beyond this point, the viscosity of the system starts to increase, although the rise is quite gradual.

The time sweep measurement on the 6S reaction mixture (**Figure 3.9, Panel a**) follows the same trend observed from the 4S reaction mixture.

In fact, at 140 °C, the resin remains largely unchanged throughout the test. Both the storage modulus (G') and complex viscosity (η^*) stay low and stable, indicating that the curing process is not effectively triggered at this temperature (**Figure 3.9, Panel b**). These values are slightly lower than those observed in the 4-arm system, suggesting that the increased branching further limits chain mobility and delays the start of crosslinking.

At 165 °C, the 6S reaction mixture starts to show early signs of curing, with gradual increases in G' and η^* (**Figure 3.9, Panel c**). Although the initial rise in viscosity is quite fast, the progress soon slows down and after one hour, the modulus does not exceed 10000 Pa, unlike what is

observed at 180 °C, where the curing process becomes significantly more pronounced (**Figure 9, Panel d**).

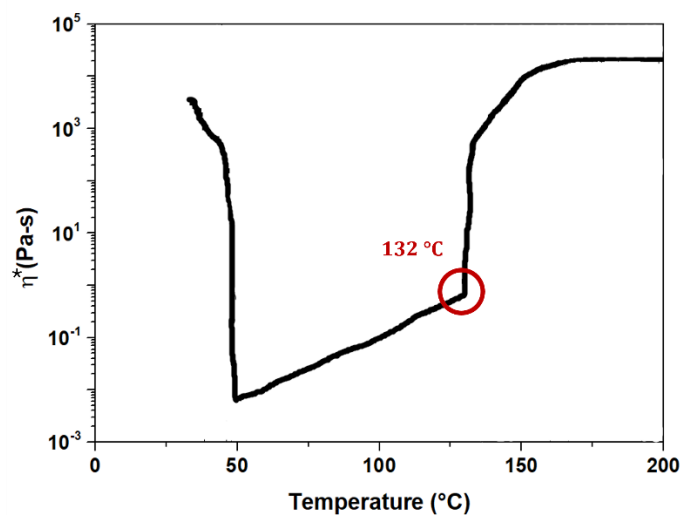


Figure 3.8 - Temperature Sweep Test of 6S reaction mixture system (30-250 °C); frequency of 1 rad/s and a 1% strain

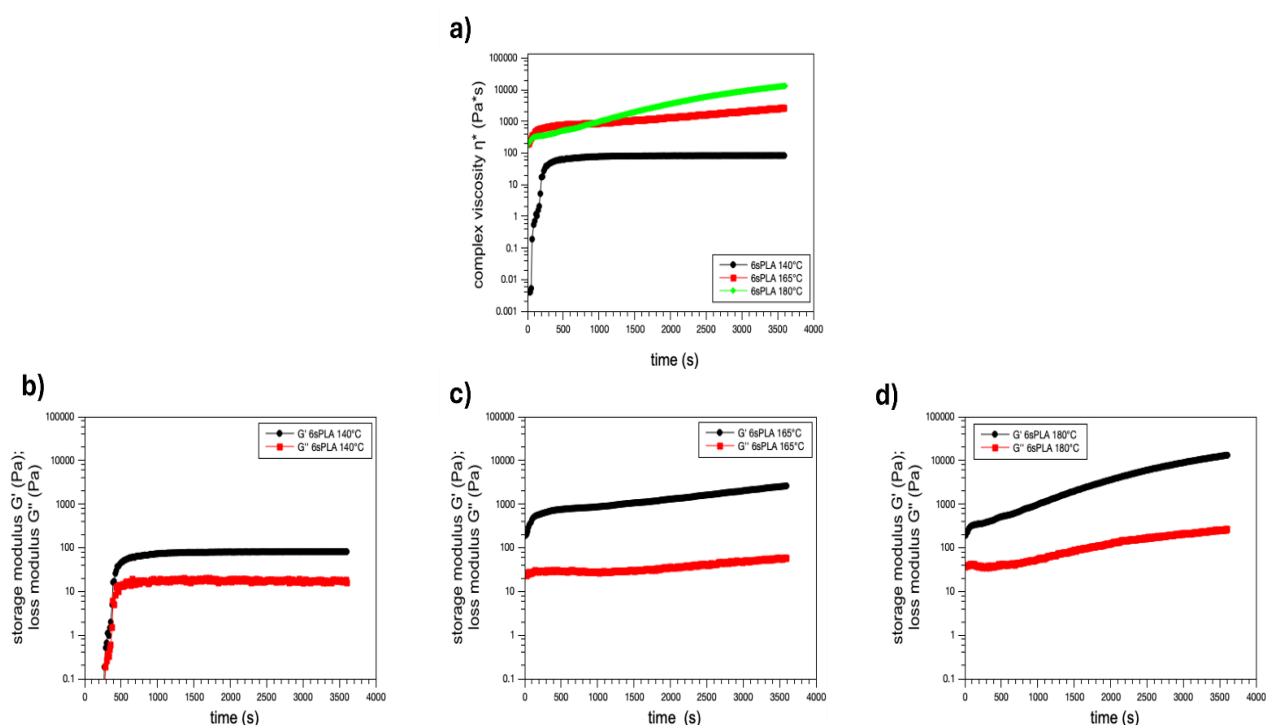


Figure 3.9 - Time sweep test showing the curing kinetics of 6S reaction mixture: (Panel a) viscosity vs. time at the three investigated temperatures; (Panel b): G' - G'' vs time at 140 °C for 1 hour, (Panel c): G' - G'' vs time at 165 °C for 1 hour, (Panel d): G' - G'' vs time at 180 °C for 1 hour.

In the end, comparing the three temperatures, for both systems, reveals a clear trend: the higher the temperature, the faster the reaction and the stronger the network that forms. At 140 °C, no curing occurs; at 165 °C, the system begins to crosslink and gradually builds structure, and at 180 °C, the reaction proceeds quickly, reaching an almost complete cure in a short time.

The rheology results and gel-fraction data show just how critical temperature is in driving the process, indicating that 180 °C is needed to achieve fast, efficient crosslinking and produce a solid, well-developed thermoset network.

3.4.2 TGA

To evaluate the thermal stability and degradation behavior of the crosslinked material obtained from *Entry 3* of **Table 3.3**, thermogravimetric analysis was carried out. The crosslinked polymer was obtained by curing the 4S-PLA-COOH prepolymer under optimized conditions in the presence of $\text{Zn}(\text{OAc})_2$ as a catalyst.

The TGA profile of the 4S-PLA-COOH prepolymer (**Figure 3.10**) reveals a single, well-defined decomposition event, with a Td5% (the decomposition temperature at which the sample has lost 5% of its initial mass) around 209.23°C and a peak degradation rate at approximately 253.6 °C. The material undergoes a total mass loss of about 96.95%, indicating that it is almost entirely organic and fully decomposes under the test conditions.

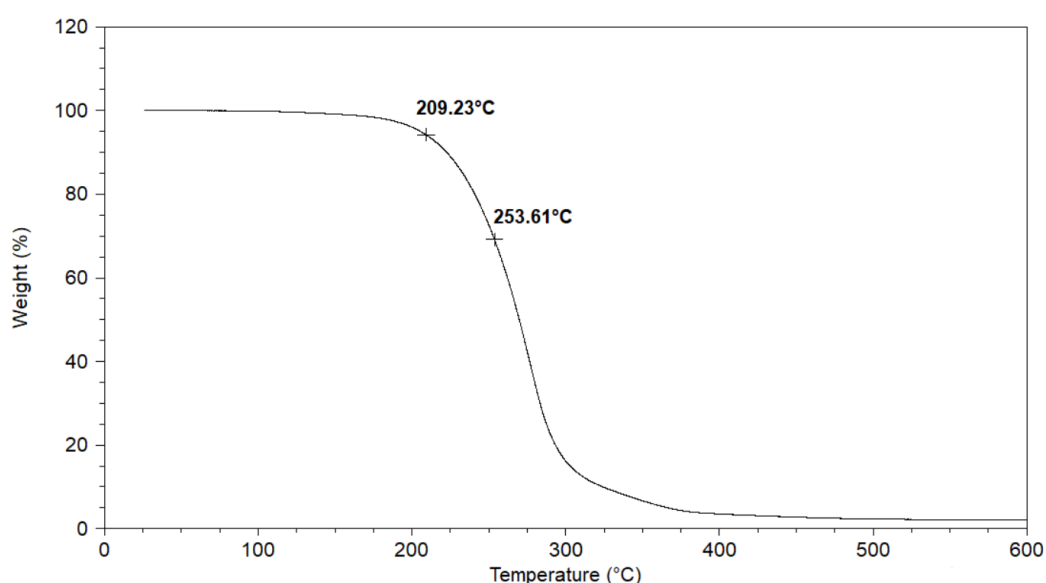


Figure 3.10 - TGA thermogram of 4S-PLA-COOH prepolymer

In contrast, the TGA thermogram of the 4-arms cured material (**Table 3.3, Entry 3**), reported in **Figure 3.11**, shows a significantly different thermal degradation profile. The Td5% is at a higher temperature of approximately 216.85 °C, with the maximum rate of mass loss occurring at around 310.75 °C. The total mass loss is reduced to 84.38%, and a solid residue of approximately 15.6% remains at the end of the analysis. This residue likely consists of non-volatile inorganic components, possibly deriving from the zinc catalyst

The increase of ~70 °C in the degradation onset temperature, along with the higher residual mass, clearly demonstrates the improved thermal stability imparted by the crosslinked network. These findings are in line with similar hybrid epoxy-PLA systems and indicate the formation of a more robust and thermally resistant polymer matrix.

Interestingly, both materials exhibit a single major degradation step, suggesting a high degree of chemical homogeneity. However, the shift in thermal behavior after curing confirms that the crosslinking reaction proceeded efficiently and uniformly throughout the material, with no evidence of unreacted monomers or phase separation, which would typically be reflected in a multi-step degradation pattern.

Overall, the TGA analysis highlights the significant difference between the prepolymer and the cured material. The crosslinked material of *Entry 3* demonstrates superior thermal performance and structural integrity compared to 4S-PLA-COOH, validating the effectiveness of the curing process catalyzed by $\text{Zn}(\text{OAc})_2$.

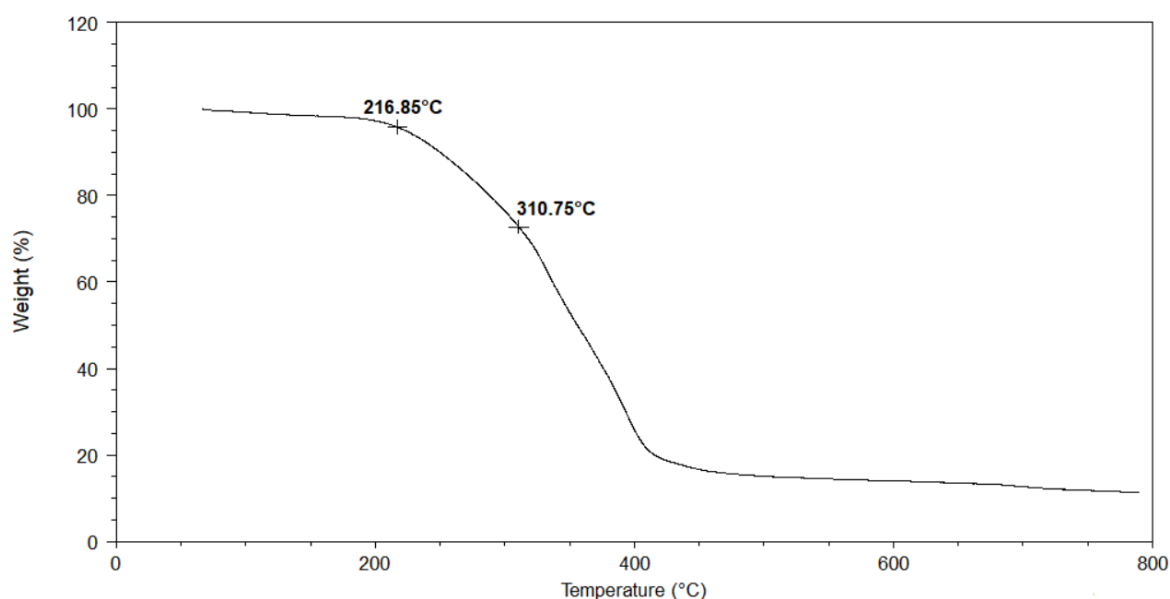


Figure 3.11 - TGA thermogram of 4-arms cured material related to Entry 3 of Table 3.3

Thermogravimetric analysis was also carried out on the 6-arms crosslinked material (**Table 3.3, Entry 8**), obtained by curing the corresponding 6S-PLA-COOH prepolymer under the same optimized conditions previously used for the 4S-based system.

Similar to the behavior observed for 4S-PLA-COOH, the 6S-PLA-COOH prepolymer displays a single, well-defined degradation step, with a Td5% of 201.48°C and reaching its maximum rate of degradation at around 262.2 °C (**Figure 3.12**). The total mass loss recorded is 95.33%, confirming that the material is largely organic and undergoes nearly complete thermal decomposition.

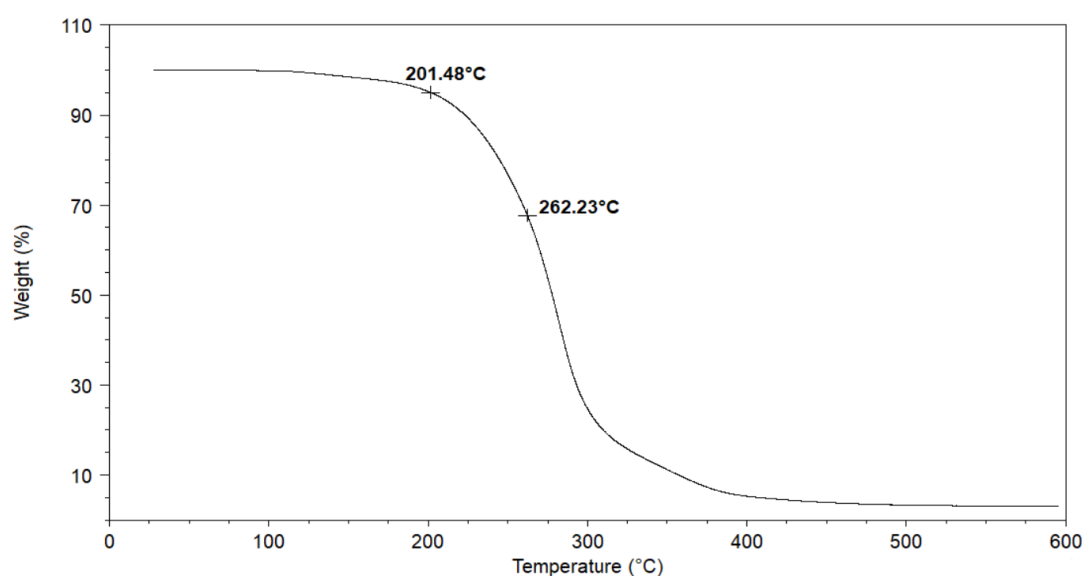


Figure 3.12 - TGA thermogram of 6S-PLA-COOH prepolymer

Once cured, the 6-arms cured material from *Entry 8* shows a thermal degradation profile very similar to that of the 4-arms in *Entry 3*, with the Td5% occurring around 227.03 °C and a peak at approximately 304.81 °C (**Figure 3.13**). The total weight loss is about 85.9%, which is in close agreement with the value observed for the 4S-based crosslinked material.

These results suggest that, despite the structural differences between the 4-arms and 6-arms systems, both formulations respond similarly to the curing process. The comparable degradation temperatures and mass losses indicate that the crosslinking reaction proceeded efficiently in both cases, leading to polymer networks with similar thermal stability.

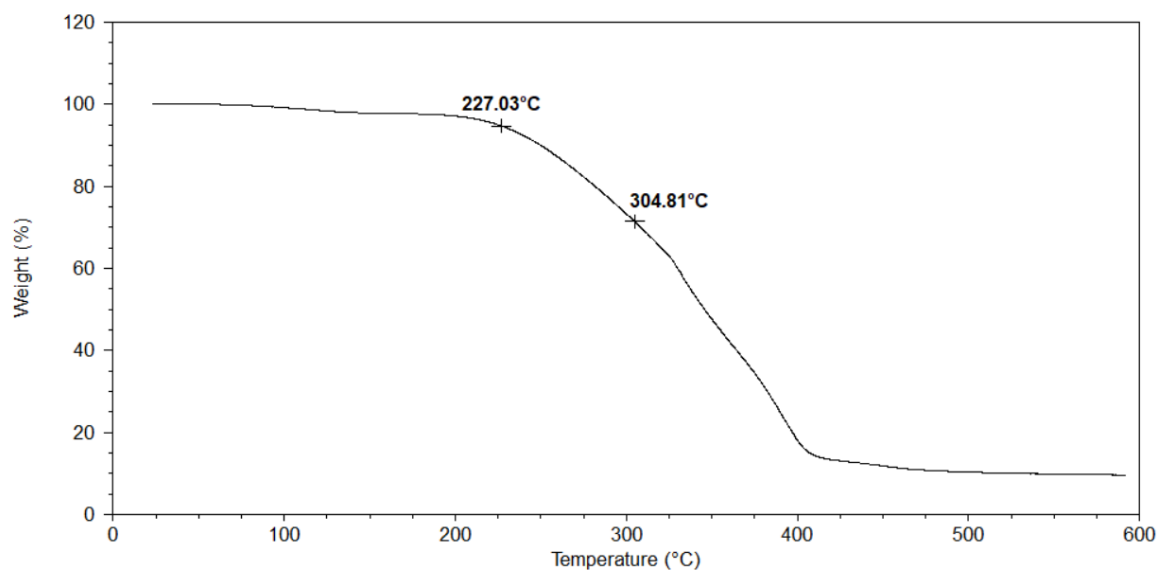


Figure 3.13 - TGA thermogram of 6-arms cured material related to Entry 8 of Table 3.3

To further advance the discussion and get a more accurate characterization of the materials, a new set of cured samples was prepared in this work using both 4S-PLA-COOH and 6S-PLA-COOH as prepolymers. The film thickness was varied in this phase so that samples of 50 μm and 250 μm were prepared (**Table 3.4**).

A sample cured at 165 °C for 3 hours was also included, since the rheological data show that the reaction, at this temperature, does proceed, although at a slower rate. After 3 hours at 165 °C, an insoluble product with a high gel fraction was indeed obtained (*Entries 11 and 13*).

For *Entry 11*, the gel fraction remains lower than the value reached after curing for 3 hours at 180 °C. In contrast, the *Entry 13* sample prepared from the 6-arm prepolymer shows a gel fraction comparable to that achieved at 180 °C for the same curing time. This behavior aligns well with the time-sweep results, where the increase in viscosity for the 6-arm system progresses at a rate much closer to that observed at higher temperatures.

Entry	ns-PLA(COOH) Acid (mmol/g _{sper})	T (°C)	Gel Fraction	Swelling (%)	Thickness (μm)
10^a	1.8	180	95%	1129	50
11^a	1.8	165	70%	1298	50
12^b	2.0	180	96%	1005	50
13^b	2.0	165	98%	957	50
14^a	1.8	180	95%	680	250
15^b	2.0	180	93%	830	250

Table 3.4 – Preparation conditions for the new set of cured samples at different thicknesses: ^a Tests carried out using 4S-PLA-COOH; ^b Tests carried out using 6S-PLA-COOH; all tests are carried out with $[F_{X_{Epoxy}}]:[F_{Z_{COOH}}] = 1:1$, 10 mol% of $Zn(OAc)_2$ (mol-% vs $[COOH]$) and 3 hours as reaction time

3.4.3 FT-IR

The films obtained from the tests corresponding to *Entries 10* and *12* in **Table 3.4**, prepared by curing the 4S-PLA-COOH and 6S-PLA-COOH prepolymers, respectively, were analyzed by Transform Infrared Spectroscopy, a qualitative technique that helps identify the functional groups in the material.

Looking specifically at the samples of *Entry 10*, the spectra show the presence of the expected functional groups (**Figure 3.14**).

A broad band around 3400 cm^{-1} corresponds to the O–H stretching of hydroxyl groups, which form as a result of epoxide ring-opening during the transesterification reaction with the terminal carboxylic acids of the prepolymer.

The ester carbonyl stretching is clearly visible around 1750 cm^{-1} . In the fingerprint region, two distinct areas between $1350\text{--}1250\text{ cm}^{-1}$ and $1200\text{--}950\text{ cm}^{-1}$ are associated with C–O stretching vibrations and the skeletal modes of the polymer backbone.

The FT-IR data show that the key functional groups are consistently retained across all samples.

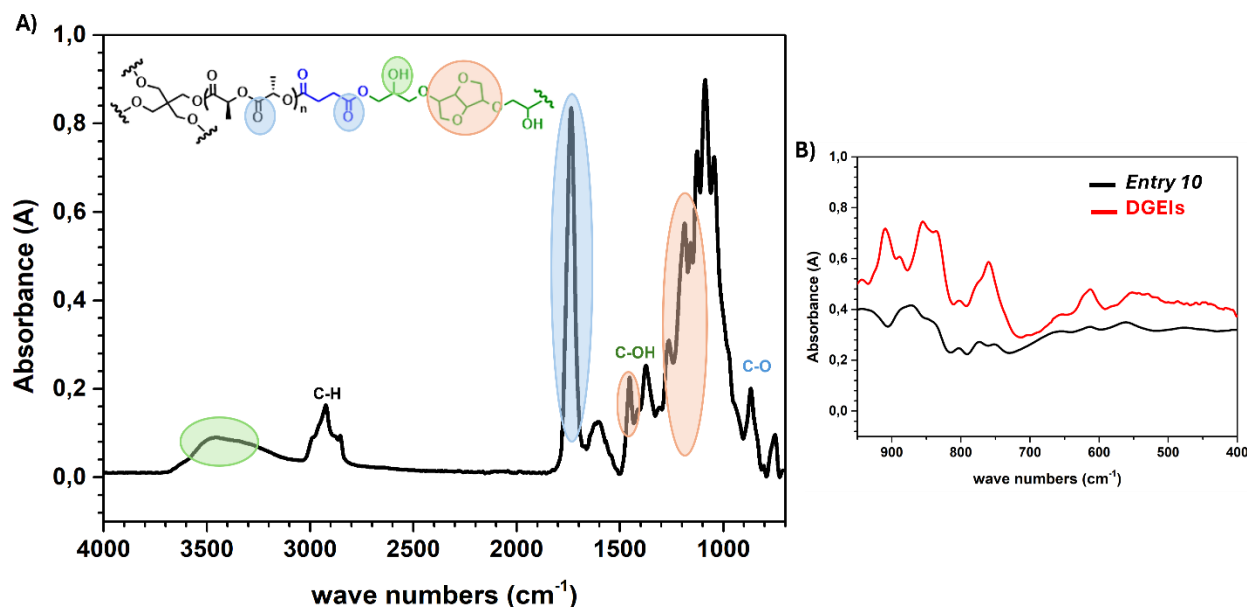


Figure 3.14 – A) FT-IR of Entry 10, Table 3.4, with the main functional groups highlighted; B) Magnification of the $<950\text{ cm}^{-1}$ region with comparison to the DGEIs FTIR spectrum (red), showing the decrease and disappearance of fingerprint signals associated with epoxide rings.

The FT-IR analysis of *Entry 12* film shows an identical pattern of signals, confirming the presence of the main functional groups typical of the product's structure (**Figure 3.15**).

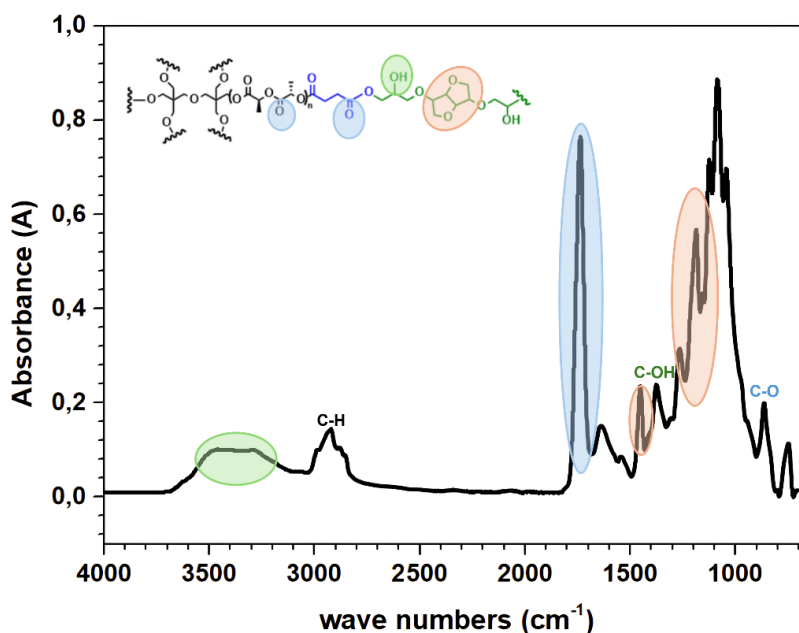


Figure 3.15 - FT-IR of Entry 12, Table 3.4, with the main functional groups highlighted

3.4.4 SEM

SEM analysis shows that both the 4-arm and 6-arm crosslinked systems cured at 180 °C (*Entries 10 and 12 in Table 3.4*), as well as those cured at 165 °C (*Entries 11 and 13*), present a fairly uniform and compact morphology. No visible cracks or fractures are detected, indicating that all samples maintain good structural integrity under the tested conditions.

In the samples cured at 180 °C reported in **Figure 3.16**, the images on the left, corresponding to the 4-arm system, display a smoother and more homogeneous surface, which suggests better phase compatibility and a more uniform curing process.

The images on the right, representing the 6-arm system, show a slightly more heterogeneous morphology, likely resulting from a different internal reorganization during curing. This behavior is consistent with the distinct molecular architecture of the 6-arm material.

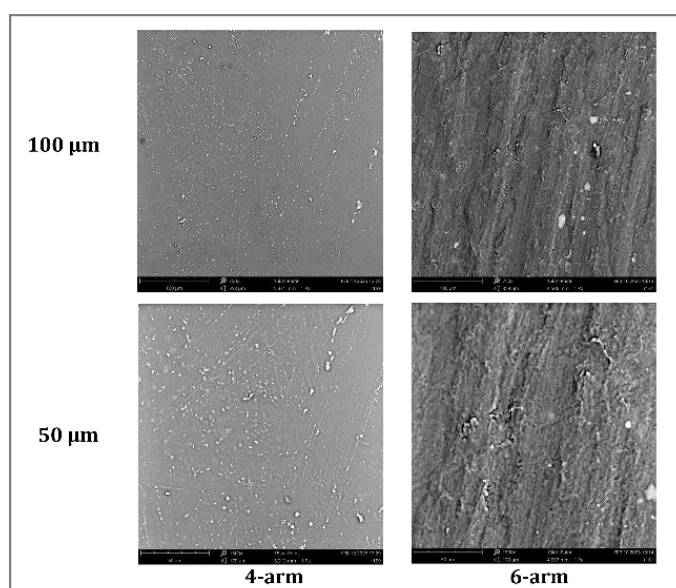


Figure 3.16 - SEM micrographs at different magnifications (100–50 μm) of Entry 10 (left) and Entry 12 (right) of Table 3.4, cured at 180 °C for 3 hours

In the samples cured at 165 °C (**Figure 3.17**), the images on the left, corresponding to the 4-arm system (*Entry 11*), display a more heterogeneous matrix, likely due to incomplete curing. At this temperature, the gel fraction reaches only about 70%, indicating that the material is not yet fully crosslinked.

In contrast, the images on the right, corresponding to the 6-arm system (*Entry 13*), show smoother and more uniform surfaces. This suggests that curing at a lower temperature allows the polymer chains in the 6-arm system to reorganize more homogeneously during the curing process.

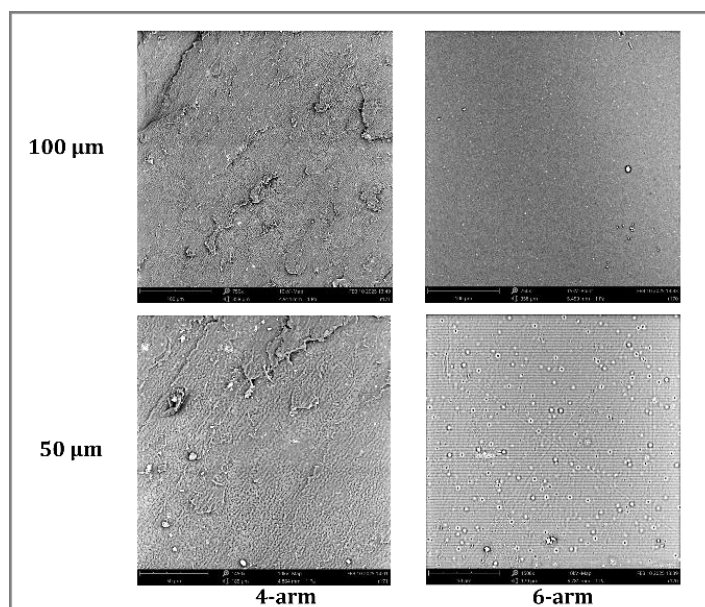


Figure 3.17 - SEM micrographs at different magnifications (100–50 μm) of *Entry 11* (left) and *Entry 13* (right) of *Table 4*, cured at 165 °C for 3 hours

In any case, for all samples, the surface is smooth and flat, with a spherulitic structure well-distributed and an average diameter of about 50 nm.

These small features appear to be connected to the presence of the Zn(II) catalyst. Overall, the microstructure suggests that the catalyst is well dispersed and stable network structure.

3.4.6 Tensile Tests

Mechanical properties were calculated for 4-arm and 6-arm samples crosslinked under the same conditions ([COOH]:[fz epox] ratio of 1:1, using 10 mol% of Zn(OAc)₂ with respect to [COOH], at 180 °C for 3h in an oven under nitrogen) but with varying thickness, 50 μm (*Samples 10* and *12*, related to *Entries 10* and *12*, **Table 3.4**) and 250 μm (*Samples 14* and *15*, of *Entries 14* and *15*, **Table 3.4**). The aim was to investigate the effect of sample thickness on the tensile properties of cross-linked networks.

