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Biotechnology*

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***Bio-Based Materials:
Advancing in Synthesis of Biopolymers and in
Natural Fiber Composites***

Cycle XXXVII

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Author's Declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for School of Advanced Studies, and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of others, is indicated as such. Any views expressed in the dissertation are those of the author.

19/01/2025



Preface

Nowadays, the concept of sustainability in the production of polymeric materials suitable for industrial and biomedical applications has assumed considerable importance and interest from the world of scientific research. The excessive use of fossil-based raw materials and the issues that arise from the manufacturing process of these contributes to increasing the global warming. In this regard, attention has shifted towards using bioresources and sustainable processes that promote the development of a bio-based economy. The synthesis and employment of biodegradable and biocompatible polymers represent a solution to reduce excessive petroleum-based polymers consumption and pollutions, as an eco-friendly solution to the environmental issues.

This work, carried out in the Prof. Marcantoni's research group at the University of Camerino (Italy) with the collaboration of HP Composites S.p.A. from November 2021 to November 2024, had the objective to develop sustainable materials for high performances composites application and the study of bio-based polymers. Following the same line of research, 6 months, from January 2024 to July 2024, were carried out in the research group of Professor Timothy Long, at the Arizona State University (Arizona), in Biodesign Center for Sustainable Macromolecular Materials and Manufacturing.

The introductory chapter focuses on the study of the state of the art of biomaterials.

A thorough examination of bio-reinforced composites, specifically the development of organic functionalization of natural fibers to enhance their durability and applicability, is presented in the second chapter; the Part II then explores the extrusion process of hemp-polyurea composites as well as the investigation of the thermal and mechanical properties of the resulting composites.

The third chapter focuses on synthetic bio-based polymers and is made up of Part I, in which the synthesis of bio-based PUA with the employment of a new non-toxic and eco-sustainable catalytic system was reported, and Part II concerning the sustainable 3D-printing of itaconic anhydride-based polymer.

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1 Introduction to Bio-based materials

1.1 The importance of polymers

Nowadays, it is impossible to imagine a world without synthetic polymers. The combination of low-cost production, versatility, durability and high strength-to-weight ratio made plastic the key material of the modern times.¹ Its increasing use is reflected in the exponential growth of its production over the last half century (Figure 1.1).

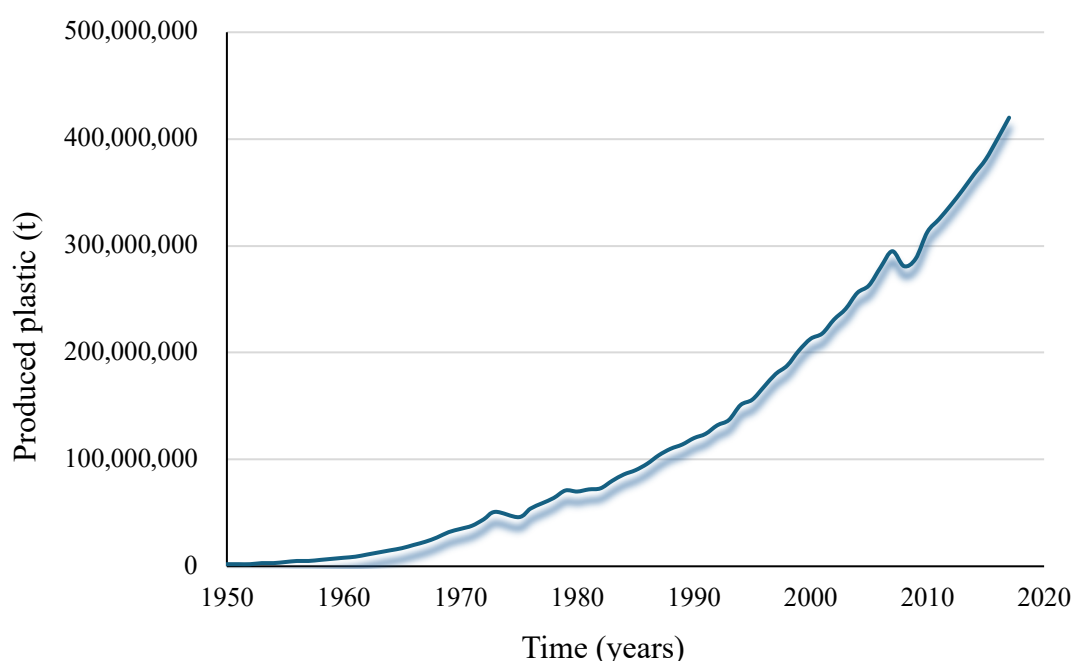


Figure 1.1. Global plastic production

The amount of plastic that is produced every year has incredibly increased from few million tons in 1950 to over 400 million tons in 2017 and its growth is expected to quadruple reaching around 1480 million tonnes by 2050.² Lightness, easily processability and resistance allowed the development of products that have improved the quality of life in sectors like the food industry, medical industry, electronics and automotive.³ Thanks to polymers, used daily in form of plastic, fibers, films and others, it is possible to package food safely, produce sterile medical devices but also built light

¹ Kibria, M. G.; Masuk, N. I.; Safayet, R.; Nguyen, H. Q.; Mourshed, M. *Environ. Res. J.* **2023**, *17*, 20.

² Geyer, R.; Jambeck, J. R.; Law, K. L. *Sci. Adv.* **2017**, *3*(7), 1700782.

³ North, E. J.; Halden, R. U. *Environ. Health Rev.* **2013**, *28*(1), 8.

vehicles and save energy. Despite their many positive aspects, polymeric materials are consequently responsible for waste and pollution when they reach the end of their life, laying the groundwork for a significant environmental challenge that must be addressed.⁴

1.2 Polymers: a material problem?

Stated the great value of polymers and how their use can facilitate everyday life, the issues related to their production, employment and disposal should not be underestimated. Polymers are very large molecules composed of repeating structural units, called monomers, linked together by covalent bonds to form long chains.⁵ They can be obtained through chemical reaction between monomers, either of the same or different type. If the reaction occurs in nature, this leads the formation of natural polymers, like cellulose, starch and natural rubber, while synthetic polymers are man-made. Although synthetic polymers have been studied since the middle of the nineteenth century and have attracted growing interest since their development, a significant problem has arisen in recent years: their negative impact on the environment.⁶ Many synthetic polymers are difficult to degrade naturally, leading to an accumulation of waste that threatens natural ecosystems. Certain type of plastics, for example, can take hundreds of years to decompose, during which time they fragment into small pieces that can enter the food chain, potentially causing adverse effects on human and animal health.⁷

In addition, the production of synthetic polymers often involves the use of non-renewable resources, such as oil and fossil-based raw materials, and can generate polluting emissions. These factors contribute to the overall environmental impact, raising concerns about the sustainability of these materials in the long term.

1.3 From linear to biocircular economy

⁴ Millican, J. M.; Agarwal, S. *Macromolecules* **2021**, 54(10), 14.

⁵ Namazi, H. *BioImpacts* **2017**, 7(2), 73.

⁶ Silva, R. R. A.; Marques, C. S.; Arruda, T. R.; Teixeira, S. C.; De Oliveira, T. V. *Macromolecules* **2023**, 3(2), 371-399.

⁷ Dey, S.; Veerendra, G. T. N.; Babu, P. A.; Manoj, A. P.; Nagarjuna, K. *Biomed. Mater. Devices*. **2024**, 2(1), 70-112.

The accumulation of plastic and other polymers in the environment is one of the greatest environmental challenges of our time. In this context, the traditional model based on "take, make, and dispose" shows its limitations. Resources are extracted, transformed into products, and disposed when no longer usable. This approach is not sustainable in the long term because it leads to the accumulation of waste and the depletion of raw materials (Figure 1.2).



Figure 1.2. Traditional linear economy model

The depletion of fossil fuels is one of the greatest problems. Composed of coal, oil and natural gas, fossil fuels come from organic material that was buried by soil and rock layers in millions of years. This process has produced reserves that account for most of the world's energy, used for electricity, heating and also serve as feedstock for a wide range of polymer products. However, extraction and consumption of these resources occur at an unsustainable rate. The increasing demand for polymers has led to an intensification of raw material extraction, which not only exhausts available resources, but also has direct economic consequences reflected in an increase in energy and material prices.⁸ The problem of fossil fuel depletion is further enhanced by climate change. The burning of these fuels releases large amounts of carbon dioxide (CO₂) and other greenhouse gases (GHG) into the atmosphere, contributing to global warming and its harmful effects. These changes not only lead to environmental problems, but they are also warring for food security and the global health.⁹

The other predominant sore point of this traditional model is the waste disposal. At the end of their life cycle, products, in the linear economy model, are made to be disposed in landfill or through incineration, with serious environmental consequences. Landfilling occupies large areas of land and can release harmful gases, including sulfur dioxide

⁸ Martins, F. F.; Castro, H. *Energy Rep.* **2020**, *6*, 417-422.

⁹ Kweku, D. W.; Bismark, O.; Maxwell, A.; Desmond, K. A.; Danso, K. B.; Oti-Mensah, E. A.; Adormaa, B. B. *J. Sci. Res. Rep.* **2018**, *17*(6), 1-9.

(SO₂) and nitrogen dioxide (NO₂), which have adverse effect for the humans. An improper waste disposal can also cause soil, water and air contamination.¹⁰ Most of non-biodegradable plastics materials are capable to persist in the environment for decades, threatening ecosystems and biodiversity. Incineration also, produces a wide range of air pollutants, including, reactive trace gases, particulate matter, and other toxic compounds.¹¹ Considering the climate change and the increase in global population the linear economy model is no longer sustainable. A promising solution is given by the bio-circular economy model in which the life cycle of products minimize waste and promote the recovery of resources, through a system in which materials are circularly reintegrated into the environment. The bioeconomy creates value-added products from renewable bio-resources; while on the other hand, the circular economy is involved with extending the life cycle of a given material through the reuse of waste. With different approaches, these two economies complement each other in forming a complete sustainability model. The circular economy (CE) has received much attention in last years as a solution to the consumption and production demands of resources given by the growing industrial activity (Figure 1.3).



Figure 1.3. Circular economy model

¹⁰ Siddiqua, A.; Hahladakis, J. N.; Al-Attia, W. A. K. *Environ. Sci. Pollut. Res.* **2022**, 29(39), 58514-58536.

¹¹ Wiedinmyer, C.; Yokelson, R. J.; Gullett, B. K. *Environ. Sci. Technol.* **2014**, 48(16), 9523-9530.

CE is reflecting a concept of sustainability which limits resource consumption by enhancing the recovery and recycle processes of materials aimed to provide an eco-friendly alternative to the framework of the linear economic model.

The core of the circular economy is based on three key foundations:

1. *reuse at the product level* (“repair” or “refurbishment”);
2. *reuse at the component level* (“remanufacturing”);
3. *reuse at the material level* (“recycling”).¹²

Consequently, this model leads to a reduction in raw material demand and depletion, emissions and pressure on ecosystems. Despite the benefits of the circular economy, attention remains high towards the depletion of fossil fuels and above all the growing emissions of greenhouse gases, in particular of carbon dioxide emitted during the combustion of fossil fuels. For this reason, the capture and storage of CO₂ are necessary to reduce the environmental effect of its emissions and to allow a more sustainable use of raw materials. In this regard, efforts are being made to replace and integrate the use of the biomass resources into this model, essential for reducing emissions and promote sustainability.¹³ To achieve an efficient use of biomass as a resource, European bioeconomy strategies are moving towards the concept of circular bioeconomy (CBE) made possible thanks to the bio-based economy.

1.4 Bio-based economy

Bioeconomy or bio-based economy refers to a set of economic systems and innovations aimed at substituting fossil resources with renewable biological resources to produce bio-derived materials and services. The use of renewable resources is important to address and limit the environmental problems largely caused by carbon dioxide emissions and exhaustion of fossil sources.

The bioeconomy recognizes biomass as the main component in the production of energy and materials. *Biomass* essentially refers to any component of an organic, animal, or vegetable matrix that has not gone through any form of fossilization and can be

¹² Morseletto, P. *Resour. Conserv. Recycl.* **2020**, *153*, 104553.

¹³ Stegmann, P.; Londo, M.; Junginger, M. *Resour. Conserv. Recycl. X* **2020**, *6*, 100029.

converted into energy or other high-valued products. Usually, biomass is classified into two basic types:

1. primary: refers to organic matter that arose from plants, animals, or aquatic algae;
2. secondary waste that arises from primary biomass (agriculture, industrial, and municipal waste). This outlook is important in not only providing renewable resources to renew; it offers a very promising sustainable system for recycling municipal waste.

Biomass can be regarded as a renewable form of clean energy that denotes a strong alternative for mitigation of greenhouse gas emissions. The adjustment of its greenhouse gas contributions is made mainly because biomass sources have the capacity to store atmospheric CO₂, capture and immobilize it through photosynthesis and, only after combustion, return carbon dioxide to the environment, taking part in the *short-term carbon cycle*. In fossil fuels, either they are oil, coal, or natural gas, free carbon that has been kept in the Earth's envelope for years is released. Due to the long duration of its “sequestration”, this carbon is outside the natural carbon cycle. The huge release contributes, in this way, to the increase of atmospheric concentrations of CO₂, aggravating the greenhouse effect and worsening the expansion of global warming (Figure 1.4).¹⁴

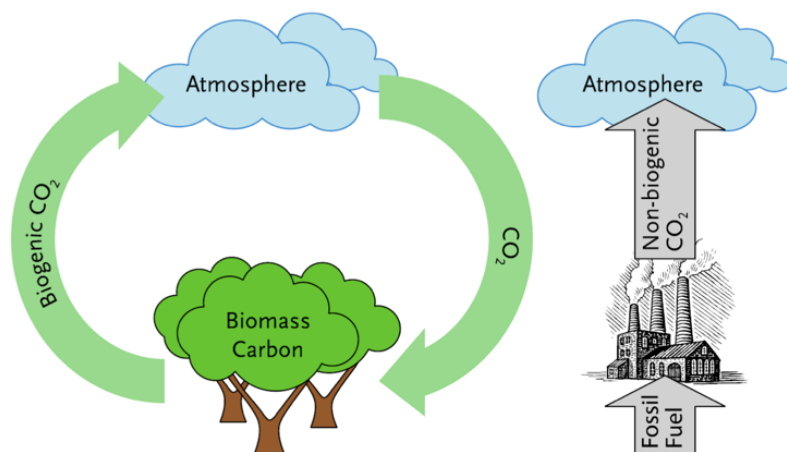


Figure 1.4. Fossil vs biogenic CO₂ emissions

¹⁴ Harris, Z. M.; Milner, S.; Taylor, G. B. *Greenhouse Gas Balances of Bioenergy Systems*; Academic Press, 2018, 55–76.

Hence, the CO₂ is absorbed by the growth of the vegetation then used energetically, and then again absorbed by the regrowth of new biomass. In principle, therefore, the biomass is a "neutral" source in terms of emissions.¹⁵ The biomass value is determined by its application and is defined by the *biomass value pyramid* (Figure 1.5). The added value is the highest at the top of the pyramid, while it is the lowest at the bottom. On the contrary, the volume of biomass needed for the applications is the lowest at the top and it is the highest at the bottom of the pyramid.¹⁶

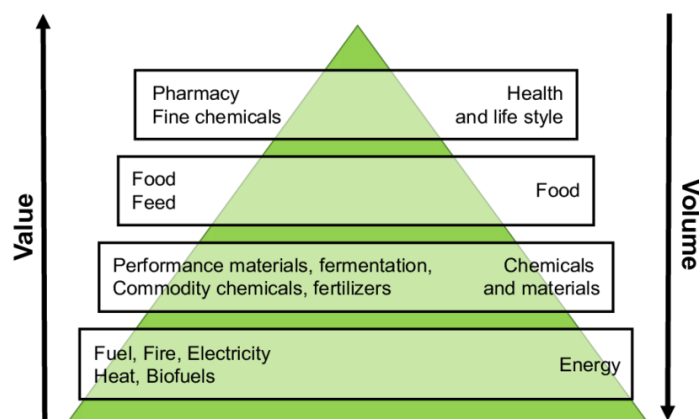


Figure 1.5. Biomass pyramid value

The conversion of biomass into energy is shown at the bottom of pyramid where the value market is large, but the price is low. The market for fine chemicals or pharmaceuticals is small but the price of these products is high. To ensure that a bio-based economy is also sustainable, it must respect 3 basic principles:

- Use the renewable resources available today for actual needs (the production of biomass must go with the consumption of bioproducts).
- Use all the parts of the biomass
- Use the most valuable parts of the biomass for the most added value products (like pharmaceutical and fine chemicals products)

Based on the principles of sustainable biomass utilization, a significant application of biomass is the production of biopolymers. By using renewable resources and ensuring that all parts of the biomass are used efficiently, biopolymers offer a green alternative to

¹⁵ Abbasi, T.; Abbasi, S. A.; *Renew. and Sust. Energ.* **2010**, *14*, 919-937.

¹⁶ Zhao, X.; Zhou, H.; Sikarwar, V. S.; Zhao, M.; Park, A. H. A.; Fennell, P. S.; Fan, L. S. *Environ. Sci.* **2017**, *10*(9), 1885–1910.

traditional fossil-based polymers. They represent a crucial solution to address environmental challenges, especially in plastic waste management.¹⁷

1.5 Biopolymers

There are different definitions of biopolymers given by acknowledged organizations. According to the International Union of Pure and Applied Chemistry (IUPAC) biopolymers are macromolecules produced by living organisms including proteins, polysaccharides and nucleic acids (DNA and RNA). An additional key definition is given by the American Society for Testing and Materials (ASTM) who considers the concept of biodegradability defining a biopolymer a “degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae”.¹⁸ It’s important, in this sense, to distinguish between bio-based and biodegradable polymers. As stated by the European Bioplastic Organization, bio-based or partially bio-based bioplastic are polymers with the same characteristics and properties to fossil-based plastic but derived from renewable resources. On the other hand, biodegradable plastics are derived from either renewable or non-renewable resources.^{19,20} Therefore, a material can be defined as bioplastic if it is bio-based or biodegradable, or if it has both characteristics. A biopolymer made from renewable and non-fossil resources that is also biodegradable could solve the main environmental problems associated with the disposal of plastic. The Figure 1.6 shows some examples of plastics that clarify the relation between biodegradable and bio-based materials.

¹⁷ Machado, G.; Santos, F.; Lourega, R.; Mattia, J.; Faria, D.; Eichler, P.; Auler, A. *Lignocellulosic Biorefin. Technol.* **2020**, 125-158.

¹⁸ Goel, V.; Luthra, P.; Kapur, G. S.; Ramakumar, S. S. V. *J. Polym. Environ.* **2021**, 29, 3079–3104.

¹⁹ Wojtowicz, A. Biodegradability and Compostability of Biopolymers. In *Thermoplastic Starch: A Green Material for Various Industries*; 2009; pp 55–76.

²⁰ Tokiwa, Y.; Calabia, B. P.; Ugwu, C. U.; Aiba, S. *Int. J. Mol. Sci.* **2009**, 10(9), 3722–3742.

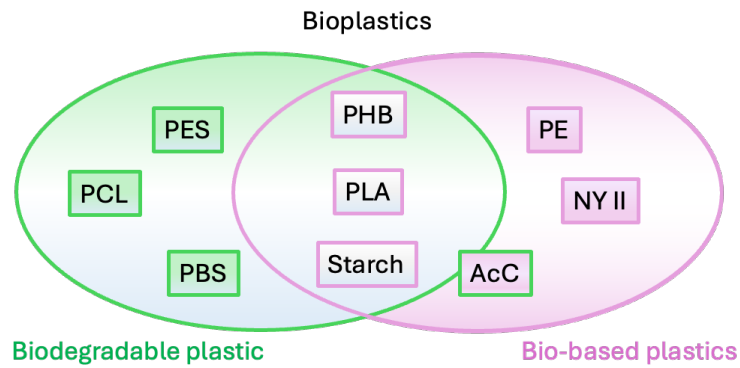


Figure 1.6. Bioplastics: Biodegradable and bio-based plastic

Plastics like polycaprolactone (PCL), polybutylene succinate (PBS) and polyethylene succinate (PES) are fossil-based, but they can degrade by the action of microorganism. At the same time, polylactide (PLA), polyhydroxybutyrate (PHB), and starch blends are produced from biomass or renewable resources and are thus biodegradable. Even though polyethylene (PE) and Nylon 11 can be produced from biomass or renewable resources, they are non-biodegradable. Some types of polymers are either biodegradable or non-biodegradable, depending on different factors. Acetyl cellulose (AcC), for example, with a low acetylation degree can be degraded, while AcC with high substitution ratios is non-biodegradable.

1.5.1 Biodegradability of polymers

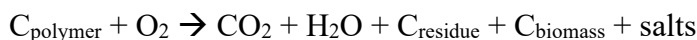
Biodegradation refers to a type of degradation made through the action of enzymes or living organism involving chemical and physical deterioration of the materials which thus become available for new natural processes. Three different steps are involved in the biodegradation process:

1. Biodeterioration. Refers to the modification of chemical, mechanical and physical properties of the macromolecule due to the microbial growth either external to or within the polymer
2. Bio-fragmentation. Indicates the conversion of polymers into species at lower molecular mass.

3. Assimilation. It is the final step in which the fragments are converted into carbon dioxide, water and biomass by the action of microorganisms supplied by carbon, energy and nutrient source.²¹

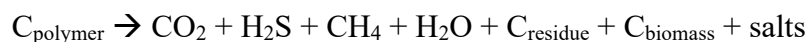
Biodegradation can occur in two different conditions:

1. Aerobic, in presence of oxygen:



These conditions lead to the formation of CO₂ and H₂O in addition to the cellular biomass of microorganisms during the degradation of the plastic forms.

2. Anaerobic, in absence of oxygen:



In these conditions, polymer biodegradation leads to the formation of CO₂ and H₂O as well as CH₄ produced by microorganisms under methanogenic conditions. In some cases, H₂S can form in a sulfidogenic environment, where specific bacteria reduce sulfate.

The presence of O₂ in aerobic process allows microorganisms to release more energy from the chemical bonds of the polymer, making the process more efficient in term of energy than the anaerobic. As a result, aerobic biodegradation is faster and more effective. Biodegradation is strongly influenced by chemical structure, complexity and length of polymer chains. In many cases plastic materials can be made of different types of polymers therefore different propensities to degradability. Humidity, temperature, pH, salinity and the supply of different nutrients are factors that influence the microbial degradation of polymers. The environment, therefore, plays a key role in the degradation process. Recent research from Max Planck Institute for Polymer Research in Mainz (Germany) have shown that polylactic acid is basically non-degradable in seawater.²² Polymer morphology also greatly affects biodegradation rates, with the degree of crystallinity being a crucial factor, since enzymes primarily target the amorphous regions of polymers, where molecules are loosely packed and more susceptible to degradation. In contrast, the crystalline regions are more resistant to degradation. A higher melting

²¹ Emadian, S. M.; Onay, T. T.; Demirel, B. *Waste Manag.* **2017**, *59*, 526–536.

²² Haider, T. P.; Völker, C.; Kramm, J.; Landfester, K.; Wurm, F. R., *Angew. Chem. Int. Ed.* **2019**, *58*, 50-62.

temperature (T_m) further reduces polymer's biodegradability. Aliphatic polyesters and polycarbonates are two examples that exhibit high potential as biodegradable polymers due to their susceptibility to lipolytic enzymes and microbial degradation. However, compared to aliphatic polyesters and polycarbonates, materials like aliphatic polyurethanes and polyamides have higher T_m values, which makes them less biodegradable.²³

1.5.2 Biopolymer's classifications

The classification of biopolymers is very diverse, with several different types. For simplicity, biopolymers can be broadly distinguished according to their origin into natural, synthetic and microbial biopolymers. Natural biopolymers are those directly produced by living organisms, synthetic biopolymers are synthesized from renewable resources, and they can be further classified into biodegradable and non-biodegradable (Figure 1.7).²⁴

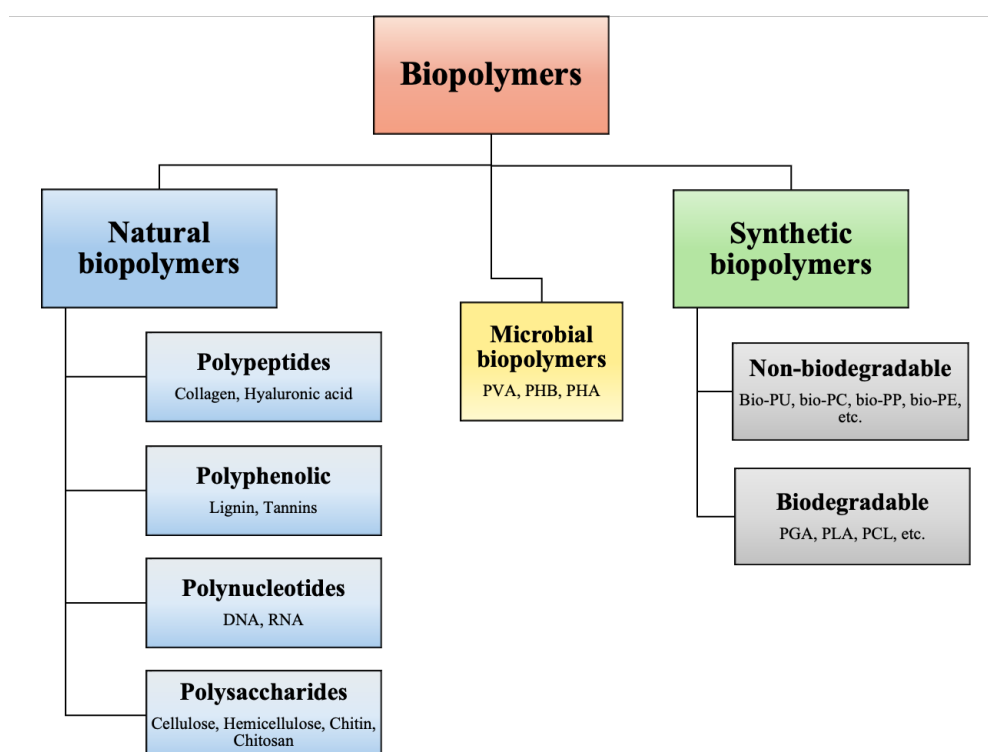


Figure 1.7. Classification of biopolymers

²³ Tokiwa, Y.; Suzuki, T. *J. Appl. Polym. Sci.* **1981**, 26, 441–448.

²⁴ Ekiert, M.; Mlyniec, A.; Uhl, T. *Diagnostyka* **2015**, 16 (4), 63–70.

Biopolymers can also be classified based on the ways in which they respond to heat as:

- *thermoplastics*: materials that can be heated, remolded and cooled as needed without any chemical changes
- *thermosets*: tough materials that cannot be remolded or heated after initial forming
- *elastomers*: polymer that has elastic properties, such as natural and synthetic rubbers.²⁵

1.5.3 Natural biopolymers

Natural biopolymers are polymers produced by living organisms, such as plants, animals, bacteria, and fungi, through biological processes. They are synthesized by living microorganism and they are made from natural monomers such as amino acids, sugars or nucleotides. Natural biopolymers structures are capable of being functionalized due to their chemical compositions full of reactive sites, therefore they can be used in a wide range of applications such as industrial, medical, and environmental. The modification of biopolymers offers promising possibilities to design structures for specific applications especially in the biomedical field such as drug delivery systems, tissue engineering, medical implants, biosensors and wearable electronic devices.²⁶ Cellulose, lignin and hemicellulose are the most abundant natural biopolymers, since they are the compounds present in the highest ratio in biomass and extracted directly from that.

- Cellulose

Cellulose is a linear polysaccharide polymer consisting of chain with several hundred to many thousands glucose monosaccharide units linked together by β -1,4-glycosidic bonds (Figure 1.8). Due to the arrangement of the glucose subunits, each glucose monomer is oriented in the opposite direction to the one next to it, leading to a linear, fibrous structure. Cellulose is found in nature mainly in plants, but it is also produced from microorganisms in the form of microbial cellulose; it constitutes one of the most abundant biopolymers with a large range of applicability in pharmaceutical industry.

²⁵ Niaounakis, M. *Biopolymers: Processing and Products*; William Andrew: 2014

²⁶ Jian, M.; Zhang, Y.; Liu, Z.; Chin. *J. Polym. Sci.* **2020**, *38*, 459-490.

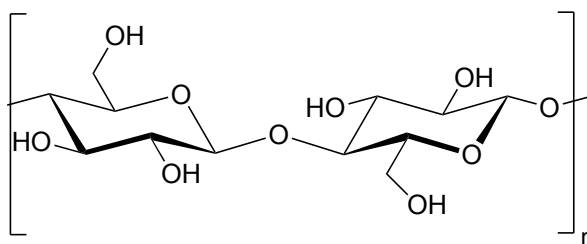


Figure 1.8. Cellulose structure

The molecular structure imparts cellulose its main properties: hydrophilicity, chirality, degradability, and high reactivity of the -OH groups which can form hydrogen bond networks contributing to the cellulose crystalline characteristics.²⁷

- Hemicellulose

Hemicellulose is a polysaccharide made of a combination of sugars (Figure 1.9), whose chemical composition is difficult to determine, as it varies depending on the environmental conditions in which the fiber grows and its age.

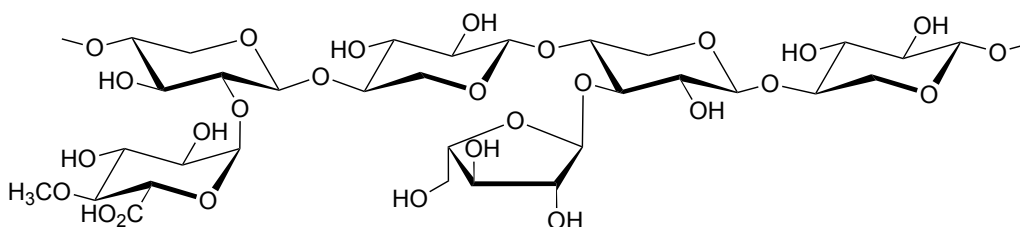
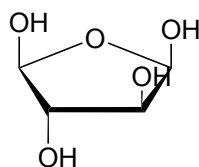


Figure 1.9. Hemicellulose structure

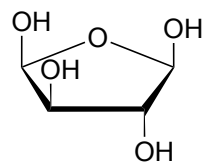
Generally, monomers that make up hemicellulose are pentoses and hexoses. The most important pentoses are arabinose and xylose, while the hexoses are glucose, mannose and galactose (Figure 1.10).

²⁷ Drumright, R. E.; Gruber, P. R.; Henton, D. E., *Adv. Mater.* **2000**, *12*, 1841-1846.

Pentoses:

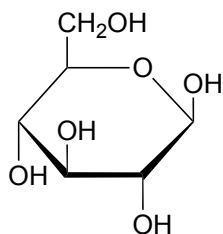


Arabinose

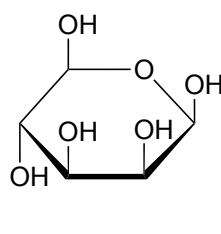


Xylose

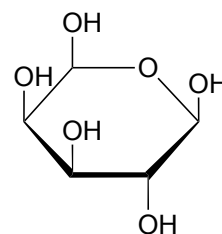
Hexoses:



Glucose



Mannose



Galactose

Figure 1.10. Hexoses and pentoses structures of hemicellulose

Hemicellulose differs from cellulose in four aspects:

- It contains different sugar units
- More branched structure
- Lower degree of polymerization
- Its constituents differ from the type of plant, while in cellulose they remain unaltered.²⁸

- Lignin

Lignin is an amorphous polyphenolic biopolymer, characterized by a complex structure (Figure 1.11), that serves as a structural support material in plants.

²⁸ John, M. J., Thomas, S. *Carbohydr. Polym.*, **2008**, 71, 343.

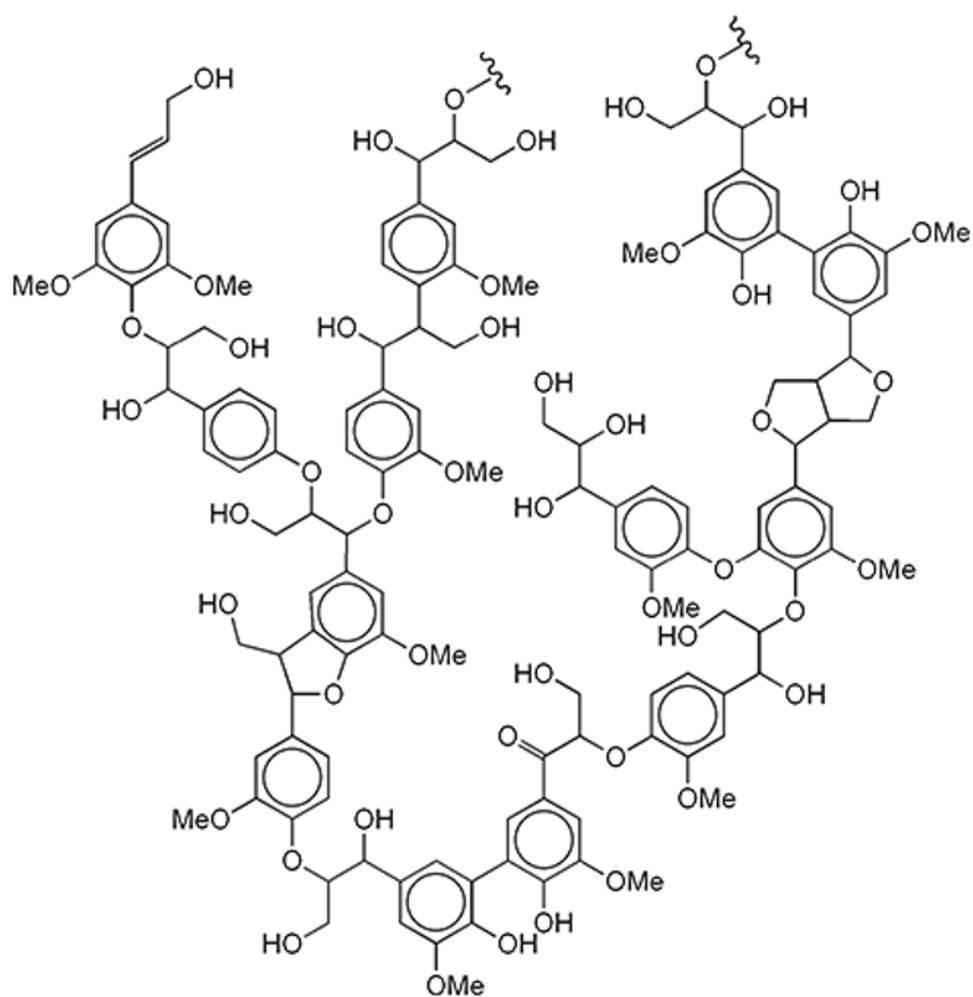


Figure 1.11. Lignin chemical structure

Lignin biosynthesis results from the polymerization of different phenylpropyl acids and alcohols. The main monomeric units that make up lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 1.12).²⁹

²⁹ Chakar, F. S., Ragauskas, A. J. *Ind. Crops. Prod.*, **2004**, 20, 131.

Lignin monomers

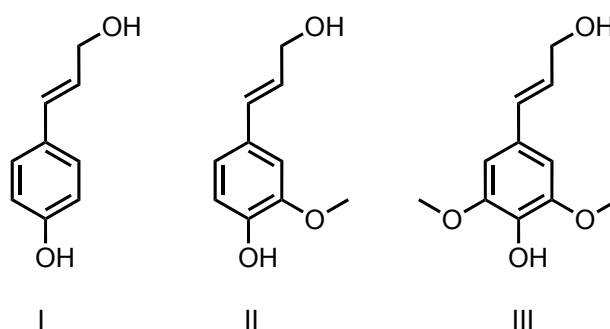


Figure 1.12. Lignin structure and monomers: *p*-coumaryl alcohol (I), coniferyl alcohol (II), sinapyl alcohol (III).

Although most of the functional groups of lignin and the units that compose it have been identified, its exact chemical nature has not yet been determined due to the lack of an effective method to isolate it in its native state. Its chemical structure, in fact, can be modified during the different extraction methods. In this regard, lignin can be categorized according to its origin in hardwood, softwood, or grass lignin but mostly on the base of the extraction method used (kraft lignin, lignosulfonate, organosolv lignin).³⁰

- Collagen

Collagen is a natural polymer that represents the matrix material of bone, teeth and connective tissue and can be extracted from animal or human sources. Collagen is the most important structural protein in our body and strengthens tendons and elastic sheets that support the skin and internal organs. It is composed of three chains, wrapped together in a compact triple helix. The resistant structure is formed by a repeated sequence of only three amino acids: glycine, proline and hydroxyproline (Figure 1.13).

³⁰ Mohanty, A. K., Misra, M. A., Hinrichsen, G. I. *Macromol. Mater. Eng.*, **2000**, 276, 1-24.

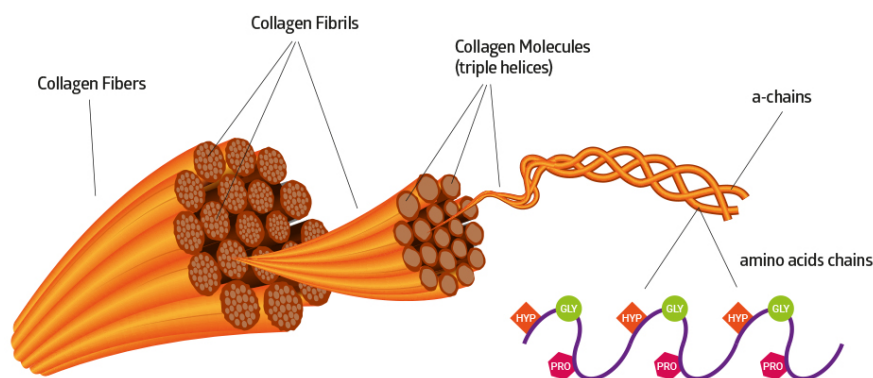


Figure 1.13. Collagen structure

The excellent biocompatibility and safety due to its biological properties made collagen a fundamental resource in biomedical applications. The main applications of collagen concerns drug delivery systems, sponges for burns-wounds, antiaging creams, tissue engineering including skin replacement, bone substitutes, and artificial blood vessels and valves.³¹

- Chitin and chitosan

Chitin is a natural polysaccharide consisting of repeating units of N-acetyl glucosamine linked with β -(1-4) glycosidic bonds. Chitin is the second most abundant polymer present in nature after cellulose. It is found in the form of crystalline microfibrils ordered in the exoskeleton of arthropods, particularly in marine crustaceans such as shrimps and crabs. Thanks to its biodegradability, hydrophilicity, non-toxicity, antibacterial properties and affinity for proteins, chitin has found use in various applications such as in biosensors. Chitosan is the most important derivative of chitin (Figure 1.14) and is obtained by partial deacetylation of chitin under alkaline conditions or by enzymatic hydrolysis. It is used in the biomedical application and is much easier to process than chitin, but the stability of chitosan materials is generally lower, owing the higher hydrophilic character and the sensibility to pH.³²

³¹ Lee, C. H.; Singla, A.; Lee, Y., *Int. J. Pharm.* **2001**, *221*, 1-22.

³² Rinaudo, M., *Prog. Polym. Sci.* **2006**, *31*, 603-632.

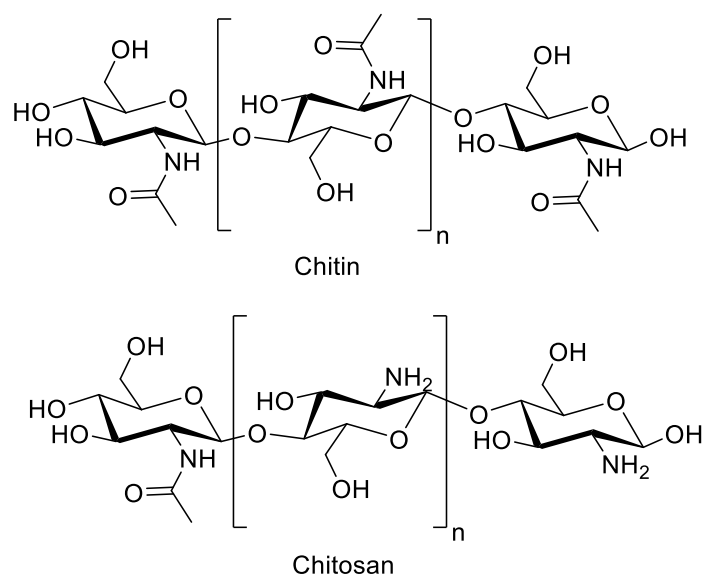


Figure 1.14. Structure of chitin and chitosan

- Hyaluronic acid (HA)

Hyaluronic acid is a polysaccharide that is naturally present in the fluids and joints of human body. It consists of alternating units of *N*-acetyl-*D*-glucosamine and glucuronic acid (Figure 1.15). Hyaluronic acid (HA) is naturally synthesized by the body's cells to maintain the elastoviscosity of liquid connective tissues, to lubricate the moving parts of the body, such as joints and muscles, and to help water transport.³³

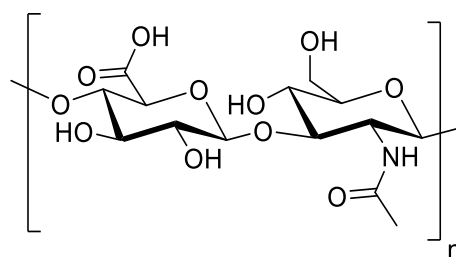


Figure 1.15. Structure of hyaluronic acid

- DNA and RNA

DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) are biopolymers made up of nucleotides repeating units, linked together in long chains. Nucleotides are composed of three main components: a nitrogenous base (adenine, thymine or

³³ Necas, J.; Bartosikova, L.; Brauner, P.; Kolář, J. *Vet. Med.* **2008**, 53, 397-411.

carboxylate chain are characteristics that make this biopolymer useful in pharmaceutical and biomedical applications.³⁵

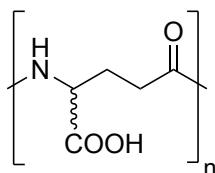


Figure 1.17. Structure of poly-γ-glutamic acid

- Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates are thermoplastic polyester biopolymers (Figure 1.18) synthesized by various bacteria through the fermentation of sugars or lipids. These are biodegradable and biocompatible polymers therefore their use is frequent in formulation of bioplastic for packaging and medical applications (such as sutures, repair patches, orthopedic pins, nerve guides and bone marrow scaffolds).³⁶

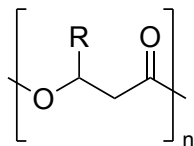


Figure 1.18. Structure of polyhydroxyalkanoates

³⁵ Ogunleye, A.; Bhat, A.; Irorere, V. U.; Hill, D.; Williams, C.; Radecka, I. *Microbiology* **2015**, 161, 1-17.