At a lower sample thickness of 50 μm , the measured mechanical properties from tensile testing are presented in **Table 3.5**, and the stress-strain curves are shown in **Figure 3.18**:

Sample (see Table 3.4)	Young Modulus E (Mpa)	Tensile strength σ (Mpa)	Elongation at break ϵ_b (%)	Thickness (μm)
10 ^{a,c}	854 $\pm$ 12	13 $\pm$ 1.8	6.4 $\pm$ 1.8	50
11 ^{a,d}	925 $\pm$ 6	16.0 $\pm$ 1.6	3.8 $\pm$ 2	50
12 ^{b,c}	910 $\pm$ 8	14.4 $\pm$ 2	3.8 $\pm$ 0.6	50
13 ^{b,d}	914 $\pm$ 16	14.7 $\pm$ 1	4 $\pm$ 0.3	50

Table 3.5 – Mechanical properties from tensile tests: elastic modulus (E), yield strength (σ_y), and elongation at break (ϵ_B), extracted from the corresponding stress–strain curves. The tests were performed at 25 °C on prismatic specimens (width = 5 mm, length = 30 mm, thickness $\approx$ 50 μm), using a constant crosshead speed of 1 mm/min until sample failure. Each test was conducted on a minimum of eight replicates. ^a Tests carried out using 4S-PLA-COOH as prepolymer; ^b Tests carried out using 6S-PLA-COOH as prepolymer, ^c cured at 180 °C for 3 hours, ^d cured at 165 °C for 3 hours

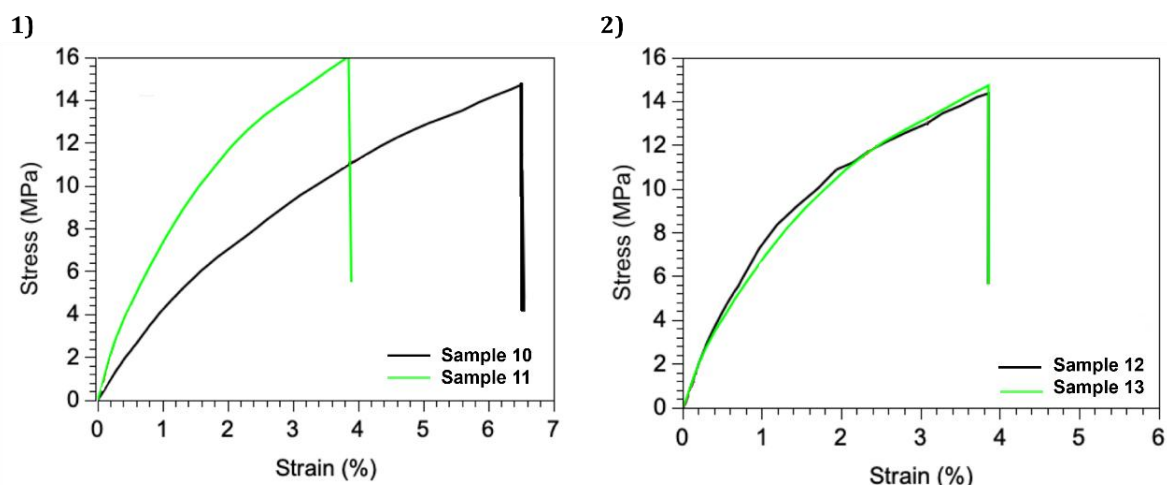


Figure 3.18 – Stress-strain curves: 1) Tests carried out using 4S-PLA-COOH as prepolymer at 180 °C (black) and 165 °C (green); 2) Tests carried out using 6S-PLA-COOH as prepolymer at 180 °C (black) and 165 °C (green)

For the thinner samples (50 μm), cured at 180 °C for 3 hours, the results show that the 4-arm based system (*Sample 10*) is slightly stiffer and stronger than the 6-arm based system (*Sample*

12), with a Young's modulus of 910 ± 8 MPa and tensile strength of 14.4 ± 2 MPa, compared to 854 ± 12 MPa and 13 ± 1.8 MPa for *Sample 10*. However, this comes at the expense of flexibility: the elongation at break for *Sample 12* is significantly lower ($3.8 \pm 0.6\%$) than that of *Sample 10* ($6.4 \pm 1.8\%$), suggesting a more brittle behavior.

When comparing the properties of samples cured at different temperatures (*Samples 10* and *12* at 180°C , and *Samples 11* and *13* at 165°C), distinct differences emerge between the 4-arm and 6-arm systems, consistent with the trends observed in earlier characterizations (**Figure 3.18**).

For the 4-arm materials (*Samples 10* and *11*, **Table 3.5**), reducing the curing temperature from 180°C to 165°C leads to an increase in Young's modulus and tensile strength (from 854 MPa to 925 MPa and from 13 MPa to 16 MPa, respectively), while the elongation at break drops from 6.4 % to 3.8 %. This indicates a stiffer, yet less ductile material, likely due to incomplete crosslinking at the lower temperature.

In contrast, the 6-arm system (*Samples 12* and *13*) shows very similar mechanical properties regardless of the curing temperature, with Young's modulus around 910–914 MPa, tensile strength between 14.4 and 14.7 MPa, and elongation at break of about 4 %.

When the thickness increases to 250 μm , both materials show a marked improvement in mechanical performance (**Table 3.6, Figure 3.19**). The stiffness more than doubles for the 4-arm based system (*Sample 14* related to *Entry 14, Table 3.4*), reaching 1900 MPa, and increases to 1400 MPa for the 6-arm based material (*Sample 15* related to *Entry 15, Table 3.4*).

At the same time, ductility increases dramatically in both systems, with elongation at break values of $43 \pm 5\%$ and $48 \pm 3\%$ for *Sample 14* and *Sample 15*, respectively.

These improvements suggest that thicker samples allow for more complete network formation during curing, likely due to better thermal retention and more uniform reaction progression throughout the material.

Sample (see Table 3.4)	Young Modulus E (Mpa)	Tensile strength σ (Mpa)	Elongation at break ϵ_b (%)	Thickness (μm)
14 ^a	1900 ± 2	11 ± 0.5	43 ± 5	250
15 ^b	1400 ± 1.5	10 ± 1	48 ± 3	250

Table 3.6 - Mechanical properties from tensile tests: elastic modulus (E), yield strength (σ_y), and elongation at break (ϵ_b), extracted from the corresponding stress-strain curves. The tests were performed at 25 °C on prismatic specimens (width = 5 mm, length = 30 mm, thickness $\approx 50 \mu\text{m}$), using a constant crosshead speed of 1 mm/min until sample failure. Each test was conducted on a minimum of eight replicates. ^a Tests carried out using 4S-PLA-COOH as prepolymer; ^b Tests carried out using 6S-PLA-COOH as prepolymer; ^c cured at 180 °C for 3 hours; ^d cured at 165 °C for 3 hours

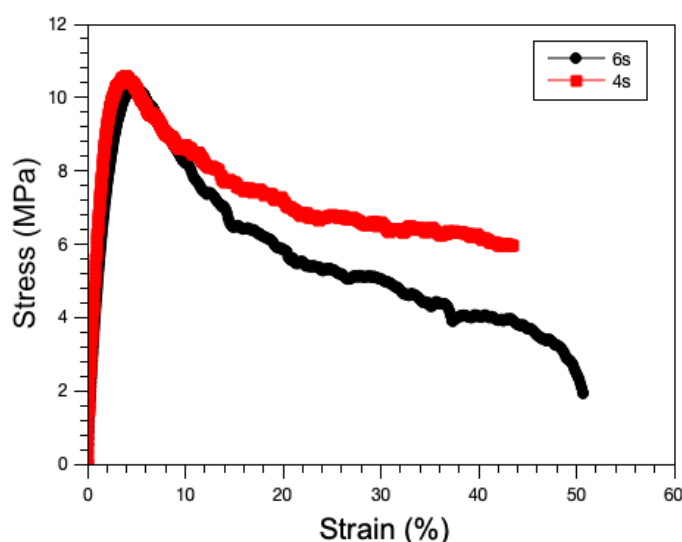


Figure 3.19 – Stress-strain curves of thicker samples; tests carried out on Sample 14 (red); tests carried out on Sample 15 (black)

Interestingly, tensile strength remains relatively stable across both thicknesses and formulations, with values ranging between 10.5 and 14.4 MPa. This consistency implies that ultimate strength is less sensitive to these parameters, possibly being more affected by inherent material properties or failure mechanisms like microcrack formation.

Comparing the two formulations, cured at 180 °C, a few trends emerge. In the thin samples, the 6-arm-based material appears stiffer but more brittle, while the 4-arm-based system is slightly more flexible.

In the thick samples, however, the differences between the two systems are less pronounced: the 4-arm-based shows higher stiffness, while the 6-arm-based maintains slightly better elongation.

This suggests that formulation influences become more evident when the network is less developed, as in thinner films, while thicker samples benefit more from curing conditions and geometry, leading to overall improved and more comparable performance.

These observations highlight that mechanical behavior is determined by formulation and sample thickness.

3.4.7 Dynamic Mechanical Analysis

Due to the significant improvement in mechanical properties observed in *Samples 14* and *15* and considering that thicker specimens allow for more accurate measurements because of the sensitivity of the instrument, only the thicker samples were selected for further testing.

DMA analysis was therefore performed to gain a deeper understanding of their viscoelastic behavior and thermal transitions, and to evaluate the impact of network architecture on the performance of these optimized vitrimeric systems.

The key results are summarized in **Table 3.7**.

Sample (see Table 3.4)	E' (GPa)	E'' (GPa)	T _g (°C)
14 ^a	2.26	283	34
15 ^b	1.97	213	35

Table 3.7 - Mechanical properties from DMA of crosslinked samples. Tests were performed within the range 25-60 °C with a heating rate = 1 °C/min, 0.05% of dynamic strain amplitude, and 1 Hz as frequency.
^a Test carried out using 4S-PLA-COOH as prepolymer; ^b Test carried out using 6S-PLA-COOH as prepolymer

Figure 3.20 below presents, in Panel A, the storage modulus as a function of temperature and the loss modulus as a function of temperature (Panel B), with E' highlighted for *Sample 14* (black) and *Sample 15* (red).

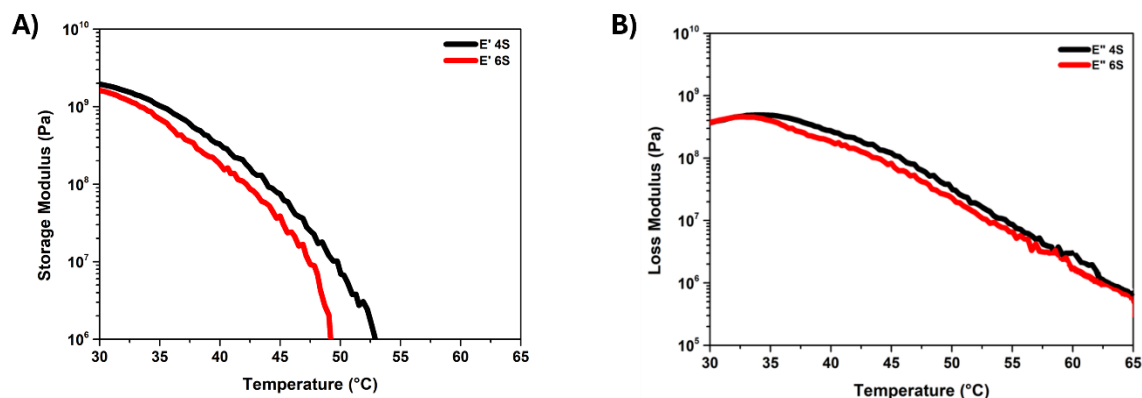


Figure 3.20 - DMA curves. Panel A: storage modulus vs Temperature, Panel B: loss modulus vs temperature of Sample 14 (black curve) and Sample 15 (red curve)

Upon reviewing the data, it appears that the mechanical behavior of the two samples is broadly similar. Both samples demonstrate high stiffness, with E' values exceeding 1.9 GPa. Moreover, the loss modulus curves, presented in **Figure 3.20, Panel b**, display comparable trends, with the 4-arm-based sample exhibiting a slightly lower T_g than the 6-arm-based sample (34 vs 35 °C). These findings indicate that the two systems possess a well-formed and highly crosslinked network. This is an encouraging result that confirms the effectiveness of the formulation strategies employed.

However, *Sample 14* shows slightly higher values for both the storage modulus (E') and the loss modulus (E''). Despite these subtle differences, it's important to highlight that the two systems behave remarkably similarly overall, which is a strong indication that both network architectures offer good crosslinking efficiency and mechanical integrity. This makes both materials viable candidates for applications where reprocessability, dimensional stability, and dynamic performance are essential.

3.4.8 Stress-Relaxation Test

Stress relaxation tests were carried out on the 4-arm-based system (*Sample 14*) at three different temperatures to explore the viscoelastic response of the materials: 60 °C, 120 °C, and 140 °C. The tests were conducted with 3% of static strain, a heating rate of 5 °C/min and 0.5 N of maximum applied force. The results are shown in **Figure 3.21 Panel A**, where the normalized shear modulus (G_t/G_0) is plotted over time on a logarithmic scale.

At the lower temperature of 60 °C, the network retained most of its stiffness over time, indicating very limited relaxation and a predominantly elastic behavior. As the temperature increased, a clear acceleration in stress relaxation was observed. At 120 °C and even more so at 140 °C, the material softened more rapidly, which is consistent with the thermal activation of dynamic bond exchange reactions characteristic of vitrimers.

T (°C)	τ^* (s)
60	503
120	306
140	113

Table 3.8 – Relaxation time τ^* values for each temperature studied for Sample 14

This behavior is quantified by the relaxation time (τ^*), the point at which the modulus drops to about 37% (1/e) of its initial value. At higher temperatures, τ^* decreases significantly, highlighting that the network becomes more mobile and able to rearrange its internal structure more quickly.

Figure 3.21 Panel B further illustrates the Arrhenius-type dependence of the stress relaxation process. Plotting $\log(\tau^*)$ against the inverse of temperature ($1000/T$) reveals a linear trend, confirming that the material follows an Arrhenius-type behavior.

From this linear fit, the activation energy (E_a) for the bond exchange process was calculated to be 28 kJ/mol using the Arrhenius equation:²⁴

$$\tau^* = \tau_0 e^{-\frac{E_a}{RT}}$$

R= ideal gas constant, T= temperature,
 τ_0 = pre-exponential factor

Based on this relationship, the vitrimeric transition temperature (T_v), the point at which the polymer network becomes sufficiently dynamic to allow significant flow due to bond exchange, was extrapolated to be 43 °C, using a reference relaxation time of 10^4 seconds. This temperature is commonly associated with a network viscosity of 10^{12} Pa·s, a standard benchmark for defining T_v in vitrimers. The relatively low T_v indicates that the material

remains dimensionally and mechanically stable at room temperature, while still capable of topological rearrangement, reprocessing, or self-healing when exposed to moderately elevated temperatures.

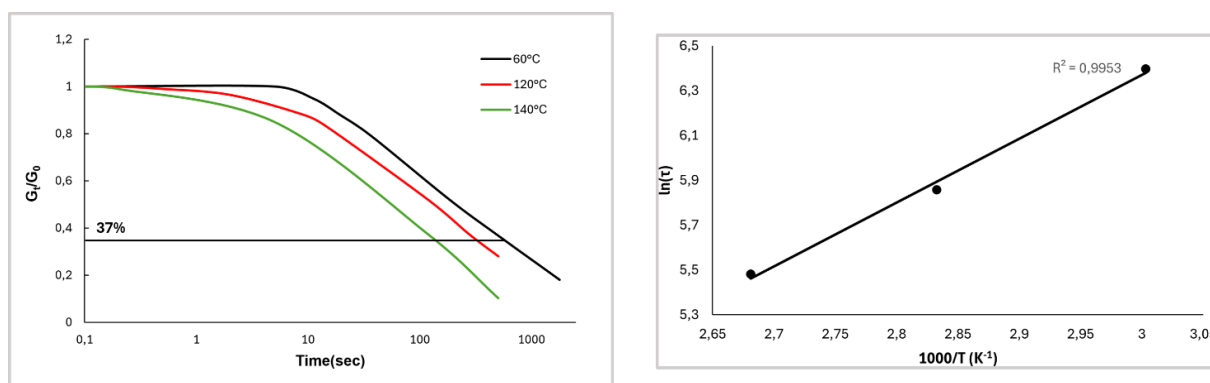


Figure 3.21 – Stress-relaxation graphs. Panel A: stress relaxation behavior of Sample 14 (140 °C (green), 120 °C (red), 60 °C (black)); Panel B: Arrhenius analysis. Tests were conducted with 3% of static strain, a heating rate of 5 °C/min and 0.5 N of maximum applied force.

Figure 3.22 shows the stress relaxation behavior of a 6-arm-based system, *Sample 15* (Panel A) and its related Arrhenius analysis (Panel B). As expected, the normalized shear modulus (G_t/G_0) decreases as temperature rises, indicating the material's gradual softening.

At intermediate temperatures, especially at 120 °C, the 6-arm network maintains its stiffness longer than the previously studied four-arm system. This slower relaxation suggests that the material takes more time to start flowing, likely because the extra arms in the network create a tighter, more interconnected structure that resists movement.

From the τ^* values obtained for *Sample 15* and reported in **Table 3.9**, it is possible to determine E_a and T_v of the material.

T (°C)	τ^* (s)
60	900
120	203
140	101

Table 3.9 - Relaxation time τ^* values for each temperature studied for Sample 15

The activation energy for the 6-arm system is 32 kJ/mol, slightly higher than the 28 kJ/mol calculated for the 4-arm system. This difference is also reflected in the vitrimeric transition temperature, which increases from 43 °C in the 4-arm system to 66 °C in the 6-arm system.

Although the 4-arm and 6-arm vitrimeric materials have different transition temperatures (43 °C and 66 °C), both values are low enough to allow reprocessing under mild conditions. This makes both systems suitable for applications requiring recyclability, reconfigurability, or self-healing, depending on specific performance needs.

The difference in network architecture mainly offers a way to fine-tune the balance between flowability and structural integrity, without limiting either material to a narrow set of applications.

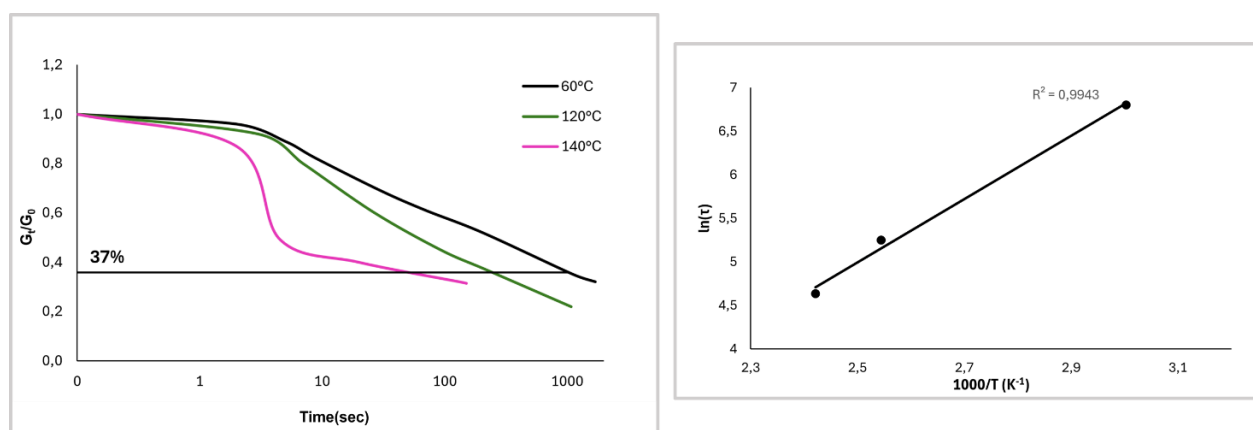


Figure 3.22 - Stress-relaxation graphs. Panel A: stress relaxation behavior of a Sample 15 (140 °C (pink), 120 °C (green), 60 °C (black)); Panel B: Arrhenius analysis

3.5 Water Contact Angle

The contact angle is a widely used macroscopic parameter for characterizing the wettability of solid surfaces.²⁵ It offers valuable insights into the surface's chemical composition, physical structure, and interfacial energy.²⁶ By analyzing the contact angle formed between a liquid droplet and a solid substrate, one can determine important surface properties, such as surface free energy, surface roughness, and whether the surface is hydrophobic or hydrophilic (**Figure 3.23**). This information is particularly relevant for various industrial and technological applications, including coating processes, adhesion, lubrication, and adsorption phenomena.²⁷

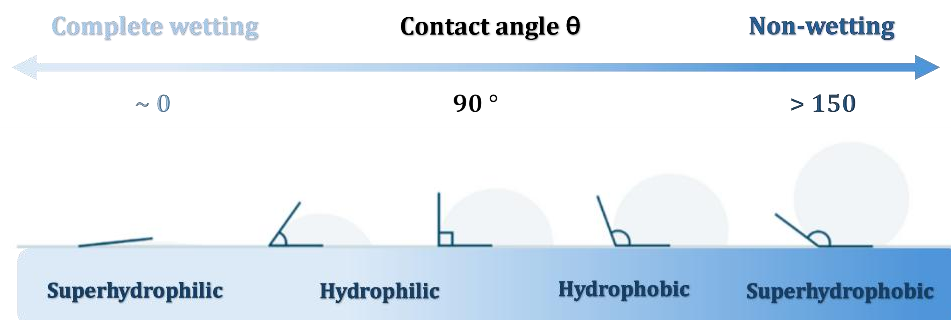


Figure 3.23 - Classification of surface wettability based on contact angle measurements

Time-dependent water contact angle measurements, along with droplet shape analysis, highlight noticeable differences in surface wettability and energy across the vitrimer formulations (**Figure 3.24**, left). The 4-arm-based material (*Sample 10*, **Table 3.5**), tends to show more hydrophobic and stable surface behavior over time compared to its 6-arm-based counterparts (*Sample 12*, **Table 3.5**).

In particular, *Sample 10* exhibits relatively high initial contact angles, around 65° , that remain quite stable over a 1000-second measurement window (**Figure 3.24**, right).

This suggests lower surface energy and limited water affinity, possibly due to a reduced presence of polar groups at the surface or restricted water uptake.

In contrast, the 6-arm *Sample 12* displays significantly lower contact angles, around 38° , and shows faster spreading over time, indicating greater wettability and a more hydrophilic surface nature (**Figure 3.24**, right).

These differences can be attributed to the underlying network architecture.

Compared to the 6-arm systems, the 4-arm vitrimer networks show a more hydrophobic surface. This points to a less wettable, lower-energy interface, likely because fewer polar groups are available at the surface.

In fact, after curing, a hydroxyl group is formed due to the opening of the epoxide (see **Scheme 3.1**), so the 6-arm system ends up with approximately 50% more OH groups in the final network, providing a straightforward explanation for its higher surface wettability.

Moreover, the limited chain mobility and greater steric hindrance in these 4-arm systems not only contribute to their surface stability but also influence how the material responds mechanically and behaves at interfaces.

This structural difference likely explains the more stable and higher contact angles observed in *Sample 10* compared to the 6-arm formulation.

Overall, the comparison shows that 4-arm vitrimeric materials offer more hydrophobic and temporally stable surfaces.

These characteristics are especially valuable in applications where water resistance, surface durability, and controlled interfacial behavior are crucial, such as in advanced coatings, moisture barriers, and materials used in challenging environments.

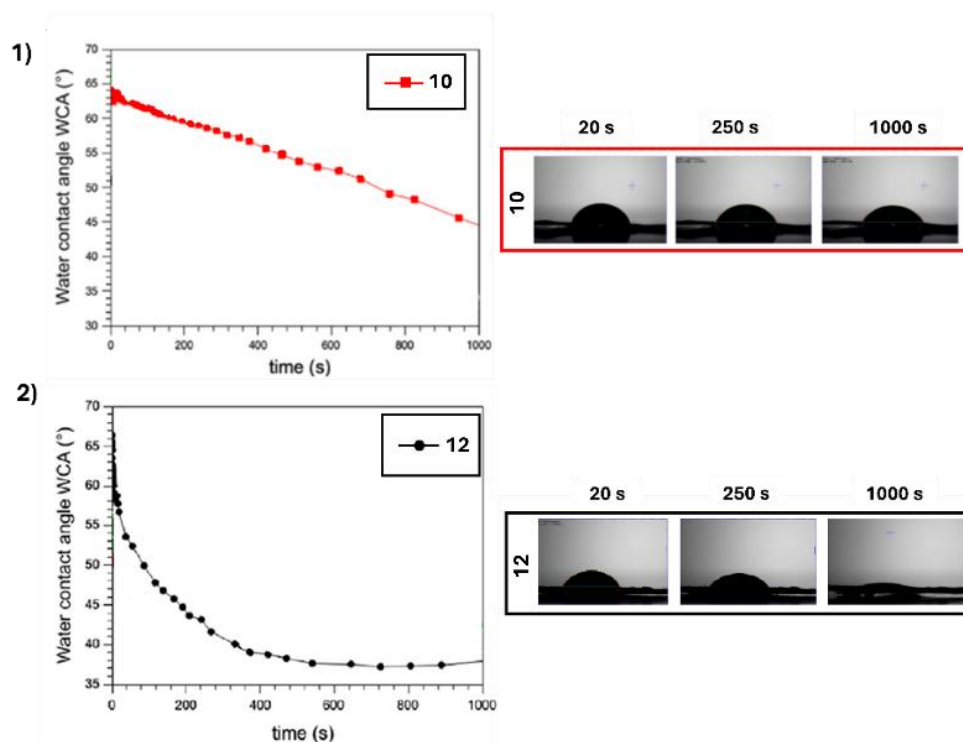


Figure 3.24 - WCA measurements (left), 1) 4-arm Sample 10; 2) 6-arm Sample 12. Droplet shape analysis (right) of 4-arm Sample 10 (top) and 4-arm Sample 12 (bottom)

3.6 Shape Memory Behavior

Shape memory polymers are a type of smart material that can return to their original shape after being temporarily deformed when exposed to specific external stimuli, such as heat, light, or pH changes. Interest in these materials has grown quickly in recent years due to their

wide range of potential uses, from aerospace and flexible electronics to advanced biomedical devices. Their unique ability to combine lightweight properties with programmable mechanical responses makes them especially desirable for next-generation functional materials and devices.²⁸

First qualitative examinations were performed for a crosslinked *Sample 14* film to determine its performance in terms of shape memory behavior, specifically its ability to recover its original shape upon an external stimulus, in this case, temperature.

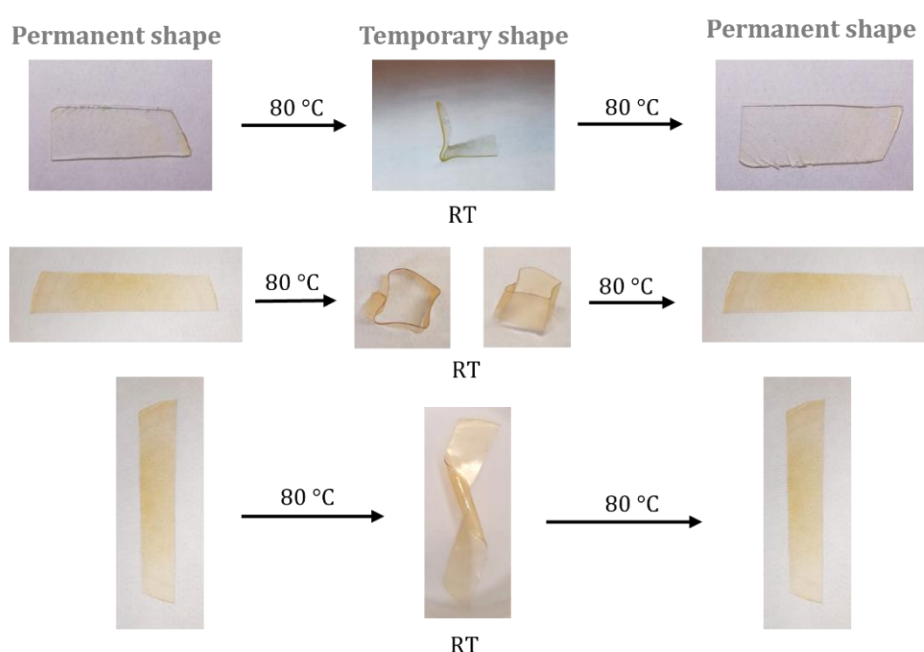


Figure 3.25 – Qualitative shape memory test of *Sample 14* film

Three thin strips (4x1 cm) of the same film were heated to 80 °C, a temperature above the T_g . Once softened, the strip was manually shaped in three different ways to create distinct temporary forms: in **Figure 3.25**, at the top section, the strip was bent to form an angle of approximately 90°, at the middle section was folded over itself into a square shape, and at the bottom section was tightly rolled.

After cooling to room temperature, the material retained all three deformed shapes, indicating the fixation of the temporary configurations.

When the film was reheated at 80 °C, the material gradually began to unfold and unroll, eventually returning to its original flat shape across all sections. This simple yet effective demonstration clearly showed that the crosslinked 4-arm-based system is capable of thermal shape memory; it can be programmed into temporary shapes and, with heat, "remembers" and recovers its original form.

Conclusion

This chapter explores the development of a new class of bio-based epoxy systems obtained by crosslinking star-shaped PLA prepolymers with DGEIs, highlighting the role of end-group functionalization, macromolecular architecture, and curing conditions in determining network formation and the properties of the resulting material.

Preliminary tests showed that -OH-terminated 4S-PLA-OH prepolymers display very low reactivity toward DGEIs, even in the presence of a catalyst, meaning that a chemical modification of the chain ends is required to afford a correct network formation.

The conversion of -OH groups to -COOH functionalities by reaction with succinic anhydride was found to be a straightforward, efficient, and highly reproducible method, as assessed by NMR, GPC, and acid-base titration.

Curing-screening experiments on the 4S-PLA-COOH as prepolymer identified optimal and reproducible conditions: 180 °C, an [epoxy]:[COOH] ratio of 1:1, and 10 mol% Zn(OAc)₂, yielding gel fractions >90% within 3 hours.

Lower temperatures led to slower kinetics and incomplete networks, as shown by gel-fraction values and isothermal rheology.

Prepolymer architecture strongly influenced the processability and quality of the final materials: 4-arm and 6-arm PLA produced uniform films, whereas 3-arm systems were unstable.

Several samples of both 4-arm and 6-arm based systems were prepared and subjected to mechanical and thermal characterization to investigate the materials' properties and the influence of their molecular architecture.

Thermal and rheological analyses confirmed successful network formation and enhanced thermal stability.

SEM revealed smooth, homogeneous surfaces with well-distributed nanospherulites, attributed to the presence of the Zn-catalyst.

Mechanical properties depended on architecture and film thickness: 4-arm systems were more flexible, 6-arm ones stiffer and less ductile; both improved markedly in thicker films.

DMA showed similar T_g values ($\sim 34\text{--}35\text{ }^\circ\text{C}$) and high storage moduli ($\approx 2\text{ GPa}$ for 4-arm, $\approx 1.9\text{ GPa}$ for 6-arm).

Contact-angle measurements showed that prepolymer architecture affects surface properties as well: 4-arm materials provided more hydrophobic and time-stable surfaces than their 6-arm analogs, in agreement with their lower content of residual OH groups and a less densely populated network of polar functionalities.

Stress-relaxation experiments demonstrated clear vitrimer behavior for both systems, with Arrhenius-controlled relaxation and ester-exchange dynamics. Activation energy increased with branching ($28\text{ to }32\text{ kJ mol}^{-1}$), and the vitrimer temperature T_v rose from $43\text{ }^\circ\text{C}$ to $66\text{ }^\circ\text{C}$. This confirms that both networks are reprocessable above T_v while retaining dimensional stability at room temperature.

3.7 Experimental Part

3.7.1 Materials and Methods

Reactions sensitive to air or moisture were carried out under a nitrogen atmosphere, using either a glovebox or Schlenk techniques, depending on the experiment's needs. All glassware was dried overnight at 120 °C and flushed with nitrogen to ensure dry conditions. Deuterated solvents were purchased from Aldrich, and methanol was dried over sodium and freshly distilled before use. Both L-lactide (Lumilact® L) and the polyalcohols were pre-dried overnight using phosphorus pentoxide (P₂O₅). Unless specified otherwise, all other reagents were used as received from commercial suppliers.

3.7.2 Instruments and Measurements

NMR spectra were recorded using Bruker Avance instruments operating at 300, 400, or 600 MHz (Ascend 3 HD), depending on availability and the resolution required. Chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (J) in hertz (Hz). For ¹H-NMR, the residual CHCl₃ signal at δ 7.26 ppm in CDCl₃ was used as the reference, while for ¹³C-NMR, the CDCl₃ peak at δ 77.22 ppm served as the reference point.

Gel permeation chromatography (GPC) was used to analyze the molecular weight distribution of the samples. The measurements were carried out on an Agilent 1260 Infinity Series system, equipped with a ResiPore column (3 μ m, 300 $\times$ 7.5 mm), and operated at a flow rate of 1.0 mL/min. Both UV detection (at 250 nm) and a refractive index (RI) detector (PLGPC 220) were used to monitor the elution. The analyses were performed at a constant temperature of 35 °C, using either THF or CHCl₃ as the eluent. Calibration was done using monodisperse polystyrene standards to ensure reliable molecular weight estimation. Instrument calibration for temperature and enthalpy was carried out using high-purity indium (melting point: 156.60 °C; enthalpy: 28.45 J/g). Experimental Mn and Mw/Mn ($\bar{D}$) values were determined vs. polystyrene standards.

DSC measurements were performed using either a TA Instruments Q2000 or Q20 system. The samples were first equilibrated at -20 °C, then heated to 250 °C at a rate of 10 °C per minute and subsequently cooled back down to -20 °C at the same rate. Before running the

experiments, the instrument was calibrated for both temperature and enthalpy using high-purity indium (melting point: 156.60 °C; enthalpy of fusion: 28.45 J/g) as a standard.

TGA analysis was performed using a TA Instruments Q500 device produced by TA Instruments (Waters/TA Instruments), with polymer samples placed in platinum crucibles and tested under a nitrogen atmosphere flowing at 40.0 mL per minute.

Rheological analyses were carried out using an Advanced Rheometric Expansion System (ARES) from RHEO Service GmbH & Co. KG (Reichelsheim, Germany). For the temperature sweep tests, a strain of 1% and a frequency of 1 rad/s were applied, while for the time sweep tests, a strain of 5% at 1 rad/s was used.

FTIR-ATR spectra were recorded using a Perkin-Elmer FT-IR/NIR Spectrum 400 spectrophotometer over the range 4000–450 cm⁻¹, with a resolution of 4 cm⁻¹ and 16 scans accumulated per spectrum.

DMA measurements were performed using a DMA 50 instrument (Metravib, France). Temperature-sweep experiments were conducted from 25 to 60 °C under the following conditions: heating rate of 1 °C/min, dynamic strain amplitude of 0.05%, and frequency of 1 Hz.

Relaxation tests were carried out on the same instrument, applying a 3% static strain while heating from 25 to 160 °C at a rate of 5 °C/min.

The sample morphology was examined by SEM using a Phenom ProX instrument (Thermo Fisher Scientific, USA) on gold-sputtered specimens.

WCA measurements were performed at room temperature using an FTA 1000 instrument (First Ten Angstroms, UK). A 4 µL droplet of deionized water was deposited onto the sample surface using an automated drop-dispensing system. Images of the droplet were captured at different time intervals, from the initial contact (0 s) up to 1000 s.

3.7.3 Synthesis of Carboxyl End-Capped 3-Arm, 4-Arm and 6-Arm Star-Shaped Poly(L-Lactic Acid) Oligomers

4S-PLA-OH (15 g), prepared as described earlier, is dissolved in a small amount of 1,4-dioxane (30 mL). Then, 3.1 g of succinic anhydride is added to the flask, keeping the ratio of [OH] to

succinic anhydride at 1:1. After it fully dissolves, the organic catalysts DMAP (0.075 g) and TEA (0.1 mL), each about 0.5% by weight relative to the prepolymer, are added. The mixture is stirred at room temperature (around 25 °C) overnight. Subsequently, the dioxane is removed under vacuum at 80 °C. It's extracted three times with chloroform and water to purify the product. The organic layer is dried over magnesium sulfate and filtered. After that, the product is precipitated by adding it to hexane, forming a white solid, which is collected by decanting. This solid is dried first using a rotary evaporator, then further dried under vacuum at 120 °C to ensure all solvent traces are gone. A sample aliquot of the product is dissolved in a 1:1 mixture of chloroform and benzyl alcohol and titrated with 0.1 M KOH in methanol to measure how many acidic groups are present.

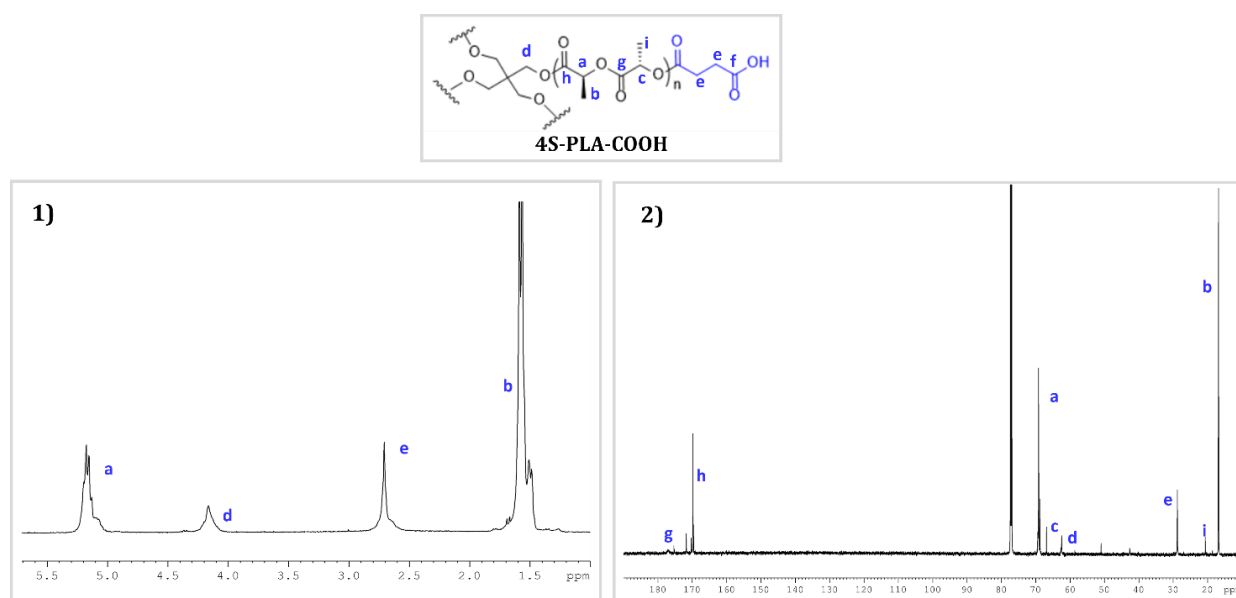


Figure 3.26 - 1) ^1H -NMR, 400 MHz, CDCl_3 , 297 K; 2) ^{13}C -NMR, 100 MHz, CDCl_3 , 297 K of 4S-PLA-COOH

^1H -NMR (400 MHz, CDCl_3 , 297 K): δ 5.18 (m, 4nH, a), 4.17 (br, 2H, d), 2.68 (s, 4H, e), 1.59 (d, 3nH, $J = 6.6$ Hz, b)

^{13}C -NMR (100 MHz, CDCl_3 , 297 K): δ 175.17 (g), 171.58 (f), 169.61 (h), 69.01 (a), 66.72 (c), 62.29 (d), 28.61 (e), 20.49 (i), 16.64 (b).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	2694	2111	3050	4252	5532	2891
PD						
1.445						

Figure 3.27 – Molecular weight averages of 4S-PLA-COOH calculated by GPC analysis in CHCl₃, using polystyrene standard.

The same procedure is followed for the 3S-PLA-COOH and 6S-PLA-COOH synthesis. In particular, for the 6S-PLA-COOH, the synthesis was carried out by reacting 15 g of the prepolymer with 3.5 g of succinic anhydride in 30 mL of 1,4-dioxane. To this solution, 0.1 mL of TEA and 0.075 mL DMAP were added to catalyze the reaction. The mixture was stirred at room temperature (25 °C) overnight to ensure complete conversion. The product was then recovered using the same procedure previously described for the 4S-PLA-COOH sample.

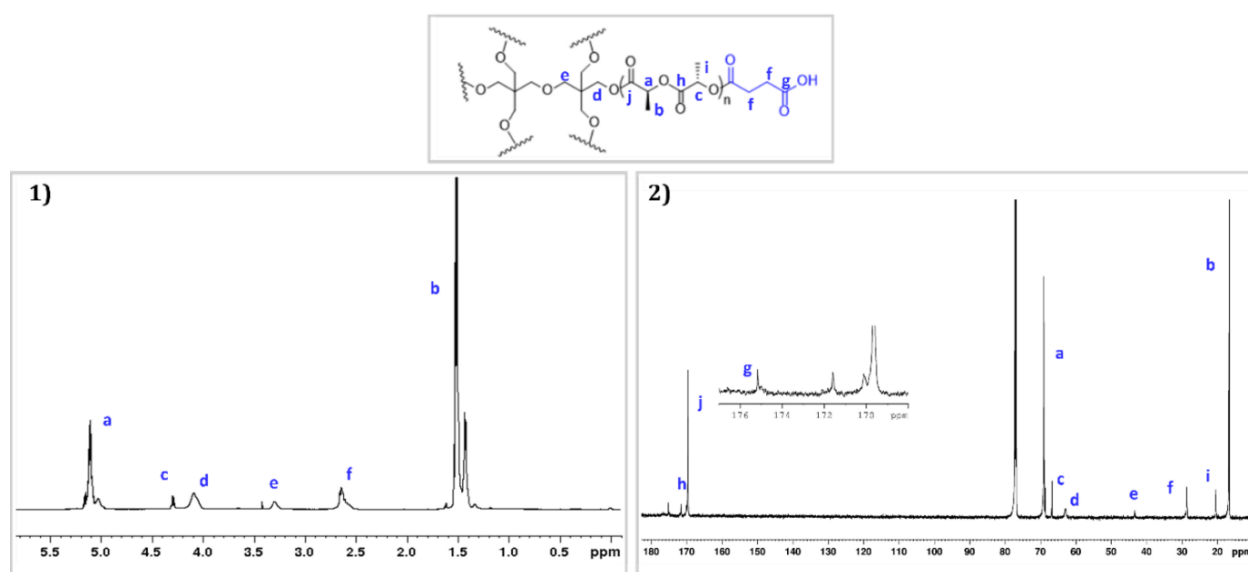


Figure 3-28 - 1) ¹H-NMR, 400 MHz, CDCl₃, 297 K; 2) ¹³C-NMR, 400 MHz, CDCl₃, 297 K of 6S-PLA-COOH

¹H-NMR (400 MHz, CDCl₃, 297 K): δ 5.16 (m, 6nH, a), 4.34 (q, 1H, J= 7.0 Hz, c), 4.15 (br, 2H, d), 3.34 (br, 2H, e), 2.70 (s, 4H, f), 1.57 (d, 3nH, J=6.8 Hz)

¹³C-NMR (100 MHz, CDCl₃, 297K): δ 175.16 (g), 171.58 (h), 169.61 (j), 69.01 (a), 66.72 (c), 62.87 (d), 43.34 (e), 28.62 (f), 20.50 (i), 16.64 (b).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	4655	3513	6820	11893	17517	6208
PD						
1.941						

Figure 3.29 - Molecular weight averages of 6S-PLA-COOH calculated by GPC analysis in CHCl_3 , using polystyrene standard.

For the synthesis of 3S-PLA-COOH, 15 g of the prepolymer were dissolved in 30 mL of 1,4-dioxane and reacted with 3.1 g of succinic anhydride. Catalysis was promoted by the addition of 0.1 mL of triethylamine (TEA) and 0.075 mL of 4-dimethylaminopyridine (DMAP). The reaction was maintained under stirring at ambient temperature (25 °C) and left to proceed overnight to allow full conversion. The final product was isolated following the same recovery procedure adopted for the last two syntheses.

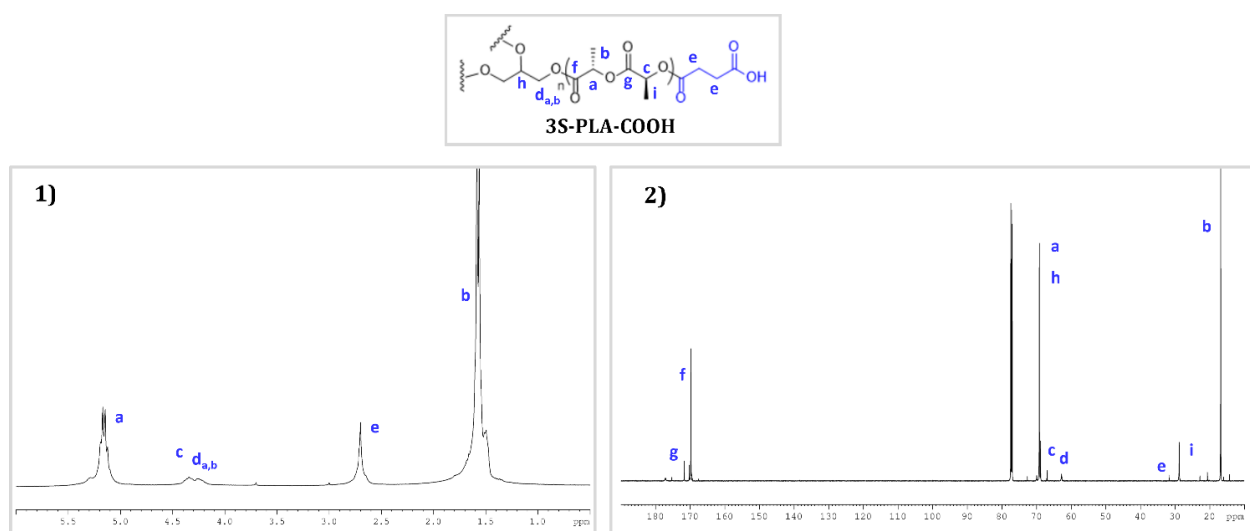


Figure 3.30 - 1) ^1H -NMR, 400 MHz, CDCl_3 , 297 K; 2) ^{13}C -NMR, 100 MHz, CDCl_3 , 297 K of 3S-PLA-COOH

^1H -NMR (400 MHz, CDCl_3 , 297 K): δ 5.18 (m, 3nH, a), 4.25 (br, 3H, c and $d_{a,b}$), 2.68 (s, 4H, e), 1.59 (d, 3nH, J = 6.4 Hz, b).

^{13}C -NMR (100 MHz, CDCl_3 , 297 K): δ 171.7 (g), 169.7 (f), 69.1 (a, h), 68.7 (c), 69.8 (d), 31.6 (e), 28.7 (i), 16.7 (b)

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	1992	1715	2574	3788	5153	2421
PD						
	1.501					

Figure 3.31 - Molecular weight averages of 3S-PLA-COOH calculated by GPC analysis in CHCl₃, using polystyrene standard.

3.7.4 Curing Process

To carry out the crosslinking reaction, the mixture was cast into a Teflon Petri dish. First, the required amounts of nS-PLA-COOH and DGEIs were dissolved in dichloromethane in one vial, while Zn(OAc)₂ was dissolved separately in methanol (Reported in **Table 3.10**). The two solutions were then combined and sonicated for 30 minutes to ensure proper mixing. The resulting solution was gently transferred to the Petri dish using a Pasteur pipette and left at room temperature overnight to allow the solvents to evaporate. The next day, the dish was placed in an oven under a nitrogen atmosphere. The temperature was gradually increased from 25 °C to 180 °C at a rate of 1 °C per minute, allowing any remaining solvent to fully evaporate and helping to prevent bubbles in the final film. Once the target temperature was reached, the sample was held at 180 °C for 3 hours to complete the process.

Entry (see Table 3.4)	nS-PLA-COOH	DGEIs	Zn(OAc) ₂	Thickness
10 ^a	0.5 g	110 mg	15.6 mg	50 μm
12 ^b	0.5 g	131 mg	18.1 mg	50 μm
14 ^a	1.5 g	475 mg	67.5 mg	250 μm
15 ^b	1.5 g	395 mg	56.1 mg	250 μm

Table 3.10 - Reagent quantities used in the curing reactions, ^a4S-PLA-COOH as prepolymer, ^b6S-PLA-COOH as prepolymer

3.7.5 Gel Fraction and Swelling Tests

To evaluate swelling and determine the gel fraction, a small portion of the sample (M_i) was weighed and placed in a vial with either chloroform or ortho-dichlorobenzene, using a ratio of 50 mg of sample per 5 mL of solvent. The vial was then immersed in a preheated oil bath, set to 55 °C for chloroform or 150 °C for ortho-dichlorobenzene, and left for 8 hours to allow

the sample to swell. After that, the swollen sample was filtered, gently dried with filter paper, and weighed to assess how much solvent had been absorbed. The same sample was then dried overnight in a vacuum oven at 60 °C and weighed again (M_f) to calculate the gel fraction.

3.7.6 Shape Memory

To visually display the shape memory behavior, a strip 4x1 cm of 4S-PLA-COOH film was cut, and then the strip was shaped into a hollow sphere at 80 °C. After cooling to room temperature to freeze the new temporary shape of the film. After the strip was reheated at 80 °C to determine if there was a memory of the initial form.

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CHAPTER 4

Results and Discussion

*Studies on the Degradation and
Chemical Depolymerization of
the New Vitrimeric Materials*

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Introduction

The growing demand to reduce the environmental impact of plastic products has led to the development of biobased, degradable, and recyclable polymers to the forefront, without sacrificing the chemical, physical, and mechanical properties of fossil-based polymers available in the marketplace today.

In particular, the pressure originating from tightening European and global environmental regulations (e.g., the Single-Use Plastics Directive (SUP)¹ and the goals of the European Green Deal²) has driven the transition towards materials aligning with the principles of the circular economy.

In this context, the ability to produce high-performance polymers that are also degradable or recyclable at the end of their lives is a primary challenge for materials science.

This new generation of PLA-derived vitrimers, which are crosslinked using an equally biobased molecule, suggests this way forward as a new family of materials that captures the characteristics of thermosetting resins, thermal and mechanical stability, with reprocessability.

Since PLA is already known to undergo chemical depolymerization under the right conditions,^{3,4} introducing dynamic covalent bonds into the network takes this a step further, making it possible to not only reshape the material but also break it down in a controlled way and potentially recover its original constituent elements at the end of its lifecycle.

This chapter describes a study of the hydrolytic degradation of the 4-arm-based *Sample 10* and 6-arm-based *Sample 12*, treated in **Chapter 3, Table 3.4**, in collaboration with Prof. *Scaffaro's* group at the Department of Engineering of the University of Palermo.

The goal is to understand the impact of changes in molecular design on the stability of the materials in water media, a key variable not only for sustainability and potential future regulatory requirements for plastic materials, but also for the functionality and potential applications of such systems.

The study is divided in three main investigative approaches. Gravimetric analysis was first employed to monitor mass loss in acidic and basic environments to provide a quantitative approximation of the stability of the networks under hydrolytic conditions. This was

complemented by a morphological examination through SEM analysis, which enabled monitoring of surface and inner structure changes as degradation progressed. Lastly, a depolymerization test was also conducted to explore the prospects of monomers and low-molecular-weight fragments recovery from the crosslinked matrix, thereby assessing the material's chemical recyclability.

4.1 Degradation Study

The degradation study of the crosslinked materials, *Samples 10* and *12*, provides a clear and systematic comparison between 4-arm and 6-arm PLA-derived vitrimeric networks under accelerated hydrolytic conditions at pH=5 and pH=9.

The collected data highlight the influence of macromolecular architecture, specifically the degree of branching, on the materials' degradability and susceptibility to chemical depolymerization.

Films of both systems were prepared following the optimized conditions described in the previous chapter.

From these films, strips measuring 5 mm in width (with variable height but the same weight of 0.1 g) were cut and used for degradation testing.

Each strip was immersed in 20 mL of buffer solution, either acidic (pH=5) or basic (pH=9), and stored at ambient temperature (25 °C).

The weight loss of each sample was assessed after 10 and 20 days of immersion. After each time point, samples were dried at 60 °C for 24 hours and then reweighed.

The percentage mass loss for both 4-arm and 6-arm networks over time and under the two pH conditions is reported in the graph shown in **Figure 4.1**.

The results clearly indicate that the 6-arm-based *Sample 12* undergoes significantly faster degradation, particularly under alkaline conditions (pH=9), where it shows nearly 50% mass loss after 20 days. In contrast, 4-arm-based *Sample 10* retains nearly 90% of its initial mass under the same conditions.

A similar trend, although less pronounced, is observed under mildly acidic conditions (pH=5), where 6-arm-based *Sample 12* still exhibits a more accelerated degradation rate compared to its 4-arm-based counterpart.

The enhanced degradability of the 6-arm-based *Sample 12* network may be attributed to its higher number of reactive chain ends, leading to a greater density of hydroxyl groups that form during the crosslinking reaction with bis-epoxide. These hydroxyl-rich regions contribute to increased hydrophilicity, facilitating water uptake and accelerating hydrolytic cleavage, particularly under basic conditions, where ester saponification is favored.

In contrast, the 4-arm-based system, with fewer arms and likely a denser crosslinked structure, forms a more compact network. This reduced chain-end density and tighter network make it less susceptible to hydrolytic attack, resulting in slower erosion and superior mass retention over time.

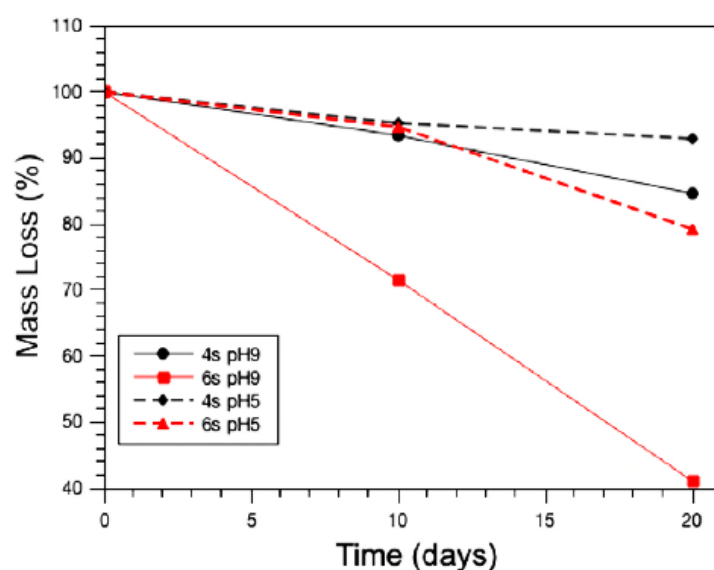


Figure 4.1 - Mass loss kinetics of *Sample 10* (black) and *Sample 12* (red), in acidic (dashed line) and alkaline (solid line) conditions

Figure 4.2 provides a visual comparison of the 4-arm-based *Sample 10* and 6-arm *Sample 12* resins before and after 20 days of immersion in a basic solution (pH=9). The differences between the two systems are immediately apparent.

After the degradation period, the 6-arm-based *Sample 12* appears significantly more fragile and fragmented. This visual deterioration is consistent with the high mass loss measured in the quantitative analysis. The material shows clear signs of delamination and partial dissolution, indicating a substantial breakdown of the polymer network.

In contrast, the 4-arm-based *Sample 10* retains much of its original shape and structural integrity. Although some surface changes may be present, the 4-arm-based system looks far more intact overall, confirming its greater resistance to hydrolytic degradation under alkaline conditions.

These visual cues provide intuitive support for the gravimetric data, reinforcing the idea that molecular architecture plays a critical role in how these materials degrade.

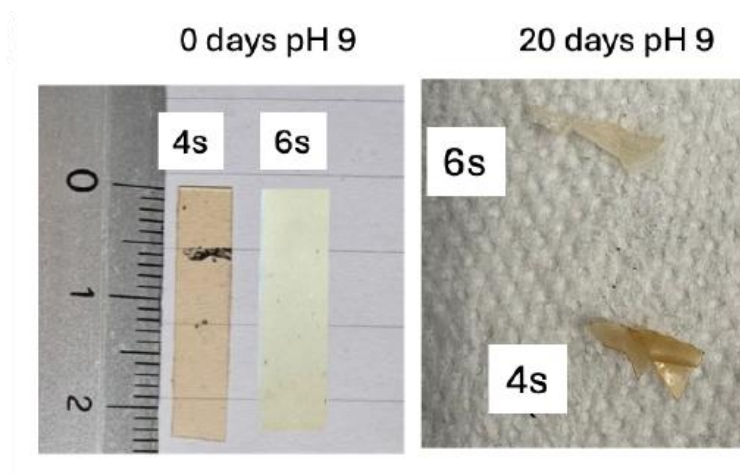


Figure 4.2 - visual comparison of *Sample 10* and *Sample 12* morphology before (left) and after immersion in a buffer solution at pH=9 (right)

4.2 Surface Erosion and Morphological Evolution (SEM Analysis)

SEM was employed to gain a deeper understanding of how degradation impacts the surface morphology and internal structure of the vitrimeric PLA-based networks. The comparison between the 4-arm-based *Sample 10* and 6-arm-based *Sample 12* systems revealed clear differences in their erosion behavior and microstructural integrity over time and under different pH conditions.

At the initial time point ($t = 0$), both *Samples 10* and *12* displayed relatively smooth and homogeneous surfaces, with only minimal imperfections or embedded features (**Figure 4.3**, white). These observations suggest that the curing process was effective in producing well-formed, uniform materials with consistent bulk properties.

After 20 days of immersion in mildly acidic conditions ($\text{pH}=5$), both systems exhibited visible signs of surface erosion (**Figure 4.3**, orange). However, degradation was notably more pronounced in the 6-arm-based samples, which showed deeper surface cavities and greater disruption of the polymer matrix. While the 4-arm-based ones were also affected, their surfaces remained comparatively less porous and more structurally coherent.

Under alkaline conditions ($\text{pH}=9$), the degradation process intensified, particularly for the 6-arm-based networks (**Figure 4.3**, blue).

SEM cross-sectional analysis revealed a well-defined erosion front of approximately $30\text{ }\mu\text{m}$, accompanied by internal fragmentation and partial delamination of the layers. In contrast, the 4-arm-based samples still displayed some internal cracking, but overall retained greater cohesion and network integrity.

These findings underscore the increased vulnerability of 6-arm systems to alkaline hydrolysis. The more open and branched network architecture of 6-arm allows deeper penetration of the degrading medium, resulting in more extensive bulk degradation rather than mere surface erosion. It also leads to a greater exposure of hydrolytically labile ester bonds, particularly at chain ends and junction points. Consequently, these systems are more susceptible to degradation in both acidic and basic environments.

Conversely, the 4-arm system, with its less branched architecture, shows slower degradation kinetics and enhanced resistance to hydrolytic attack. This makes it more suitable for long-term applications where environmental stability and resistance to aqueous conditions are critical.

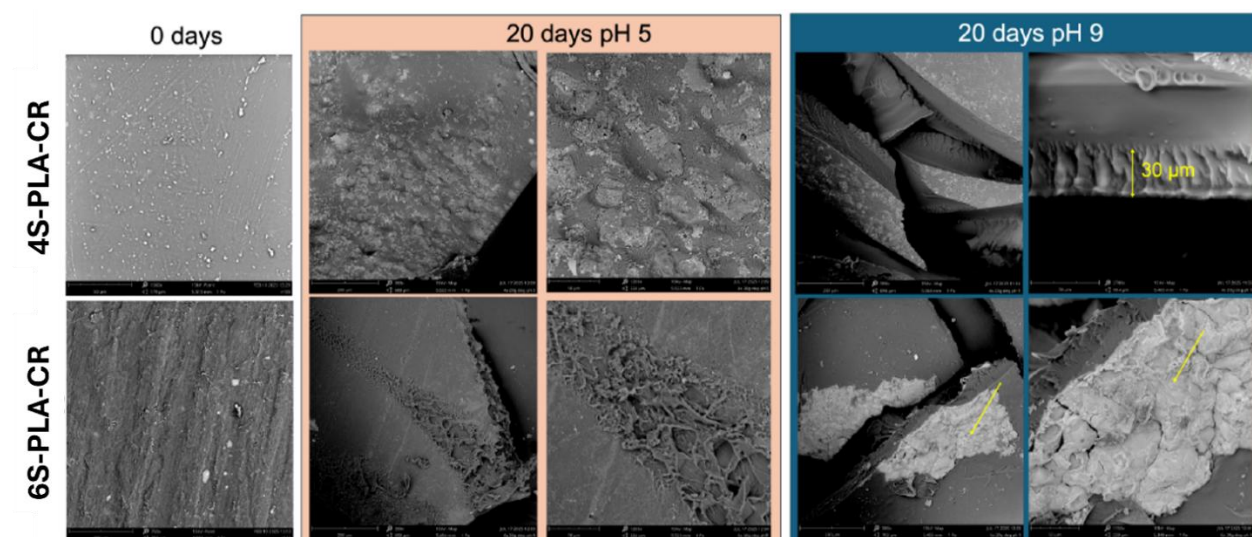


Figure 4.3 - SEM of 4-arm-based Sample 10 (top line) and 6-arm-based Sample 12 (bottom line) at time=0 (white), after 20 days of immersion at pH=5 (orange) and pH=9 (blue)

4.3 Depolymerization test

According to the result obtained from the degradation tests, which clearly indicate that alkaline conditions are favorable in catalyzing the degradation of the crosslinked materials synthesized, a primary depolymerization experiment was set up for a new sample (*Sample 16*) prepared in the same optimized conditions of the 4-arm previous one: 4S-PLA-COOH as prepolymer, [fz epox]:[fz carbox]=1:1, 10 mol% of $\text{Zn}(\text{OAc})_2$ in respect to the carboxylic groups at 180 °C for 3 hours in oven under nitrogen flow, with a gel fraction of 97%.

This experiment was designed to explore if the crosslinked network could be selectively hydrolyzed under basic conditions, with potential recovery of its monomeric or oligomeric building blocks.

The promising degradation behavior observed in basic media motivated this approach, as it may represent a first step toward the chemical recyclability of such materials.

After a series of trials aimed at optimizing reaction conditions, an effective depolymerization procedure was identified.

Specifically, 200 mg of crosslinked polymer was treated with 2 equivalents of potassium hydroxide based on the estimated number of ester bonds present in the sample. The reaction was carried out in water as a solvent and the resulting mixture was kept at 55 °C for 2 hours.

Under these conditions, the material was completely dissolved (**Figure 4.4**), which indicated that hydrolysis of ester linkages had gone through successfully.

In an effort to separate the corresponding carboxylic acid from its salt form, hydrochloric acid (HCl) was used to acidify the reaction mixture to reduce lactate to lactic acid.

The solution obtained was again washed with chloroform to separate the organic components. The organic layer was then identified using ^1H -NMR spectroscopy, which showed that the lactic acid had been successfully recovered as one of the major degradation products (**Figure 4.5**).

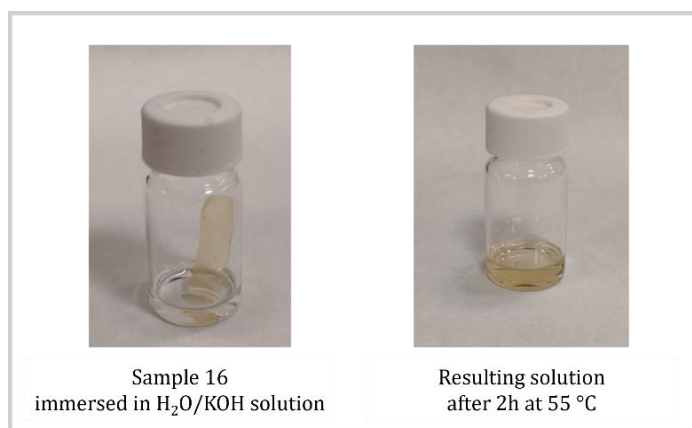


Figure 4.4 – Comparison between a Sample 16 strip at time=0 (left) and after 2 hours at 55 °C in a basic solution of KOH (right)

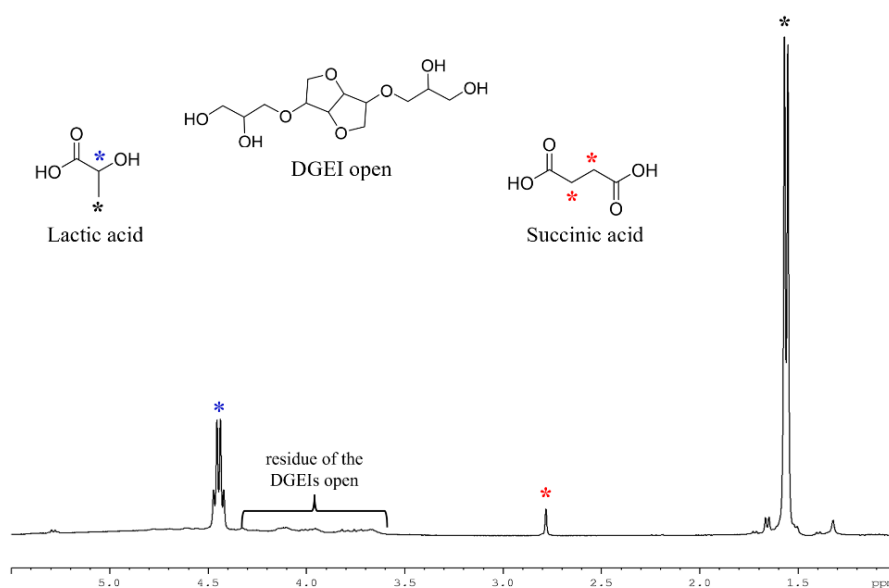


Figure 4.5 - ^1H -NMR spectrum (298K, 400MHz, CDCl₃) of the mixture obtained after degradation with KOH of a strip of Sample 16

One of the most notable features in the spectrum is a prominent quadruplet around 4.3 ppm, marked with a blue asterisk. This signal corresponds to the methine proton of lactic acid, a key indicator that PLA-based segments within the network were successfully broken down. Its position aligns well with known values in the literature, offering a clear confirmation of the recovery of this monomer after hydrolysis.