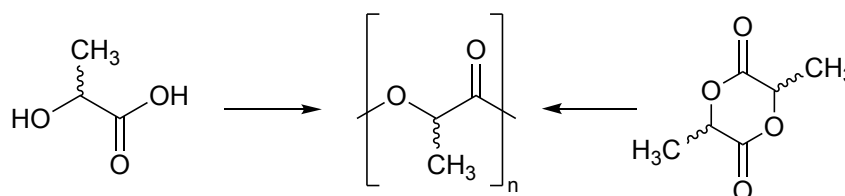
³⁶ Verlinden, R. A. J.; Hill, D. J.; Kenward, M. A.; Williams, C. D.; Radecka, I. *J. Appl. Microbiol.* **2007**, 102, 1437-1449.

1.5.5 Synthetic biopolymers

By accepted definition, synthetic biopolymers are those polymers that are obtained from modifications of synthetic polymers as well as from polymerization of synthetic monomers, and which in any case have the characteristic of being able to undergo natural degradation, without leaving residues harmful to the living and natural environment. However, there are several advantages of natural biopolymers over synthetic biopolymers, including no toxicity, better bioactivity and biocompatibility, effective biological function and extreme hydrophilicity. However, the poor processability of natural biopolymers often limits their practical applications, leading to significant drawbacks such as: high batch-to-batch inconsistency, poor solubility that blocks fabrication processes, easily contaminable by pathogens, limited material properties like strength, elasticity and shelf life, and finally high cost. At the same time, synthetic biopolymers present improved control over chemical composition, particularly in terms of processability and mechanical properties, but at the expense of a decreased bioactivity, a low capacity of cellular specificity and a limited recognition of surface cells. Nevertheless, synthetic biopolymers can be produced and modified under controlled conditions allowing for the prediction and reproduction of their physical and mechanical properties, as well as the target function of the final material avoiding any type of impurities.³⁷

- Poly(Lactic acid) (PLA)

Poly(lactic acid) (PLA) is a polyester derived from renewable resources such as corn and sugar beets. It can be prepared by both direct polycondensation of lactic acid and by the ring opening polymerization of the cyclic lactide (Scheme 1.1).



Scheme 1.1. Synthesis of PLA

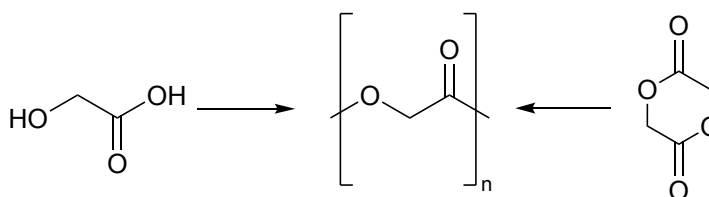
³⁷ Reddy, M. S.; Ponnamma, D.; Choudhary, R.; Sadasivuni, K. K. *Polymer*, **2021**, *13*, 1-51.

Thanks to its biodegradable, biocompatible and thermoplastic character PLA offers great promise in several commodity and biomedical applications (sutures for example) even if its commerce is limited by high production costs.³⁸

Many current studies focus on the bulk modification of PLA to enhance toughness in consumer applications as well as the introduction of reactive functional groups beneficial for biomedical applications.³⁹

- Poly(glycolic acid) (PGA)

Poly(glycolic acid) has a chemical structure similar to that of PLA without the methyl side group, it is synthesized through polymerization of glycolic acid or ring opening of glycolide (Scheme 1.2). Poly(glycolic acid) is both biodegradable and compostable, making it valuable for drug delivery and tissue engineering applications. It presents high mechanical properties and gas barrier performance that make it promising for coatings, membranes, thermal management and packaging.⁴⁰



Scheme 1.2. Synthesis of PGA

- Polycaprolactone (PCL)

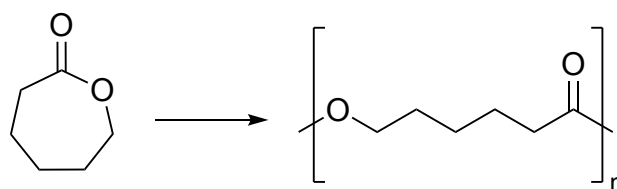
Polycaprolactone is a biodegradable aliphatic polyester synthesized by ring-opening polymerization process of ϵ -caprolactone (Scheme 1.3).⁴¹ PCL is known for its excellent biocompatibility and bioresorbability properties. It is widely used in the field of human therapy, including drug delivery systems, tissue engineering as well as a component in biodegradable plastics.

³⁸ Drumright, R. E.; Gruber, P. R.; Henton, D. E., *Adv. Mater.* **2000**, *12*, 1841-1846.

³⁹ Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog. Polym. Sci.* **2010**, *35*, 338-356.

⁴⁰ Samantaray, P. K.; Little, A.; Haddleton, D. M.; McNally, T.; Tan, B.; Sun, Z.; Huang, W.; Ji, Y.; Wan, C., *Green. Chem.* **2020**, *22*, 4055-4081.

⁴¹ Ali, S. A. M.; Zhong, S. P.; Doherty, P. J.; Williams, D. F. *Biomaterials* **1993**, *14*, 648-656.



Scheme 1.3. Synthesis of PCL

- Polyanhydrides (PAs)

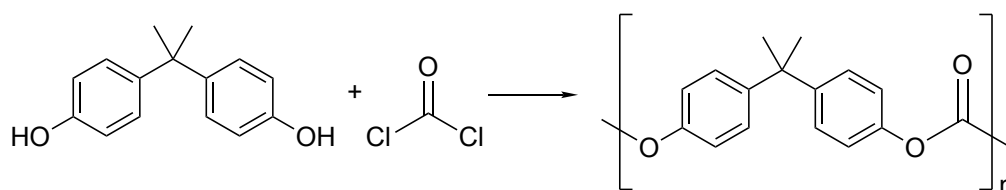
PAs constitute an important class of biodegradable and biocompatible polymers derived by fatty acids. They come from the polymerization of dicarboxylic acid that form repeating unit connected by anhydride bonds (Scheme 1.4). The degradation of polyanhydrides results in the formation of non-toxic diacid byproducts, making these ideal polymers for biomedical applications such as antibiotics, chemotherapy, and controlled drug delivery systems.⁴²



Scheme 1.4. Synthesis of PAs

- Polycarbonate (PC)

Polycarbonate is a thermoplastic aliphatic polymer characterized by a strong biocompatibility in conjunction with good impact resistance. Typically, PC is obtained by the polycondensation of bisphenol A and phosgene (COCl_2) (Scheme 1.5). It is a tough, durable and hard polymer normally used in applications like lenses, medical devices, and electronic components. It is resistant to degradation caused by microorganisms or environmental factors; though, it is usually blended with other polymers to improve its biodegradability. However, it is easy to recycle and reuse.

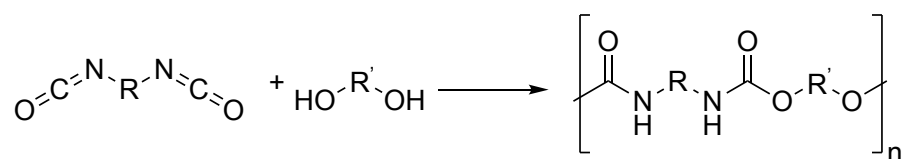


Scheme 1.5. Synthesis of PC

⁴² Basu, A.; Domb, A. *J. Adv. Mater.* **2018**, *30*, 1-10

- Polyurethanes (PUs)

Polyurethanes are synthetic polymers which contain urethane groups -HNCOO- in the main polymer chain. The urethane linkage is formed by the reactions between NCO groups of diisocyanates and OH groups of polyols (Scheme 1.6).⁴³ Traditional polyurethanes are not biodegradable due to their stable chemical bonds, but they can be designed to be more environmentally friendly, making use of bio-based building block.



Scheme 1.6. Synthesis of PU

There are different types of polyurethane (thermoplastic, flexible foam, rigid foam, water-borne, ionomers) and each of them is aimed at a certain type of use. They can be utilized in a wide range of products, such as liquid coatings, adhesives, elastic fibers, foams and in biomedical applications (like drug delivery systems, breast implants, surgical dressings and others).⁴⁴

⁴³ Kwon, O.-J.; Yang, S.-R.; Kim, D.-H.; Park, J.-S. *J. Appl. Polym. Sci.* **2007**, *103*, 1544-1553.

⁴⁴ Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. *RSC Advances* **2016**, *6*, 114453-114482.

1.5.6 Biocompatibility of polymers

Biocompatibility is defined as the ability of a material to perform its medical function without undesirable effects in the individual but rather by generating responses that are more appropriate to the specific situation and optimizing clinically performance.⁴⁵ Biocompatibility represents a huge challenge to the manufacturing of medical devices and drug delivery systems, affecting everything from production to the approval process of the final product. The assessment of the biocompatibility of biomaterials for medical devices is a complex task influenced by several factors including first the chemical nature and physical properties of the material and secondly the type and the duration of contact with biological system. To make the material usable, these factors must be rigorously tested. Since biomaterials are being applied in various and increasingly complex fields such as tissue engineering, invasive sensors, drug delivery, gene transfection, medical nanotechnologies and implantable medical devices, these uncertainties associated with the mechanisms and conditions necessary for biocompatibility have become serious barriers to progress. Not all biomaterials are biocompatible and there is still confusion about what biocompatibility means and the mechanisms that contribute to it, despite the fact that this expression has become very widespread in the field of biomaterials science. This property varies depending on several factors, like polymers chemical composition, physical properties, and the specific biological context in which they are used. In the modern world, several characteristics are taken into consideration to define whether a polymer can be classified as biocompatible:

- Reaction of the body towards a material which may be site dependent, meaning biocompatibility is not only dependent upon the material itself, but also on the specific context in which it is being used
- An increasing number of applications require the material to specifically interact with the surrounding tissues, rather than being inert and ignored by the body.
- In some cases, the material must be designed to degrade over time within the body, rather than remaining permanently.⁴⁶

⁴⁵ Tanaka, M.; Sato, K.; Kitakami, E.; Kobayashi, S.; Hoshiba, T.; Fukushima, K. *Polymer* **2015**, *47*, 114-121.

Consequently, biocompatibility is better redefined as follows: “*Biocompatibility refers to the ability of a material to perform with an appropriate host response in a specific situation*” (Figure 1.19).⁴⁶

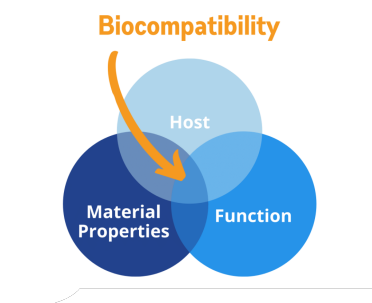


Figure 1.19. Biocompatibility

1.5.7 Biopolymers for biomedical applications

Biopolymers can play important functions in our body. They hold the cells together in tissues, they provoke chemical signals in cells to guide their behavior, they improve the smoothness and elasticity of the skin, and they protect the organism from pathogens. However, a biopolymer should possess specific properties to perform its biocompatible function and be environmentally sustainable in the same way. For this reason, biomaterials, thanks to their eco-friendly potential and beneficial properties, are considered promising alternatives to fossil-based materials in biomedical and pharmaceutical applications including drug delivery system, dental treatment, tissue engineering, wound healings, and other as wells (Figure 1.20).

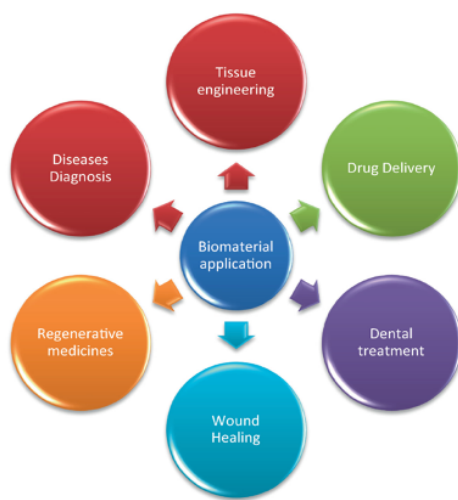


Figure 1.20. Biomaterials in biomedical application

⁴⁶ Donaruma, L. G. *J. Polym. Sci. Part C Polym. Lett.* **1988**, 26, 414–414.

1.6 Bio-composites

Despite the advantages of biopolymers, they have some limitations compared to petroleum-based materials, such as relatively low stiffness, lower tensile strength, high permeability, and reduced thermal stability. To improve the properties and increase the commercial value of biopolymers, "biopolymer composites", obtained by adding reinforcing materials at the micro or nanoscale, are widely studied.^{47,48,49} These composites find use in a wide range of applications, including construction, medicine, electronics, packaging, and automotive. Bio-composites are defined as eco-friendly and sustainable materials. Composites, in general, are made up of two or more phases in which one of the components is present in a higher concentration and acting as matrix while the component present in a smaller amount forms the reinforcement improving properties and inducing enhanced performance. In most cases, the matrix is a polymer, as it is characterized by a low density, which provides lightness to the final material. The reinforcement, on the other hand, is usually made up of fibers, which guarantee high resistance to the product. From the combination of these two components, it is possible to obtain a material that enhances the best characteristics of both phases in terms of performance and weight. Although the numerous advantages that characterize composites, the evaluation of their life cycle often yields issues due to the limited recyclability and the high energy consumption of the disposal processes.⁵⁰ For example, glass fibers, which are used as reinforcement in many polymers, still cause environmental problems, both in mechanical recycling and in end-of-life disposal through incineration.^{51,52} Current trends towards the production of eco-sustainable materials are thus focused on the development of bio-composites, materials mainly consisting of a polymeric matrix and a natural fiber reinforcement (Figure 1.21).

⁴⁷ Deshmukh, K.; Ahamed, M. B.; Sadasivuni, K. K.; Ponnammam, D.; AlMaadeed, M. A. A.; Deshmukh, R. R.; Pasha, S. K.; Polu, A. R.; Chidambaram, K. *J. Appl. Polym. Sci.* **2017**, *134*,

⁴⁸ Ashik, K.; Sharma, R. S.; Guptha, V. J. *Mater. Today Proc.* **2018**, *5*, 3000–3007.

⁴⁹ Galvez, P.; Abenojar, J.; Martinez, M. A. *Compos. Part B Eng.* **2019**, *176*, 107194.

⁵⁰ Matabola, K. P.; De Vries, A. R.; Moolman, F. S.; Luyt, A. S. *J. Mater. Sci.* **2009**, *44*, 6213.

⁵¹ Loos, J.; Schimanski, T.; Hofman, J.; Peijs, T.; Lemstra, P. J. *Polymer* **2001**, *42*, 3827.

⁵² Thomason, J. L. *Compos. Sci. Technol.* **2002**, *62*, 1455.

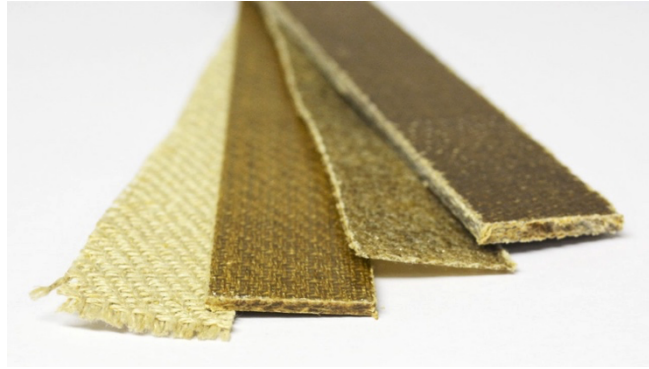


Figure 1.21. Natural fiber reinforced composites

1.6.1 Matrix

General information

The matrix is a fundamental component of composite materials, it represents the continuous and homogeneous phase. It plays several key roles within the material, including enclosing the reinforcement, ensuring the cohesion of the composite, ensuring the good dispersion of the dispersed phase, transferring the load to the reinforcement phase, protecting the reinforcement phase from any external agents and delaying the propagation of cracks. Matrices in composite materials can be classified in:

- polymeric
- ceramic
- metallic.

Polymeric matrices are the mostly used, as they have a high resistance/weight ratio and allow to obtain objects with different shapes and sizes. They are divided into two main groups:

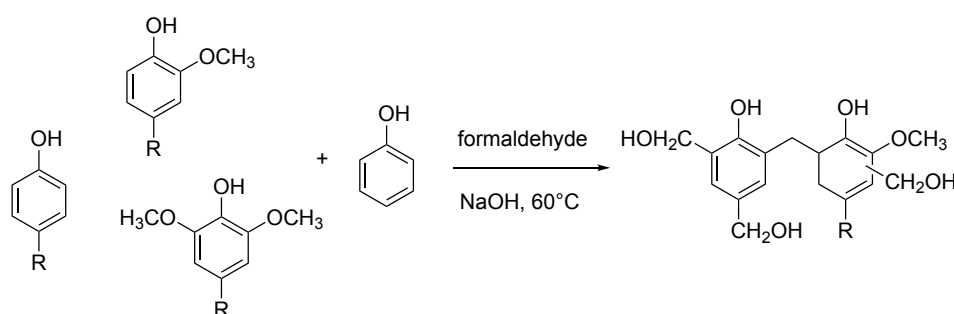
- thermoplastic resins: (such as PP, PE, PVC, PTFE), are characterized by a relatively low glass transition temperature (T_g) and melting temperature (T_m) they are not optimal for the manufacture of composites for high-temperature applications;
- thermosetting resins: (such as epoxy, acrylic or phenolic resins), are formed from monomers with multiple reactive functional groups. These resins are characterized by a highly stable structure with a high glass transition temperature and, unlike thermoplastics, these resins do not exhibit a distinct melting temperature.

Thermoplastic resins are made up of linear or branched polymers, which can be reshaped at high temperatures and have a high impact resistance and toughness. Thermosetting resins, on the other hand, are polymers that have a cross-linked structure, due to the formation of covalent bonds that act as a bridge between the polymer chains, thus giving the final material high rigidity and performances. The cross-linking process takes place during radical polymerization through the application of heat or in presence of UV light and specific agents, known as radical photo-initiators. This process is irreversible, as the resulting material will degrade rather than melt when exposed to additional heat, unlike thermoplastic polymers. Generally, thermosetting resins are mostly used in composite industry, as they require lower temperatures and pressures, during the processing compared to thermoplastic materials. Furthermore, they have low viscosity, good matrix-fiber interaction and better control over the orientation of the fibers during the production process.

Efforts are being made in the production of bio-based thermoplastic and thermosetting resins that are derived from renewable resources, such as carbohydrates, lignocellulosic compounds, vegetable oil and plant extracts. The most common bio-based thermosetting resins are:

- Phenolic resins

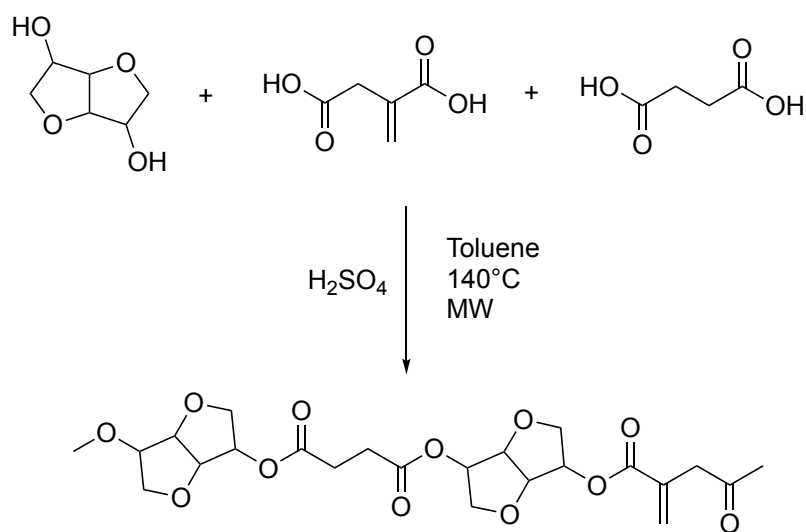
Derived from natural and oil-derived phenols and aldehydes, used to produce heat-resistant materials (Scheme 1.7).⁵³



Scheme 1.7. Bio-based phenolic resin from phenols in bio-oil

⁵³ Cho, E. C.; Chang-Jian, C. W.; Lu, C. Z.; Huang, J. H.; Hsieh, T. H.; Wu, N. J.; Weng, H. C. *Polymers* **2022**, *14* (3), 575

that the use of isosorbide can be a unique tool to develop new bio-based high-performance dimethacrylate UPs (Scheme 1.10).⁵⁶



Scheme 1.10. Synthesis of bio-based UPs

Nowadays, different studies focus on the production of bio-based thermosets using monomers of biological origin and on new methodologies for the recycling these materials once they reach the end of their life, with the aim of making these materials not only environmentally sustainable, but also circular.⁵⁷

1.6.2 Reinforcement

The reinforcement phase is a key element of composite materials, as it absorbs most of the external load and provides mechanical strength and stiffness to the composite material. The contribution of the reinforcement phase depends on several factors, including the mechanical properties of the reinforcement material, the interface between the matrix and the reinforcement, the reinforcement's volume and orientation within the material.

Composite materials can be classified according to the type of material used as reinforcement. The different types of reinforcement are:

⁵⁶ Li, Q.; Ma, S.; Xu, X.; Zhu, J. Bio-Based Unsaturated Polyesters. In *Unsaturated Polyester Resins*; Elsevier: 2019; pp 515–555

⁵⁷ Liu, J.; Wang, S.; Peng, Y.; Zhu, J.; Zhao, W.; Liu, X. *Prog. Polym. Sci.* **2021**, *113*, 101353.

- Particles: like silica, aluminum, calcium carbonate; these reinforcements improve hardness, wear resistance, and physical properties.
- Fibers: such as glass, carbon and natural fibers; the fibers provide mechanical strength and stiffness to the composite material.
- Lamellae or sheets: these contribute to fracture resistance and dimensional stability.

For high performances composites the most used type of reinforcement are the fibers. These offer superior mechanical properties like high strength, stiffness, and lightweight characteristics making fiber-reinforced composites ideal for applications in aerospace, automotive sector where performance and weight reduction are critical.

Glass fibers

The industrial production of glass fibers began in the 1930s to make electrical insulators.⁵⁸ Glass fibers are mainly composed of silica (SiO₂), to which metal oxides are added such as calcium oxide, silicon oxide, magnesium oxide, aluminum oxide and boron oxide, to facilitate processing operations. Their production involves melting silica, alumina, and CaO (lime) at a temperature of 1550 °C. The molten mixture is then fed into a die, where it is extruded and cooled forming thin, highly durable filaments of variable length. After this operation the filaments are joined in a bundle which in turn is passed through a winder, forming a coil. Glass fibers are characterized by a good mechanical resistance, light weight, resistance to humidity and corrosion.

Carbon fibers

Discovered in 1878 by Edison, while he was working on the development of the first incandescent lamp, they were commercially produced only later, in the aeronautical field.⁵⁹ Carbon fibers show superior properties compared to glass fibers, both in terms of lightness and resistance, at the expense of their cost. Nowadays they are obtained from residues of the distillation of petroleum or tar. The production process begins with drawing, or its reduction into fibers, followed by stretching at a temperature of 200°C and a carbonization phase, which orders the main axes of each molecule, at a temperature

⁵⁸ Zu, Q.; Solvang, M.; Li, H. Commercial Glass Fibers. In *Fiberglass Science and Technology: Chemistry, Characterization, Processing, Modeling, Application, and Sustainability*; Springer: 2021; pp 1–87.

⁵⁹ Savage, G. Carbon Fibres. In *Carbon-Carbon Composites*; Springer Netherlands: Dordrecht, 1993; pp 37–83.

between 1100°C and 1500°C. Both glass and carbon fibers have a production process that requires high temperatures and therefore greater energy consumption.

Natural fibers

Natural fibers offer numerous advantages, including high sustainability, ease of production, wide availability, low cost, biodegradability, and generally lower density compared to synthetic carbon and glass fibers. These features are therefore allowing for the creation of lightweight and sustainable composites, driving many industries, interested in ecological transition, to consider these fibers as promising reinforcements in composite materials. Natural fibers are divided according to their origin into:

- Mineral fibers
- Animal fibers
- Plant fibers

Mineral fibers come from natural geological materials (asbestos, basalt fibers, glass wool, stone wool and clay fibers) and they are typically used for their excellent thermal insulation, fire resistance, and durability.⁶⁰ Animal fibers come from animal fur or insect secretions, and they are mostly used in the clothing and fabric industry. Plant fibers come from a broad variety of sources including stem fibers (jute, ramie, flax, rattan, soybeans, hemp, and kenaf), leaf fibers (abaca, banana, sisal, and pineapple), seed fibers (cotton, coir, and kapok), tufted fibers (corn, wheat, bamboo, barley, and rice), core fibers (corn and wheat), woody fibers, and root fibers (luffa).⁶¹ The structure and chemical composition of plant fibers are influenced by the different climatic conditions, the growing area and the age of the plant. Despite the different advantages, natural fibers present critical issues compared to synthetic fibers. The hydrophilic nature of these fibers enhances their hygroscopicity, leading to challenges with water absorption. In addition, their hydrophilicity clashes with the non-polar and hydrophobic character of most polymeric materials, resulting in non-uniform fiber dispersion within the matrix and to compatibility issues. For these reasons, the fibers have to undergo chemical or physical treatments before they can be used as reinforcements in bio-composites (this will be further discussed in the following chapter).

⁶⁰ Gualtieri, A. F. Mineral Fibre-Based Building Materials and Their Health Hazards. In *Toxicity of Building Materials*; Woodhead Publishing: 2012; pp 166–195.

⁶¹ Sfiligoj Smole, M.; Hribernik, S.; Stana Kleinschek, K.; Kreže, T. Plant Fibres for Textile and Technical Applications. In *Advances in Agrophysical Research*; 2013; pp 369–398.

1.7 Bio-composites classification

Bio-composites can generally be classified, depending on the nature of the matrices and the fibers used, into three broad categories (Figure 1.22):

- Partially biodegradable
- Hybrid bio-composites
- Completely biodegradable

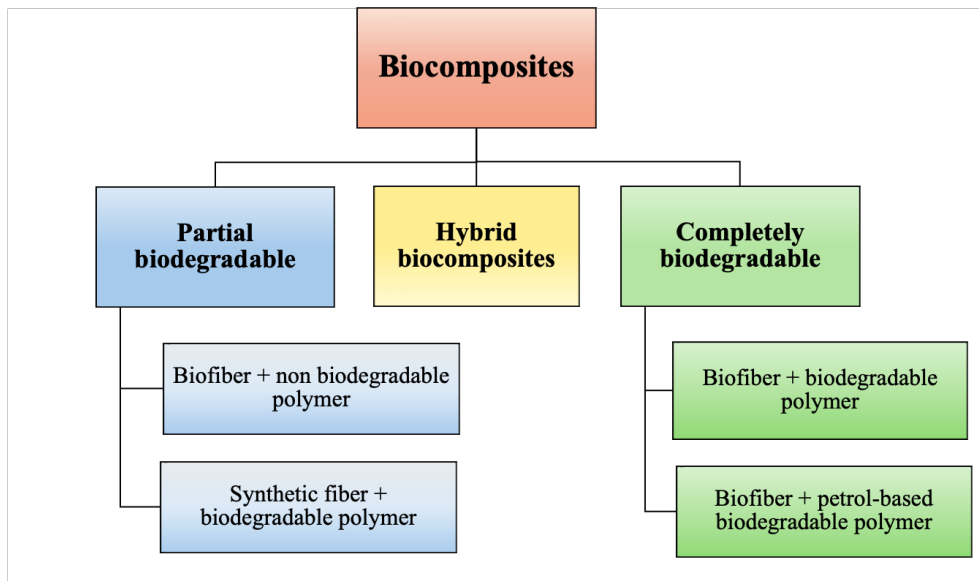


Figure 1.22. Classification of bio-composite

1.7.1 Partially biodegradable bio-composites

In partially biodegradable bio-composites, non-biodegradable polymer matrices, such as traditional thermoplastic polymers (polypropylene, polyethylene, and others) or thermosetting polymers (epoxy, polyester, and others), are reinforced with natural fibers. Another possibility within this category is represented by bio-based polymers reinforced with synthetic fibers. It is important to note that this classification does not consider the time or amount of degradation, as these aspects depend on variables such as environment, temperature and microorganisms, and can be assessed through standard degradation tests.

1.7.2 Hybrid bio-composites

Another class of bio-composites that is receiving increasing interest is that of hybrid composites. These types of composites are usually made up of a polymer matrix and two or more different reinforcements (Figure 1.23) to produce an advanced material with an innovative and better applicability, in terms of functionality but also sustainability.

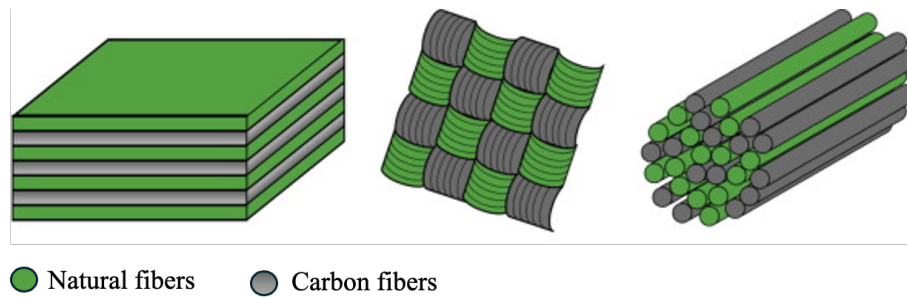


Figure 1.23. Hybridization of natural and synthetic fibers

The properties of hybrid composites depend on the constituent materials and combine advantages and the individual characteristics of each component.⁶² In the field of composite materials, the integration of two or more types of fillers or fibers within a matrix allows to mitigate the disadvantages of one type of reinforcement thanks to the benefits provided by another. For example, by hybridizing natural fibers with synthetic fibers, although some of the main advantages of natural fiber-based composites are reduced, such as biodegradability, easy handling and availability of natural resources, hybridization can effectively help to reduce the costs, weight and environmental impact associated with synthetic fiber composites. Numerous studies demonstrate that hybridization synthetic-natural fibers techniques improve the mechanical, thermal and dynamic properties of composites, reducing moisture absorption and increasing fire resistance.⁶³ Fiber-reinforced hybrid materials can be realized in general by two distinct approaches: either by homogeneously mixing the fibers within a common matrix or by laminating alternating layers of composites with each type of fiber and a specific arrangement is determinant for specific properties in relation of the application goal. The strength and uniqueness of these materials depend on several factors. The most important factor is the nature of the reinforcements, then their arrangement within the composite

⁶² Bunsell, A. R.; Harris, B. *Composites* **1974**, 5(4), 157–164.

⁶³ Bahrami, M.; Abenojar, J.; Martínez, M. Á. *Materials* **2020**, 13(22), 5145.

as well as their orientation. Other determinant factors are the degree of interaction, the length of the individual fibers and the adhesion of these with the polymer matrices. The mechanical properties of the individual fibers play a key role in determining the overall strength of the hybrid composite. The properties of a hybrid system can be defined and predicted by the following formula:

$$P_H = P_1 V_1 + P_2 V_2$$

where P_H is the property to be investigated, P_1 the property of the first system and P_2 the property of the second system. V_1 and V_2 are the relative volume fractions of the two components, with $V_1 + V_2 = 1$.⁶⁴

Bio-hybridized materials are used recently in a variety of applications such as automotive, aerospace, civil engineering, medicine, electronic devices, and other scientific fields. The choice of the type of reinforcing materials is obviously strongly related to the type of application.⁶⁵ For example, in the automotive sector it is increasingly common to develop composites consisting of carbon fibers coupled with natural fibers in epoxy matrices to make more eco-friendly interior materials.⁶⁶ Hybrid composites offer a promising approach for optimizing material performance by combining the benefits of different fibers, while enhancing both sustainability and efficiency of the final material.

1.7.3 Fully biodegradable bio-composites

In fully biodegradable bio-composites, natural fibers (such as hemp, flax, jute and others) are combined with biodegradable polymers made from renewable materials (such as cellulose, soy, starch and others) or degradable fossil-based polymers (such as aliphatic co-polyesters and polyesteramides). These two combinations aim to reduce environmental impact caused by non-degradable polymers and the long-term waste accumulation of composites. Biodegradable composites are increasingly being used for interior components of vehicles where weight reduction and sustainability are required. They are being used to replace single use plastics in packaging, offering eco-sustainable alternative material that can decompose after disposal. Additionally, products such as

⁶⁴ Sreekala, M. S.; George, J.; Kumaran, M. G.; Thomas, S. *Composites Sci. Technol.* **2002**, 62 (3), 339–353.

⁶⁵ Zuo, P.; Srinivasan, D. V.; Vassilopoulos, A. P. *Compos. Struct.* **2021**, 274, 114358.

⁶⁶ Tirupathi, Kumar, J. S.; Hiremath, S. S. *Fibers Polym.* **2022**, 23(13), 3505–3515.

furniture, clothing and agriculture stuff can be made from fully biodegradable bio-composites to reduce environmental impact and minimize the waste production.

1.8 Natural-fiber composites in the automotive application

The use of natural fibers in composite materials is increasing, driven by the regulation that encourages the recycling and reuse of materials, especially within the automotive industry (Figure 1.24).



Figure 1.24. Natural fiber-reinforced composite for automotive application

Natural fibers, due to their eco-friendly properties, light weight, strength and low cost, are increasingly replacing glass and mineral fillers in several engineering applications, such as vehicles and construction. The automotive industry has recognized the advantages of natural fiber composites (NFCs), obtained by combining these fibers with mostly thermoset resins. Fiber-reinforced composites are particularly appreciated for their dimensional stability and low weight, which are essential for automobiles. However, the use of natural fibers also presents challenges, including sensitivity to moisture, growth of microorganism and poor interfacial adhesion with polymer matrices. In addition, there remain concerns about the quality, durability of natural fibers, and limitations related to processing temperatures.⁶⁷ Therefore, research and deep studies are needed to solve these issues related to water absorption, fiber durability, and interaction with polymer matrices in order to maximize the properties and performances of natural fiber reinforced composites for the automotive sector.

⁶⁷ Huda, M. S.; Drzal, L. T.; Ray, D.; Mohanty, A. K.; Mishra, M. Natural-Fiber Composites in the Automotive Sector. In *Prop. Perform. Nat. Fibre Compos.*; Woodhead Publ., 2008; pp 221–268

Research objectives

The growing demand for sustainable alternatives to fossil-based materials has driven extensive research into bio-based polymers and composites. As highlighted in this chapter, several challenges remain in improving the performance, processability, and applicability of these materials. In response to these challenges, this thesis aims to:

- Improve the durability and applicability of natural fibers by developing organic functionalization strategies that reduce their moisture sensitivity and enhance their compatibility with polymer matrices.
- Optimize the processing of bio-based composites through advanced reactive extrusion techniques, ensuring the recycling of polymers with employment of natural fibers.
- Develop innovative bio-based synthetic polymers, focusing on sustainable catalytic systems and the use of renewable precursors.
- Investigate eco-friendly techniques such as the 3D-printing enabling the design of more efficient and sustainable bio-based materials.

2 Chapter 2: Natural fiber for bio-composites

PART I. Organic functionalization of natural fibers

2.1 Structure of natural fibers

The structure of plant fibers is mainly composed of three fundamental components: cellulose, lignin and hemicellulose (Figure 2.1). Other elements are present in smaller quantities, such as pectins, waxes and pigments.

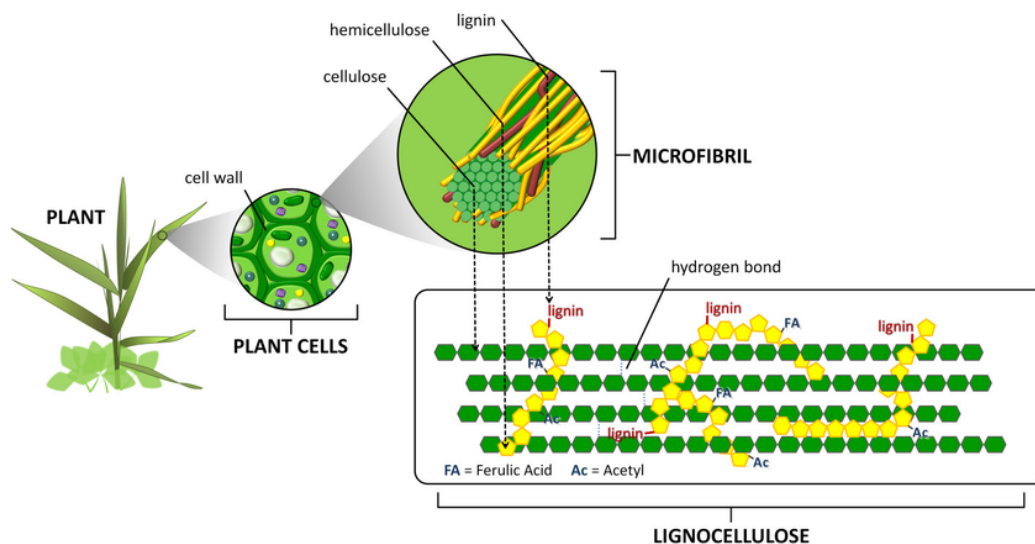


Figure 2.1 Structure of plant fibers

Cellulose represents the main structural component, giving the fibers mechanical resistance and stability. Generally, each fiber has a variable amount of cellulose that depends on the species and age of the plant. In various natural fibers, the chemical structure of cellulose remains unchanged, however the degree of polymerization (DP) changes, which reflect the length of the polymer chains and has a direct impact on the mechanical properties of the fiber.

Lignin, on the other hand, has the main role of providing rigidity to the lignocellulosic matrix, placing itself around the cellulose microfibrils, thus providing stability and

compactness even against biological degradation. It gives strength to the entire plant and makes the fiber more resistant.⁶⁸

Hemicellulose is a low molecular weight polysaccharide made up of different sugars (in contrast of the only glucose unit of cellulose), in particular sugars with five carbon atoms, pentoses such as arabinose and xylose and sugars with six carbon atoms, such as glucose, mannose and galactose. In plant fiber context hemicellulose acts as a matrix that can hold together the cellulose microfibrils. Hemicellulose, together with lignin, gives further integrity to the cell wall, providing flexibility but at the same time strength.⁶⁹ Given its structure made up of different sugars, hemicellulose can form networks that are able to stabilize the cellulose, providing structural strength without compromising cellulose ability to move. In addition to its support function, hemicellulose also influences the porosity of the cell wall and regulates water absorption. Hemicellulose is essential for the growth and expansion of plant cells, allowing them to respond to mechanical and environmental stresses.

Pectins and waxes constitute the minor components of plant cells. Pectins act as glues between cells, providing flexibility and cohesion of cell walls and regulating water passage and osmotic pressure. They work together with hemicellulose, strengthening the interactions between cellulose microfibrils, to maintain cell wall integrity and guide proper growth. Waxes, on the other hand, coat the external surfaces of plants, forming a hydrophobic barrier that protects against water and pathogens.

2.2 Characterization techniques of natural fibers

Qualification and quantification of fiber's components are essential in the production of composite materials to ensure a good and optimized interaction with various polymeric matrices on the base of the type of natural reinforcement. The amount and the structure of these components can vary significantly depending on the plant species, the age of the plant and the environmental conditions in which they grow, such as temperature,

⁶⁸ Monties, B. *Anim. Feed. Sci. Technol.* **1991**, 32(1-3), 159-175.

⁶⁹ Khodayari, A.; Thielemans, W.; Hirn, U.; Van Vuure, A. W.; Seveno, D. *Polym.* **2021**, 270, 118364.

humidity and soil quality.⁷⁰ Chemical characterization and precise determination of these components are essential for a fibers optimal use. Through these processes, the isolation of individual constituents, such as lignin cellulose or hemicellulose, or the isolation of fibrous fractions can be performed. Component extracted from plant fibers can be in this way integrated into polymer matrices, as reinforcements or functional elements, creating green materials with unique mechanical, thermal or functional properties. This approach allows the maximum exploitation of the unique characteristics of natural fibers and their extracted components.

2.2.1 Lignin and cellulose quantification process

The first step in the fiber characterization process is delignification, the removal of lignin, which is a fundamental component of the plant cell wall together with cellulose. The chemical structure of lignin varies depending on the source of the plant biomass (e.g. softwood, hardwood or grasses). Its extraction allows to obtain purer cellulosic fibers, useful for further processing. This process is particularly relevant in the paper industry, which uses extraction techniques to remove lignin and recover cellulose, obtaining different types of paper depending on the level of purity reached with the extraction process. Conventional methods for lignin extraction can be classified into two categories: chemical and mechanical.

Chemical methods

Kraft process

One of the most common methods, used to effectively remove lignin from fibers, leaving almost pure cellulose is the Kraft process. It is the most widely used method for isolating lignin (96 % of the market), as it allows obtaining smaller chains that are soluble in water or alkali. This process takes place at high temperatures (140 -170°C), using a mixture of alkaline substances, known as “white liquor” consisting of sodium hydroxide (NaOH) and sodium sulfide (Na₂S).⁷¹ The mixture allows the separation of lignin from cellulose through breaking the bonds holding the two components together, resulting in a pulp

⁷⁰ Karimah, A.; Ridho, M. R.; Munawar, S. S.; Adi, D. S.; Damayanti, R.; Subiyanto, B.; Fatriasari, W.; Fudholi, A. *J. Mater. Res. Technol.* **2021**, *13*, 2442–2458

⁷¹ Souza, R. E.; Gomes, F. J. B.; Brito, E. O.; Costa Lelis, R. C. *J. Appl. Biotechnol. Bioeng.* **2020**, *7*, 100

containing the cellulose and an extraction liquid (black liquid), made up of lignin and other compounds. To separate the lignin from the extraction liquid, acid precipitation using an H_2SO_4 solution at 121°C is commonly used, followed by a filtration process.⁷² An alternative method for lignin separation is ultrafiltration, where no change in temperature or pH is required.⁷³ Kraft lignin may have some impurities, such as sulfur, due to the reagents used during the process. To limit this, alternative methods have been developed using soda ash alone with similar conditions of Kraft method, without the use of sodium sulfide and sulfuric acid (Figure 2.2). This process was industrialized in 1853 for biomasses such as flax, straw and others, and consists of treating the lignocellulosic material with a solution of NaOH , at high pressures and a temperature between 140°C - 170°C .