In addition, a distinct signal at around 1.5 ppm can also be observed, which is attributed to the methyl group (CH_3) of lactic acid.

The simultaneous presence of both the methine and methyl resonances further supports the formation of free lactic acid as a major degradation product.

Another important set of signals appears at approximately 2.6 ppm (highlighted with red asterisks), which can be assigned to the methylene protons of succinic acid.

This observation supports the release of the aliphatic diacid originally incorporated into the polymer backbone, again suggesting that the degradation process was effective across the entire structure.

In the region between 3.5 and 4.2 ppm, several multiplets are visible. These are attributed to protons from the open form of DGEIs, the crosslinking agent used in the formulation. Their presence in the spectrum is particularly significant, as it suggests that not only the linear segments of the polymer but also the crosslinked domains underwent cleavage, resulting in low-molecular-weight, soluble fragments.

Overall, the NMR results clearly show that the polymer network can be efficiently broken down under mild alkaline conditions, allowing the recovery of its original building blocks.

This finding highlights not only the hydrolytic degradability of the material but also its promising potential for chemical recycling and sustainable end-of-life processing.

Conclusion

The hydrolytic degradation study of the newly synthesized crosslinked material, 4-arm-based and 6-arm-based systems, demonstrates how macromolecular architecture affects their stability and susceptibility to hydrolysis in specific conditions. In particular, the higher branching of 6-arm-based systems and its more dense terminal group and hydrophilic zone concentration made degradation occur more rapidly, especially under basic conditions (pH=9), in which a mass loss of almost 50% was observed within 20 days. In contrast, the 4-arm-based system was found to be more resistant, maintaining about 90% of its initial mass for the same period of time under the same conditions.

SEM analysis supported these trends by showing greater surface erosion and internal fracture in the 6-arm-based material, while the 4-arm-based material had a denser and more coherent microstructure.

These results demonstrate how the less branched structure facilitates the formation of a denser network that is more resistant to hydrolytic degradation.

The depolymerization experiment on *Sample 16* demonstrated the potential for selectively decomposing the material under mild alkaline conditions with partial regeneration of component monomers, such as lactic acid, succinic acid, and fragments of the DGEIs crosslinker. Identification of such products by ^1H -NMR spectroscopy demonstrates the viability of a chemical recycling process, offering tangible prospects for PLA-based vitrimeric material development with an improved end-of-life.

4.4 Experimental Part

4.4.1 Materials and Methods

All the glassware used for this analysis was dried at 120°C overnight to avoid the presence of solvents or impurities resulting from its washing.

Deuterated solvents were purchased from Aldrich.

All the other reagents were purchased from Aldrich and, unless specified otherwise, were used as received from commercial suppliers.

4.4.2 Instruments and Measurements

NMR spectra were recorded using Bruker Avance instruments operating at 400 MHz (Ascend 3 HD). Chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (J) in hertz (Hz). For ^1H -NMR, the residual CHCl_3 signal at δ 7.26 ppm in CDCl_3 was used as the reference.

The morphology of the cross-linked products, both initially and after degradability testing, was studied using scanning electron microscopy (SEM), performed with a Phenom Pro X instrument (Thermo Fisher Scientific, USA) and optical microscopy (Leica MS5 stereomicroscope).

4.4.3 Degradation Test

Film strips 5 mm wide (variable height, but constant weight of 0.1 g) were cut and used for degradation tests. Each strip was immersed in a beaker containing 20 mL of buffer solution, with an acidic (pH 5) or basic (pH 9) pH, and stored at room temperature (25°C).

Weight loss was assessed after 10 and 20 days of immersion. At the end of each time interval, the samples were dried at 60°C for 24 hours and then weighed.

- Preparation of a pH 9 buffer solution: 3.10 g of boric acid are dissolved in 250 ml of distilled water in a 500 ml volumetric flask. To adjust the pH, 20.75 ml of a 1 M sodium hydroxide solution is added. The solution is then diluted to a volume of 500 ml.

- Preparation of a pH 5 buffer solution: 6.87 ml of pure acetic acid are measured and diluted to a final volume of 300 ml using distilled water to prepare a 0.4 M acetic acid solution. Separately, 9.84 g of sodium acetate are dissolved in distilled water and the solution is diluted to a final volume of 300 ml to prepare a 0.4 M sodium acetate solution. Equal volumes of the two solutions are combined to get the final buffer solution with pH 5.

4.4.4 Preparation of Sample 16 for the Depolymerization Test

1.5 g of 4S-PLA-COOH and 475 mg of DGEIs were dissolved in dichloromethane in one vial, while 67.5 mg of $\text{Zn}(\text{OAc})_2$ was dissolved separately in methanol. The two solutions were then combined and sonicated for 30 minutes to ensure proper mixing. The resulting solution was transferred to the Petri dish using a Pasteur pipette and left at room temperature overnight to allow the solvents to evaporate. The next day, the dish was placed in an oven under a nitrogen atmosphere. The temperature was gradually increased from 25 °C to 180 °C at a rate of 1 °C per minute, allowing any remaining solvent to fully evaporate and helping to prevent bubbles in the final film. Once the target temperature was reached, the sample was held at 180 °C for 3 hours to complete the process.

4.4.5 Depolymerization Test

In 20 ml vials, 200 mg of cross-linked film were treated with 2 equivalents of KOH, related to the estimated number of ester bonds present in the sample. 8 ml of distilled water was added and used as the solvent. The vial, with the resulting mixture, was introduced in a preheated oil bath at 55 °C and left for 2 hours. After this time, the starting solid film was completely solubilized, and ^1H -NMR confirmed successful depolymerization, yielding the starting reagents.

^1H -NMR (400 MHz, CDCl_3 , 298 K): δ 4.38 (q, 1H, J = 7.32, CH), 2.71 (s, 4H, CH_2), 1.49 (d, 3H, J =6.85, CH_3)

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CHAPTER 5

Results and Discussion

*Toughness Enhancement of
HDPE/Biopolymer Composites
through Dynamic Covalent Chemistry*

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Introduction

As outlined in the introductory part and as seen in the previous chapters, one solution to make materials recyclable is introducing reversible bonds that can break and reform in response to external stimuli. The plastics industry is enormous, with approximately 430 million tons produced globally in 2022, 99.4% of which came from fossil sources.¹

While it's true that thermoplastic materials are easier to recycle than thermosets, the production rate far exceeds the recycling pace. Consequently, most plastics end up in landfills or are incinerated.

Polyethylene (PE) is the most widely produced plastic in the world, accounting for approximately 26% of global production. Its popularity reflects its ease of processability, and excellent thermomechanical properties, rendering it omnipresent in consumer products – like shopping bags, milk jugs, and soap containers – and industrial applications – such as water pipes, irrigation films, and packaging materials.²

The same characteristics also make PE a very good candidate as a matrix for composite materials, whose properties can be engineered by adding reinforcing agents.

Natural fibers emerged in the last few years as a sustainable alternative to traditional synthetic reinforcement fillers, like glass or carbon fibers. Natural fibers exhibit desirable mechanical properties (e.g., stiffness and impact resistance), lower density, and advantages with respect to cost, energy use, and end-of-life disposal.

Combining recycled PE with natural fibers presents a promising direction toward more sustainable materials.^{3,4} In addition to recovering value from plastic waste, it also improves the performance of recycled plastics, promoting a more circular and sustainable approach to composites manufacture.

Cross-linking polyolefins like PE has been a way to enhance material performance.⁵ Unfortunately, traditional cross-linking typically makes materials non-recyclable. Current advances are aimed at using dynamic covalent bonds to generate Covalent Adaptable Networks (CANs). These new structures can combine the benefits of cross-linking with reprocessability and/or recyclability, and they are revealing new possibilities for creating high-performance, yet sustainable, polymer systems.⁶⁻⁹

This chapter was developed during my research period at the *École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI Paris)*, under the supervision of Professor Renaud Nicolay.

The goal of the research carried out was to investigate the introduction of bio-based fillers (like cellulose, xanthan gum, arabic gum and guar gum) within HDPE through reactive extrusion, using two dynamic chemistries previously employed on polyolefins to create CANs: azidotriazine chemistry and boronic ester chemistry.

Blending polyethylene with natural fibers is a promising route to more environmentally friendly composite materials. This valorizes not only waste plastic but also increases the mechanical properties of recycled polymers, contributing to a more circular and greener material life cycle.

The modified blends were compared to unmodified controls to assess performance improvements. The properties of the material were evaluated using various thermomechanical characterization methods.

5.1 HDPE and Biopolymers Blends – Preparation and Characterization

Blends based on HDPE and biopolymers such as cellulose (C), xanthan gum (XaG), guar gum (GuG), and arabic gum (ArG) were prepared through an extrusion process. The biopolymers were incorporated at different weight percentages (5, 10, and 20 wt%) relative to HDPE, to explore how the amount of biopolymer affects the properties of the polyolefin matrix.

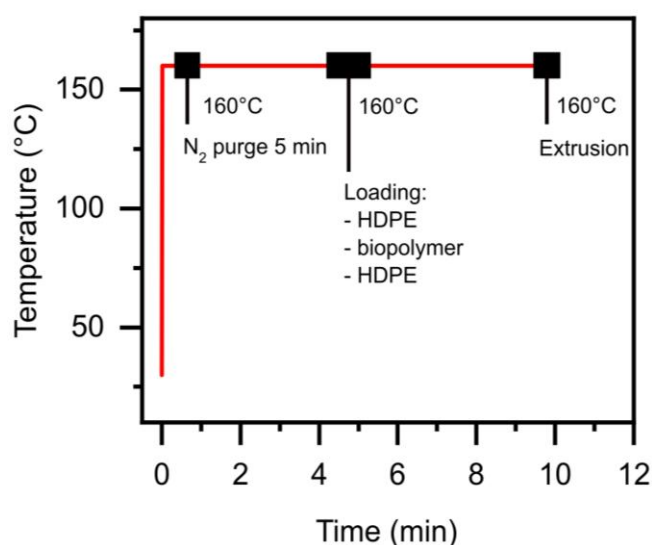


Figure 5.1 – General extrusion protocol scheme for producing different HDPE-Biopolymers blends

The blends were prepared using a three-step insertion process, which proved to be the most effective because when only HDPE is added first and then the biopolymer, the biopolymer, being a powder, mostly stays at the top of the extruder and fails to blend properly.

On the other hand, if the biopolymer is added first and then the HDPE, it tends to settle at the bottom of the extruder.

A three-step insertion process proved to be the best solution. The first addition of HDPE prevents the biopolymer powder from settling at the bottom, while the second addition of HDPE carries the powder that remained at the top of the extruder (**Figure 5.1**).

The materials were processed at 160 °C for 5 minutes inside the extruder.

When compared to the extrusion profile of pure HDPE, no significant variations in torque over time were observed for the composites (**Figure 5.2**). This indicates that the biopolymers and HDPE are mixing without undergoing chemical reactions.

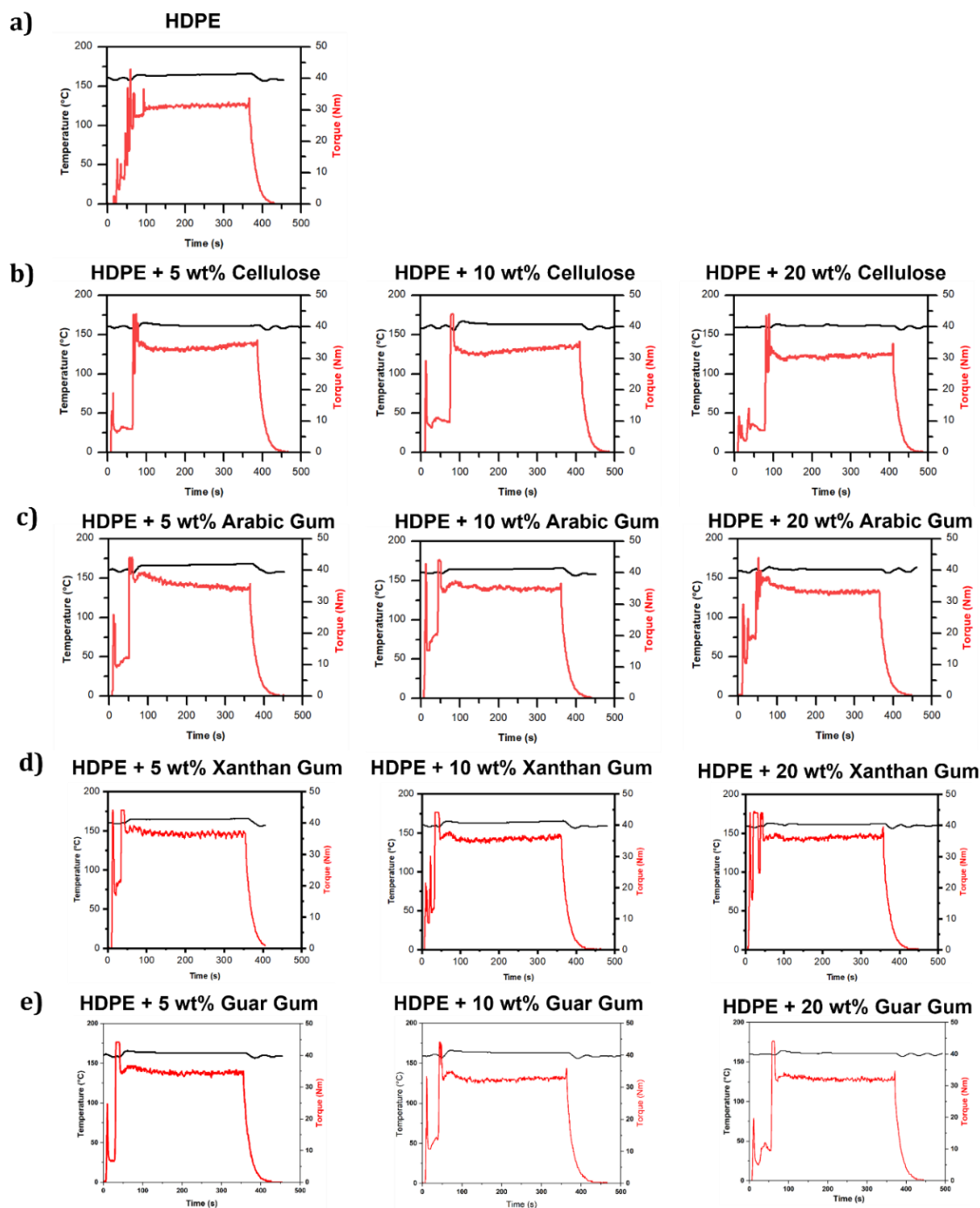


Figure 5.2 – Extrusion profiles of pure HDPE (a) and blends of HDPE with various loadings (5, 10 and 20 wt%) of different biopolymers: b) microgranular cellulose, c) arabic gum, d) xanthan gum and e) guar gum)

5.1.1 Thermogravimetric Analysis and Differential Scanning Calorimetry Analysis

The extrusion process was carried out at a temperature that does not compromise the stability of the biopolymers, as verified by TGA.

When tested without any pretreatment, the gum samples showed two distinct weight losses (**Figure 5.3**). The first, occurring around 100 °C in all cases, is linked to the evaporation of residual water. The second, associated with the actual degradation of the biopolymers, appeared at different temperatures depending on the material. Degradation temperatures are all superior to 200°C, with cellulose being the most thermally stable biopolymer.

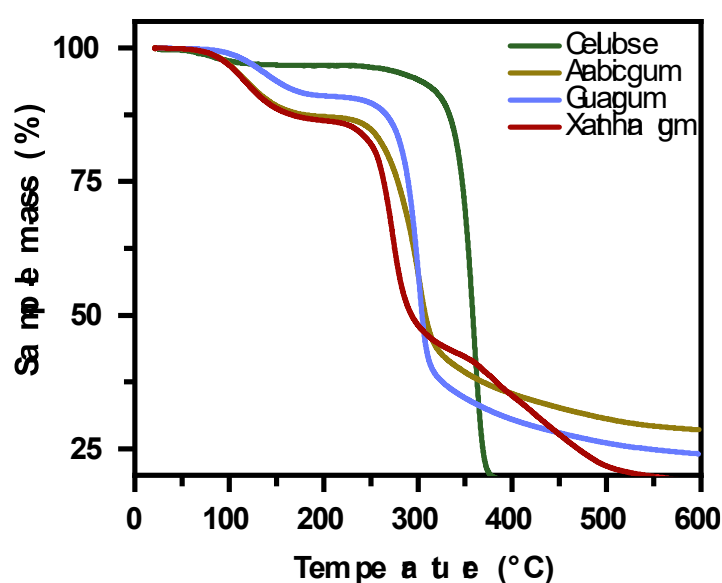


Figure 5.3 - TGA of cellulose (green), arabic gum (yellow), guar gum (blue) and xanthan gum (red) without pre-treatment

To remove water and obtain more reliable thermal profiles, all reagents were dried under vacuum at 100 °C overnight. After this treatment, the initial weight loss disappeared, confirming that it was due to residual water.

These results were further supported by DSC analysis. As an example, the thermogram of arabic gum is shown in **Figure 5.4**, reflecting the same thermal behavior observed in the TGA and reinforcing the suitability of the processing temperature used in the extrusion step.

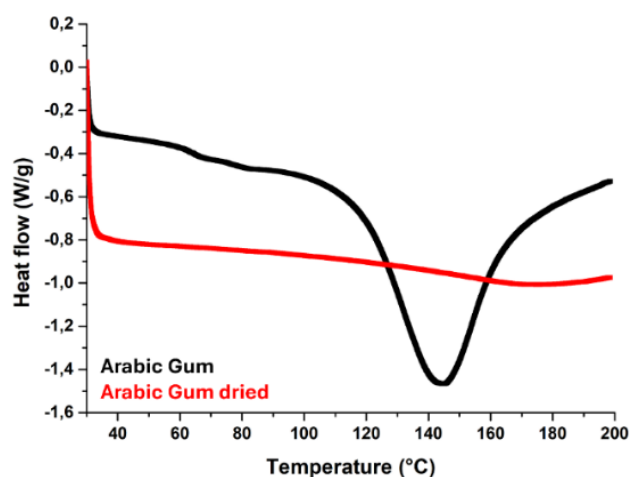


Figure 5.4 -DSC thermogram of arabic gum, exo up. Unpretreated arabic gum (black) and arabic gum after drying at 100 °C under vacuum (red).

The thermal behavior of HDPE-biopolymer blends was examined using DSC to determine how the addition of fillers impacts the melting characteristics of the polymer.

As reported in **Figure 5.5**, the overall shape of the thermograms remains essentially unchanged.

All samples, with different amounts of filler, display a melting peak for HDPE at approximately 135 °C.

This indicates that the presence of fillers does not significantly influence the melting transition of the matrix. This is further confirmed by the quantitative results summarized in **Table 5.1**, which indicate slight variations in the enthalpy of fusion (ΔH_m) and its corresponding crystallinity (X_c) across the different formulations.

The crystalline structure of HDPE remains largely intact when blended with these biopolymers.

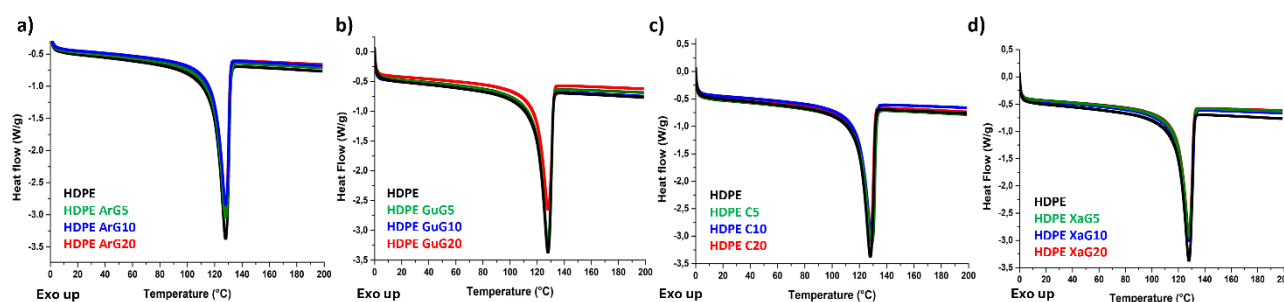


Figure 5.5 - DSC thermograms, exo up, of HDPE with different loadings (0, 5, 10, and 20 wt%) of biopolymers: 1)Arabic Gum; 2)Guar Gum; 3) Cellulose; 4) Xanthan Gum

	ΔH_m (kJ/mol)	X_c
HDPE	4.96	0.60
HDPE-GuG5	5.04	0.61
HDPE-GuG10	5.12	0.62
HDPE-GuG20	4.08	0.58
HDPE-ArG5	4.52	0.55
HDPE-ArG10	4.31	0.52
HDPE-ArG20	4.95	0.60
HDPE-C5	4.81	0.58
HDPE-C10	4.95	0.60
HDPE-C20	4.93	0.60
HDPE-XaG5	4.48	0.55
HDPE-XaG10	4.97	0.61
HDPE-XaG20	5.09	0.62

Table 5.1 - Melting enthalpy (ΔH_m) and degree of crystallinity (X_c) values for pure HDPE and for various HDPE systems modified with biopolymers (GuG, ArG, C, XaG) at different weight percentages.

5.1.2 Tensile Testing

Tensile tests were used to evaluate the mechanical performance of the blends. Based on the data provided in **Table 5.2**, it is reasonably clear that the rigidity, as demonstrated in the Young's modulus values, increased with the amount of biopolymer in the blends, regardless of the nature of the biopolymer (**Table 5.2** and **Figure 5.6**). These results suggest that biopolymers may partially reinforce the HDPE matrix, making it slightly more resistant to deformation.

Still, given the margin of error in the data, the differences between the four biopolymers may not be as pronounced as they first appear. These small changes may be more related to the structure and polarity of each biopolymer, which could affect how well they interact with the HDPE.

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ϵ_y (%)	Eng. strain at break ϵ_b (%)	Eng. stress at break (MPa)
HDPE	777 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
(HDPE-GuG5)	839 ± 64.5	24.2 ± 2.55	16.8 ± 1.6	810 ± 87.2	18.0 ± 1.92
(HDPE-GuG10)	923 ± 35.5	22.6 ± 1.01	16.5 ± 0.49	813 ± 41.3	16.7 ± 1.57
(HDPE-GuG20)	1065 ± 49.1	22.1 ± 0.52	14.9 ± 0.95	728 ± 42.5	14.1 ± 1.44
(HDPE-ArG5)	828 ± 53.5	16.1 ± 2.85	14.6 ± 1.09	833 ± 91.9	7.87 ± 5.65
(HDPE-ArG10)	921 ± 125	18.9 ± 2.04	14.5 ± 0.70	792 ± 59.6	13.8 ± 2.14
(HDPE-ArG20)	1019 ± 79.0	17.3 ± 1.43	12.4 ± 0.64	708 ± 42.2	7.67 ± 4.66
(HDPE-C5)	851 ± 64.6	19.5 ± 1.03	15.1 ± 0.66	886 ± 76.8	13.8 ± 3.00
(HDPE-C10)	960 ± 23.9	17.9 ± 0.55	13.1 ± 0.28	886 ± 30.4	10.6 ± 5.23
(HDPE-C20)	1000 ± 23.4	15.7 ± 0.72	11.0 ± 0.32	764 ± 33.1	8.58 ± 3.67
(HDPE-C40)	1424 ± 191	18.0 ± 1.84	5.85 ± 1.24	45.6 ± 9.70	4.92 ± 1.30
(HDPE-XaG5)	636 ± 411.1	21.5 ± 1.60	13.3 ± 3.53	748 ± 63.2	11.8 ± 5.82
(HDPE-XaG10)	862 ± 26.4	18.9 ± 1.37	14.4 ± 0.81	723 ± 35.5	11.0 ± 3.07
(HDPE-XaG20)	982 ± 43.9	17.8 ± 2.00	11.6 ± 0.60	634 ± 48.0	3.35 ± 1.84
(HDPE-XaG40)	1437 ± 99.1	19.9 ± 4.13	6.50 ± 1.52	32.8 ± 10.3	7.18 ± 4.12

Table 5.2 - Tensile test values of HDPE and Biopolymers blends with 5, 10, and 20 wt% of biopolymer. Tests performed at 25 °C using a deformation rate of 10 mm/min on dogbone-shaped specimens (13 mm × 2 mm × 1.4 mm); each test was conducted on five replicates.

The modified HDPE samples exhibit substantial changes in engineering yield stress and toughness as a function of filler type and content.

In general, fillers increase the yield stress over pure HDPE at relatively low filler loadings; this suggests that an increased resistance to the onset of plastic deformation has been achieved with the addition of the filler.

At higher concentrations, however, some formulations exhibit a decrease in yield stress, which implies excessive filler content can inhibit efficient stress transfer within the polymer matrix. Most of the filled systems show a progressive reduction in toughness as the filler content increases. Higher filler concentrations usually result in reduced elongation and, in some instances, more brittle behavior. This trend is consistent with the common trade-off observed

in filled polymers, where stiffness and yield properties may improve, but often at the expense of ductility and overall toughness.

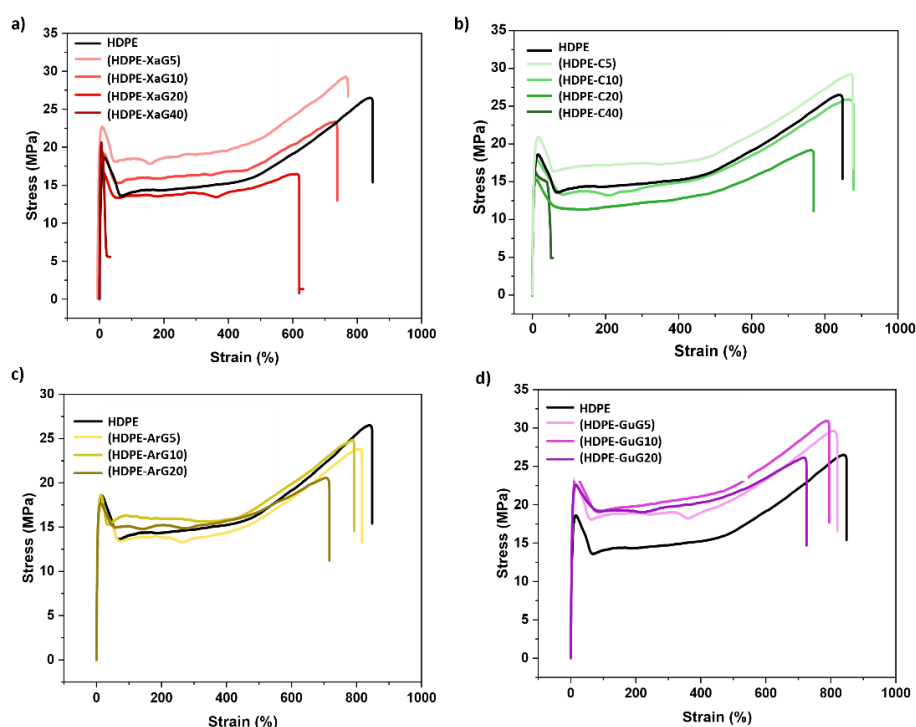


Figure 5.6 – Engineering stress-strain curves of HDPE with various loadings (5, 10 and 20 wt%) of different biopolymers (b) cellulose, c) arabic gum, d) guar gum and e) xanthan gum. The curves closest to the average are presented.

5.2 Introduction of Grafting Agent – Azidotriazine

This section focuses on the incorporation of an azidotriazine grafting agent into the HDPE–biopolymer blends during reactive processing. The aim was to investigate whether this molecule could effectively promote grafting and possible cross-linking reactions, and to assess how such chemical modifications might influence the structural and mechanical properties of the resulting materials.

This molecule had previously been studied by Van Zee, Nicolay et al.,¹⁰ who applied it to upcycle blends of PE and PP into high-performance materials. Their findings showed that, under reactive extrusion at industrially relevant temperatures, the decomposition of the azidotriazine triggers a series of chemical reactions that form amorphous, phase-separated nanostructures. These nanostructures tend to form at the interfaces between different polymers. Interestingly, these nanostructures behave as multivalent thermomechanically

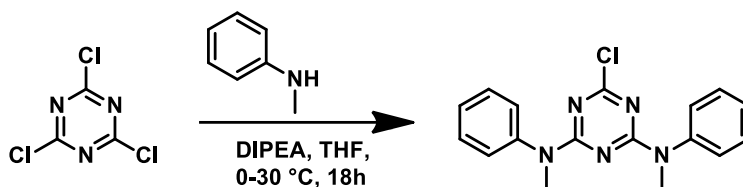
reversible cross-linkers, helping to reinforce the material. As a result, the treated blends show a significant improvement in ductility compared to their untreated counterparts. In addition, they demonstrate excellent dimensional stability even at high temperatures, along with good mechanical recyclability. Altogether, this strategy offers a promising path toward more sustainable polymer processing and the development of advanced, high-performance materials from unsorted polyolefin blends.

5.2.1 Synthesis and Characterization of 6-Azido-*N*²,*N*⁴-dimethyl-*N*²,*N*⁴-diphenyl-1,3,5-triazine-2,4-diamine (**Tr-N₃**)

The synthesis of 6-Azido-*N*²,*N*⁴-dimethyl-*N*²,*N*⁴-diphenyl-1,3,5-triazine-2,4-diamine (**Tr-N₃**) was carried out in two steps, following a protocol reported in literature.¹⁰

In the first step, 6-Chloro-*N*²,*N*⁴-dimethyl-*N*²,*N*⁴-diphenyl-1,3,5-triazine-2,4-diamine (**Tr-Cl**) was obtained by reacting cyanuric chloride with *N*-methylaniline in the presence of *N,N*-diisopropylethylamine (DIPEA), which acted as a base (**Scheme 5.1**). The reaction was performed in dry THF.

The resulting product, **Tr-Cl**, was isolated as a yellowish solid, with a purity of 91.7% (calculated by ¹H-NMR) and a yield of 87.5% by weight.



Scheme 5.1 - Synthesis of **Tr-Cl**

The formation of the desired product was confirmed through ¹H-NMR and ¹³C-NMR analysis. Spectra and signal assignments are shown below (**Figure 5.7**).

Additional confirmation came from GC-MS (EI) analysis, which revealed a molecular ion peak at 325.20 m/z [M]⁺, a value in excellent agreement with the expected theoretical mass of 325.11 m/z.