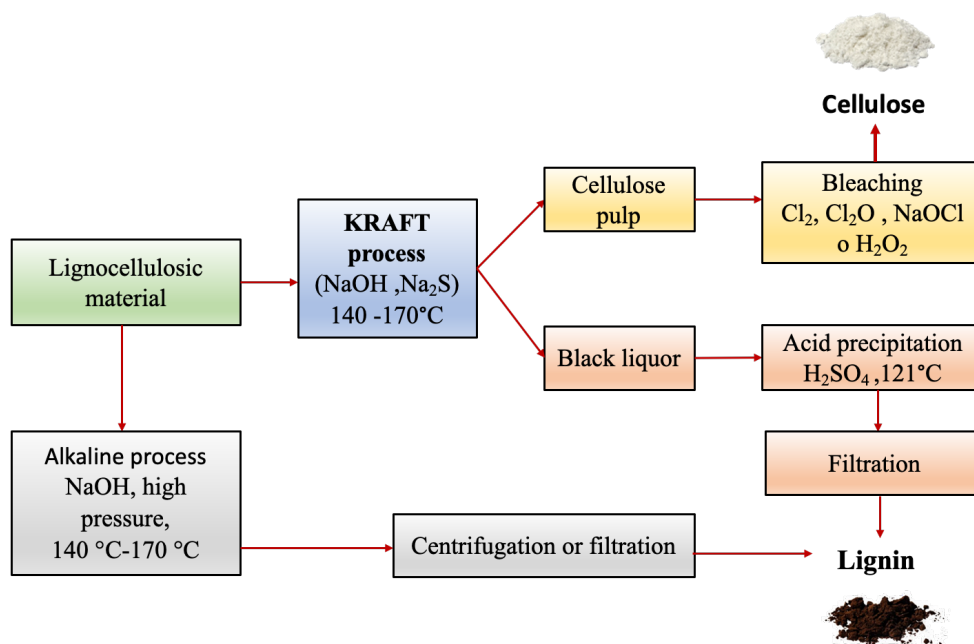


Figure 2.2. Kraft process

Acid extraction:

Involves the use of strong acids to dissolve lignin. The process aims to isolate the lignin from the rest of the components by solubilizing it, breaking the glycosidic bonds, sensitive to the common acids (sulfuric acid H_2SO_4 , phosphoric acid H_3PO_4 , hydroiodic

⁷² Tribot, A.; Amer, G.; Alio, M. A.; de Baynast, H.; Delattre, C.; Pons, A.; Mathias, J. D.; Callois, J. M.; Vial, C.; Michaud, P.; Dussap, C. G. *Eur. Polym. J.* **2019**, *112*, 228

⁷³ Jönsson, A. S.; Nordin, A. K.; Wallberg, O. *Chem. Eng. Res. Des.* **2008**, *86*, 1271

acid HI, hydrofluoric acid HF, and others) and then being recovered at the end of the process as a precipitate (Figure 2.3).⁷⁴

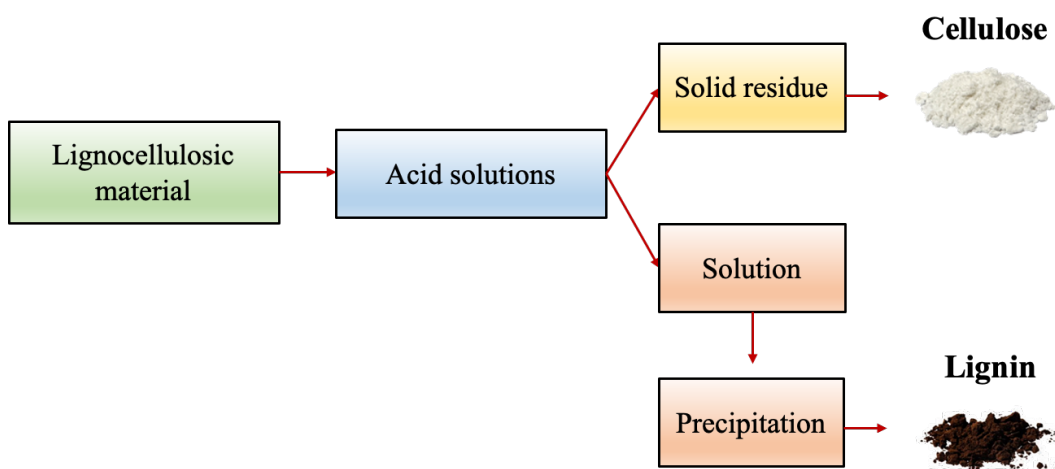


Figure 2.3. Acid extraction

The acids treatment acts directly on aryl ether linkages (β -O-4 linkages) of lignin, leaving the acid-insoluble part precipitating as residue (Figure 2.4).

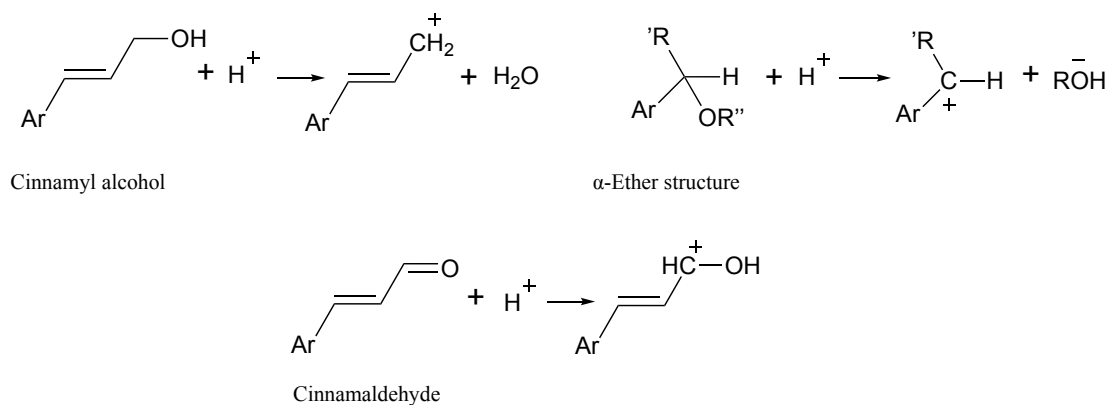


Figure 2.4. Acid treatment

The carbon ions, generated by cinnamyl alcohol, cinnamaldehyde and α -ether, end up in condensation reaction creating more stable polymeric structure and thus making difficult the applicability of the process in industrial scale.⁷⁵

⁷⁴ Xu, J.; Kong, Y.; Du, B.; Wang, X.; Zhou, J. *Prog. Sustainable Energy* **2022**, 41 (3), 13785.

⁷⁵ Río, J. del; Gutiérrez, A.; Rodríguez, I.; Ibarra, D.; Martínez, A. *J. Anal. Appl. Pyrolysis* **2007**, 79, 39-46.

Ionic liquids extraction

In this process substances solubilize lignin and regenerate it through reorganization of hydrogen bonds.⁷⁶ Ionic liquids (IL) anions form hydrogen bonds with lignin creating stronger interaction than that between lignin and lignin, enabling the dissolution of lignin in ionic liquid. In addition, also cations of ionic liquid play an important role in lignin dissolution, those coming from strong polar double bonds are able of reducing the lignin-lignin structural units interaction generating hydrogen bonds with hydroxyl groups of lignin.⁷⁷ The lignin is then reprecipitated by water given the grater interaction force between H₂O and IL.

Deep eutectic solvents (DES)

DES extraction process constitutes an innovative method, using mixtures of organic compounds, to solubilize and isolate lignin in a more sustainable way. DES promotes the cleavage of unstable ether bonds between phenyl propane units producing low molecular weight lignin while maintaining the overall structural features. Deep eutectic solvents are prepared by reacting a molecule acceptor with one or two hydrogen bond donors. By changing their chemical nature and molar ratio, it is possible to tune properties and extraction capability of the final DES.⁷⁸ In general, alcohols, amides, acids and polyols are used as donors, while the most widely used hydrogen bond acceptor is choline chloride (ChCl) due to its convenient price, biocompatibility and biodegradability.⁷⁹

Physical methods

The most used physical methods for lignin extraction and treatment are pyrolysis and microwave technique. The pyrolysis, which exploits high temperature, is generally used to produce value added chemicals from lignin.⁸⁰ All methods of selective extraction of

⁷⁶ Ji, W.; Ding, Z.; Liu, J.; Wang, H.; Zhang, Y.; Xu, Y. *Energy Fuels* **2012**, *26*, 6393-6403.

⁷⁷ Kilpeläinen, I.; Xie, H.; King, A.; Granström, M.; Heikkinen, S.; Argyropoulos, D. *J. Agric. Food Chem.* **2007**, *55*, 9142-9148.

⁷⁸ Francisco, M.; Van Den Bruinhorst, A.; Kroon, M. C. *Green Chem.* **2012**, *14*, 2153.

⁷⁹ Mbous, Y. P.; Hayyan, M.; Hayyan, A.; Wong, W. F.; Hashim, M. A.; Looi, C. Y. *Biotechnol. Adv.* **2017**, *35*, 105.

⁸⁰ Gayubo, A. G.; Valle, B.; Aguayo, A.; Olazar, M.; Bilbao, J. *J. Chem. Technol. Biotechnol.* **2010**, *85*, 132-144.

lignin from biomass result in the formation of a treatment-insoluble fraction consisting primarily of cellulose, then hemicellulose and other waxy residues. Typically, this pulp is then subjected to bleaching processes, often based on soda and hydrogen peroxide, to further cleanse the pulp of any residual lignin and obtain pure cellulose.⁸¹ The type of treatment and purification is strictly dependent on the final application.

2.3 Advantages and disadvantages of natural fibers

As mentioned above, the use of natural fibers to replace synthetic fibers (glass or carbon fibers) has gained attention in recent years due to the growing environmental problems related to climate change and depletion of raw materials. In fact, the main advantages of natural fibers, in addition to their wide availability and low cost, are their recyclability and biodegradability.⁸² All these positive aspects, combined with good mechanical properties, make them potential substitutes to synthetic fibers in composite materials. In particular, flax, hemp, jute and sisal exhibit mechanical properties such as high strength, low density and high stiffness. However, low thermal stability and poor compatibility with polymeric matrixes limit their use, it is therefore necessary to use compatibilizers and reduce processing temperatures. The thermal degradation of natural fibers occurs in different stages: in the temperature range of 220-280 °C, the degradation of hemicellulose begins, followed by lignin in the range of 280-300 °C, and finally cellulose degradation in the range of 300-350 °C.^{83,84} However, the main obstacles encountered when using plant fibers are their hydrophilic nature and high tendency to absorb water due to the presence of hydroxyl groups (-OH) in the cellulose, which contrasts with most hydrophobic polymer matrices. This leads to poor adhesion and non-homogeneous dispersion of the fibers in the matrix, compromising the mechanical properties of the composite.⁸⁵

Therefore, the key problems to be solved in the production of fiber-reinforced composites are:

- the thermal stability of fibers

⁸¹ Al-Dulaimi, A. A.; Wanrosli, W. D. *J. Polym. Environ.* **2017**, *25*, 192.

⁸² Sanjay, M. R.; Siengchin, S.; Parameswaranpillai, J.; Jawaid, M.; Pruncu, C. I.; Khan, A. *Carbohydr. Polym.* **2019**, *207*, 108.

⁸³ Saheb, D. N.; Jog, J. P. *Adv. Polym. Technol.* **1999**, *18*, 351-363.

⁸⁴ Mui, E. L.; Cheung, W. H.; Lee, V. K.; McKay, G. *Ind. Eng. Chem. Res.* **2008**, *47*, 5710-5718

⁸⁵ Cruz, J.; Figueiro, R. *Procedia Eng.* **2016**, *155*, 285-290.

- the adhesion between fibers and polymer matrix
- the water absorption of fibers

To solve these problems, methods for treating fibers and chemically modifying their surface have been studied.

2.4 Treatment of natural fibers

The most common treatments used for natural fibers are classified into physical, chemical and biological treatments.

2.4.1 Physical treatments

Among the common physical methods to treat natural fibers, the most employed are plasma, ultrasound and UV light treatments. These are used to activate the surface of the fibers, extracting individual filaments from the fiber bundles and modifying the surface structure improving their compatibility with the supporting material.

Plasma treatment

Plasma treatment is used to remove pollutants present on the surface of fibers, increasing their purity. The plasma gas, made of particles like atoms, free electrons, ions and molecules, establish a chemical and physical alteration on the surface of material when an electric field is applied. This treatment can modify surface properties, such as the ability to absorb liquids, the reactivity with dyes and flame retardants. In addition, it can increase surface roughness, improving mechanical strength and adhesion between the surface and the polymer matrix. Plasma can also generate free radicals that react with oxygen and other gases, producing surfaces with different properties in terms of hydrophilicity and hydrophobicity.^{86,87} There are two types of plasma: thermal and non-thermal. Thermal plasma can be damaging to fiber-based materials respect to non-thermal plasma treatments, both were conducted at atmospheric pressure and at low

⁸⁶ Borcia, G.; Anderson, C. A.; Brown, N. M. D. *Surf. Coat. Technol.* **2006**, 201 (6), 3641–3648.

⁸⁷ Skundric, P.; Kostic, M.; Medovic, A.; Pejic, B.; Kuraica, M.; Vuckovic, A.; Obradovic, B.; Mitrovic, D.; Puric, J. *J. Nat. Fibers* **2007**, 4 (4), 13–27.

pressure or vacuum.⁸⁸ Basically, plasma is a gas characterized by a mixture of atomic, molecular, ionic and radical species, with free electrons and photons. Its generation occurs by applying an electric field between two electrodes immersed in a gaseous medium. The properties of the plasma are influenced by the characteristics of the gases used for its formation, as well as the electrical power, the geometry and dimensions of the electrodes.

Vacuum plasma treatment requires the use of a low-pressure chamber, where a gas, such as oxygen, nitrogen or helium, is introduced and subsequently ionized to determine chemical and morphological changes. These chemical processes are complex and generally involve the removal of atoms or the breaking of bonds that produce free radicals. However, this method has limitations related to the size of the vacuum chamber and is also a batch process.⁸⁹

Atmospheric pressure plasma treatment has become more widely used recently for a wide range of materials, including fibers, polymers, ceramics and composites. The most important feature of this method is the opportunity to treat the sample in situ, avoiding the limitation of the vacuum chamber dimensions. Furthermore, it allows continuous and uniform treatments, it is reliable and reproducible, and it is cheaper than low pressure treatments that require the use of expensive vacuum systems.

The four main atmospheric plasma technologies are: Corona Treatment, Dielectric Barrier Discharge (DBD), Atmospheric Pressure Plasma Jet (APPJ) and Glow Discharge (APGD).

Corona treatment

Corona treatment is a technique able to induce surface oxidation of different materials and improve the compatibility between hydrophilic fibers and hydrophobic matrices. This process is based on the application of high-frequency discharges between electrodes that ionize the atmosphere, creating a visible blue plasma. The sample is placed in the gap between the electrodes and it is bombarded with high-speed electrons. The power of these electrons is sufficient to break the molecular bonds of the material surfaces,

⁸⁸ Mukhopadhyay, S.; Fanguero, R. J. *Thermoplast. Compos. Mater.* **2009**, 22 (2), 135–162.

⁸⁹ Kusano, Y.; Løgstrup Andersen, T.; Sørensen, B. F.; Toftegaard, H. L.; Teodoru, S.; Hansen, C. M. Adhesion Improvement of Fibres by Continuous Plasma Treatment at Atmospheric Pressure. In *Proceedings of the Risoe International Symposium on Materials Science*; Risoe National Laboratory: Roskilde, Denmark, 2013; pp 123–130.

inducing surface oxidation. In this context, corona treatment can produce oxidants such as ozone, atomic oxygen and free oxygen radicals, which act on the surface of the material increasing the wettability and adhesiveness of the materials.⁹⁰ Corona treatment is characterized by low cost and energy consumption and it is very effective as a pre-treatment for textiles, due to its ability to clean and improve the roughness of the surfaces. However, corona treatment has a limitation: the penetration depth is variable, and, in some cases, it is not able to reach the desired depth in yarn or fabric.⁹¹

Dielectric Barrier Discharge

The dielectric barrier discharge (DBD) method presents similarities with corona treatment, but has a fundamental difference: in corona treatment, discharges occur between bare metal electrodes, while in DBD the electrodes are separated by a dielectric layer. This dielectric layer accumulates the charge transported on its surface and distributes it uniformly over the entire surface of the electrode.⁹² In terms of surface treatment, DBD generates high-energy electrons through collisions during discharge, which can produce radicals and excited particles efficiently. These can activate different reaction pathways leading to the production of reactive intermediates, which promote the surface activation of materials. This technology is often used to treat textiles, polymers, plastic sheets, metal surfaces and others. However, a major problem of DBD technology is the unavoidable non-uniformity of the treatment and its short duration.

Atmospheric Pressure Plasma Jet (APPJ)

The pulsed plasma jet is an innovative technology that uses two tubular metal electrodes separated by a gap to generate a plasma that can be directed onto a specific sample.⁹³ The inside of the electrodes is surrounded by a quartz tube through which a gas, such as helium, flows to generate plasma. The management of parameters, like wave pulse, pulse frequency and gas flow rate, allows to optimize the plasma formation. The APPJ offers

⁹⁰ Zenkiewicz, M.; Richert, J.; Rytlewski, P.; Moraczewski, K. *Process. Polym.* **2009**, 6 (10), 649–657.

⁹¹ Shishoo, R. Introduction and the Potential of Plasma Technology in the Textile Industry. In *Plasma Technologies for Textiles*; Woodhead Publishing: Cambridge, U.K., 2007; pp 1–24.

⁹² Kogelschatz, U. *Plasma Chem. Plasma Process.* **2003**, 23 (1), 1–46.

⁹³ Ptasinska, S.; Bahnev, B.; Stypczynska, A.; Bowden, M.; Mason, N. J.; Braithwaite, N. S. J. *Phys. Chem. Chem. Phys.* **2010**, 12 (28), 7779–7781.

several advantages, including the possibility of applying local treatments with high density of charged particles and reactive oxyhydrogen and nitrogen species. In addition, the treatment can be highly precise, and the high gas velocity allows the penetration of plasma components into small cavities. APPJ is suitable for various industrial and research applications, such as surface modification, sterilization of biological materials, ozone formation and treatment of heat-sensitive materials.⁹⁴

Atmospheric Pressure Glow Discharge (APGD)

The main feature of APGD is the emission of a homogeneous and stable plasma, which can be generated in helium or other gases such as argon and nitrogen. APGD is performed by applying relatively low voltages between symmetrical conductive electrodes at high frequencies, producing a homogeneous plasma inside the electrodes with a current pulse for every half cycle. This APGD plasma is characterized by high electronic energies and densities of excited and charged gaseous species at low temperature, making it ideal for surface treatment without overheating of materials. APGD is used in several applications, including surface modification, thin film deposition, ozone generation, degradation of organic compounds, sterilization, disinfection, biological and chemical decontamination, surface cleaning and waste treatment.⁹⁵

Ultrasound and UV light treatments

Ultrasonic treatments, although less frequently used than plasma treatments, present a remarkable effectiveness in removing substances and pollutants from surfaces, even without the use of surfactants. This phenomenon can be explained by the process of formation and collapse of acoustic bubbles, responsible for effects observed in solid-liquid or liquid-liquid systems. Ultrasonic treatment can modify the crystalline morphology of natural fibers, significantly influencing their mechanical and chemical properties. Ultraviolet (UV) light, with a wavelength between 10 and 400 nm can induce chemical reactions with organic molecules, generating more complex effects than those of simple heating. UV radiation represents a potential energy source able to promote

⁹⁴ Elaragi, G. M.; Elaraby, H. S. *Int. J. Appl. Sci. Eng.* **2015**, *13* (1), 25–33.

⁹⁵ Hussain, S.; Qazi, A.; Imran, H.; Niaz, S.; Badar, M. *Pramana* **2016**, *87* (6), 90.

photochemical reactions inside natural fibers, altering their mechanical properties and offering a clean method to modify the fiber surface. Its low cost and simplicity make it a very promising technique for industrial applications.^{96,97}

2.4.2 Chemical treatments

Chemical processes on natural fibers are used to modify the surface characteristics and improve the mechanical properties of natural fibers by forming or breaking bonds through chemical agents. For example, alkali treatment can significantly improve the mechanical properties of natural fibers by modifying the crystalline structure and removing components such as hemicellulose and lignin from the fiber. In addition, specific chemical treatments can reduce the moisture absorption and subsequent swell the fibers, thus improving their performances and durability. The use of silane coupling agents is particularly effective in this regard, since it can improve the interactions at the fiber-matrix interface through the formation of strong chemical bonds.⁹⁸ Some of the existing chemical treatments for the modification of natural fibers will be briefly described in the following sections.

Alkaline treatment

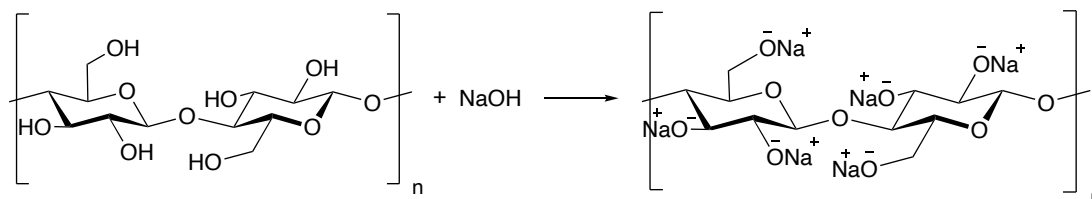
Alkali treatment, known as mercerization, is a well-established chemical approach to improve the properties of natural fibers. This treatment consists of exposing the fibers to a sodium hydroxide (NaOH) solution, with a certain concentration (usually 5/10% V/V) at specific temperature and time, which leads to the breaking of the fiber bundles into smaller fibers. The surface of the fiber becomes rough, its diameter decreases, increasing the aspect ratio and mechanical properties. This treatment also determines the removal of constituents from natural fibers such as hemicellulose and lignin from natural fibers, as well as the complete elimination of organic substances such as pectin, wax and oils. This allows to expose and increase the number of available reaction sites, improving the

⁹⁶ Di Benedetto, R. M.; Gelfuso, M. V.; Thomazini, D. *Res.* **2015**, *18* (6), 1219–1227.