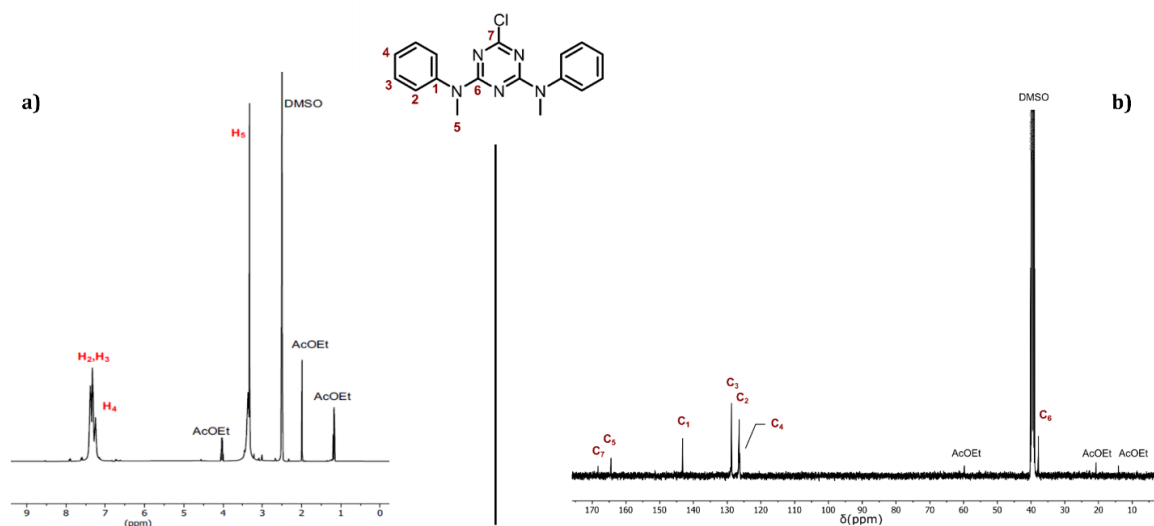
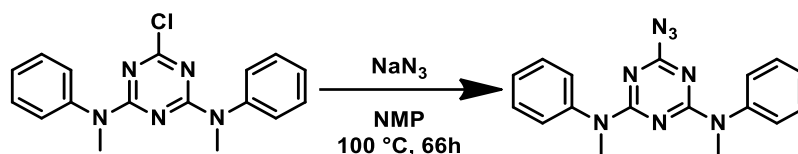


Figure 5.7 – a) $^1\text{H-NMR}$ of **Tr-Cl**, 400 MHz, DMSO-d_6 , 298 K; b) $^{13}\text{C-NMR}$ of **Tr-Cl**, 101 MHz, DMSO-d_6 , 298 K

In the second step, the chlorine atom on the triazine ring is substituted by an azido group through a reaction between **Tr-Cl** (obtained in step 1) and sodium azide (NaN_3) (**Scheme 5.2**).

The reaction is performed in anhydrous *N*-methyl-2-pyrrolidone (NMP) as solvent.

Tr-N₃ was obtained as a yellowish solid, with a yield of 95% by weight.



Scheme 5.2 - Synthesis of **Tr-N₃**

Similarly, the successful formation of the desired product was confirmed by both $^1\text{H-NMR}$ analysis and infrared spectroscopy (**Figures 5.8** and **5.9**).

The IR spectrum shows the characteristic peak at 2127 cm^{-1} , corresponding to the asymmetric stretching vibration of the N_3 group of **Tr-N₃**.

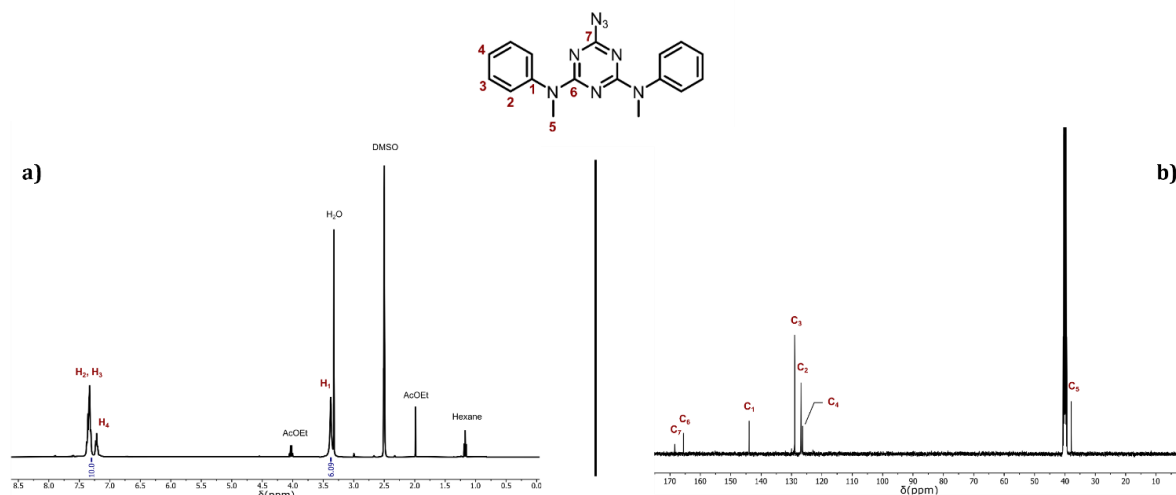


Figure 5.8 – a) ^1H -NMR of **Tr-N₃**, 400 MHz, DMSO-d_6 , 298 K; b) ^{13}C -NMR of **Tr-N₃**, 400 MHz, DMSO-d_6 , 298 K

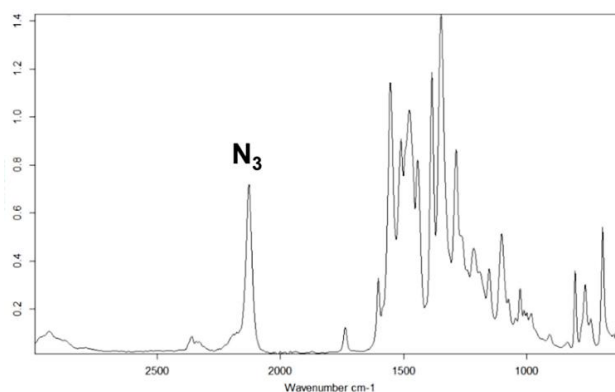


Figure 5.9 – FT-IR spectrum of **Tr-N₃**

5.2.2 Synthesis of Masterbatch of **Tr-N₃** in PE (40 wt%)

To make the introduction of **Tr-N₃** into the reactive extrusion process more straightforward and consistent, a masterbatch containing 40 wt% of **Tr-N₃** in HDPE was prepared. This strategy was chosen to improve the handling and dispersion of the grafting agent in the polyolefin blend.

The masterbatch was synthesized by first dissolving **Tr-N₃** in xylene at 100 °C. At the same time, a suspension of HDPE in xylene was heated to 140 °C under a nitrogen atmosphere to prevent any thermal oxidation. Once both mixtures were fully homogeneous, they were combined and stirred together at 140 °C for 5 minutes. After mixing, the solvent was removed under vacuum, yielding a yellowish solid. The product was then thoroughly dried under

vacuum to eliminate any residual solvent, resulting in a stable, solid masterbatch that could be easily used for reactive extrusion

5.3 Reactive Extrusion

Reactive extrusion was performed using two different processing approaches, schematically shown in **Figure 5.10**:

- In the first approach (E1), all the components (**Tr-N₃**, the biopolymer, and HDPE) were added to the extruder at the same time and mixed at 160 °C for 5 minutes. The temperature was then raised to 214 °C to decompose **Tr-N₃** and initiate the grafting reaction (**Figure 5.10, left**).

The goal of this method was to test the possibility of producing a grafted polymer, with nitrene grafting occurring in the presence of both the synthetic and bio-based polymers.

- The second approach (E2) entailed a stepwise process. Initially, only the HDPE and **Tr-N₃** were introduced and mixed at 160 °C for 5 minutes. After this period, the temperature was raised to 214 °C to activate the azidotriazine, and the reaction was allowed to proceed for 10 minutes. The system was cooled down to 160 °C after 10 minutes, and the biopolymer was added (**Figure 5.10, right**).

This protocol was designed to produce HDPE cross-linked with thermomechanically reversible polyazane oligomers. In this case, the biopolymer acts as a structural filler.

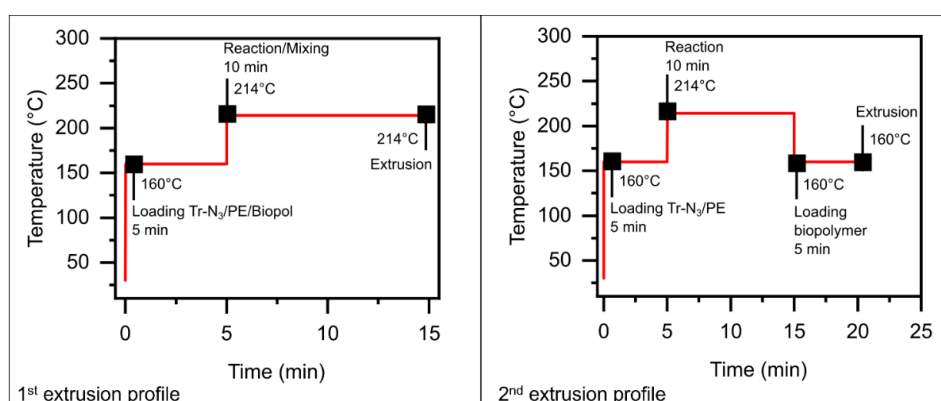


Figure 5.10 - Reactive extrusion protocols: on the left, the first extrusion profile (E1), used to produce a grafted polymer; on the right, the second profile (E2), where the biopolymer is added as a filler.

The suitability of the four biopolymers for the reactive extrusion process was investigated using TGA with a 30 minutes isotherm at 214°C (**Figure 5.11**). Among the materials tested, cellulose and xanthan gum were the most thermally stable and were selected to conduct reactive processing.

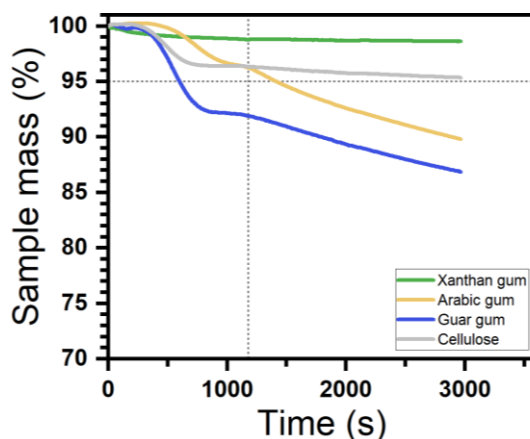


Figure 5.11 - Isotherm TGA of biopolymers (xanthan gum (green), Arabic gum (yellow), guar gum (blue), cellulose (grey)); 30min at 214 °C.

5.4 Compatibilization of HDPE and Cellulose using Tr-N₃

For the compatibilization reaction by reactive extrusion, a cellulose content of 20 wt%, named as **C20**, was chosen. This composition seemed to offer an interesting combination of biopolymer loading and mechanical properties (see **Table 5.1**).

To further explore the effects of functionalization, two different concentrations of azidotriazine-based grafting agent (**Tr-N₃**) were tested: 1 wt% (T1) and 5 wt% (T2), corresponding to approximately 0.1 mol% and 0.5 mol%, respectively. These concentrations were based on a study by Nicolay, Van Zee *et al.*¹¹

In this study, it was found that modifying polyethylene with **Tr-N₃** at concentrations below 0.50 mol% induced chain branching. This improved the material's melt strength while staying below the gel point. At concentrations of 0.50 mol% or higher of **Tr-N₃**, the materials exhibit an insoluble fraction and behave more like thermosets.

In the two extrusion protocols, we observed a steady increase in torque over time (**Figure 5.12**). This increase in torque is typically associated with changes in the melt viscosity, which

in this case can be taken as an indication of ongoing chemical reactions, such as grafting, branching and cross-linking.

The torque increase was much more noticeable when 5 wt% of **Tr-N₃** was used, indicating a higher degree of branching and network formation compared to the 1 wt% formulation.

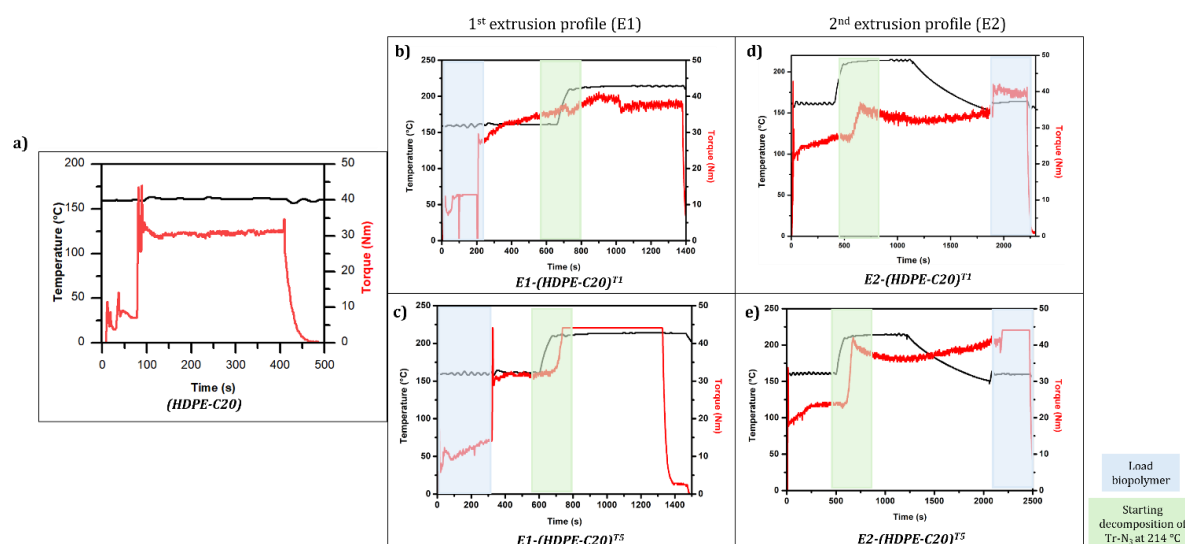


Figure 5.12 - Comparison of the extrusion profiles, highlighting the zones where cellulose is introduced (light blue) and the point where **Tr-N₃** decomposes (light green). a) HDPE-C20; b) E1-(HDPE-C20)^{T1}; c) E1-(HDPE-C20)^{T5}; d) E2-(HDPE-C20)^{T1}; e) E2-(HDPE-C20)^{T5}.

The samples obtained were analyzed through thermal and dynamic mechanical testing to investigate the impact of the addition of **Tr-N₃** on the properties of these new materials.

5.4.1 Differential Scanning Calorimetry Analysis

DSC analysis of the second thermal scan reveals a minimal reduction in crystallinity for the HDPE samples with 5 wt% **Tr-N₃** (**Figure 5.13**). This reduction suggests that grafting and cross-linking reactions resulting from the decomposition of **Tr-N₃** produce a slightly less ordered structure. Specifically, E1(HDPE-C20)^{T1} and E2(HDPE-C20)^{T1} exhibit ΔH_m values of 4.77 and 4.61 kJ/mol and crystallinity (X_c) values of 0.58 and 0.56. In contrast, E1(HDPE-C20)^{T5} and E2(HDPE-C20)^{T5} exhibit ΔH_m values of 4.07 and 4.33 kJ/mol, with X_c values of 0.49 and 0.53. In contrast, the use of two different extrusion protocols does not seem to significantly affect the thermal properties of the material in this case.

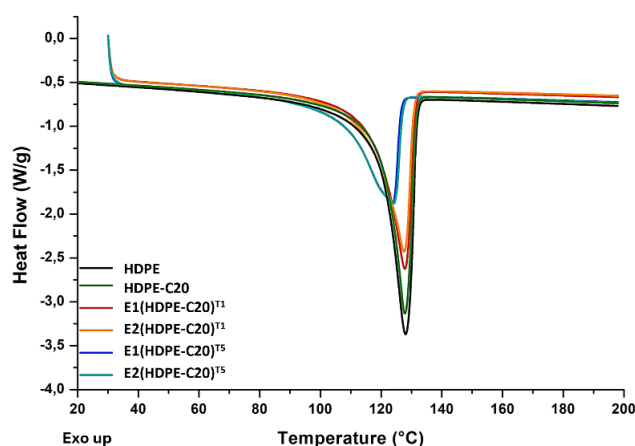


Figure 5.13 - DSC thermograms, 2nd heating, exo up, of HDPE (black); HDPE and 20 wt% of cellulose (green); HDPE, 20 wt% of cellulose and 1 wt% of Tr-N₃ (E1, red, E2, orange); HDPE, 20 wt% of cellulose and 5 wt% of Tr-N₃ (E1, blue, E2, turquoise)

5.4.2 Tensile Testing and Dynamic Mechanical Analysis

As shown in **Table 5.3**, the tensile test results for HDPE-C20 blends containing **Tr-N₃** reveal a marked increase in engineering yield stress ($\sigma_y > 21$ MPa) compared to the unprocessed samples, both in samples with different amounts of azidotriazine and in those produced under different extrusion profiles (**Figure 5.14**).

This trend suggests that the chemical modifications and processing conditions used here may be strengthening the material, either by increasing its stiffness or by promoting a more efficient network within the polymer matrix.

Moreover, the E1(HDPE-C20)^{T1} sample also shows a high Young's modulus ($E = 1045$ MPa). This suggests that introducing and activating Tr-N₃ during the first step of the extrusion profile, in the presence of only HDPE, may have promoted a greater degree of grafting onto the polymer matrix.

However, these improvements come at the expense of ductility, which decreases, especially for the samples E2(HDPE-C20)^{T1}, E1(HDPE-C20)^{T5} and E2(HDPE-C20)^{T5}. This is expected, as the formation of a grafted system generally leads to a material that is stiffer and more brittle.

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ϵ_y (%)	Eng. strain at break ϵ_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
(HDPE-C20)	1003 ± 23.4	15.7 ± 0.72	11.0 ± 0.32	764 ± 33.1	8.58 ± 3.67
E1(HDPE-C20) ^{T1}	1045 ± 47.2	23.4 ± 1.70	12.3 ± 0.14	573 ± 83.5	8.45 ± 5.08
E2(HDPE-C20) ^{T1}	870 ± 61.5	21.4 ± 1.39	10.6 ± 0.84	31.6 ± 13.7	4.51 ± 3.42
E1(HDPE-C20) ^{T5}	870 ± 51.6	24.6 ± 2.70	16.0 ± 1.37	27.1 ± 6.80	12.3 ± 1.38
E2(HDPE-C20) ^{T5}	779 ± 41.8	22.9 ± 1.16	16.7 ± 4.21	38.2 ± 11.1	5.86 ± 2.80

Table 5.3 – Tensile test values reported Young's Modulus, Eng. yield stress, Eng. yield strain, Eng. strain at break, Eng. stress at break for pure HDPE, (HDPE-C20), E1(HDPE-C20)^{T1}, E1(HDPE-C20)^{T5}, E2(HDPE-C20)^{T5}

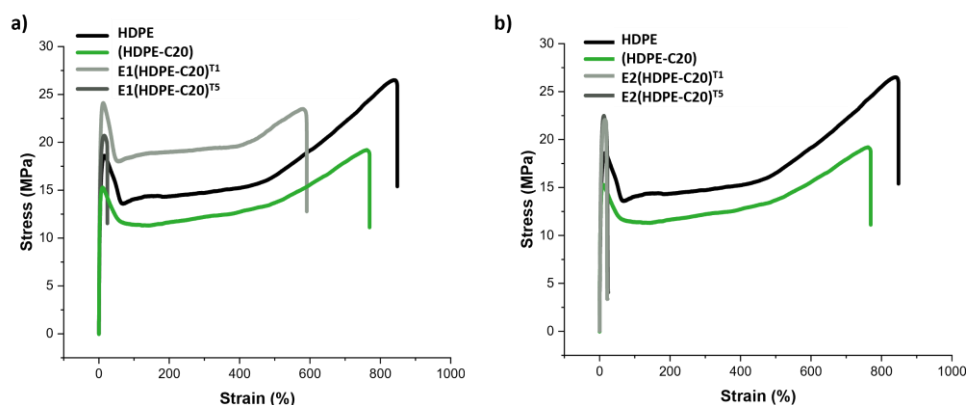


Figure 5.14 - Engineering stress versus strain curves at room temperature of HDPE and modified HDPE blended with cellulose containing Tr-N₃. a) Following 1st extrusion profile; b) Following 2nd extrusion profile

The thermomechanical properties were investigated at 1% strain and 1 Hz frequency. Compared to pure HDPE, all the materials with 20 wt% cellulose and different **Tr-N₃** contents showed similar or slightly higher E' values below the T_m of HDPE, around 130-140 °C. Notably, samples with lower **Tr-N₃** content (T1) showed a modest increase in E' compared to those with higher content, suggesting subtle differences in network formation. (**Figure 5.15, Panel A**)

To facilitate the comparison, looking at the storage modulus at 180 °C, further differences become apparent. While E1(HDPE-C20)^{T5} and E2(HDPE-C20)^{T5} reach plateaus of 1.02 and 0.82 MPa, respectively, their networks seem less densely cross-linked than the control sample

reported for similar systems consisting of pure HDPE and **Tr-N₃**, as described by *Sun et al.*¹¹, which shows an E' of 1.33 MPa. This points to a lower crosslink density or weaker interactions within the modified systems.

Relative to the samples with 1 wt% **Tr-N₃**, the E1 extrusion profile softened and flowed under its own weight at 170 °C, whereas the E2 profile held its shape throughout the DMA temperature ramp. The corresponding E' values of 0.19 and 0.17 MPa, respectively, reflect differences in how effectively the grafting agent reacted during the reactive extrusion process.

The loss modulus (E'') and tan delta ($\tan \delta$) curves show that all samples undergo transitions around 130–140 °C. Adding **Tr-N₃** slightly changes the peaks, and higher amounts tend to broaden or shift them, reflecting more complex chain relaxation behavior (**Figure 5.15, Panel B**). Moreover, these composites exhibit lower and broader $\tan \delta$ peaks compared to neat HDPE, indicating that the addition of the filler and the grafting agent may enhance energy dissipation, vibration damping, and mechanical stability. (**Figure 5.15, Panel C**)

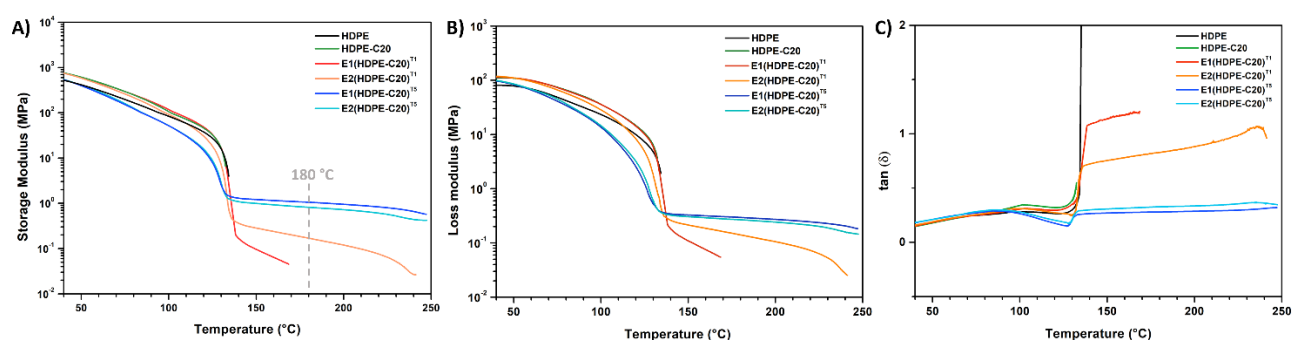


Figure 5.15 – DMA analysis (1% strain and 1 Hz frequency) of HDPE (black curve) and HDPE modified samples; A) Storage modulus (MPa) vs Temperature (°C), E' is highlighted with gray dashed line; B) Loss modulus (MPa) vs Temperature (°C); C) $\tan \delta$ vs Temperature (°C)

5.4.3 Upcycling of HDPE+Cellulose (>20 wt%) using **Tr-N₃**

Because the addition of triazine led to a noticeable drop in toughness, we increased the cellulose content to further challenge the material and determine whether our additive could help recover some of the lost performance.

As expected, grafting or crosslinking led to a decrease in elongation at break, while the composites became significantly stiffer and exhibited a marked increase in engineering yield stress compared to both neat HDPE and HDPE/cellulose. This response is consistent with

what is normally seen in crosslinked systems, where gains in stiffness often come at the cost of reduced toughness.

The results from the stiffness values found so far indicate that cellulose could be acting as a reinforcing filler since Young's modulus values increased with the higher loading of the biopolymer.

Following the attempts to prepare blends with 40 wt% cellulose (HDPE-C40) compatibilized by adding **Tr-N₃**, using two extrusion protocols, the produced materials possess a Young's modulus greater than that of their equivalents produced with HDPE-C20 (**Figure 5.16**). Most importantly, these are significantly higher compared to those reported for similar systems consisting of pure HDPE and **Tr-N₃**, as described by *Sun et al.*¹¹

The most remarkable effect is obtained in the case of the E1(HDPE-C40)^{T1} and E2(HDPE-C40)^{T1} samples, both containing 1 wt% azidotriazine (**Table 5.4**). These display a significant improvement in both Young's modulus and engineering yield stress, as compared to their non-functionalized counterparts.

The elastic modulus reaches 1256 MPa for E1 and 1421 MPa for E2, values that are comparable to, or higher than, those of the unmodified HDPE-C40 sample, while providing a more balanced mechanical response.

Another significant enhancement involves yield stress, which rises from approximately 18 MPa for HDPE-C40 to 31.2 MPa (E1) and 29.0 MPa (E2), reflecting an increase of over 60%. This increase suggests that azidotriazine may enhance the interface between the polymer matrix and cellulose, potentially due to stronger interactions with the cellulose surface. These hypotheses will be explored further in future studies.

However, the values obtained in this work seem considerably higher than those reported by *Sun et al.*¹¹, who recorded much lower modulus values for HDPE/Tr-N₃ systems without cellulose: 670 MPa for the sample containing 1 wt% **Tr-N₃** and 517 MPa for the sample containing 5 wt% **Tr-N₃**.

These results clearly suggest that extrusion protocols 1 and 2 help optimize the cellulose reinforcing effect in the polymer matrix. This yields significantly stiffer materials.

The increased Young's modulus and engineering yield stress observed in composites prepared with 1 wt% **Tr-N₃** and 40 wt% cellulose are of great interest; for this reason, additional application-oriented tests should be performed, such as creep resistance and environmental stress cracking resistance tests.⁸

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ϵ_y (%)	Eng. strain at break ϵ_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
(HDPE-C30)	1127 ± 61.9	22.8 ± 1.25	10.6 ± 0.96	430 ± 235.2	9.32 ± 3.89
(HDPE-C40)	1424 ± 191	18.0 ± 1.84	5.85 ± 1.24	45.6 ± 9.70	4.92 ± 1.30
(HDPE-C50)	1607 ± 31.7	19.8 ± 1.63	4.67 ± 1.11	27.1 ± 6.32	8.23 ± 1.84
E1(HDPE-C40) ^{T1}	1256 ± 39.9	31.2 ± 1.70	8.74 ± 1.06	16.9 ± 10.6	16.8 ± 1.86
E2(HDPE-C40) ^{T1}	1421 ± 78.8	29.0 ± 1.75	6.47 ± 0.48	10.8 ± 3.23	12.9 ± 2.80
E2(HDPE-C40) ^{T5}	1114 ± 160	22.9 ± 2.33	7.93 ± 0.08	12.6 ± 2.55	9.61 ± 3.59

Table 5.4 - Tensile test values reported Young's Modulus, Eng. yield stress, Eng. yield strain, Eng. strain at break, Eng. stress at break for pure HDPE, HDPE blended with 30, 40, 50 wt% of cellulose and systems 40 wt% cellulose compatibilized by adding **Tr-N₃** (1 wt% and 5 wt%) with both extrusion profiles

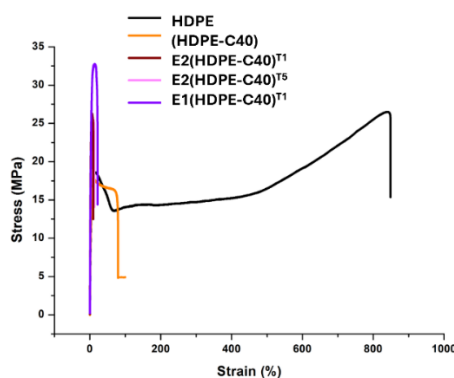


Figure 5.16 -Engineering stress versus strain curves of HDPE and modified HDPE; pure HDPE (black), (HDPE-C40) (orange), E2(HDPE-C40)^{T1} (brown), E2(HDPE-C40)^{T5} (pink), E1(HDPE-C40)^{T5} (purple)

Figure 5.17, Panel A, presents the temperature-dependent storage modulus curves of pure HDPE and its composites with 20 and 40 wt% cellulose, including the formulations containing different amounts of the **Tr-N₃** (T1, T2) additive and processed according to the E1 and E2 extrusion profiles. The storage moduli of the HDPE-C40 composites are significantly higher compared to their 20 wt% previously treated counterparts. At 180 °C, E2(HDPE-C40)^{T5}

exhibits a substantially greater plateau modulus of 3.3 MPa, which is well above the values observed for all C20 counterparts. This reflects a much stronger network that maintains stiffness even deep into the melt region. Samples containing 1 wt% **Tr-N₃** (with both E1 and E2) show lower moduli of 0.96 MPa and 0.37 MPa, respectively, but still remain significantly stiffer than their respective C20 composites. This suggests that at 40 wt% cellulose, the material retains most of its solid-like characteristics, likely due to a constrained fiber network that stabilizes the melt. As in the C20 system, the C40 composites show transitions in E'' and $\tan \delta$ around 130–140 °C (**Figure 5.17, Panels B and C**). The addition of **Tr-N₃** slightly shifts and broadens the peaks, reflecting more complex chain relaxation, while the overall lower and broader $\tan \delta$ compared to pure HDPE indicates enhanced energy dissipation, damping, and mechanical stability.

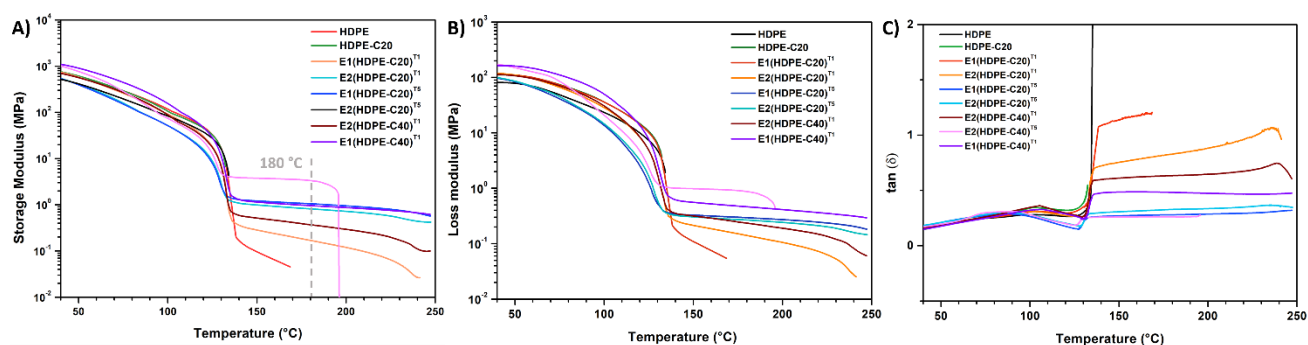


Figure 5.17 - DMA analysis (1% strain and 1 Hz frequency) of HDPE (black curve) and HDPE modified samples; A) Storage modulus (MPa) vs Temperature (°C), E' is highlighted with gray dashed line; B) Loss modulus (MPa) vs Temperature (°C); C) $\tan \delta$ vs Temperature (°C)

5.5 Compatibilization of HDPE and Xanthan Gum using **Tr-N₃**

The reactive extrusion was conducted using 20 wt% xanthan gum while examining the two **Tr-N₃** concentrations (1 wt% and 5 wt%).

However, unlike the trials with cellulose, only the second extrusion protocol was suitable, as the product from the first extrusion seemed to be burned. This occurrence was probably due to xanthan gum degradation processes triggered by the conditions of the process, even though previous TGA measurements at 214 °C showed that the gum was the most stable of the four biopolymers considered under these conditions.

The torque values, reported in the graphs in **Figure 5.18**, indicate a two-stage process for both concentrations of **Tr-N₃**. Initially, there is an increase during the reaction between HDPE and **Tr-N₃**, followed by a second increase upon the addition of the gum.

This suggests a two-step process: the first increase seems to be related to the decomposition of **Tr-N₃** and its consecutive grafting of HDPE, while the second rise likely reflects the additional effects of processing as the gum is incorporated, which appears to change the material's rheological properties.

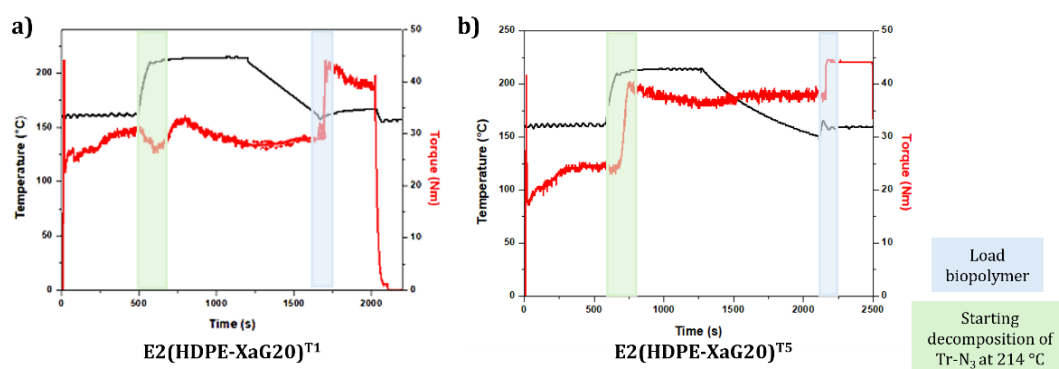


Figure 5.18 - Comparison of the extrusion profiles, highlighting the zones where cellulose is introduced (light blue) and the point where **Tr-N₃** decomposes (light green). a) E2(HDPE-XaG20)^{T1}; b) E2(HDPE-XaG20)^{T5}

Looking at the exothermic-up DSC thermograms from the second heating ramp (**Figure 5.19**), there might seem to be a slight decrease in crystallinity for the HDPE/Xanthan Gum/**Tr-N₃** systems.

However, the ΔH_m and crystallinity values, E2(HDPE-XaG20)^{T1}: 4.82 kJ/mol, $X_c = 0.58$; E2(HDPE-XaG20)^{T5}: 4.98 kJ/mol, $X_c = 0.60$, are actually very close to those of pure HDPE.

This suggests that, in this case, the presence of the filler and the grafting agent doesn't appear to noticeably affect the polymer's structure. Additional experiments will be carried out to better understand any subtle effects.

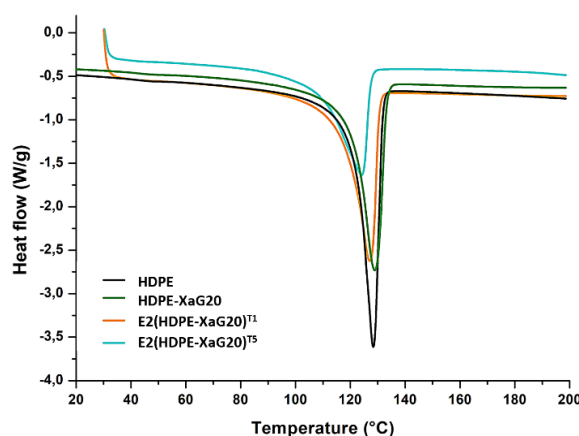


Figure 5.19 – DSC thermograms, 2nd heating, exo up, of HDPE (black); HDPE and 20 wt% of xanthan gum (green); HDPE, 20 wt% of xanthan gum and 1 wt% of Tr- N_3 (E2, orange); HDPE, 20 wt% of xanthan gum and 5 wt% of Tr- N_3 (E2, turquoise)

5.5.1 Tensile Testing and Dynamic Mechanical Analysis

The samples were subjected to uniaxial tensile testing at room temperature to investigate their mechanical performance. The obtained values remain very similar to those of pure HDPE or the HDPE/xanthan gum blend.

Table 5.5 indicates that the incorporation of azidotriazine leads to tensile test results comparable to those obtained under the same conditions using cellulose as a filler.

Notably, in this case, the E2(HDPE-X20)^{T1} sample exhibits a remarkable increase in engineering yield at break, reaching 159%, which indicates a significant enhancement in the material's ability to undergo plastic deformation before failure.

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ε_y (%)	Eng. strain at break ε_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
(HDPE-XaG20)	982 ± 43.9	17.8 ± 2.00	11.6 ± 0.60	634 ± 48.0	3.35 ± 1.84
E2(HDPE-XaG20) ^{T1}	958 ± 50.9	23.9 ± 1.24	11.9 ± 0.33	159 ± 10.4	4.80 ± 3.46
E2(HDPE-XaG20) ^{T5}	787 ± 57.9	20.9 ± 0.94	13.8 ± 1.44	85.5 ± 27.3	4.79 ± 3.48

Table 5.5 - Tensile test values reported Young's Modulus, Eng. yield stress, Eng. yield strain, Eng. strain at break, Eng. stress at break for pure HDPE, (HDPE-XaG20), E2(HDPE-XaG20)^{T1}, E2(HDPE-XaG20)^{T5}

Thermomechanical properties were measured at 1% strain and 1 Hz. Below the T_m of HDPE (≈ 130 – 140 °C), E2(HDPE-XaG20)^{T5} shows slightly lower E' values than pure HDPE, while E2(HDPE-XaG20)^{T1} is slightly higher. At 180 °C, T1 and T5 plateau at 0.13 and 0.72 MPa, respectively, indicating less densely cross-linked networks compared to the reference system of pure HDPE/**Tr-N₃** reported by Sun et al.¹¹ ($E' = 1.33$ MPa) (**Figure 5.20, Panel a**). This suggests a lower crosslink density or weaker interactions in the modified HDPE systems. As seen in *Panels b and c* of **Figure 5.20**, the xanthan gum-based composites also show E'' and $\tan \delta$ transitions around 130 °C. The addition of **Tr-N₃** causes a slight shift and widening of these peaks, suggesting more complex chain motions, while the overall lower and broader $\tan \delta$ relative to pure HDPE points to improved energy dissipation and greater mechanical stability.

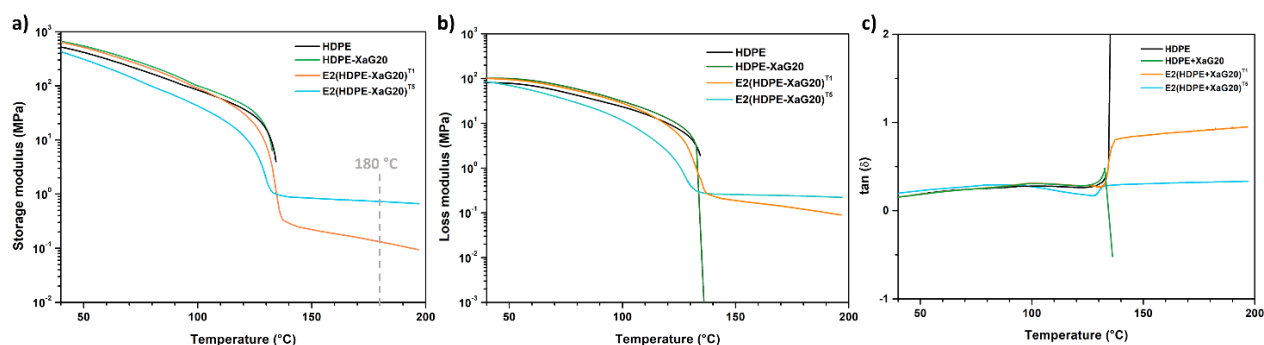


Figure 5.20 - DMA analysis (1% strain and 1 Hz frequency) of HDPE (black curve) and HDPE modified samples; a) Storage modulus (MPa) vs Temperature (°C), E' is highlighted with gray dashed line; b) Loss modulus (MPa) vs Temperature (°C); c) $\tan \delta$ vs Temperature (°C)

5.6 Introduction of Grafting Agent – Maleimide

In addition to the azidotriazine-based study, inspired by previous work by Van Zee, *Nicolaÿ et al.*, we also investigated a strategy involving boronate chemistry, aiming to assess whether the properties and overall effect could be modified or enhanced.^{8, 12}

Dioxaborolane groups, particularly, have attracted increasing interest due to their ability to undergo catalyst-free metathesis reactions through an associative exchange mechanism.

These reactions offer several advantages, including high thermal stability and strong chemical orthogonality, which make them highly suitable for creating dynamic covalent networks.^{8,13,14} In addition, dioxaborolanes are especially promising for developing vitrimers, thanks to their

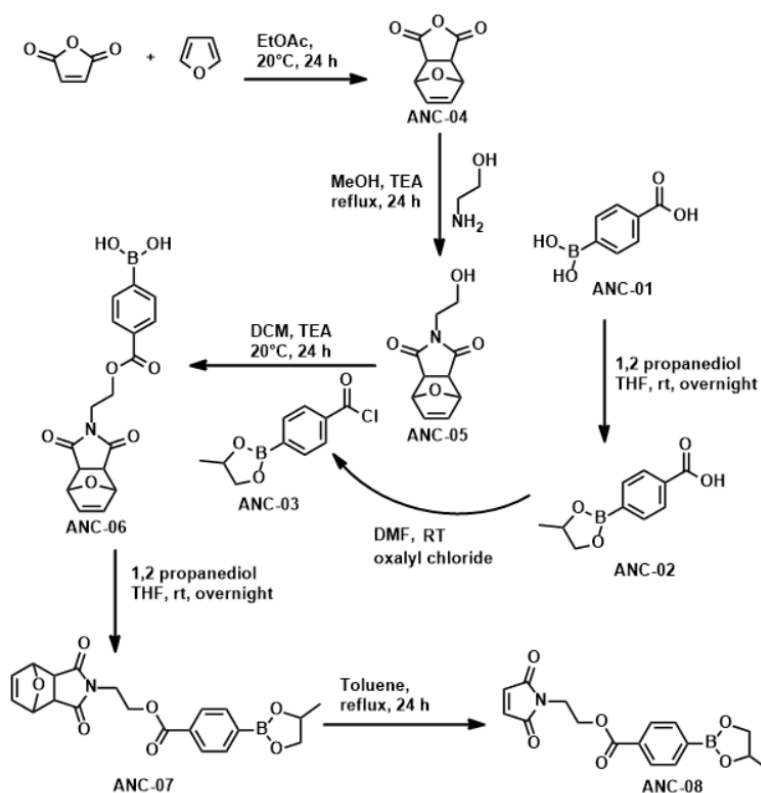
exceptionally high bond dissociation energy.¹⁵⁻¹⁷ These properties open up interesting possibilities for designing adaptable and reprocessable polymer systems.

To implement this strategy, we adopted a two-step reactive extrusion process. The first step involved the radical-initiated grafting of maleimide groups onto the polymer backbone, setting the stage for the introduction of dioxaborolane functionalities. The second involves the introduction of the filler.

This strategy was designed to investigate whether the use of a different covalent chemistry influences the interfacial compatibility of HDPE and biopolymer components in blends and their performance in terms of mechanical properties.

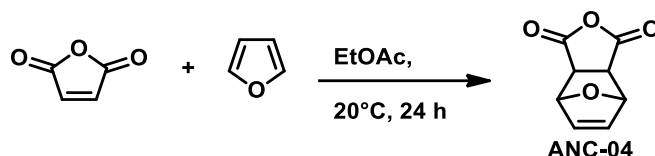
5.6.1 Synthesis and Characterization of 2-(2,5-dioxo-2,5-dihydro-pyrrol-1-yl)ethyl 4-(4-methyl-1,3,2-dioxaborolan-2-yl)benzoate (**ANC_08**)

The new dioxaborolane-maleimide grafting agent (**ANC_08**) was synthesized through a seven-step process by adapting and modifying the protocol reported by Formon *et al.* (**Scheme 5.3**).^{18,19}



Scheme 5.3 – Synthetic route for maleimide-based boronic ester **ANC_08**

The first step is the preparation of 3,6-epoxy-1,2,3,6-tetrahydropthalic anhydride (**ANC_04**), which was prepared by a Diels–Alder reaction between maleic anhydride and furan in ethyl acetate at room temperature (**Scheme 5.4**). After 24 hours of stirring, the formation of colorless crystals reflected the success of the reaction. $^1\text{H-NMR}$ spectroscopy confirmed the formation of the desired cyclic adduct (**Figure 5.21**).



Scheme 5.4 - **ANC_04** synthesis

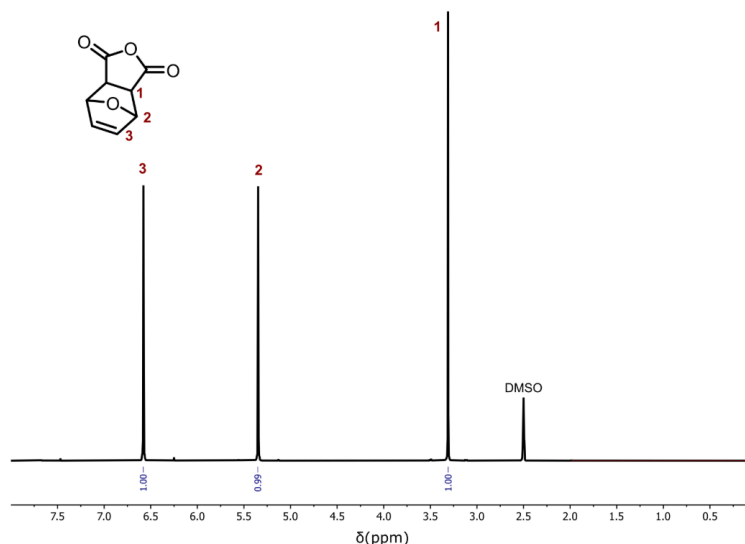
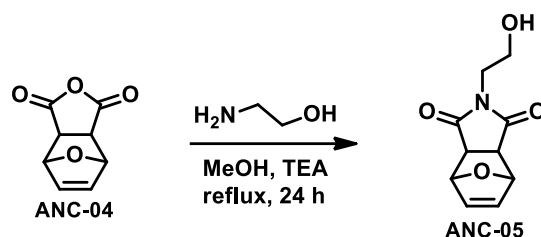


Figure 5.21 - $^1\text{H-NMR}$ of **ANC_04** (400 MHz, DMSO-d_6 , 298 K)

Starting from **ANC_04**, 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-4,7-epoxyisoindole-1,3-dione (**ANC_05**) was synthesized through a two-step one-pot transformation: first, the ring opening of the anhydride, followed by imide formation using ethanolamine and triethylamine as the base (**Scheme 5.5**). The reaction was carried out in methanol. To enable reagent addition under controlled conditions, the methanol was initially cooled to 0 °C. The mixture was then refluxed for 24 hours. As the reaction progressed, the solution gradually turned orange, an observation that aligned with the expected course of imide formation.

The successful synthesis of **ANC_05** was later confirmed by ^1H -NMR analysis, highlighted by the appearance of a multiplet at 3.67 ppm, attributed to the CH_2 protons directly attached to the imidic nitrogen atom (**Figure 5.22**).



Scheme 5.5 - *ANC_05* synthesis

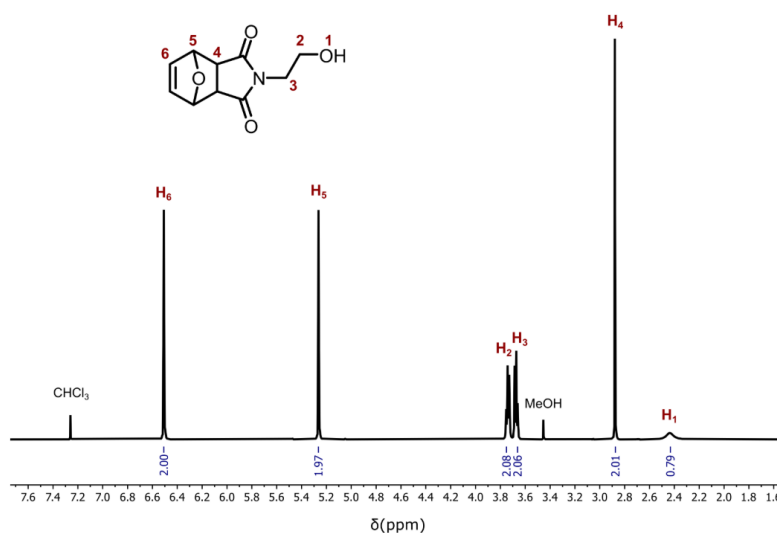
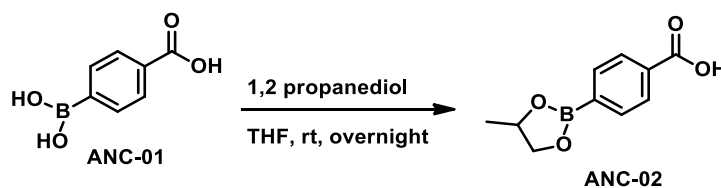


Figure 5.22 - ^1H -NMR of *ANC_05* (400 MHz, CDCl_3 , 298 K)

To introduce the boronic ester functionality, 4-(4-methyl-1,2,3-dioxaborolan-2-yl)benzoic acid (**ANC_02**) was synthesized via condensation of 1,2-propanediol onto 4-carboxyphenylboronic acid under reflux in THF (**Scheme 5.6**). The process went smoothly over 14 hours, and following the removal of the solvent, the product was isolated as a white solid in an excellent yield of 99%.



Scheme 5.6 - *ANC_02* synthesis

To activate the carboxylic acid group for the subsequent esterification reaction, **ANC_02** was converted into the corresponding acid chloride, *4-(4-Methyl-1,2,3-dioxaborolan-2-yl) benzoyl chloride* (**ANC_03**), using oxalyl chloride in anhydrous dichloromethane under a nitrogen atmosphere (**Scheme 5.7**). A catalytic quantity of DMF was added to initiate the reaction. After the addition of oxalyl chloride, intense bubbling was observed, indicating the release of CO and CO₂. This bubbling slowed down after about two hours, signaling the completion of the reaction. After evaporation of the solvent under reduced pressure, the acid chloride was obtained as a dry solid in 92% yield.

The successful conversion was further confirmed by ^1H -NMR spectroscopy, showing the disappearance of the singlet at $\delta=13.09$ ppm, which corresponds to the hydroxyl proton of the original carboxylic acid group (**Figure 5.23**).



Scheme 5.7 - ANC_03 synthesis

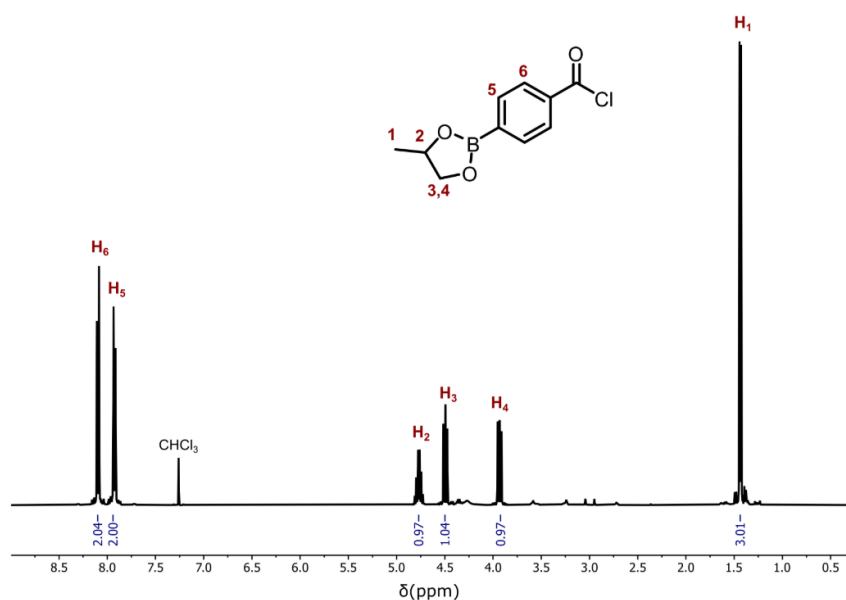
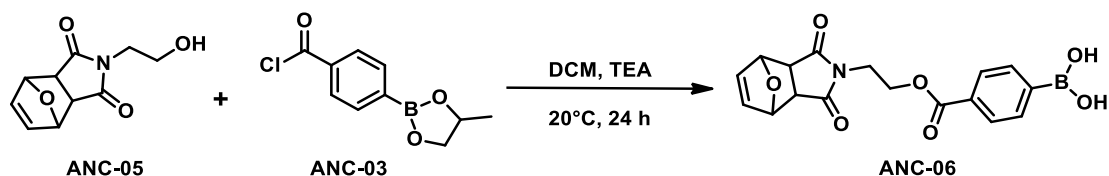


Figure 5.23 - ^1H -NMR of **ANC_03** (400 MHz, CDCl_3 , 298 K)

The next step was to couple the boronic acid derivative (**ANC_03**) to the imide intermediate (**ANC_05**) to form (4-((2-(1,3-dioxo-3a,4,7,7a-tetrahydro-4,7-epoxyisoindol-2-yl)

ethoxy)carbonyl)phenyl)boronic acid (**ANC_06**), which was the goal structure containing the maleimide and boronic ester functional groups (**Scheme 5.8**). This coupling reaction was performed by adding **ANC_03** to a cooled solution of **ANC_05** in dry dichloromethane and triethylamine under nitrogen (the mixture was kept at 0 °C during the addition to reduce side reactions). The reaction vessel was not allowed to warm above 0 °C during the addition, then stirred at room temperature for 18 hours. Upon completion, the solvent was removed in vacuo, and the crude material was washed with water and extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated to generate the product. The ^1H NMR spectrum showed a duplicated set of signals, likely due to the presence of stereoisomers (**Figure 5.24**). Interestingly, this pattern disappeared in the following reaction step, suggesting that the stereoisomeric mixture was resolved during the process. The successful formation of the ester linkage was further supported by ^1H -NMR data, which revealed the expected chemical shifts associated with both the boronic ester moiety and the imide unit (**Figure 5.24**).



Scheme 5.8 - **ANC_06** synthesis

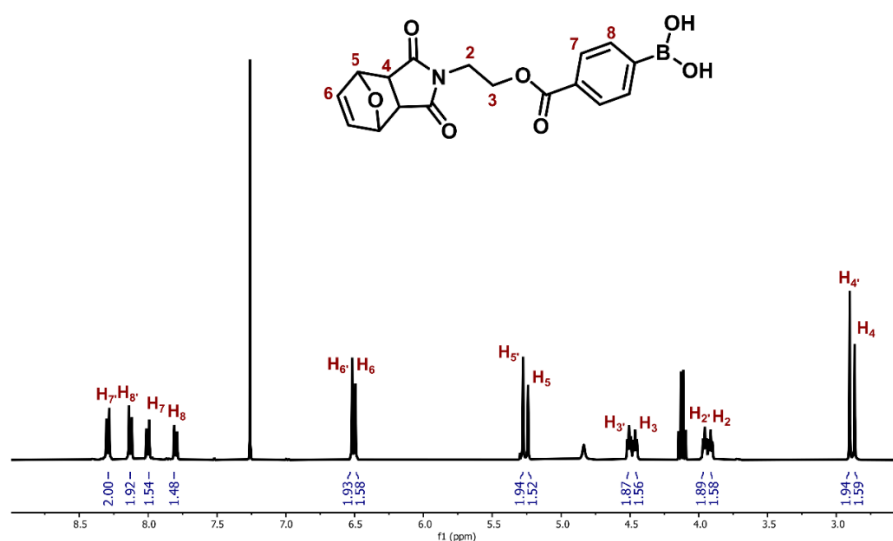
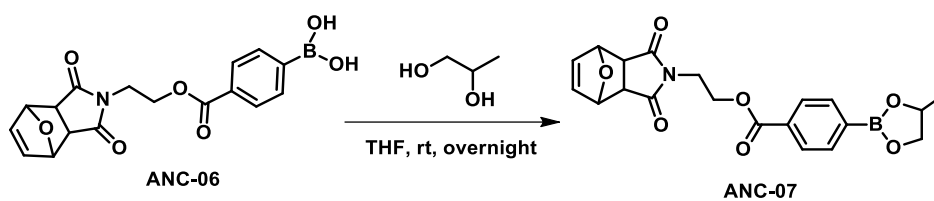


Figure 5.24 - ^1H -NMR of **ANC_06** (400 MHz, CDCl_3 , 298 K)

During the aqueous work-up of the previous reaction, the boronic ester group in **ANC_06** was partially hydrolyzed, leading back to the boronic acid form. To restore the ester functionality, **ANC_06** was treated with 1,2-propanediol in THF at room temperature (**Scheme 5.9**).

A small amount of water was added to help dissolve the starting material, while anhydrous magnesium sulfate was included to gradually remove moisture and shift the equilibrium toward ester formation.

The reaction was stirred overnight under mild conditions. After filtration to remove the drying agent and evaporation of the solvent, 2-(1,3-dioxo-3a,4,7,7a-tetrahydro-4,7-epoxyisoindol-2-yl)ethyl 4-(4-methyl-1,3,2-dioxaborolan-2-yl)benzoate (**ANC_07**) was obtained as a crude solid. $^1\text{H-NMR}$ analysis confirmed that the dioxaborolane ring had successfully re-formed, with the expected signals visible, including the characteristic methyl group of the boronic ester (**Figure 5.25**).



Scheme 5.9 - **ANC_07** synthesis

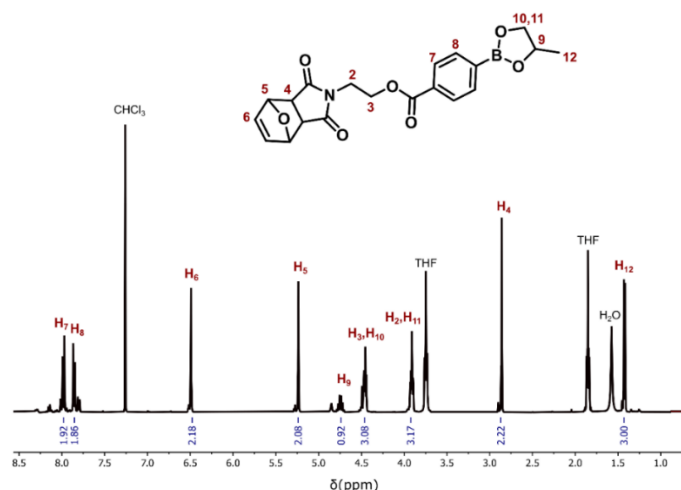
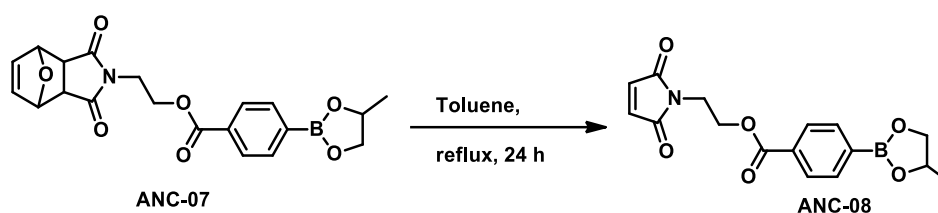


Figure 5.25 - $^1\text{H-NMR}$ of **ANC_07** (400 MHz, CDCl_3 , 298 K)

The final step in **ANC_08** synthesis was the thermal rearrangement of the cyclic imide in **ANC_07** to the corresponding maleimide via a retro Diels–Alder reaction (**Scheme 5.10**).

This is a process that removes the furan moiety that had been formed in the first cycloaddition (step 1), restoring the characteristic conjugated double bond of the maleimide ring.

To accomplish this, **ANC_07** was dissolved in toluene and refluxed overnight. After the removal of solvent under reduced pressure, the product was isolated as a white solid. ^1H -NMR ensured the success of the conversion, indicating the disappearance of the tetrahydro ring signals and the appearance of new, downfield-shifted signals as expected for the maleimide double bond formation (**Figure 5.26**).



Scheme 5.10 - ANC_08 synthesis

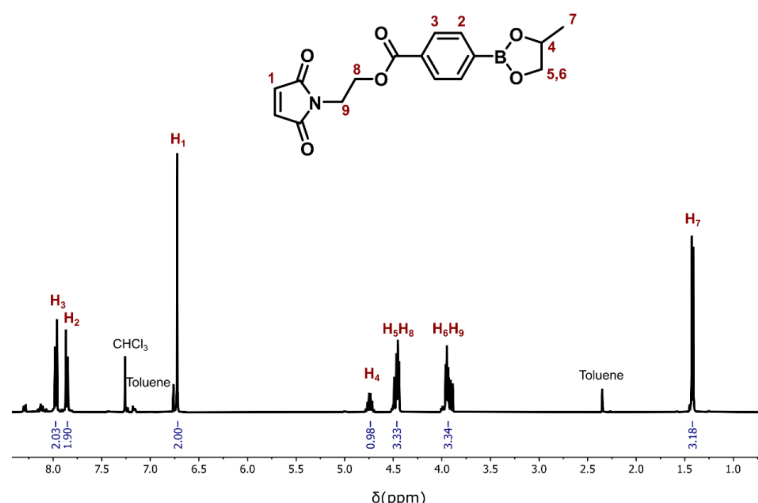


Figure 5.26 - ^1H -NMR of ANC_08 (400 MHz, CDCl_3 , 298 K)

5.7 Compatibilization of HDPE and Biopolymers with Maleimide Grafting Agent (Cellulose and Xanthan Gum)

Maleimide grafting onto HDPE by reactive extrusion is usually made possible by a radical-induced process, in which a peroxide initiator, here dicumyl peroxide (DCP), is essential for producing the necessary free radicals. Maleimide-based additives and HDPE are first mixed to achieve a homogeneous blend before adding the radical initiator, which breaks down when heated to produce free radicals. After that, the mixture is heated in an extruder so that the

grafting can take place during the extrusion process. These radicals then react with the maleimide groups, leading to their grafting onto the polyethylene backbone.

This procedure yields a polyethylene material that has been chemically treated with maleimide groups, increasing its compatibility with other materials or its reactivity for additional chemical modifications. We try to improve its interaction with diol-rich biopolymers, aiming to improve the overall toughness of the material. Accordingly, and following procedures reported in the literature, the grafting was assumed to be quantitative.¹²

5.7.1 Reactive Extrusion

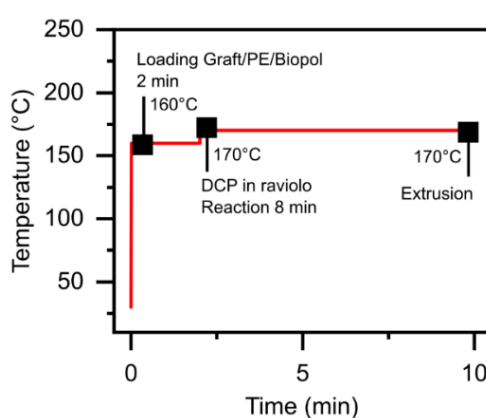


Figure 5.27 - Extrusion protocol of HDPE and biopolymers compatibilization with maleimide-based grafting agent

To explore the potential of the maleimide grafting approach, it was applied to the reactive extrusion of cellulose and xanthan gum, each incorporated at 40 wt%. The process was carried out in two main stages, schematically reported in **Figure 5.27**.

In the initial stage, the HDPE matrix, the selected biopolymer, and 0.37 mol% with respect to HDPE repeating units of the **ANC_08** were added to the extruder at 160 °C and mixed for 2 minutes. This step ensured that the components were well dispersed before initiating the chemical reaction. The temperature was then raised to 170 °C, and DCP was introduced as the radical initiator (0.005 wt% relative to the matrix). At this point, the system reached the conditions needed to activate the peroxide, allowing the grafting reaction between the maleimide and the polymer chains to begin. The reaction was allowed to proceed for 10 minutes with continuous mixing, after which the material was extruded. During this step, a clear increase in torque was observed (**Figure 5.28**). This behavior is consistent with the

formation of grafted structures and suggests the possible development of network-like interactions within the polymer matrix.