⁹⁷ Mahzan, S.; Fitri, M.; Zaleha, M. *Conf. Ser.: Mater. Sci. Eng.* **2017**, *226*, 012122.

⁹⁸ Xie, Y.; Hill, C. A. S.; Xiao, Z.; Militz, H.; Mai, C. *Compos. Part A Appl. Sci. Manuf.* **2010**, *41* (7), 806–819.

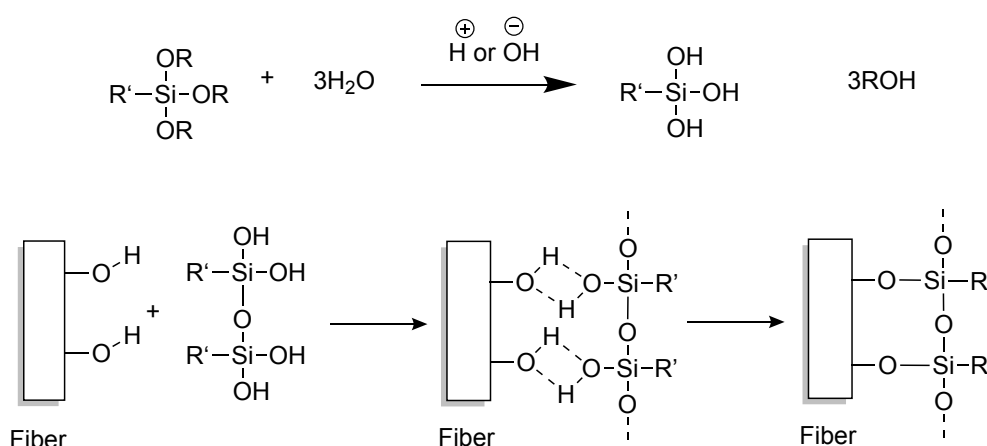
adhesion of the fibers to the polymer matrix.⁹⁹ Scheme 2.1 illustrates the general reaction of alkali treatment, where sodium hydroxide induces the ionization of the hydroxyl groups of natural fibers, forming alkoxides.



Scheme 2.1. Mercerization of cellulose

Silane treatment

Silane treatment involves the reaction of the lignocellulosic fiber with a silane-based coupling agent, which enhances the degree of cross-linking in the interfacial region, thus ensuring greater adhesion. This process is usually applied to lignocellulosic fibers pretreated with NaOH, which increases the effectiveness of the coupling with the silane agent. The employment of silane improves the interfacial properties, facilitating the interaction between the reinforcement and the matrix. Silane coupling agents, once hydrolyzed, react with the -OH groups present in the fiber to form stable covalent bonds (Scheme 2.2).¹⁰⁰



Scheme 2.2. Silanization process on natural fibers

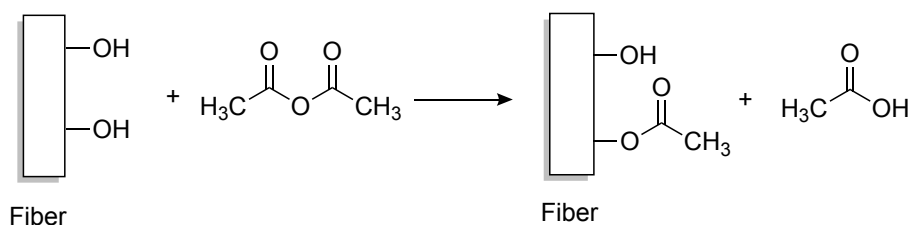
⁹⁹ Oushabi, A.; Sair, S.; Oudrhiri Hassani, F.; Abboud, Y.; Tanane, O.; El Bouari, A. *S. Afr. J. Chem. Eng.* **2017**, 23, 116–123.

¹⁰⁰ John, M. J.; Anandjiwala, R. D. *Polym. Compos.* **2008**, 29 (2), 187–207.

To ensure an effective coupling the silane agent must have a bifunctional structure (R') that can act as a bridge between the two phases. Different types of silanes have been examined as coupling agent for natural fiber reinforced composites, including trialkoxysilane, which has shown promising results. These groups can include glycidyl, vinyl, amino, mercapto or methacrylate. The choice of the silane depends on the type and characteristics of the matrix involved in the composites. Treatment of sisal fiber, for example, with an aminoalkyl reagent resulted in the formation of a thin layer of siloxane and polysiloxane on the fiber surface, thereby influencing the decomposition properties of sisal fiber.¹⁰¹ The results regarding the effect of silane treatment on fiber strength are variable. For example, alcohol-silane treatment with triethoxysilane-3-aminopropyl showed a significant improvement in tensile and flexural properties in nonwoven composites made of short kenaf fiber and PP.¹⁰² Fiber coupling with silane is a promising method to improve fiber durability and adhesion. Furthermore, it has been showed an increase in hydrophobicity in flax fiber, accompanied by a significant improvement in mechanical properties in derived bio-composites.¹⁰³

Acetylation treatment

The acetylation process is highly effective in modifying the surface of natural fibers, contributing to increasing their hydrophobicity. Typically, the treatment involves the use of acetic anhydride and acetic acid with forming an ester functionality. During this esterification, the acetyl groups (CH₃CO-) react with the hydroxyl groups (-OH) present in the fibers (Scheme 2.3).¹⁰⁴



Scheme 2.3. Acetylation of natural fibers

¹⁰¹ Zhou, F.; Cheng, G.; Jiang, B. *Ind. Crops Prod.* **2014**, 52, 341–348.

¹⁰² Asumani, O. M. L.; Reid, R. G.; Paskaramoorthy, R. *Compos. Part A Appl. Sci. Manuf.* **2012**, 43 (9), 1431–1440.

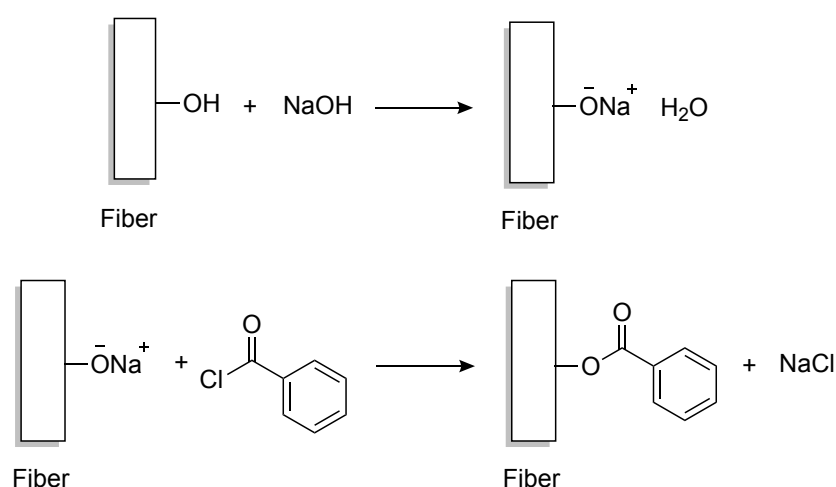
¹⁰³ Le Moigne, N.; Longerey, M.; Taulemesse, J. M.; Bénézet, J. C.; Bergeret, A. *Compos. Sci. Technol.* **2014**, 100, 226–232.

¹⁰⁴ Pickering, K. L.; Efendy, M. G. A.; Le, T. M. *Compos. Part A Appl. Sci. Manuf.* **2016**, 83, 98–112.

This chemical modification facilitates the replacement of the polar hydroxyl groups, which are found on the cell wall of the fiber, with acetyl groups, which are less polar. This results in a decrease in the hydrophilic nature of the fiber itself, favoring greater compatibility with non-polar matrices. Acetylation treatments are effective in limiting moisture absorption in natural fibers thus improving the mechanical properties of composites, including interfacial shear strength, tensile strength and flexural strength.¹⁰⁵ In some cases, to obtain optimal results, acetylation can be preceded by an alkaline pretreatment.¹⁰⁶

Benzoylation treatment

Benzoylation process is used to increase the hydrophobicity of the fibers. It is normally performed, after the alkaline treatment, through the reaction of benzoyl chloride with the activated hydroxyl groups of the natural fibers (Scheme 2.4).¹⁰⁷



Scheme 2.4. Benzoylation of natural fibers

This chemical reaction promotes the introduction of benzoyl functional groups (C₆H₅CO), which are useful to improve the adhesion with the non-polar matrix. In

¹⁰⁵ Ahmad, F.; Choi, H. S.; Park, M. K. *Macromol. Mater. Eng.* **2015**, 300 (1), 10–24.

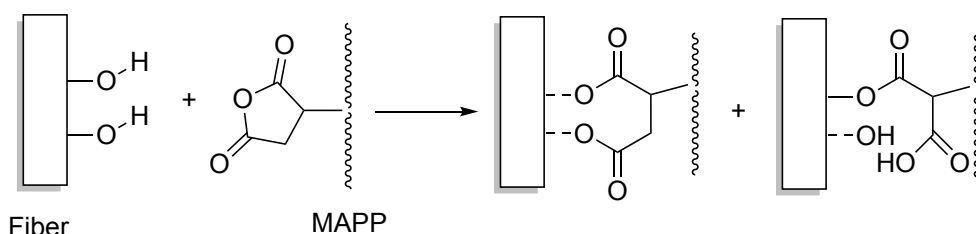
¹⁰⁶ Lu, N.; Oza, S.; Tajabadi, M. G. Surface Modification of Natural Fibers for Reinforcement in Polymeric Composites. In *Surface Modification of Biopolymers*; John Wiley & Sons, Inc.: Hoboken, NJ, 2015; pp 63–85.

¹⁰⁷ Kalia, S.; Dufresne, A.; Cherian, B. M.; Kaith, B. S.; Avérous, L.; Njuguna, J.; Nassiopoulou, E. *Int. J. Polym. Sci.* **2011**, 2011, 837875.

addition to the improvement of the fiber-polymer interaction, the benzoylation treatment increases the thermal stability of the fibers conferring better mechanical performances to the resulting composite (increase in the elastic modulus, T_g and a better tensile strength).¹⁰⁸

Maleic anhydride treatment

The functionalization of natural fibers with maleic anhydride is particularly useful for making them optimal reinforcement in bio-composites. Unlike other chemical treatments, maleic anhydride (MA) is not only used to modify the surfaces of natural cellulosic fibers, but also the surface of polymer matrices, to better improve interfacial adhesion and increase the mechanical properties of both phases involved. An example in this context is polypropylene (PP), which in the presence of maleic anhydride generates maleated polypropylene (MAPP). During this treatment, MAPP can interact with the hydroxyl groups -OH of cellulose, favoring the formation of hydrogen or covalent bonds between the reinforcement and the matrix (Scheme 2.5).¹⁰⁹



Scheme 2.5. Natural fiber-MAPP interaction

Graft copolymerization

Graft copolymerization is a process that involves the lateral polymerization of various monomers on a polymeric skeleton already formed, which in the case of natural fibers is represented by cellulose chains. A monomer widely used in the graft copolymerization of natural fibers is the acrylic acid, in the presence of a radical initiator, an ester bond is created between the hydroxyl groups of the fiber and the carbonyl of acrylic acid. To

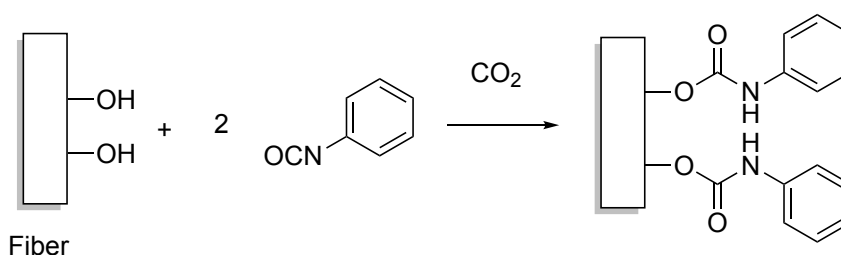
¹⁰⁸ Li, X.; Tabil, L. G.; Panigrahi, S. J. *Polym. Environ.* **2007**, *15*, 25–33.

¹⁰⁹ Punyamurthy, R.; Sampathkumar, D.; Ranganagowda, R. P. G.; Bennehalli, B.; Srinivasa, C. V. *J. King Saud Univ. Eng. Sci.* **2017**, *29*(1), 33–41.

perform graft copolymerization of vinyl monomers on natural fibers, redox initiators, such as cerium (IV) ions, can be used, some of the salts that can be used are ammonium cerium (IV) nitrate and cerium (IV) sulfate. Another option to use free radical initiators, includes azobisisobutyronitrile, potassium persulfate and ammonium persulfate, which promote the incorporation of various monomers into natural fibers.¹¹⁰ Graft copolymerization, depending on the type of monomer, can significantly modify the physicochemical properties of natural fibers. It can improve chemical and heat resistance, reduce moisture absorption, improve swelling behavior in various solvents, and improve interaction with matrices.

Isocyanate treatment

Isocyanates are organic molecules characterized by R-N=C=O functional group. Isocyanate acts as effective coupling agent in reinforced composites combining with hydroxyl groups of cellulose to form urethane bond (Scheme 2.6).



Scheme 2.6. Isocyanate treatment of natural fibers

Based on the nature of R group of isocyanate molecule is possible to tune and drive specific interaction with polymeric matrices. In this context, isocyanate treatment emerges as a valid alternative to alkalization, due to its superior effectiveness in eliminating free hydroxyl groups on the fiber surface. Isocyanate is mostly used to reduce water absorption, while improving the mechanical properties of fibers.¹¹¹

¹¹⁰ Meena, R.; Bhattacharya, A. *Grafting on Cellulosics: Progress Toward Purpose*. In *Cellulose-Based Graft Copolymers*; CRC Press: 2015

¹¹¹ Liu, W.; Qiu, R.; Li, K. *Polym. Compos.* **2016**, 37(6), 1748–1756

Permanganate treatment

Potassium permanganate (KMnO_4) in acetone produces highly reactive MnO_4^- ions, which combine with the hydroxyl groups present in cellulose, giving rise to the cellulose-manganate complex. Usually preceded by an initial alkaline cleaning, KMnO_4 treatment is performed through immersion at specific concentrations in acetone solvent. This treatment not only provides interaction with the hydroxyl groups of cellulose but also acts on the lignin located in the cell wall, contributing to its elimination. The result is a significant increase in hydrophobicity. The hydrophilic character of the fibers tends to decrease as the KMnO_4 concentration increases.¹¹² Oxidation by permanganate modifies the fiber surface making it rougher, leading to a better interfacial adhesion and increasing the chemical interaction between the matrix and the fibers. The strength of this welding between the matrix and the fibers, generated by oxidation, is comparable to the chemical bonds created with silane-based treatments. The application of potassium permanganate on fiber-reinforced composites also leads to improvements in ductility, flexural strength, impact resistance, thermal stability and flexural modulus.^{113,114}

Etherification treatment

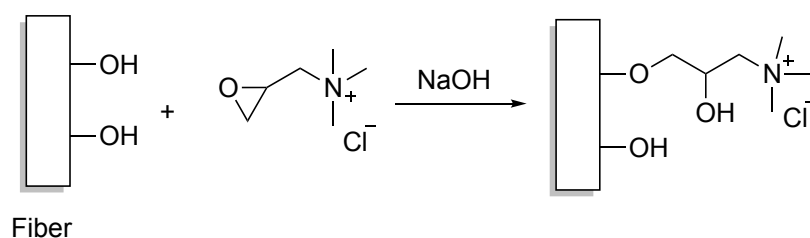
Etherification is a treatment aimed at obtaining ether bonds on the fiber surface, using bifunctional monomers. The process improves the interaction between the fibers and the polymeric chain of the matrix leading a significant increase in thermal stability of the reinforced composites. These modifications do not have a significant influence on the native structure of natural fibers and their morphology. The most used molecules to functionalize the fiber through etherification, under highly alkaline conditions, are alkyl halides as well as epoxides (Scheme 2.7). Etherification has also been used to attach alkyne groups to cellulose surfaces, thus allowing various types of tailored functional groups to be introduced onto these surfaces through *click chemistry*.¹¹⁵

¹¹² Paul, A.; Joseph, K.; Thomas, S. *Compos. Sci. Technol.* **1997**, 57(1), 67–79

¹¹³ Birniwa, A. H.; Kehili, S.; Ali, M.; Musa, H.; Ali, U.; Kutty, S. R. M.; Jagaba, A. H.; Abdullahi, S. S.; Tag-Eldin, E. M.; Mahmud, H. N. M. E. *Separations* **2022**, 9(8), 138.

¹¹⁴ He, L.; Li, W.; Chen, D.; Lu, G.; Chen, L.; Zhou, D.; Yuan, J. *Polym. Compos.* **2018**, 39(5), 1399–1409.

¹¹⁵ Rahman, N. S. A.; Ahmad, N. A.; Yhaya, M. F.; Azahari, B.; Ismail, W. R. *J. Appl. Polym. Sci.* **2016**, 133(25), 43493

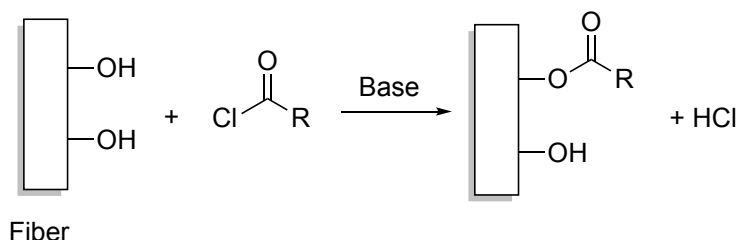


Scheme 2.7. Etherification of natural fibers with epoxides

Also, in this case the treatment is usually preceded by an alkaline treatment and is normally performed to enhance the thermal properties and the interaction of the fibers with the polymer matrices.

Esterification treatment

The chemical modification of lignocellulosic fibers with fatty acid chlorides is used to convert the hydrophilic surface of cellulose chains into hydrophobic surface. This process, which leads the formation of ester bonds generates a fatty acid residue on the surface of the fiber (Scheme 2.8).



Scheme 2.8. Esterification of natural fibers with fatty acid chlorides

The choice of the solvent, as well as the specific reaction conditions, in this type of treatment is important as it can impact the effectiveness of functionalization. The choice of solvent can drive fiber's swelling, increasing the accessibility of the hydroxyl groups, thus improving the success of the reaction. Other factors, such as temperature, reaction time, amount of derivatizing agent, volume ratio also contribute to the extent of the modification.¹¹⁶ The introduction of long carbon chains on fibers -OH groups, through

¹¹⁶ Corrales, F.; Vilaseca, F.; Llop, M.; Gironès, J.; Méndez, J. A.; Mutjè, P., *J. Hazard. Mater.* **2007**, 144, 5.

esterification with fatty acid derivatives, promotes the reduction of water absorption in response of an increase of hydrophobicity. The hydrophobicity given by this type of functionalization is also responsible for a better wettability when the fibers are used as reinforcement for specific polymeric matrices, thus allowing better mechanical and thermal properties. The degree of branching, the length of the chain, and the degree of unsaturation of fatty acid derivatives used, significantly influence the effectiveness of this type of treatment. It has been seen how long-chain fatty acids are responsible for an increase in tensile properties and ductility of the fiber, and how the presence of unsaturation leads to a reduction in stress to strain compared to fiber grafted with saturated fatty acids.¹¹⁷ In addition, the degree of functionalization, for esterification with fatty acids chlorides, is not always related to better properties. Indeed, it has been demonstrated that a slight functionalization in cellulose nanocrystal (CNC) for epoxy composites gives better results in terms of mechanical properties (dynamic mechanical analysis and stress to strain) respect to higher degree of substitution but still a high degree of substitution is necessary to maintain a good level of hydrophobicity.¹¹⁸

2.4.3 Biological treatments

Although chemical and physical treatments are currently the most widely used treatments for natural fibers that will then be used as reinforcements for polymer matrices, these still present disadvantages related to sustainability and the energy impact of the entire process. The use of microorganisms, such as fungi, bacteria, and enzymes, could offer a solution to these problems, since they are able to modify the surface of natural fibers with a lower energy investment. Therefore, it may be possible to develop more environmentally friendly surface treatments for the extraction and treatment of natural or raw fibers. The different enzymatic, fungal, and bacterial treatment techniques will be explored.¹¹⁹

¹¹⁷ Kulomaa, T.; Matikainen, J.; Karhunen, P.; Heikkilä, M.; Fiskari, J.; Kilpeläinen, I., *RSC adv.* **2015**, 5, 6.

¹¹⁸ Trinh, B. M.; Mekonnen, T., *Polymer* **2018**, 155, 10.

¹¹⁹ Ferreira, D. P.; Cruz, J.; Fangueiro, R. Surface Modification of Natural Fibers in Polymer Composites. In *Green Composites for Automotive Applications*; Baillie, C., Ed.; Woodhead Publishing: Cambridge, U.K., 2019; pp 3–41.