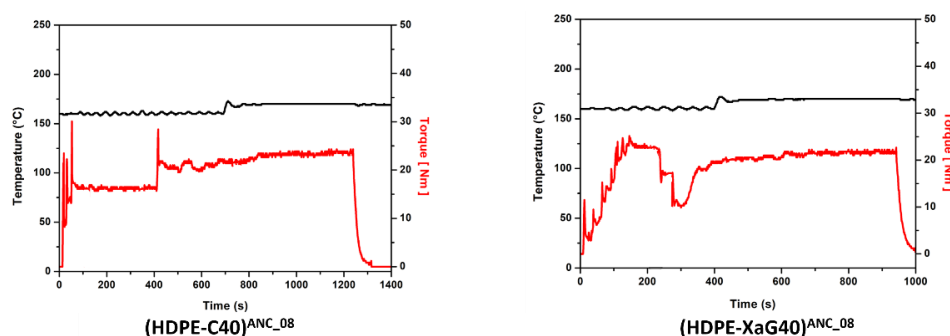


Figure 5.28 - Extrusion profiles of: on the left HDPE+Cellulose 40 wt%+**ANC_08** at 0.37 mol% with respect to HDPE repeating units; on the right HDPE+Xanthan gum 40 wt%+**ANC_08** at 0.37 mol% with respect to HDPE repeating units. The torque trend is shown in red, and the temperature over time is shown in black.

5.7.2 Tensile Testing and Dynamic Mechanical Analysis

The grafting agent **ANC_08** (0.37 mol% relative to HDPE repeating units) was incorporated into the (HDPE-C40) and (HDPE-XaG40) blends following the extrusion procedure shown in **Figure 5.27**. The aim was to evaluate whether our synthesized additive could enhance the toughness of the material.

As reported in **Table 5.6** and in **Figure 5.29, Panel a**, the Young's modulus decreases significantly from 1424 MPa to 234 MPa for the (HDPE-C40)^{ANC_08} compared to its HDPE-C40 counterpart. This drop indicates increased flexibility and a plasticizing effect. Additionally, both the yield strain and the strain at break see substantial increases (from 5.85% to 56.4% and from 45.6% to 119%, respectively).

This suggests that the material can absorb much more energy before failing, leading to a considerable improvement in toughness. It appears that **ANC_08** acts as a plasticizer, interposing itself between polymer chains and enhancing the mobility of the matrix in the studied case.

This trend is less pronounced in the case of XaG40, likely due to the distinct structure of the biopolymers that interact differently with the matrix (**Figure 5.29, Panel b**).

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ε_y (%)	Eng. strain at break ε_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
HDPE-C40	1424 ± 191	18.0 ± 1.84	5.85 ± 1.24	45.6 ± 9.70	4.92 ± 1.30
E1(HDPE-C40) ^{T1}	1256 ± 39.9	31.2 ± 1.70	8.74 ± 1.06	16.9 ± 10.6	16.8 ± 1.86
E2(HDPE-C40) ^{T1}	1421 ± 78.8	29.0 ± 1.75	6.47 ± 0.48	10.8 ± 3.23	12.9 ± 2.80
E1(HDPE-C40) ^{T5}	1114 ± 160	22.9 ± 2.33	7.93 ± 0.08	12.6 ± 2.55	9.61 ± 3.59
(HDPE-C40) ^{ANC_08}	234 ± 76.0	31.8 ± 1.23	56.4 ± 2.54	119 ± 16.0	9.92 ± 2.59
HDPE-XaG40	1437 ± 93.1	19.9 ± 4.13	6.50 ± 1.52	32.8 ± 10.3	7.18 ± 4.12
E2(HDPE-XaG40) ^{T1}	958 ± 50.9	23.9 ± 1.24	11.9 ± 0.33	159 ± 104	4.80 ± 3.46
E2(HDPE-XaG40) ^{T5}	787 ± 57.9	20.9 ± 0.94	13.8 ± 1.44	85.5 ± 27.3	4.79 ± 3.48
(HDPE-XaG40) ^{ANC08}	1004 ± 217	15.1 ± 2.25	7.89 ± 3.04	23.0 ± 5.37	1.53 ± 0.23

Table 5.6 - Tensile test values obtained at room temperature for pure HDPE compared with: HDPE containing 40 wt% of cellulose or xanthan gum; HDPE containing 40 wt% of cellulose and 1 or 5 wt% of Tr-N₃ with both extrusion profiles (E1, E2); HDPE containing 40 wt% of cellulose or xanthan gum and 0.37 mol% of ANC_08, following the extrusion protocol of Figure 5.27; HDPE containing 40 wt% of xanthan gum and 1 or 5 wt% of Tr-N₃ with E2 extrusion profiles.

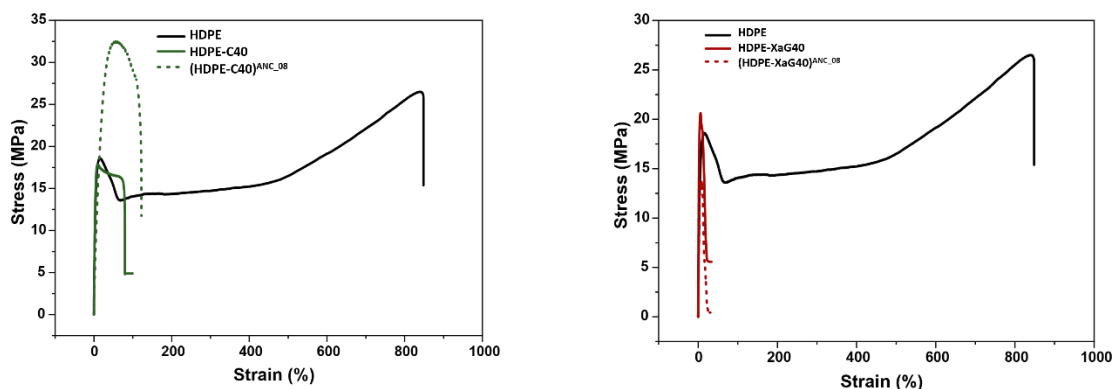


Figure 5.29 - Engineering stress versus strain curves of HDPE and modified HDPE; a) pure HDPE (black line), HDPE with 40 wt% of cellulose (green line), HDPE with 40 wt% of cellulose and 0.37 mol% of ANC_08 (dashed green line); b) pure HDPE (black line), HDPE with 40 wt% of xanthan gum (red line), HDPE with 40 wt% of xanthan gum and 0.37 mol% of ANC_08 (dashed red line); following the extrusion protocol of Figure 5.27.

5.8 Upcycling of HDPE with Maleimide Grafting Agent and Bio-based Crosslinker (Tannic Acid and Xylitol)

5.8.1 Tannic Acid

To improve the molecular design for better performance in future functionalization or crosslinking reactions, we added tannic acid, a larger and more rigid molecule with a high density of diol functional groups. Tannic acid was selected because of its polyphenolic structure, reported in **Figure 5.30**, which provides more diol groups for potential interactions, and its rigid, dendritic structure that could increase affinity for maleimide-based grafting agents.

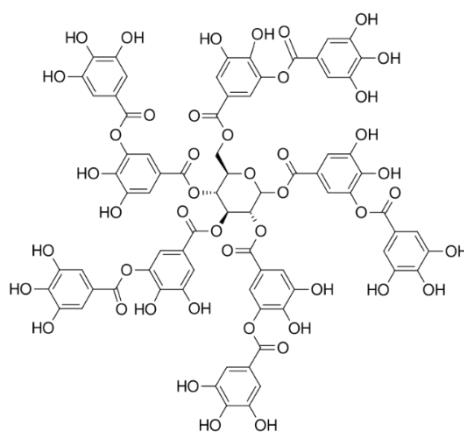


Figure 5.30 - Tannic acid structure

The influence of adding tannic acid to the HDPE matrix was initially examined by varying its weight fraction. HDPE was extruded using the same protocol applied to other biopolymers (**Figure 5.1**). The processes were carried out at 160 °C for 5 minutes, with tannic acid added at 10%, 20%, or 40% by weight.

Tensile test results show that tannic acid behaves quite differently from the other biopolymers discussed earlier. Under these processing conditions, it does not act as a conventional filler (**Table 5.7**). This is likely due to its unique molecular nature: tannic acid is a dendritic oligomer with a defined molar mass and a measurable melting point, while the other biopolymers considered are much larger in molar mass and typically degrade before melting. These structural and thermal differences mean that tannic acid interacts with the polymer

matrix in a different way, which is reflected in the distinct mechanical and thermal responses observed (**Figure 5.31**).

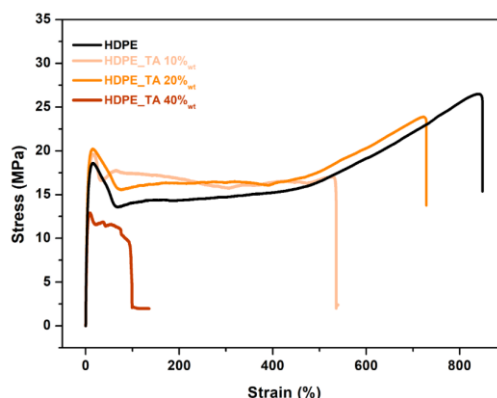


Figure 5.31 – Representative stress-strain curves at room temperature from the tensile test of HDPE (black), HDPE-TA10 (light orange), HDPE-TA20 (orange), and HDPE-TA40 (dark orange); extrusion at 160 °C for 5 min.

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ϵ_y (%)	Eng. strain at break ϵ_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
HDPE-TA10 ^a	724 ± 57.8	20.0 ± 1.18	14.9 ± 2.21	602 ± 346.9	8.83 ± 7.77
HDPE-TA20 ^a	787 ± 31.4	19.4 ± 1.78	15.2 ± 0.97	720 ± 133.9	11.8 ± 4.98
HDPE-TA40 ^a	756 ± 63.6	16.2 ± 3.69	9.83 ± 3.07	335 ± 313.2	6.32 ± 4.93
HDPE-TA40 ^b	898 ± 52.3	23.0 ± 1.45	15.3 ± 0.83	886 ± 88.1	17.3 ± 2.57

Table 5.7 - Tensile test values of pure HDPE vs HDPE and tannic acid in different wt%. ^a extrusion at 160 °C for 5 min, ^b extrusion at 140 °C for 5 min

To avoid the thermal degradation of tannic acid, we first lowered the extrusion temperature to 140 °C. As reported in **Table 5.7**, this adjustment proved to be effective. Tensile test results highlighted better mechanical performance compared to samples processed at 160 °C.

Building on these results, we chose to maintain the lower extrusion temperature and explore the use of the **ANC_08** grafting agent aimed at promoting crosslinking in the HDPE matrix.

In this approach, we followed a stepwise method: **ANC_08** was first mixed with HDPE at 140 °C for 2 minutes. The temperature was then increased to 170 °C to allow the radical

initiator to activate the grafting reaction, which continued for 8 minutes. After this grafting step, the temperature was brought back down to 140 °C, and tannic acid was added (**Figure 5.32**).

Because of its multiple diol groups, tannic acid was expected to react with the boronic acid moieties of **ANC_08**, forming boronate esters that could bridge different polymer chains and create a crosslinked structure.

The final blend was extruded after 2 minutes of mixing under these conditions.

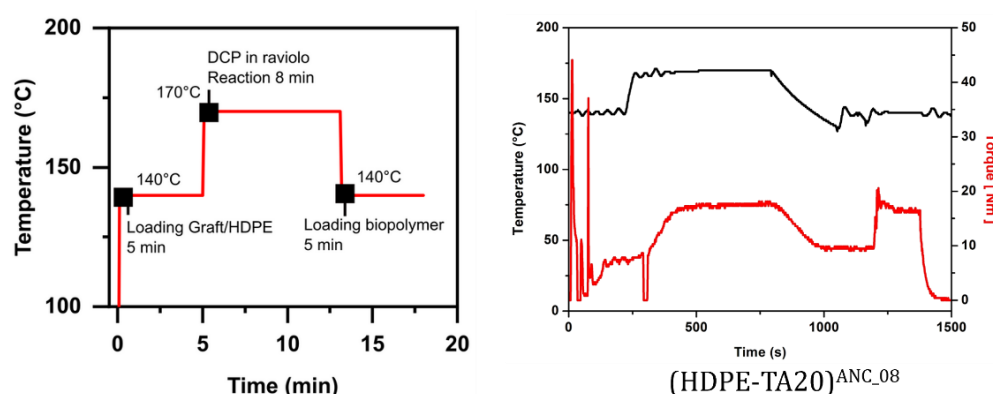


Figure 5.32 – HDPE+Tannic acid 20 wt%+**ANC_08** extrusion protocol (left) and extrusion profile of HDPE-TA20 with 0.37 mol% of **ANC_08** with respect to HDPE repeating units, and 0.005 wt% of DCP relative to the matrix (right); the torque is shown in red, and the temperature over time is shown in black

5.8.1.1 Tensile Testing and Dynamic Mechanical Analysis

Although the mechanical enhancement was limited, the tensile test results show that the addition of tannic acid and **ANC_08** resulted in mechanical properties broadly comparable with the pure HDPE (**Figure 5.33**). HDPE-TA20^b showed a slight enhancement in Young's modulus and yield stress with respect to neat HDPE, indicating a moderate stiffening effect.

The (HDPE-TA20)^{ANC_08} specimen also exhibited a higher modulus, while at the same time its yield strain and strain at break were smaller, which suggests a possible compromise between stiffness and ductility for the tested state (**Table 5.8**).

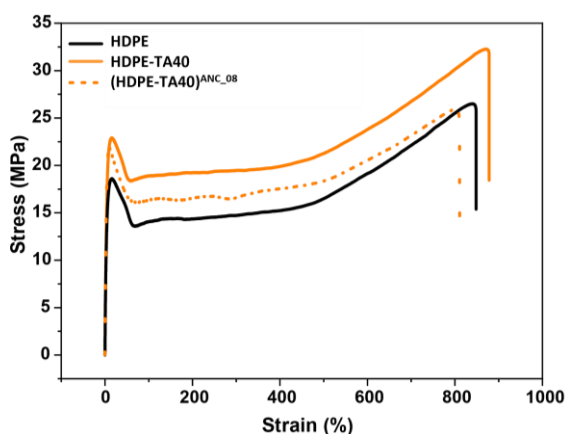


Figure 5.33 - Representative stress-strain curves at room temperature from the tensile test of pure HDPE (black), HDPE containing 20 wt% tannic acid extruded at 140 °C (orange), and HDPE with 20 wt% tannic acid additionally formulated with 0.37 mol% ANC_08 (relative to HDPE repeating units) and 0.005 wt% DCP (relative to the matrix) (orange dashed line), following the extrusion protocol described in Figure 5.32.

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ϵ_y (%)	Eng. strain at break ϵ_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
HDPE-TA20 ^b	843 ± 52.3	23.0 ± 1.45	15.3 ± 0.83	886 ± 88.1	17.3 ± 2.57
(HDPE-TA20) ^{ANC08}	898 ± 24.0	20.0 ± 2.23	9.27 ± 0.36	827 ± 59.0	12.4 ± 4.13

Table 5.8 - Tensile test values obtained at room temperature for pure HDPE compared with HDPE containing 20 wt% tannic acid, and HDPE with 20 wt% tannic acid additionally formulated with 0.37 mol% ANC_08 (relative to HDPE repeating units) and 0.005 wt% DCP (relative to the matrix), following the extrusion protocol described in Figure 5.33; ^b extruded at 140 °C.

Analyzing the DMA results, the storage modulus versus temperature curve in **Figure 5.34** displays that the E' behavior remains mostly unaffected by the modifications. The curve for the modified sample ((HDPE-TA40)^{ANC_08}) almost perfectly overlaps with that of pure HDPE throughout the temperature range, reflecting the typical softening and viscoelastic response of the polymer. The absence of a rubbery plateau above the T_m of pure HDPE suggests that, under the tested conditions, the blend did not achieve the structural connectivity typically associated with crosslinked polymer systems.

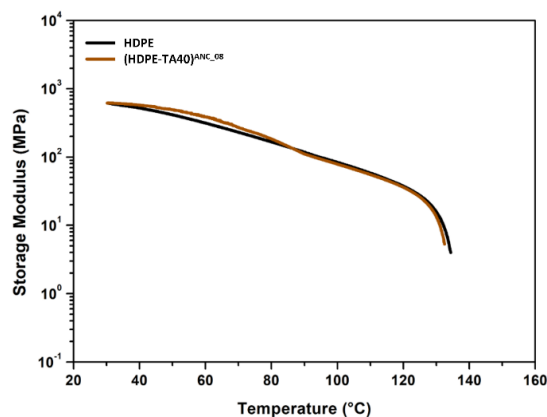


Figure 5.34 – DMA storage modulus (E') as a function of temperature for pure HDPE (black line) and modified HDPE containing 20 wt% tannic acid, 0.37 mol% ANC_08 (relative to HDPE repeating units) (brown line).

5.8.2 Xylitol

At this stage, we focused on a smaller, more adaptable molecule that could enhance the system's overall compatibility and better facilitate interaction between the grafting agent and the biobased crosslinker.

Xylitol proved to be a suitable choice due to its low melting point (93 °C), as reported in **Figure 5.35**, low molar mass, and high density of hydroxyl groups, making it ideal for forming interactions with boronic compounds.

Its reactivity with boronic ethers has already been studied in the literature, particularly in the synthesis of bio-based materials used in various applications, including food additives, cosmetic ingredients, pharmaceutical products, plasticizers, and non-ionic surfactants.²⁰

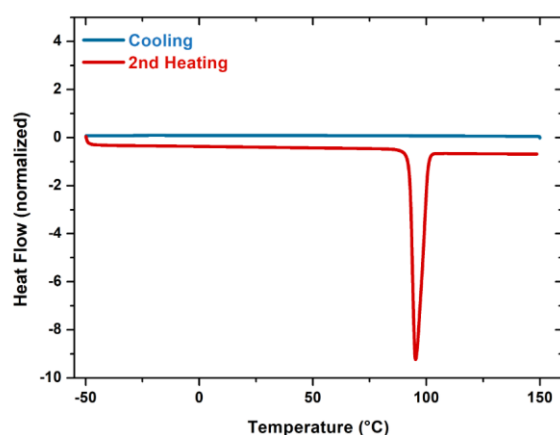


Figure 5.35 – DSC of xylitol (exo up). The cooling curve is shown in blue. The second heating curve, in red, displays the endothermic peak associated with the low melting point of xylitol.

We first explored the impact of xylitol in HDPE by adding it at 10 and 20 wt% relative to the polymer matrix. The extrusion process was carried out in a single step, with all components introduced together at 160 °C and mixed for 5 minutes (**Figure 5.1**).

Following this initial approach, we also tested xylitol in combination with **ANC_08**, first at 0.37 mol% with respect to the repeating unit of HDPE, and then in stoichiometric amounts relative to the grafting agent. The same extrusion conditions used for tannic acid were applied here as well, with the only difference being the starting temperature, which in this case was set at 160 °C (**Figure 5.32, left**).

The extrusion profiles, in **Figure 5.36, Panels a and b**, show that the torque values are extremely low in the absence of the grafting agent. In contrast, when **ANC_08** is present, at 0.37 mol% (relative to HDPE repeating units), the torque reaches values comparable to that of neat HDPE (**Figure 5.36, Panels d**). However, the torque decreases upon increasing the xylitol content. This is likely due to xylitol melting at the processing temperature, which reduces the overall viscosity of the system and makes the melt easier to process.

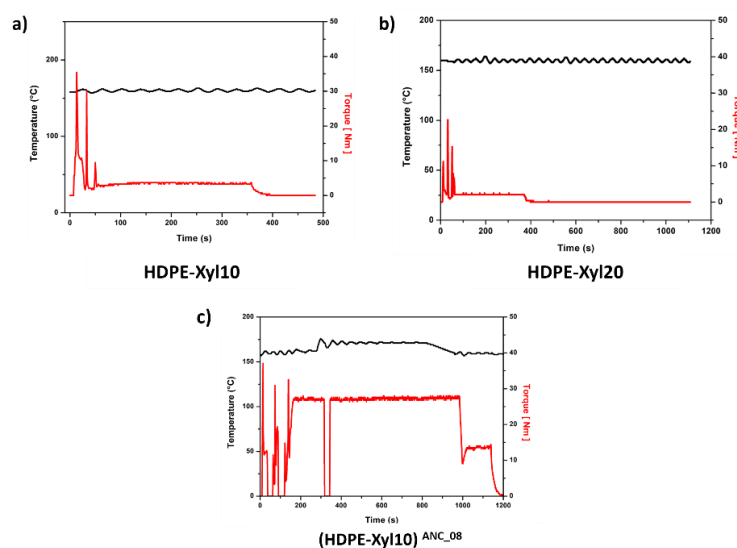
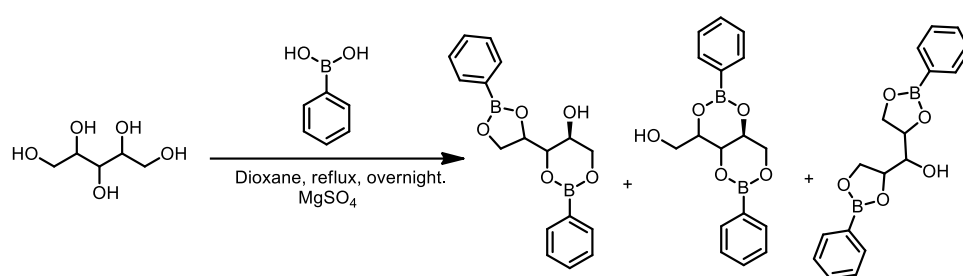


Figure 5.36 - Extrusion profiles: a) HDPE with 10 wt% of xylitol, b) HDPE with 20 wt% of xylitol, c) HDPE with 10 wt% of xylitol, 0.37 mol% **ANC_08** (relative to HDPE repeating units) and 0.005 wt% DCP (relative to the matrix). Torque vs time in red, temperature vs time in black.

To further optimize and enhance the results from the dynamic mechanical analysis presented in the following sections, we performed additional tests using xylitol and **ANC_08** at 1 mol% in a stoichiometric ratio.

At the same time, we also synthesized two new boronic ester-based molecules containing xylitol to better explore its role and potential in the system.

The first molecule, **Xyl-BE**, was synthesized by reacting xylitol with phenylboronic acid in a 1:2 ratio, allowing two boronic acid units to bind to a single sugar molecule (**Scheme 5.11**). The reaction was carried out overnight under reflux in 1,4-dioxane, using anhydrous magnesium sulfate to remove water. ^1H -NMR analysis confirmed the reaction by the disappearance of the typical OH signals of free xylitol (**Figure 5.37**). However, the final product showed multiple conformers, likely due to different hydroxyl groups participating in the boronate formation.



Scheme 5.11 - **Xyl-BE** synthesis

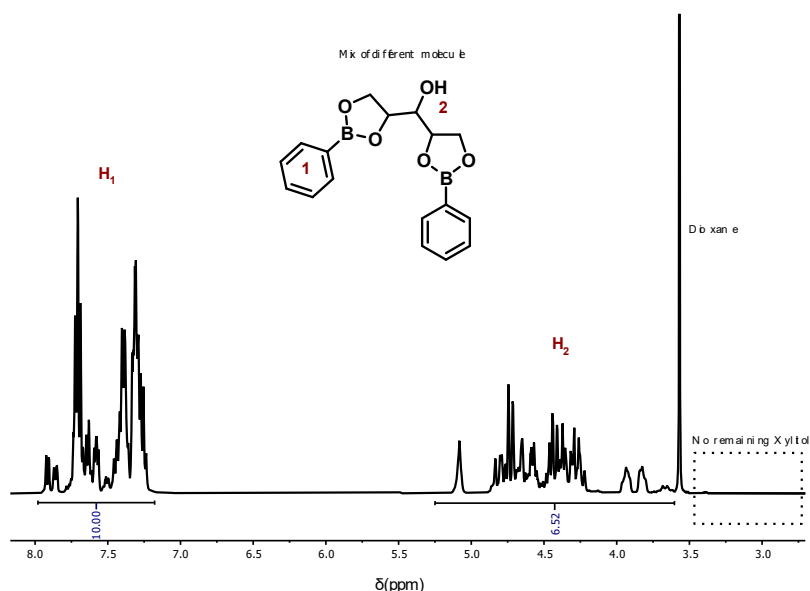


Figure 5.37 – ^1H -NMR spectrum of **Xyl-BE** (400 MHz, DMSO-d_6 , 298 K)

The second molecule, **XANC_08**, was synthesized following the same procedure (reported in the *Experimental Section*) as the first, but in this case, **ANC_08**, previously prepared, was used instead of phenylboronic acid. In **Figure 5.38**, the formation of the desired product is clearly

confirmed by the proton NMR spectrum, which shows all the expected signals for the newly synthesized species and no trace of the signals around 3 ppm from the starting xylitol.

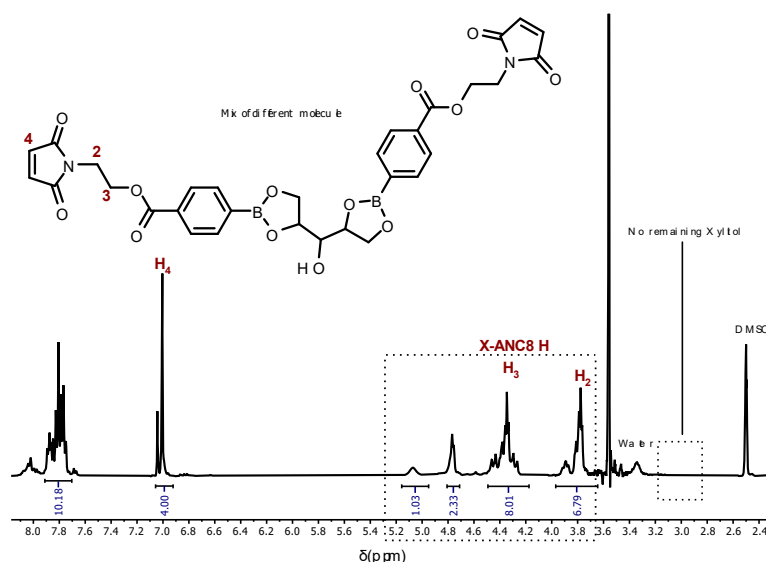


Figure 5.38 - ^1H -NMR spectrum of **XANC_08** (400 MHz, $\text{DMSO}-d_6$, 298 K)

5.8.2.1 Tensile Testing

Table 5.9 compares the main mechanical parameters of pure and modified HDPE samples. The addition of xylitol at 10 and 20 wt% does not significantly affect the Young's modulus (751–771 MPa), which remains comparable to that of pure HDPE. A slight increase in the yield stress (22.8–23.5 MPa) is observed, indicating a modest mechanical reinforcement, although accompanied by a reduction in ductility.

The most relevant results concern the samples containing xylitol and 1 mol% **ANC_08** in stoichiometric ratio $\alpha(\text{HDPE-Xyl}10)^{\text{ANC}_08}$, as well as in those incorporating **Xyl-BE** at a mol% equivalent to the 10 wt% xylitol used previously. These effects are observed both with and without the addition of **ANC_08** (β), suggesting an improvement in mechanical strength and a more favorable balance between stiffness and ductility compared to the samples containing only xylitol.

Moreover, the samples containing **Xyl-BE** together with **ANC_08** ($\alpha(\text{HDPE-Xyl-BE})^{\text{ANC}_08}$ and $\beta(\text{HDPE-Xyl-BE})^{\text{ANC}_08}$) show a much higher engineering strain at break (942% and 901%), reflecting a clear increase in ductility. These values are substantially higher than those of the

samples with only xylitol (662% and 816%) and are comparable to, or even exceed, those of neat HDPE (869%).

This suggests that ANC_08 might assist Xyl-BE in integrating more effectively into the polymer structure, potentially by enhancing compatibility or facilitating mild crosslinking.

This is further illustrated by the stress-strain curve shown in **Figure 5.39**, specifically in *Panel a* (dashed green curve) and *Panel b* (green curve).

In the sample prepared with HDPE containing 0.37 mol% of XANC_08 (relative to the repeating units of HDPE), a yield stress of 26.1 MPa has been reported.

This yield stress is the highest among all the samples discussed, indicating that the addition of **XANC_08** enhances mechanical strength.

Sample	Young's Modulus E (MPa)	Eng. yield stress σ_y (MPa)	Eng. yield strain ϵ_y (%)	Eng. strain at break ϵ_b (%)	Eng. stress at break (MPa)
HDPE	776 ± 17.0	18.8 ± 0.47	15.9 ± 0.56	869 ± 97.3	15.5 ± 2.15
HDPE-Xyl10	751 ± 26.6	23.5 ± 0.41	17.9 ± 0.51	662 ± 118	11.2 ± 5.00
HDPE-Xyl20	771 ± 32.7	22.8 ± 0.43	17.6 ± 0.70	816 ± 61.5	17.2 ± 1.18
(HDPE-Xyl10) ^{ANC_08}	901 ± 84.7	24.8 ± 1.48	16.2 ± 1.02	677 ± 51.7	14.1 ± 1.49
α (HDPE-Xyl10) ^{ANC_08}	825 ± 67.9	24.0 ± 1.07	15.4 ± 0.87	780 ± 46.6	15.7 ± 1.90
α (HDPE-Xyl-BE) ^{ANC_08}	643 ± 17.6	19.5 ± 1.30	18.9 ± 0.48	942 ± 70.0	16.9 ± 1.68
β (HDPE-Xyl-BE)	1040 ± 93.2	20.4 ± 0.57	10.0 ± 0.68	744 ± 49.6	12.9 ± 0.96
β (HDPE-Xyl-BE) ^{ANC08}	924 ± 47.1	20.4 ± 0.95	16.6 ± 0.28	901 ± 41.1	16.1 ± 2.47
HDPE-XANC_08	881 ± 34.5	26.1 ± 1.80	16.4 ± 0.91	816 ± 110	16.1 ± 7.65

Table 5.9 - Tensile test values obtained at room temperature for pure HDPE compared with HDPE containing 10 or 20 wt% xylitol; 10 wt% of xylitol and 0.37 mol% **ANC_08** (relative to HDPE repeating units)(HDPE-Xyl10)^{ANC_08 eq}; α samples containing xylitol and **ANC_08** at 1 mol% in stoichiometric ratio; β samples containing **Xyl-BE** at a mol% equivalent to the 10 wt% xylitol; HDPE with 0.37 mol% **XANC_08** (relative to HDPE repeating units)

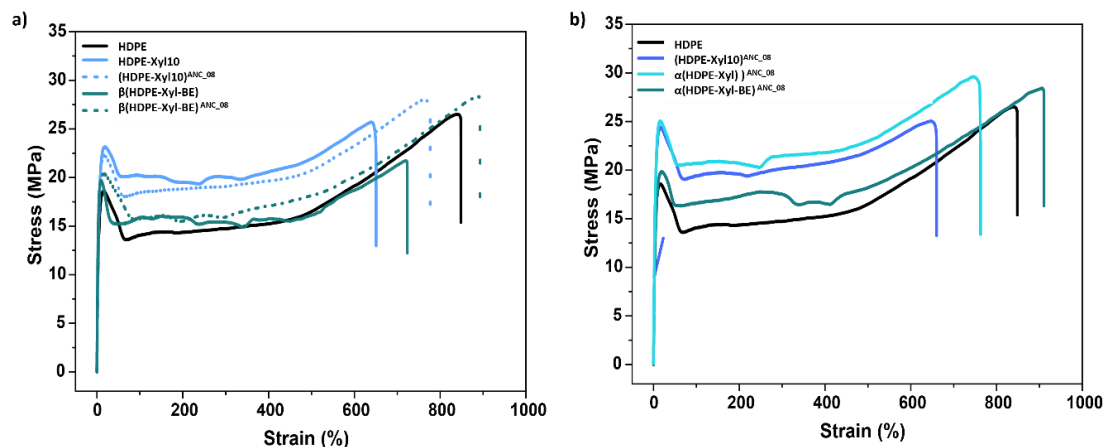


Figure 5.39 - Tensile test values obtained at room temperature for pure HDPE compared with HDPE containing 10 wt% of xylitol (light blue curve, Panel a); 10 wt% of xylitol and 0.37 mol% **ANC_08** (relative to HDPE repeating units)(HDPE-Xyl10)^{ANC_08 eq} (light blue curve dashed in Panel a and solid in Panel b); α samples containing xylitol and **ANC_08** at 1 mol% in stoichiometric ratio (mint and green curves, Panel b); β samples containing **Xyl-BE** at a mol% equivalent to the 10 wt% xylitol (dark green and dashed dark green curves, Panel a)

Conclusion

In this chapter, we focused on the development of bio-based blends composed of HDPE with biopolymers, including cellulose, xanthan gum, arabic gum, and guar gum, or with bio-based crosslinkers such as tannic acid and xylitol. This was achieved through reactive extrusion, utilizing two dynamic chemistries previously applied to polyolefins for creating CANs: azidotriazine and boronic ester chemistries. Specifically, we studied the use of dynamic covalent chemistries, such as **Tr-N₃** and the newly synthesized **ANC_08** grafting agents. The obtained materials were mechanically characterized to evaluate if their properties showed an improvement compared to neat HDPE.

We successfully incorporated various biopolymers into HDPE at different concentrations, demonstrating that these natural additives can act effectively as fillers while preserving the core mechanical properties of HDPE. This is already a meaningful result, especially considering the growing interest in partially replacing fossil-based plastics with renewable content.

The incorporation of **Tr-N₃** into HDPE/cellulose blends, particularly those containing 40 wt% cellulose, led to a notable enhancement in mechanical performance, as evidenced by the increased Young's modulus and engineering yield stress values. These improvements are not only superior to those achieved with lower cellulose content (20 wt%), but also significantly outperform previously reported HDPE/**Tr-N₃** systems lacking cellulose. The comparison with literature data highlights the synergistic effect between cellulose and **Tr-N₃**, especially when using optimized processing conditions.

Very encouraging results were obtained, especially on materials containing 40 wt% cellulose with the addition of **Tr-N₃**. For this reason, further studies, such as creep resistance and environmental stress cracking tests, are certainly needed and will be carried out in Paris.

Also, ANC-based systems revealed valuable insights. Though no rubbery plateau was observed in some cases, this was mostly due to known limitations like phase separation or overly fast exchange reactions. Importantly, xylitol and its derivative **Xyl-BE** showed promising behavior: even without a rubbery plateau, they exhibited good processability and maintained the material's structural integrity.

The functionalized version, **XANC_08**, offers a particularly interesting platform for future development. Its controlled structure and reactivity could be key in achieving tailored, reversible networks with better long-term stability and adaptability.

In summary, this work confirms that combining dynamic chemistries with biopolymers in a polyolefin matrix is not only feasible but also full of potential. While some challenges remain, especially in tuning the network behavior, the results provide a solid foundation and clear direction for future research. Further structural characterizations, including SAXS, TEM, and SEM, are needed to better understand the material architecture and will be carried out in subsequent studies.

The approach taken here opens the door to smarter, more sustainable plastics, moving closer to a circular materials economy.

5.9 Experimental Part - Materials and Methods

Chemicals and reagents were obtained from Merck, while solvents were purchased from Carlo Erba and used as received. Despite extensive drying, some synthesized compounds retained trace amounts of residual solvent. Compound purity was evaluated by ^1H NMR spectroscopy. High-density polyethylene (PE, Hostalen 4131B) was supplied by LyondellBasell via Albis Plastique France. Microgranular cellulose (MGC) and other reagents were purchased from Merck and used as received, unless otherwise stated.

5.9.1 Instruments and Measurements

Differential Scanning Calorimetry (DSC)

The DSC measurements were carried out using a TA Instruments Discovery 250 DSC, featuring an autosampler and a liquid nitrogen cooling system, and calibrated with indium. The samples were placed in disposable, single-use aluminum pans. The thermal program involved a heating ramp from 0 °C to 250 °C at +10 °C/min, a cooling ramp from 250 °C to 0 °C at -10 °C/min, followed by another heating ramp from 0 °C to 250 °C at +10 °C/min.

Thermogravimetric Analysis (TGA)

TGA analyses were conducted using a Netzsch TG 209 F1 Libra under a controlled nitrogen atmosphere. The temperature profile involved heating the sample from 30 to 600 °C at a rate of 10°C/min. Isotherms were performed at 214 °C for 30 minutes. The sample was placed in a single-use aluminum pan for the analysis.

Compression-Molding

After the reactive extrusion process, the samples were shaped through compression molding using a hydraulic press (Carver). The sample was cut, placed into the appropriate stainless-steel molds, and pressed at 160 °C for 30 minutes with an applied pressure equivalent to 30 kN. Afterward, the samples were allowed to cool down to ambient temperature on the workbench.

Tensile Testing

Tensile tests were conducted at room temperature on an Instron Universal testing system, applying a rate of deformation of 10 mm/min. During the tests, engineering stress ($\sigma = F/A_0$, where F is the applied force and A_0 represents the original cross-sectional area) was recorded

as a function of engineering strain (ϵ , based on the displacement of the grips). Dogbone-shaped samples (ISO 527-2 type 5B; 13 mm $\times$ 2 mm $\times$ 1.4 mm) were produced using compression molding. To ensure consistent results, a minimum of five specimens from each material composition were tested. Young's modulus (E), engineering yield stress (σ_y), engineering yield strain (ϵ_y), and engineering strain at break (ϵ_b) were calculated in accordance with ISO 527-1:2012(E). Young's modulus was determined as the slope of the stress-strain curve between strain values of 0.05% and 0.25% elongation. The engineering yield stress and engineering yield strain were identified at the first local maximum in the stress-strain curve. The engineering strain at break was measured at the last recorded data point before the stress fell to 10% or less of the yield stress.

Gas Chromatography coupled with Mass Spectroscopy (GC-MS)

GC-MS with electron impact (EI) analyses were carried out in ethyl acetate, using a Shimadzu GCMS-QP 2010s (70 eV).

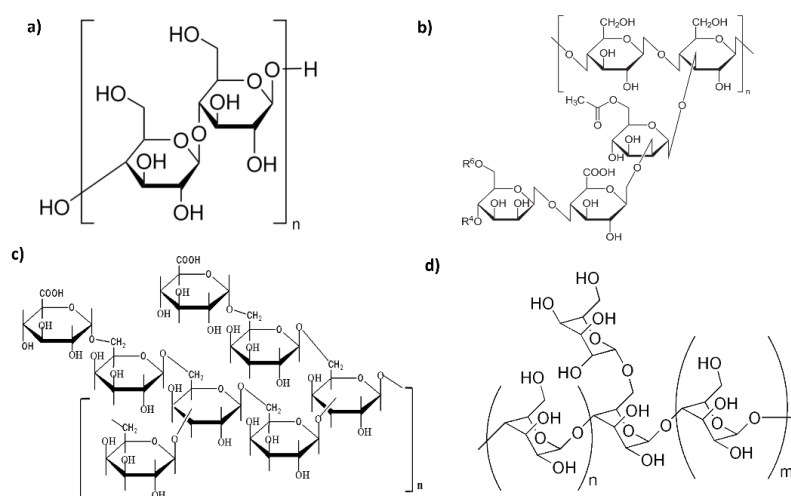


Figure 5.40 – a) cellulose structure, b) xanthan gum structure, c) arabic gum structure, d) guar gum structure

5.9.2 Extrusion Procedure – HDPE, Biopolymer Blends (Cellulose and Gums)

The procedure was carried out using a 15 cc extruder. Before starting, the barrel was preheated to 160 °C and purged with nitrogen for 5 minutes to ensure an inert atmosphere. The screw speed was set at 100 rpm. The materials were added in a stepwise manner: first, a

portion of virgin PE (with weights of 11.40 g, 10.8 g, or 9.6 g, indicating the total amount), then the biopolymer (at 0.6 g, 1.2 g, or 2.4 g), followed by the remaining quantity of HDPE. The mixture was blended at 160 °C for 5 minutes. Once the process was complete, the material was extruded and allowed to cool at room temperature, resulting in a PE control sample.

5.9.3 Extrusion Procedure – Reactive Extrusion (Cellulose or Gums and Tr-N_3)

Reactive extrusion was carried out on a 15 cc extruder. The barrel was first preheated to 160 °C, purged with nitrogen for 5 minutes and the screw speed was set to 100 rpm. Two distinct extrusion protocols were studied, using Tr-N_3 loadings of 0.1 or 0.5 mol% with respect to the moles of repeating units of HDPE, corresponding to approximately 1 wt% and 5 wt% relative to the HDPE. A masterbatch of 40 wt% of Tr-N_3 in HDPE was used in both situations. In the first extrusion protocol, the materials were added to the barrel in order: HDPE (9.3 g or 8.3 g, depending upon target composition), biopolymer (2.3 g), and the Tr-N_3 masterbatch (0.3 g or 1.4 g). The mixture was then processed at 160 °C for 5 minutes. The temperature of the barrel was then ramped to 214 °C over about 5 min, followed by 10 minutes of residence time at 214 °C, after which the material was extruded and cooled to the ambient temperature. In the second protocol, the same amounts of materials were used, but the order and timing of addition were modified. First, only the HDPE and the masterbatch were introduced and mixed at 160 °C for 5 minutes. The temperature was then raised to 214 °C and maintained for 10 minutes to allow the reaction to occur. After this step, the barrel was cooled back to 160 °C over approximately 15 minutes, and the biopolymer was added. Mixing continued for a further 5 minutes.

All extrusion procedures were done under nitrogen atmosphere.

5.9.4 Synthetic Procedures of Tr-N_3

The synthesis of 6-Azido- N^2,N^4 -dimethyl- N^2,N^4 -diphenyl-1,3,5-triazine-2,4-diamine (Tr-N_3) was carried out in two steps, following a protocol reported in literature.¹⁰

1) 1st Step: 6-Chloro- N^2,N^4 -dimethyl- N^2,N^4 -diphenyl-1,3,5-triazine-2,4-diamine (Tr-Cl)

In a 250 mL single-neck flask, 9.90 g of cyanuric chloride (53.7 mmol, 1.00 eq) is dissolved in 80 mL of THF (distilled over CaH_2) and cooled in an ice bath to 0 °C. To the flask, a solution of

6.94 g of DIPEA (53.7 mmol, 1.00 eq) in 10 mL of dry THF is added dropwise, followed by a solution of 6.04 g of *N*-methylaniline (56.4 mmol, 1.05 eq) in 10 mL of dry THF, also added dropwise. The mixture is stirred at 0°C for 1 hour. Subsequently, an additional amount of DIPEA (6.94 g, 53.7 mmol, 1.00 eq) and *N*-methylaniline (6.04 g, 56.4 mmol, 1.05 eq) were added dropwise. The mixture was stirred at 0°C for 10 minutes and then at 30°C overnight. The work-up was performed by removing the THF under reduced pressure, adding 200 mL of distilled water, and extracting the product with 4 × 100 mL of ethyl acetate. The organic phase was washed with 5 × 100 mL of 0.05M aqueous HCl, 2 × 100 mL of saturated aqueous NaHCO₃, and 1 × 100 mL of brine. The organic phase was then dried over MgSO₄ and concentrated under reduced pressure. The product, 6-chloro-*N*²,*N*⁴-dimethyl-*N*²,*N*⁴-diphenyl-1,3,5-triazine-2,4-diamine (Tr-Cl), was obtained as a yellowish solid with a product purity of 91,7% and a yield of 87.5 wt%.

¹H-NMR (DMSO-d₆ 400 MHz, Figure 8) δ: 7.7-7.0 (m, 10H), 3.36 (s, 6H)

¹³C-NMR (DMSO-d₆ 101 MHz, Figure 9) δ: 168.32, 164.42, 143.20, 128.72, 126.44, 126.25, 37.81

2) 2nd Step: 6-Azido-*N*²,*N*⁴-dimethyl-*N*²,*N*⁴-diphenyl-1,3,5-triazine-2,4-diamine (**Tr-N₃**)

In a round-bottom flask, 15.3 g of **Tr-Cl** (1 equiv, 47.0 mmol) were dissolved in 30 mL of *N*-Methyl-2-pyrrolidone (NMP). To this, 6.2 g of sodium azide (NaN₃, 2 equiv, 94 mmol) were added slowly, and the reaction mixture was stirred gently for 64 hours at 100°C. After the reaction was complete, the mixture was allowed to cool to room temperature. For the workup, 300 mL of distilled water were added, and the product was extracted with diethyl ether (3 × 200 mL). The combined organic phases were washed five times with 200 mL of brine, dried over magnesium sulfate, and filtered. The filtrate was split into three small aliquots and concentrated under reduced pressure. The resulting dry product was dissolved in a 50:50 v:v mixture of hexane and ethyl acetate and filtered through a double pad of silica gel and aluminum oxide. As before, the filtrate was split into three small aliquots, concentrated under reduced pressure, and allowed to dry completely under vacuum at 50°C overnight in a vacuum bell. A white solid was obtained (15.3 g) with an isolated yield of 95%

¹H-NMR (DMSO-d₆ 400 MHz, 298 K) δ: 7.7-7.0 (m, 10H), 3.36 (s, 6H)

¹³C-NMR (DMSO-d₆ 101 MHz, 298 K) δ: 167.97, 165.06, 143.47, 128.46, 126.35, 125.82, 37.40
FTIR (ATR) σ cm⁻¹: 3063, 3038, 2936, 2127 (N₃), 1604, 1554, 1511, 1493, 1475, 1445, 1385, 1349, 1287, 1263, 1213, 1190, 1153, 1103, 1075, 1027, 1010, 1001, 980, 905, 834, 805, 763, 741, 691, 648, 636, 612

3) Masterbatch Preparation (40% wt of **Tr-N₃**)

9 g of Hostalen HDPE were dissolved in 250 mL of xylene under a nitrogen atmosphere. The mixture was heated to 130°C. Concurrently, 6 g of **Tr-N₃** were dissolved in 15 mL of xylene at 100°C. The dissolved **Tr-N₃** was then added to the reaction mixture. After two minutes, the xylene was evaporated under reduced pressure at 90 °C. The product was subsequently dried under vacuum at 90°C overnight in a vacuum bell.

5.9.5 Synthesis of the Maleimide Grafting Agent

1) Synthesis of 3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride (**ANC_04**)

Furan (46.3 g, 47.2 mL, 680 mmol, 1.33 equiv.) was mixed with maleic anhydride (50.0 g, 510 mmol, 1.00 equiv.) in ethyl acetate (62.5 mL). The solution was stirred at room temperature for 24 hours. After this time, colorless crystals had formed and were collected by filtration, then dried under vacuum to obtain 76.3 g of final product. Purity >99%, yield 90%

¹H-NMR (400 MHz, DMSO-d₆, 298 K) δ: 6.58 (t, 2H), 5.35 (t, J = 3.4, 2.5 Hz, 2H), 3.31 (s, 2H)
¹³C-NMR (101 MHz, DMSO-d₆, 298 K) δ: 172.02, 137.33, 82.09, 49.63

2) Synthesis of 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-4,7-epoxyisoindole-1,3-dione (**ANC_05**)

ANC_04 (38.0 g, 1.0 eq) was dissolved in 130 mL of methanol in a 250 mL round-bottom flask under ambient conditions. Once fully dissolved, the solution was cooled to 0 °C. Ethanolamine (15.26 mL, 1.1 eq) and triethylamine (32.2 mL, 1.1 eq) were then added slowly, dropwise, using a dropping funnel for 30 minutes. After the addition was complete, the reaction mixture was brought to reflux and maintained at this temperature for 24 hours. During this time, the solution gradually turned orange. After cooling to room temperature, the flask was stored in a refrigerator for 48 hours to allow crystallization to occur. The resulting colorless solid (41.6

g) was collected by filtration and dried under vacuum at 40 °C overnight. The yield was 87%. The identity and purity (99%) of the product were confirmed by ¹H NMR spectroscopy.

¹H-NMR (400 MHz, CDCl₃, 298 K) δ: 6.51 (t, J = 1.0 Hz, 2H), 5.26 (t, J = 1.0 Hz, 2H), 3.78 – 3.64 (m, 4H), 2.88 (s, 2H)

¹³C-NMR (400 MHz, CDCl₃, 298 K) δ: 43.6, 48.3, 61.2, 83.7, 136.4, 175.7

3) Synthesis of 4-(4-Methyl-1,2,3-dioxaborolan-2-yl) benzoic acid (**ANC_02**)

6 g of 4-carboxyphenylboronic acid (36.2 mmol, 1 eq) and 2.73 mL of 1,2-propanediol (36.3 mmol, 1 eq) were dissolved in 64 mL of THF in a 100 mL round-bottom flask equipped with a magnetic stirrer. The reaction mixture was refluxed for 14 hours. Afterward, the solvent was evaporated under reduced pressure, giving a white powder (7.40 g) with a 99% yield.

¹H-NMR (400 MHz, DMSO-d₆) δ: 8.11 (m, 2H), 7.92 (m, 2H), 4.77 (tq, J = 13.8, 6.3 Hz, 1H), 4.49 (dd, J = 8.9, 7.7 Hz, 1H), 3.93 (dd, J = 8.9, 7.3 Hz, 1H), 1.44 (d, J = 6.2 Hz, 3H)

¹³C-NMR (101 MHz, DMSO-d₆) δ: 167.72, 135.03, 131.59, 129.04, 128.50, 71.5, 72.55, 21.52

4) Synthesis of 4-(4-Methyl-1,2,3-dioxaborolan-2-yl) benzoyl chloride (**ANC_03**)

8.0 g of **ANC_02** (38.8 mmol, 1 eq) was dissolved in 200 mL of dry dichloromethane (DCM) in a 500 mL round-bottom flask equipped with a magnetic stir bar, under a nitrogen atmosphere. Once the compound was fully dissolved, 0.26 mL of dimethylformamide (DMF) was added using a syringe. When the solution appeared homogeneous, 6.8 mL (9.84 g, 77.6 mmol, 2 eq) of oxalyl chloride was added slowly, dropwise. The reaction mixture was stirred at room temperature, during which bubbling was observed. After approximately two hours, the bubbling stopped, indicating the reaction had reached completion. The solvent was then removed under reduced pressure using a rotary evaporator. The resulting dry yellowish solid (8.72 g) was obtained in 92% yield and stored in the refrigerator until further use.

¹H-NMR (400 MHz, CDCl₃) δ: 8.11 (m, 2H), 7.93 (m, 2H), 4.77 (tq, J = 7.6, 6.2 Hz, 1H), 4.50 (dd, J = 8.9, 7.8 Hz, 1H), 3.93 (dd, J = 7.3, 4.0 Hz, 1H), 1.44 (m, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ: 168.78, 135.31, 134.95, 130.52, 129.40, 74.42, 72.97, 21.89

5) *Synthesis of 4-((2-(1,3-dioxo-3a,4,7,7a-tetrahydro-4,7-epoxyisoindol-2-yl)ethoxy)carbonyl)phenyl)boronic acid (ANC_06)*

ANC_03 (6.4 g, 28.5 mmol, 1.0 eq) was dissolved in 250 mL of anhydrous dichloromethane (DCM) in a 500 mL flask under a nitrogen atmosphere. In a separate two-neck round-bottom flask, **ANC_05** (7.00 g, 33.5 mmol, 1.2 eq) was mixed with triethylamine (TEA, 3.9 mL, 28.5 mmol, 1.0 eq) in 240 mL of anhydrous DCM. The solution was cooled to 0 °C under nitrogen, and the ANC-03 solution was added slowly, dropwise, with continuous stirring. Once the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred for 18 hours. Once the reaction was complete, the solvent was removed under reduced pressure. The resulting residue was washed with water and then dissolved in ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated to yield the crude product as white crystals (4.5 g). Yield 70%

¹H-NMR (400 MHz, DMSO-d₆, 298 K) δ: 7.91 – 7.80 (m, 4H), 6.53 (t, *J* = 0.9 Hz, 2H), 5.14 – 5.05 (m, 2H), 4.36 – 4.29 (m, 2H), 3.76 (t, *J* = 5.3 Hz, 2H), 2.95 (s, 2H).

¹³C-NMR (101 MHz, DMSO-d₆, 298 K) δ: 176.44, 165.64, 136.48, 134.69, 134.08, 130.62, 128.07, 80.39, 61.10, 47.18, 37.07.

6) *Synthesis of 2-(1,3-dioxo-3a,4,7,7a-tetrahydro-4,7-epoxyisoindol-2-yl)ethyl 4-(4-methyl-1,3,2-dioxaborolan-2-yl)benzoate (ANC_07)*

4.47 g (12.5 mmol) of ANC_06 was dissolved in 60 mL of THF in a 100 mL single-neck round-bottom flask equipped with a magnetic stir bar. To the solution, 0.989 g of propanediol (13.0 mmol, 1.02 eq) was added, followed by 5 drops of deionized water and 5.717 g (47.5 mmol) of MgSO₄, which was added gradually while stirring. The reaction mixture was stirred at room temperature and left to react overnight. After the reaction, the mixture was filtered to remove solids, and the solvent was removed under reduced pressure using a rotavapor. Product weight 4.81 g, yield 98%

¹H-NMR (400 MHz, CDCl₃, 298 K) δ: 8.04 – 7.90 (m, 2H), 7.90 – 7.77 (m, 2H), 6.49 (q, *J* = 1.3 Hz, 2H), 5.24 (t, *J* = 1.0 Hz, 2H), 4.78 – 4.66 (m, 1H), 4.53 – 4.42 (m, 3H), 3.91 (td, *J* = 7.1, 2.7 Hz, 3H), 2.86 (d, *J* = 2.2 Hz, 2H), 1.43 (d, *J* = 6.2 Hz, 2H)

¹³C-NMR (101 MHz, CDCl₃, 298 K) δ: 171.1, 166.9, 135.0, 133.3, 129.9, 128.7, 73.2, 72.4, 61.2, 36.7, 21.8

7) *Synthesis of 2-(2,5-dioxo-2,5-dihydro-pyrrol-1-yl)ethyl 4-(4-methyl-1,3,2-dioxaborolan-2-yl)benzoate (ANC_08)*

In a 1 L single-neck round-bottom flask equipped with a magnetic stir bar, 4.4 g of **ANC_07** (0.012 mol, 1 eq) were dissolved in 900 mL of toluene, and the mixture was refluxed overnight. After completion, the solvent was removed under reduced pressure, resulting in a white solid (3.84 g) with a yield of 98%.

¹H-NMR (400 MHz, CDCl₃, 298 K) δ: 8.04 – 7.93 (m, 2H), 7.94 – 7.81 (m, 2H), 6.72 (s, 2H), 4.74 (ddt, *J* = 13.8, 7.5, 6.2 Hz, 1H), 4.54 – 4.41 (m, 3H), 4.03 – 3.86 (m, 3H), 1.42 (d, *J* = 6.2 Hz, 3H).
¹³C-NMR (101 MHz, CDCl₃, 298 K) δ: 170.51, 166.42, 134.90, 134.40, 132.06, 129.38, 128.95, 74.17, 72.84, 62.34, 36.95, 21.91

5.9.6 Synthesis **XANC_08**

In a 25 mL round-bottom flask, 0.32 g of xylitol (1 equivalent, 2.1 mmol) and 1.5 g of **ANC_06** (2 eq, 4.2 mmol) were dissolved in 16 mL of 1,4-dioxane at room temperature. To prevent the formation of boroxines, one drop of deionized water was added. Magnesium sulfate (1.50 g, 6 eq) was then added gradually in three aliquots, and the reaction mixture was left stirring for 6 hours at room temperature. Then, the solution was heated under reflux for 18 hours. After completion, the reaction mixture was dried under reduced pressure at 70 °C. Toluene was added to dissolve the product and the solution was left stirring at reflux overnight. Upon drying, **XANC_08** was obtained as white solid (1,75 g) . Yield 99%.

¹H-NMR (400 MHz, DMSO-d₆, 298 K)δ: 7.8 (m, 10H), 7.0 (s, 4H), 5.3 (br, 1H), 4.8 (br, 2H), 4.4 (m, 8H), 3.8 (m, 7H)

5.9.7 Extrusion Procedure – Reactive Extrusion

1- Cellulose or Xanthan Gum and **ANC_08**

Reactive extrusion was performed on a 15 cc extruder. The barrel was first preheated to 160 °C, purged with nitrogen for 5 minutes and the screw speed was set to 100 r.m. In a single step, 6.9 g of HDPE, 4.8 g of cellulose or xanthan gum (corresponding to 40 wt% relative to the matrix), and 0.30 g of ANC08 (0.37 mol% with respect to HDPE repeating units) were introduced. After 2 minutes of pre-mixing, the barrel temperature was raised to 170 °C, and

0.3 mg of DCP (0.005 wt% relative to the matrix) was added. After 8 minutes, the resulting polymer was extruded.

2- Tannic Acid and **ANC_08**

Reactive extrusion was performed on a 15 cc extruder. The barrel was first preheated to 140 °C, purged with nitrogen for 5 minutes and the screw speed was set to 100 rpm. The process started by mixing HDPE (9.2 g) and **ANC_08** (0.37 mol% with respect to HDPE repeating units) at 140 °C for 2 minutes. Then, the temperature was increased to 170 °C, and DCP (0.005 wt% relative to the matrix) was added to trigger the reaction, which was left to run for 8 minutes. After that, the barrel temperature was lowered to 140 °C, and tannic acid (20 wt%, 2.4 g) was added. The mixture was then blended for an additional 2 minutes before being extruded.

3- Xylitol and **ANC_08**

Reactive extrusion was performed on a 7 cc extruder. The barrel was first preheated to 160 °C, purged with nitrogen for 5 minutes and the screw speed was set to 100 rpm. The process started by mixing HDPE and **ANC_08** (0.37 mol% with respect to HDPE repeating units) at 160 °C for 2 minutes (The quantities of each component are listed in **Table 5.9**). Then, the temperature was increased to 170 °C, and DCP (0.005 wt% relative to the matrix) was added to trigger the reaction, which was left to run for 8 minutes. After that, the barrel temperature was brought back down to 160 °C, xylitol (10 %wt) or **Xyl-BE** was added, and the mixture was blended for another 2 minutes before being extruded. Based on the selected ratio, the following components were added:

	HDPE	Xylitol	Xylitol-BE	XANC08	ANC_08
(HDPE-Xyl10)^{ANC_08}	10.4 g	1.2 g			0.449 g
α(HDPE-Xyl10)^{ANC_08}	4.77 g	0.272 g			0.559 g
α(HDPE-Xyl-BE)^{ANC_08}	4.54 g		0.519 g		0.533 g
β(HDPE-Xyl-BE)	4.41 g		1.19 g		
β(HDPE-Xyl-BE)^{ANC_08}	4.22 g		1.19 g		0.183 g
HDPE-XANC_08	5.36 g			0.233 g	

Table 5.10 - Quantities of each component used for the HDPE and Xyl with or without **ANC_08**, HDPE and **Xyl-BE** with or without **ANC_08**, relative to the procedure 3 of 5.9.7 paragraph. α samples containing xylitol and **ANC_08** at 1 mol% in stoichiometric ratio; β samples containing **Xyl-BE** at a mol% equivalent to the 10 wt% xylitol; only (HDPE-Xyl10)^{ANC_08 eq} was performed in a 15 cc extruder, all the others in a 7 cc extruder

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Concluding Remarks

This PhD work demonstrates that designing and developing thermosetting materials with a lower environmental footprint while maintaining performance for advanced applications is achievable.

The synthesis of branched and highly functionalized PLA-based prepolymers, the investigation of bio-based crosslinkers, and the optimization of curing strategies have enabled the production of robust polyester networks. These networks exhibit vitrimeric behavior, tunable topology, and promising thermal-mechanical stability.

Three low-molecular-weight prepolymers, each containing approximately three lactide units per arm, were synthesized and characterized by the ROP of L-lactide with multifunctional polyalcohols as initiators.

Pentaerythritol and dipentaerythritol were used to give star-shaped architectures (4S-PLA-OH and 6S-PLA-OH), and glycerol was used to generate a comb-like structure (3S-PLA-OH).

Then, only 4S-PLA-OH and a series of analogous polymer systems, either linear or of higher molecular weight, were subjected to crosslinking reaction tests with green crosslinkers under various conditions to determine the suitable parameters for network formation.

While simple alcohols as 1-hexanol and glycerol transesterified with DEM, more complex polymeric systems exhibited very poor reactivity. This behavior suggests that steric hindrance, a low density of reactive functionalities, or lack of proper activation of the crosslinker are probable causes for preventing effective network formation.

To address the limited reactivity observed in the initial systems, efforts were directed toward enhancing the crosslinking capability of the star-shaped PLA prepolymers by introducing carboxylic acid end groups through the reaction with succinic anhydride.

Screening on 4S-PLA-COOH identified optimal curing conditions (10 mol% $\text{Zn}(\text{OAc})_2$, 1:1 epoxy/acid ratio, 180 °C, 3 h), producing highly crosslinked materials with gel fractions exceeding 90%. Both 4-arm and 6-arm PLA networks formed durable, solvent-resistant structures, as verified by thermal and rheological analysis.

Mechanical testing further confirmed that the networks were successfully formed: the DMA results showed a well-defined rubbery plateau in the storage modulus (E') between 80 °C and

120 °C, indicating that the materials remain elastic even well above their glass transition temperature.

Stress-relaxation tests revealed Arrhenius-type behavior with T_v values of 43 °C and 66 °C, demonstrating effective dynamic network formation.

Surface analyses showed that the 4-arm vitrimer had a more hydrophobic and stable surface than the 6-arm version, likely because the hydroxyl groups arrange differently at the material's surface.

Qualitative shape-memory tests also pointed to interesting possibilities for use in adaptive or responsive applications.

Finally, preliminary depolymerization experiments revealed that the material can be fully depolymerized within just two hours at 55 °C in mildly basic conditions, highlighting its strong potential for gentle and efficient chemical recycling.

Parallel work conducted during my period abroad as a visiting researcher at *École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris* (ESPCI Paris) further expanded the scope of the thesis, underlining that sustainable development in polymer science could be achieved not only by designing novel biobased thermosets but also by enhancing the circularity of existing commodity plastics. The aforementioned successful compatibilization of HDPE with renewable fillers, especially via reactive extrusion and tailored grafting agents, showed another pathway toward reduced reliance on fossil-based materials.

Poor compatibility between the hydrophobic HDPE matrix and the hydrophilic fillers was a central challenge. Several blend formulations were designed and tested, with careful evaluation of the influence exerted by each filler on mechanical and thermal properties. Interfacial adhesion is an important factor, and accordingly, compatibilization strategies were put into place, including two different grafting agents: an azidotriazine-based molecule reported previously in the literature and a novel maleimide-based agent developed for this study.

These agents were incorporated via reactive extrusion, optimizing reagent concentrations and processing conditions to effect maximum compatibilization. Comparisons with unmodified controls revealed clear improvements, most notably an increase in engineering yield stress with the azidotriazine-based grafting agent, **Tr-N₃**.

Improved filler dispersion and enhanced interfacial adhesion were confirmed via comprehensive characterization, including DMA, tensile testing and DSC.

Future polarized optical microscopy will also be useful to assess the homogeneity of the samples, but also application-oriented tests should be performed, such as creep resistance and environmental stress cracking resistance tests to evaluate the long-term mechanical stability of the material and its durability under real-world service conditions.

Overall, this work shows that it is possible to combine innovative polymer design, bio-based chemistry, and strategic compatibilization to create high-performance, sustainable, and circular materials, offering viable pathways toward the next generation of environmentally friendly plastics.

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