Enzymatic treatment

Enzyme treatment is a highly sustainable and environmentally friendly methodology used today in the treatment of natural fiber for polymer composites. This approach uses enzymes to selectively remove hydrophilic components such as pectin, lignin and hemicellulose from fibers, helping to reduce the hygroscopicity of cellulosic fibers. The primary enzyme categories, involved in enzymatic hydrolysis, include hydrolases (amylases, cellulases, proteases, pectinases and lipases/esterases) and oxidoreductases (tyrosinase, laccase and peroxidase).¹²⁰ Unlike chemical catalysis, enzymatic catalysis is characterized by higher reaction rate, favorable operating conditions (temperatures below 100 °C, atmospheric pressure and pH between 4 and 8) and higher specificity.¹²¹ Studies have shown how enzymes are able to act on the fiber improving the interaction with polymeric matrices. For example, laccase enzyme is used to remove lignin from natural fibers without damaging them. An enzyme called Novamix is able to reduce the fibers into microfibers removing useless materials but still maintaining the native characteristics of the fibers.¹²² Despite the many benefits, enzymes processes are expensive, and this remains a significant issue, even though the possibility of recycling enzymes after each treatment could offer an opportunity to reduce the costs of their use.

Fungi treatment

Similar to enzymatic treatment, fungal treatment emerges as an environmentally friendly and efficient alternative to chemical methods. This strategy is used to remove non-cellulosic components (such as wax, lignin or pectin) from the surface of fibers thanks to the action of specific enzymes. The white fungus *Schizophyllum Commune* can produce extracellular oxidases, enzymes that interact with lignin components, including lignin peroxidase. These enzymes play a crucial role in the removal of lignin from the surfaces of natural fibers, increasing their roughness and improving interfacial adhesion

¹²⁰ Araujo, R.; Casal, M.; Cavaco-Paulo, A. *Biocatal. Biotransform.* **2008**, 26(5), 332–349

¹²¹ Jayapriya, J.; Vigneswaran, C. *J. Nat. Fibers* **2010**, 7(4), 241–255.

¹²² Suwanruji, P.; Smitthipong, W.; Chollakup, R. Natural Fiber Surface Treatments and Coupling Agents in Bio-Based Composites. In *Bio-Based Composites for High-Performance Materials*; CRC Press: 2014; pp 167–189.

with the polymer matrix.¹²³ Further studies revealed that composites made with fungal processed hemp fibers presents improved mechanical properties compared to untreated fibers composites. Hemp-based polypropylene thermoplastics, fungal treatment resulted in a 32% increase in composite strength compared to alkaline treatment.¹²⁴ Fungal treatment, although slow and difficult to control, represents an eco-friendly alternative treatment, with potential in the production of green and sustainable materials.¹²⁵

Bacterial treatment

An innovative method for modifying fibers is bacterial cellulose coating, which involves the addition of a new material rather than the removal of existing ones. When bacteria are inoculated into a specific culture medium with natural fibers, they produce bacterial cellulose, which is mainly deposited on the surface of the fibers.¹²⁶ Cellulose can be synthesized by various bacterial species such as *Gluconacetobacter*, *Agrobacterium*, *Aerobacter*, *Azotobacter*, *Rhizobium*, *Salmonella*, *Escherichia*, *Sarcina*.¹²⁷

Bacterial cellulose (BC) has unique properties including high purity, high crystallinity, good biodegradability, high water absorption capacity, and excellent biological affinity.¹²⁸ The aim of coating natural fibers with bacterial cellulose is to improve the adhesion between fibers and polymers, as well as to develop eco-friendly fiber-reinforced composites with improved properties and durability.¹²⁹ Various methods of coating natural fibers with bacterial cellulose have been reported, one of which is coating sisal and hemp fibers by culturing *Acetobacter Xylinum*. This approach showed an improvement in interfacial adhesion between PLA polymer and bacterial cellulose-coated sisal and hemp natural fibers.¹³⁰

¹²³ Cragg, S. M.; Beckham, G. T.; Bruce, N. C.; Bugg, T. D. H.; Distel, D. L.; Dupree, P.; Etxabe, A. G.; Goodell, B. S.; Jellison, J.; McGeehan, J. E.; McQueen-Mason, S. J.; Schnorr, K.; Walton, P. H.; Watts, J. E. M.; Zimmer, M. *Curr. Opin. Chem. Biol.* **2015**, *29*, 108–119.

¹²⁴ Gulati, D.; Sain, M. *J. Polym. Environ.* **2006**, *14* (4), 347–352.

¹²⁵ Ismail, M.; Khoshnava, S. M.; Rostami, R.; Valipour, A. The Using Fungi Treatment as Green and Environmentally Process for Surface Modification of Natural Fibres. In *Mechanical and Materials Engineering, Applied Mechanics and Materials*; Trans Tech Publications, 2014; Vol. 564, pp 63–68.

¹²⁶ Lee, K.-Y.; Bismarck, A. Creating Hierarchical Structures in Cellulosic Fibre Reinforced Polymer Composites for Advanced Performance. In *Natural Fibre Composites*; Woodhead Publishing, 2014; pp 62–95.

¹²⁷ Ross, P.; Mayer, R.; Benziman, M. Cellulose Biosynthesis and Function in Bacteria. *Microbiol. Rev.* **1991**, *55* (1), 35–58.

¹²⁸ Hungund, B. S.; Gupta, S. G. *World J. Microbiol. Biotechnol.* **2010**, *26* (10), 1823–1828.

¹²⁹ Pomet, M.; Juntaro, J.; Heng, J. Y. Y.; Mantalaris, A.; Lee, A. F.; Wilson, K.; Kalinka, G.; Shaffer, M. S. P.; Bismarck, A. *Biomacromolecules* **2008**, *9* (6), 1643–1651.

¹³⁰ Lee, K.-Y.; Shamsuddin, S. R.; Fortea-Verdejo, M.; Bismarck, A. *J. Vis. Exp.* **2014**, 83.

Experimental part

2.5 Aim of the work

This study was done in collaboration with the company that co-funded my PhD program, HP Composite S.p.A, world leader company in carbon fiber composites production. The aim of the project is to find a method to effectively employ natural fibers in the production of high-performance composites for the automotive sector. This need stems from the fact that environmental issues, as well discussed in the introduction chapter, are rapidly worsening. Chemical modification of natural fibers that makes them suitable for composite materials and solve the issues associated to their nature was studied. A functionalization process for hemp and flax fibers, based on the chemical modification of hydroxyl groups, has been reported. A new non-dissolving pre-treatment method was developed, with several diols at different molecular weight able to replace the water molecule between chains of microcrystalline cellulose (MCC) and swell the fiber making the hydroxyl group more available for further reaction. Then the introduction of reactive functional small molecules was studied to analyze and confirm the improved -OH groups accessibility (Figure 2.5).

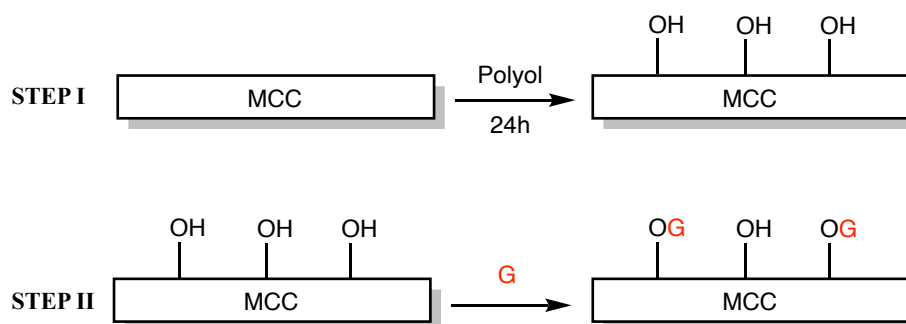


Figure 2.5. General steps of MCC derivatization

The study, once the entire process had been optimized, then focused on lignocellulosic matrices. Various fatty acid derivatives, capable of increasing adhesion with the polymeric matrices and solving the problem of fiber hygroscopicity were further tested. The general method was first optimized on matrices of a powdery nature, then validated on the whole fiber in anticipation of a scale-up process at industrial level. Specific optimizations of reaction conditions and parameters were necessary studied. Controls

and characterizations were carried out at different times to confirm the goodness of the entire process. Mechanical tests on treated fiber-reinforced composites were then reported.

2.6 Swelling pre-treatment of MCC

A new sustainable pre-treatment with different diol derivatives able to swell the polymer chains of microcrystalline cellulose were studied.¹³¹ This process makes the hydroxyl groups more available for further reactions and functionalization. Thanks to the strong affinity of polyetylen glycol (PEG) with cellulose, its ability to act as a swelling solvent was tested and an increase in volume was observed after 8 hours of soaking (Figure 2.6). The heterogeneous solution was then centrifugated to separate solid from liquid phase and MCC was washed 3 times with distilled water to ensure the total removal of PEG.

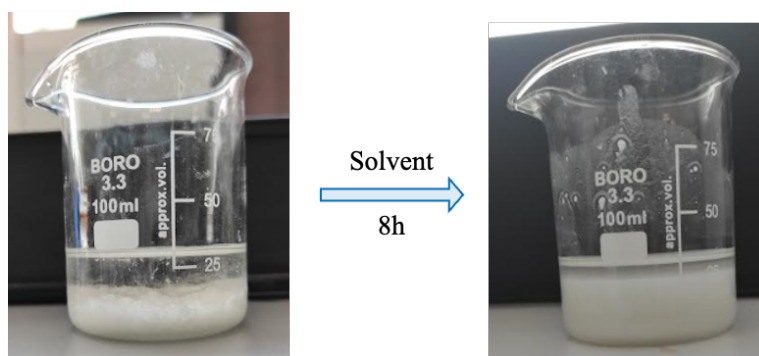


Figure 2.6. Swelling of MCC with PEG200

The solvent only acts as swelling agent and could be recovered ensuring the preservation of MCC crystalline structure, making this an efficient non-destructive method. So far studies shown that the best swelling agent, for cellulosic matrices, is water. Different types of polyols have been studied and compared with water in relation to their swelling ability. The swelling degree of different solvents were evaluated through the following formula where w it's the weight of the wet cellulose and w_0 correspond to the weight of the dry cellulose¹³²:

¹³¹ Lupidi, G.; Pastore, G.; Basileo, S.; Stella, F.; Minicucci, M.; Pettinari, C.; Guzzini, A.; Cimarelli, C.; Gabrielli, S.; Marcantoni, E. *Chem. Commun.* **2024**. Submitted

¹³² El Seoud, O.; Fidale, L. C.; Ruiz, N.; D'Almeida, M. L. O.; Frollini, E. *Cellulose* **2008**, *15*, 371–392.

$$\text{Swelling (\%)} = \frac{w - w_0}{w_0} \times 100$$

2.6.1 Solvent's screening

The effectiveness of this pre-treatment was analyzed by the swelling degree followed by functionalization with several organic small molecules. Different polyethylene glycols, varying in molecular weight (PEG 200, PEG 400 and PEG 3000), were tested and the swelling degrees obtained were compared with water's (Table 2.1).

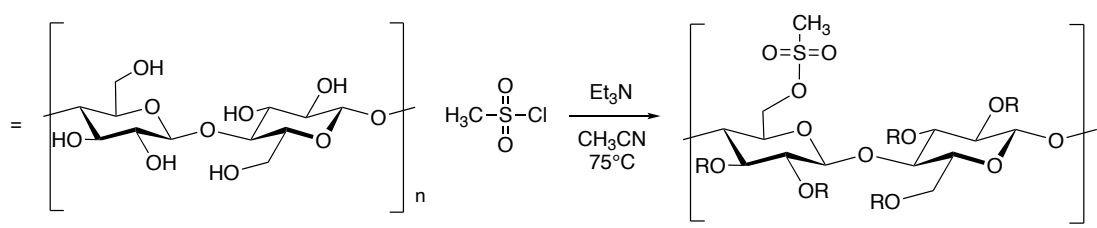
Table 2.1. Comparison data of different swelling solvent

Entry	Solvent	Swelling (%)
1	H ₂ O	55
2	PEG 400	65
3	PEG 200	85
4	PEG 3000	47

The results show that the highest swelling degree percentage was achieved using PEG 200 (Entry 3). Lower percentage has been observed for PEG 400 and PEG 3000 (Entry 2 and Entry 4) due to the difficulties of penetrating the cellulose microstructure by the highly hindered polyether chain. Lower value was achieved with water (Entry 1), confirming the goodness of this new non-dissolving method.

2.6.2 Optimization of pre-treatment conditions

The optimization of the pre-treatment was performed in function of the hydroxyl reactivity towards further chemical reactions, by comparing the degree of substitution achieved in different conditions (MCC/PEG ratio and reaction time), through the reaction with sulfonyl chloride as a functionalizing agent (Scheme 2.9).



Scheme 2.9. Functionalization of MCC with sulfonyl chloride

Degree of substitution

The degree of substitution (DS) was determined by elemental analysis (EA). DS reveals the number of grafted hydroxyl groups per anhydroglucose unit according to the following equation¹³³:

$$DS = \frac{6 \times M_C - \%C \times M_{AGU}}{M_{estergrafted} \times \%C - M_{C,estergrafted}}$$

Where M_C is the molar mass of carbon (12.01 g/mol), $\%C$ is the percentage of carbon in the sample, M_{AGU} is the molar mass of the anhydroglucose unit (162.14 g/mol), $M_{estergrafted}$ is the molar mass of the grafted ester group (g/mol) and $M_{C,estergrafted}$ is the molar mass of carbon in the grafted ester group (g/mol).

The highest value was achieved after 10 hours with 1:10 w/v% MCC/PEG. In these conditions, the swelling degree is 98%, therefore the accessibility of MCC towards further chemical modification is the highest (Table 2.2).

Table 2.2. Optimization of pre-treatment condition of MCC

Entry	MCC/PEG	Time (h)	Sw (%)	Yield (%)	DS	C (%)
5	1:10	5	85	99	0.16	43.26
6	1:5	5	83	96	0.12	43.31
7	1:20	5	88	97	0.51	40.52
8	1:10	8	95	97	0.71	39.29
9	1:10	10	98	99	1.04	37.60

Also, tests on PEG recovery were studied in relation to the amount of MCC still available after the swelling process. Five trials were conducted and more than 99% of MCC was recovered for each trial, confirming the insolubility of microcrystalline cellulose in PEG 200.

¹³³ Missoum, K.; Belgacem, M. N.; Barnes, J.-P.; Brochier-Salon, M.-C.; Bras, J. *Soft Matter* **2012**, 8, 8338.

2.6.3 Chemical, thermal and morphological characterization of pre-treated MCC

The way the pretreatment chemically impact cellulose matrix was analyzed through FTIR, TGA and SEM.

FT-IR analysis (Figure 2.7) showed no changes in functional groups before and after the swelling process with PEG 200. The process doesn't modify the chemical functionalization of MCC.

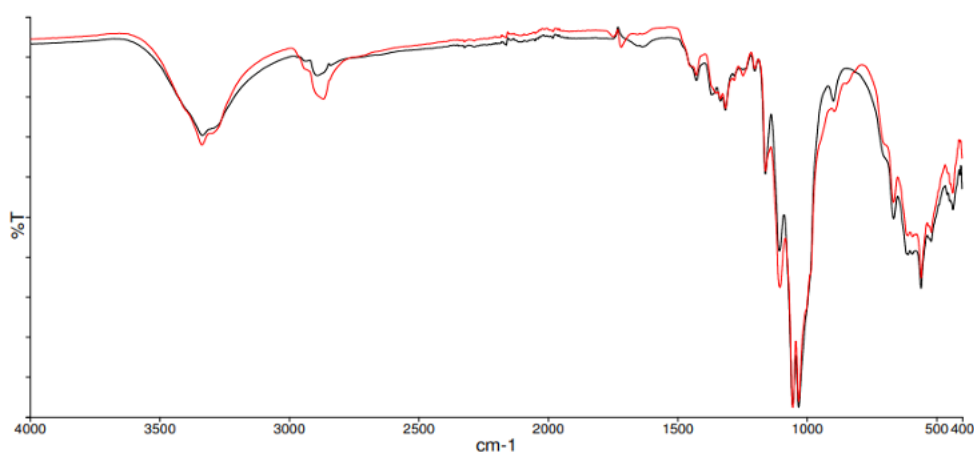


Figure 2.7. Overlay of the FT-IR spectra of pure MMC (black spectrum) and pre-treated MCC (red spectrum)

In the same way, thermal stability of samples, before and after the pre-treatment was studied. The overall thermal stability is slightly increased in pre-treated cellulose and the water weight loss, detected for the pure sample, was no longer found (Figure 2.8). This is due to the ability of PEG to penetrate the polymeric chains of MCC and replace the water molecule.¹³⁴

¹³⁴ Nguyen, T. D.; Kohdzuma, Y.; Endo, R.; Sugiyama *J. Wood Sci.* **2018**, *64*, 436.

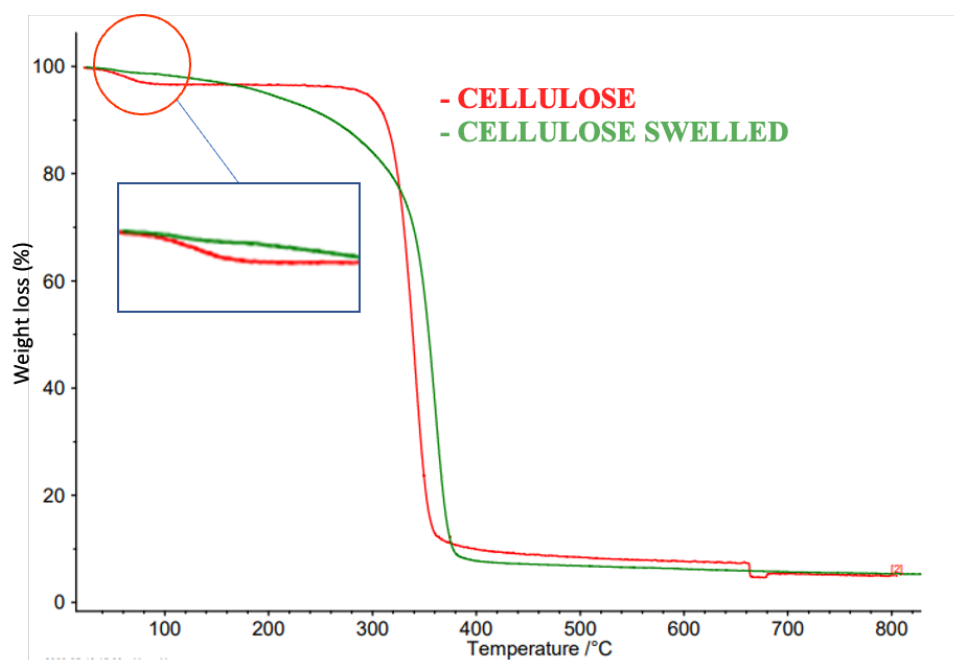


Figure 2.8. TGA thermograms of pure MMC (red curve) and pre-treated MCC (green curve)

Finally, morphological analysis was evaluated. Scanning electron microscopy (SEM) images (Figure 2.9) clearly show no deterioration on pre-treated MCC surface. Therefore, the process allows to maintain the surface characteristics of microcrystalline cellulose and can be considered as non-dissolving pre-treatment method.

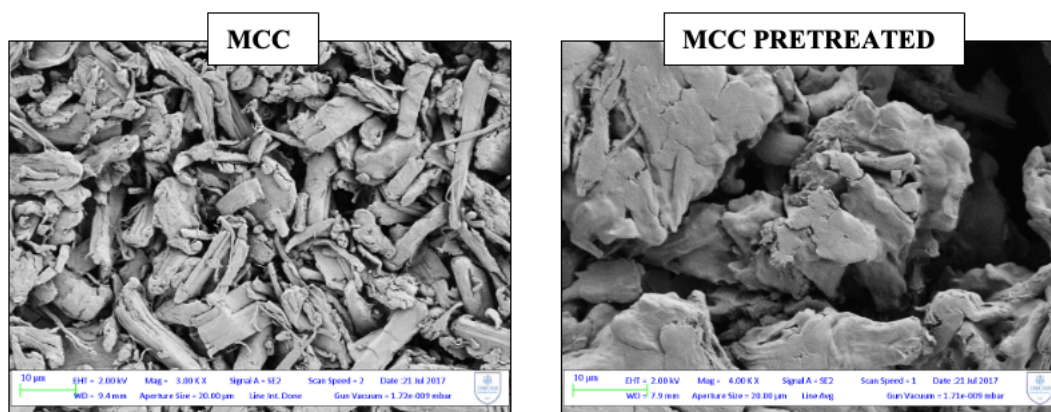


Figure 2.9. SEM images of pure MMC and pre-treated MCC

2.7 Pre-treated MCC functionalization

Once the pre-treatment was optimized, the activated cellulose was then chemically modified with various types of small molecules (Figure 2.10) to validate the whole

process aimed at the realization of unique materials acting as fillers or reinforcements in polymeric matrices (Scheme 2.10).

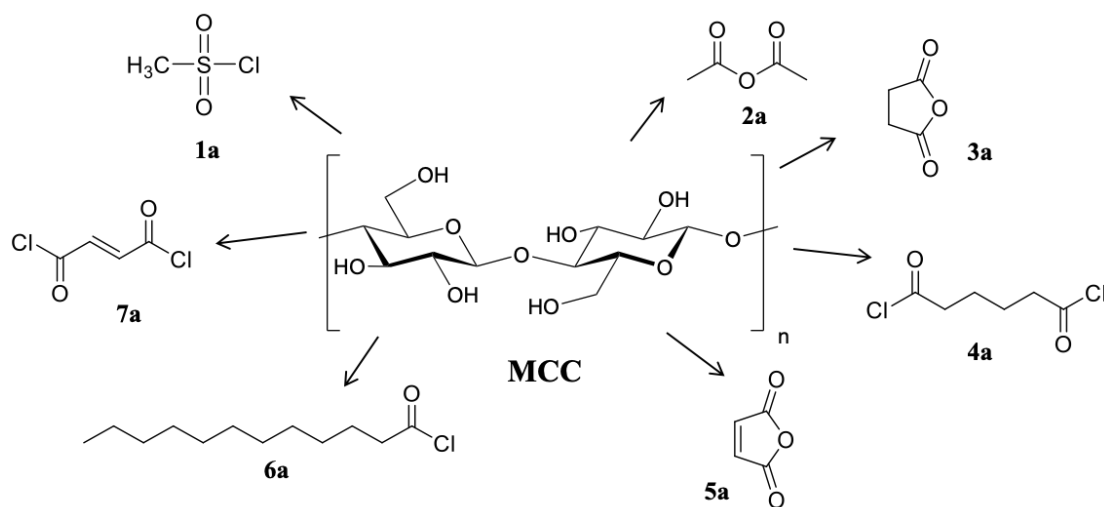
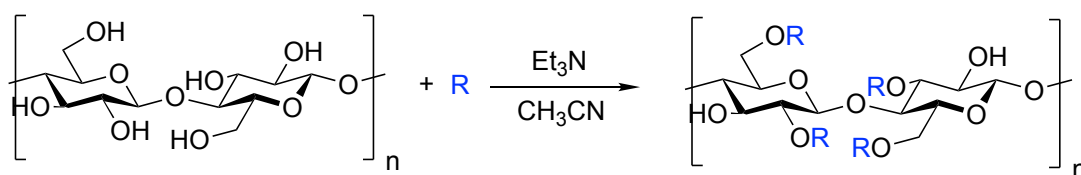


Figure 2.10. MCC and derivatizing agents



Scheme 2.10. MCC general derivatization reaction

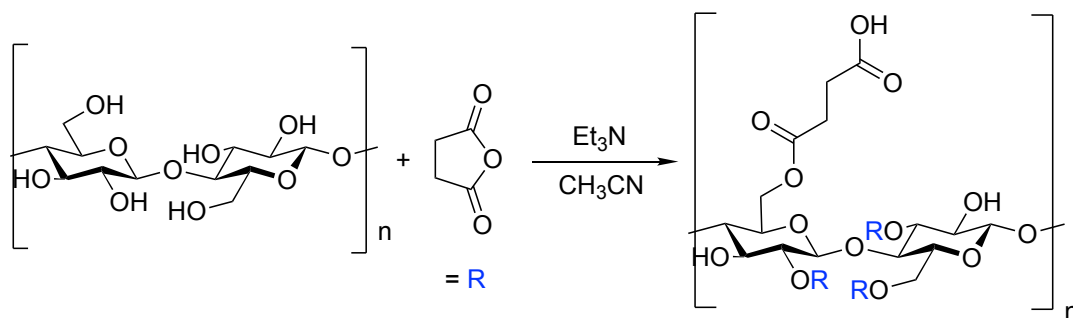
The highest degree of substitution is achieved when succinic anhydride **3a** was used as functionalizing agent (Entry 12, Table 2.3).

Table 2.3. MCC functionalization

Entry	Functionalizing agent	DS	C (%)
10	1a	1.04	37.60
11	2a	0.06	44.59
12	3a	2.70	46.34
13	4a	0.11	45.78
14	5a	1.58	45.94
15	6a	1.13	63.53

2.7.1 Optimization of functionalization conditions

The best derivatizing agent **3a** was therefore selected for the optimization of functionalization reaction conditions (Scheme 2.11).



Scheme 2.11. MCC derivatization with succinic anhydride

The highest value of DS was obtained in the Entry 20 (Table 2.4) which provides 1 equivalent of succinic anhydride and a reaction time of 16 hours.

Table 2.4. Optimization of MCC functionalization reaction condition

Entry	3a (eq.) ^a	Time (h)	DS
16	1	24	2.70
17	0.25	24	0.33
18	0.5	24	1.89
19	1	8	2.80
20	1	16	2.89

^a Equivalents to cellulose anhydroglucose unit (AGU)

This method was then compared with other processes known in literature, in particular the Urea/NaOH and LiCl/DMAc based pre-treatments (Figure 2.9).^{135,136} It's clear that the use of PEG gives the greater degree of substitution, thanks to its ability to penetrate the polymeric chains and make hydroxyl groups more available for further reactions.

¹³⁵ Wang, W.; Li, Y.; Li, W.; Zhang, B.; Liu, Y. *Cellulose* **2019**, 26, 3095.

¹³⁶ Jin, H.; Zha, C.; Gu, L. *Carbohydr. Res.* **2007**, 342, 851.

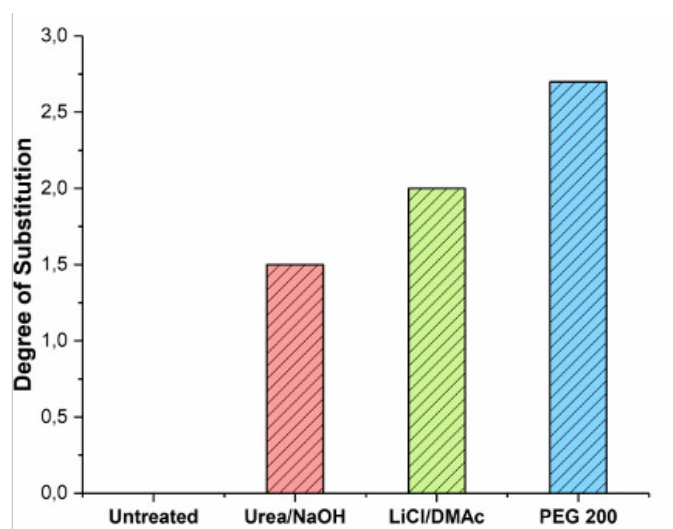


Figure 2.11. Comparison between different pre-treatment in relation of DS

2.7.2 Characterization of functionalized MCC

The chemical modification of microcrystalline cellulose has been evidenced by FT-IR spectroscopy. FT-IR spectrum of functionalized MCC (Figure 2.12) shows the characteristic peaks of cellulose functional groups (3330 cm^{-1} correspond to -OH stretching, 2900 cm^{-1} to -CH₂ and CH stretching, 1570 cm^{-1} to -OH bending and 1052-1026 cm^{-1} related to -C-O- stretching vibration).¹³⁷ Furthermore, to confirm the success of chemical functionalization, the presence of the peak at 1721 cm^{-1} , referring to -C=O stretching vibration of derivatized moiety, can be detected.¹³⁸

¹³⁷ Momzyakova, K. S.; Valishina, Z. T.; Deberdeev, T. R.; Aleksandrov, A. A.; Berlin, A. A.; Deberdeev, R. Y. *Polym. Sci. Ser. D* **2021**, *14*, 288.

¹³⁸ Cichosz, S.; Masek, A. *Molecules* **2020**, *25*, 1279.

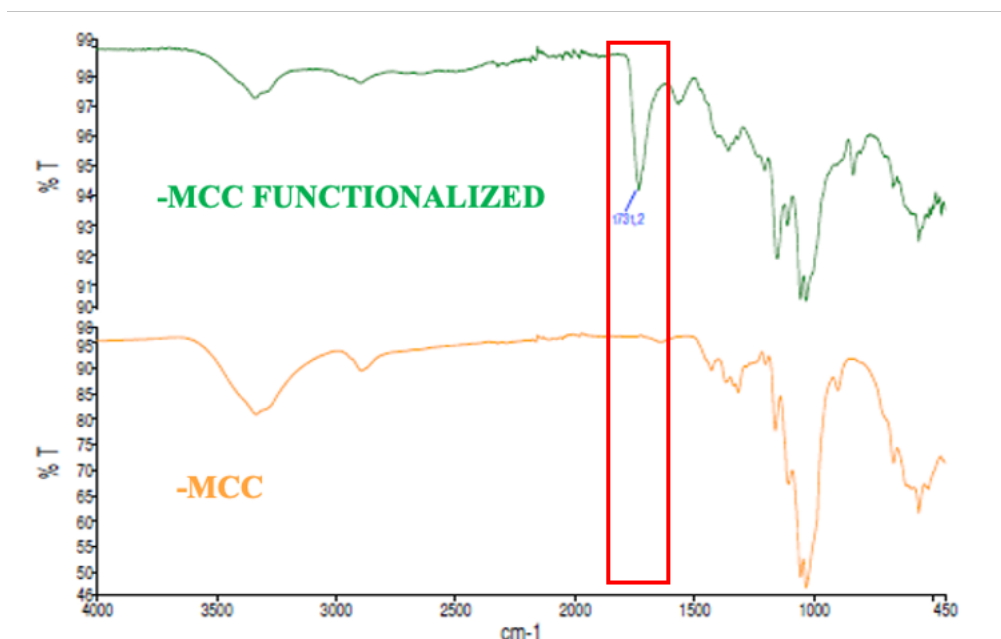


Figure 2.12. Overlay of the FT-IR spectra of pure MCC and functionalized MCC

Thermal stability of pure MCC and functionalized MCC was studied. The thermal stability of derivatized cellulose shows two loss in weight (Figure 2.13). The first one, at 168°C, is correlated to the functionalized moiety, the second one, at 357°C, is attributed to pre-treatment used. In addition, water weight loss detected for the pure sample, is still no longer found after the functionalization reaction confirming the goodness of the whole process.

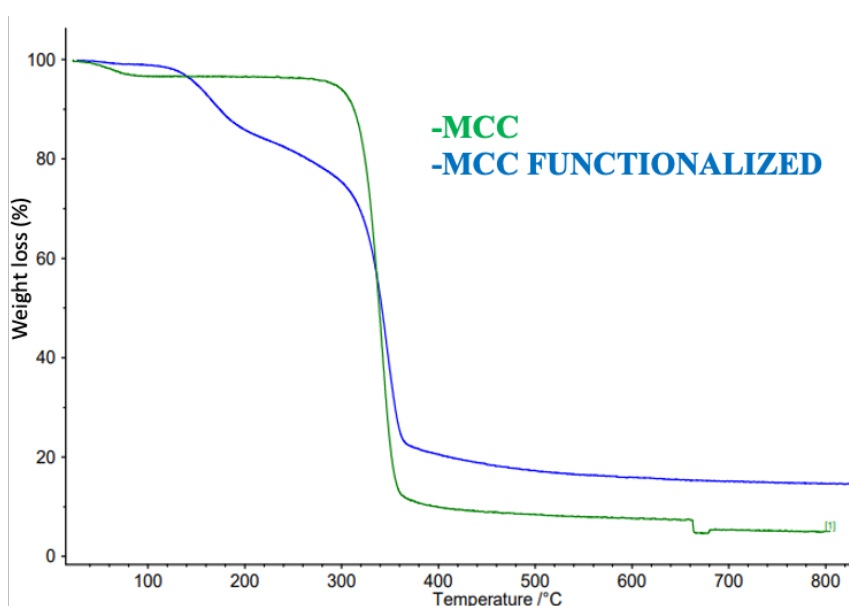


Figure 2.13. Overlay of the TGA curves of MCC and functionalized MCC

Complementary techniques like SEM and X-ray diffraction (XRD) were used to evaluate the morphological impact of the reaction on the matrix. In general, no strong irregularities or structural deformation are observed on the surface of the functionalized samples (Figure 2.14). Elemental analysis states that samples are mostly made up of carbon and oxygen that change in relation of the type of small molecule used. MCC functionalized with **1a**, also highlights the presence of the sulfur.

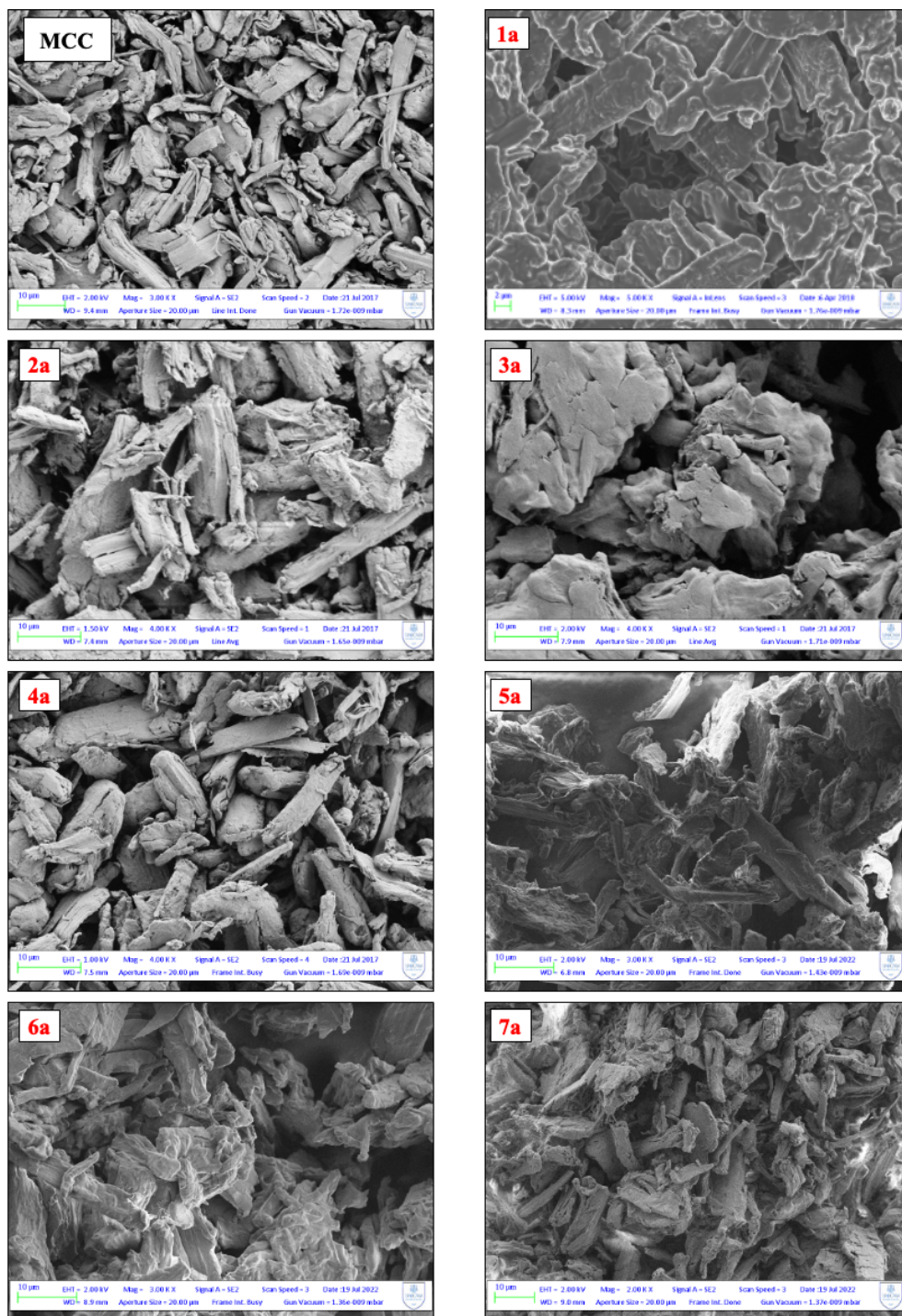


Figure 2.14. SEM images of pure MCC and functionalized MCC with small molecules: **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a**.

Then, the XRD analysis were analyzed (Figure 2.15) to state the crystallinity index of pure, swelled and functionalized MCC.

Crystallinity index

The crystallinity index of cellulose samples was depicted using the well-known *Segal method*.¹³⁹ Through this method, it's possible to calculate the index of crystallinity C_I (%) based on the height ratio between the intensity of the crystalline peak ($I_{002} - I_{AM}$) and the total intensity I_{002} after background signal subtraction:

$$C_I(\%) = \left(\frac{I_{002} - I_{AM}}{I_{002}} \right) \times 100$$

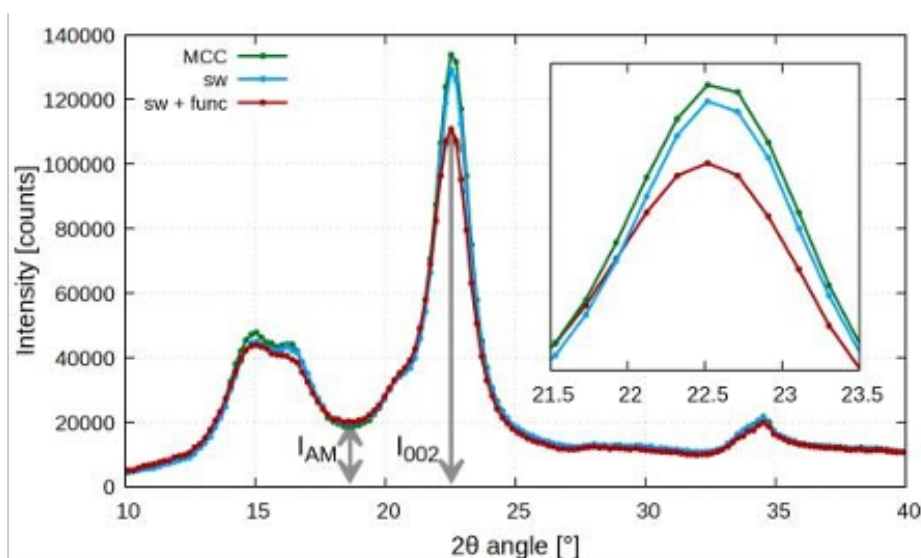


Figure 2.15. XRD patterns of pure MCC, swelled MCC and functionalized MCC

The crystallinity was also evaluated through *Agarwal method* with Raman spectroscopy (Figure 2.16). This method allows C_I detection by height ratio between peaks at 1096 cm^{-1} and 380 cm^{-1} (Figure 2.14).¹⁴⁰

¹³⁹ Segal, L.; Creely, J. J.; Martin, A. E.; Conrad, C. M. *Text. Res. J.* **1959**, 29, 786.

¹⁴⁰ Agarwal, U. P.; Reiner, R. S.; Ralph, S. A. *Cellulose* **2010**, 17, 721.

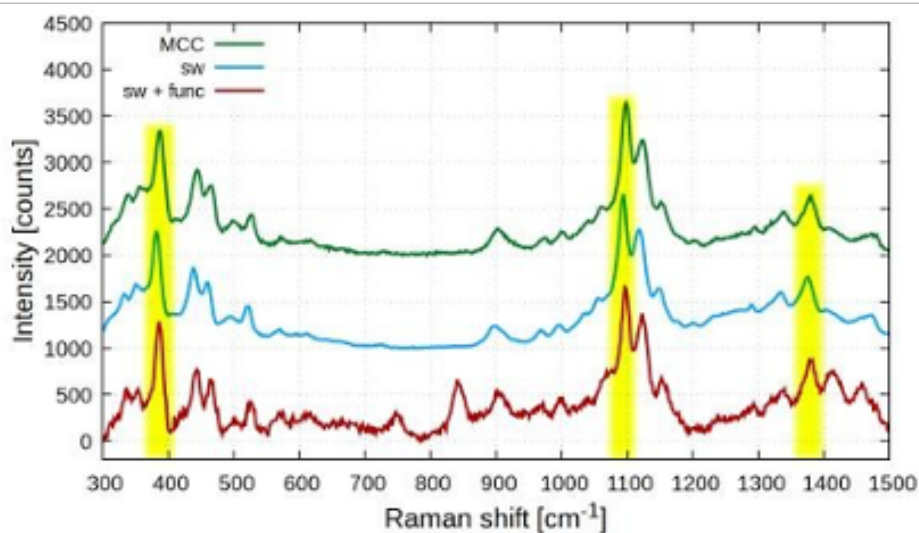


Figure 2.16. Raman patterns of pure MCC, swelled MCC and functionalized MCC

The two techniques were compared, and the results obtained are in good correlation showing very minimum loss in C_I between pure MCC, swelled MCC and functionalized MCC (Table 2.5). Raman analysis also provides information about MCC depolymerization degree by the ratio of peaks at 1376 and 1096 cm^{-1} .¹⁴¹ A slightly decrease in the I_{1096}/I_{1376} ratio is index of depolymerization reactions, observed in both the swelling and functionalization steps.

Table 2.5. Crystallinity index data of MCC

Sample	C_{IXRD} (%)	C_{IRaman} (%)	I_{1096}/I_{1376}
MCC	86	82	2.7
MCC pre-treated	85	76	2.1
MCC functionalized	82	77	1.9

¹⁴¹ Chiriu, D.; Ricci, P. C.; Cappellini, G.; Salis, M.; Loddo, G.; Carbonaro, C. M. *Raman Spectrosc.* **2018**, *1*.

2.8 Organic functionalization of natural fibers

Natural fibers characterization

To better understand and optimize the functionalization process of natural fibers, a complete characterization of pristine natural fibers was performed. Specifically, the chemical composition of lignocellulosic matrices was analyzed by FT-IR; their thermal stability, fundamental for the post process in thermoformed composites was studied with TGA; also, the quantification of the lignin and cellulose content was evaluated through DES extraction.

2.8.1 Chemical characterization of natural fibers

The overlapped spectra (Figure 2.17) show the same characteristic peaks for both flax and hemp fibers. The broad bands around 3300 cm^{-1} and $2840\text{--}2920\text{ cm}^{-1}$ relate to the --OH stretching and --CH , --CH_2 stretching vibrations. The peaks at 1730 , 1620 and 1423 cm^{-1} are attributed to the stretching vibration of --C=O , out of plane vibration of the aromatic --CH groups and in-plane bending vibration of cellulose aliphatic carbons (--CH and --CH_2), respectively.

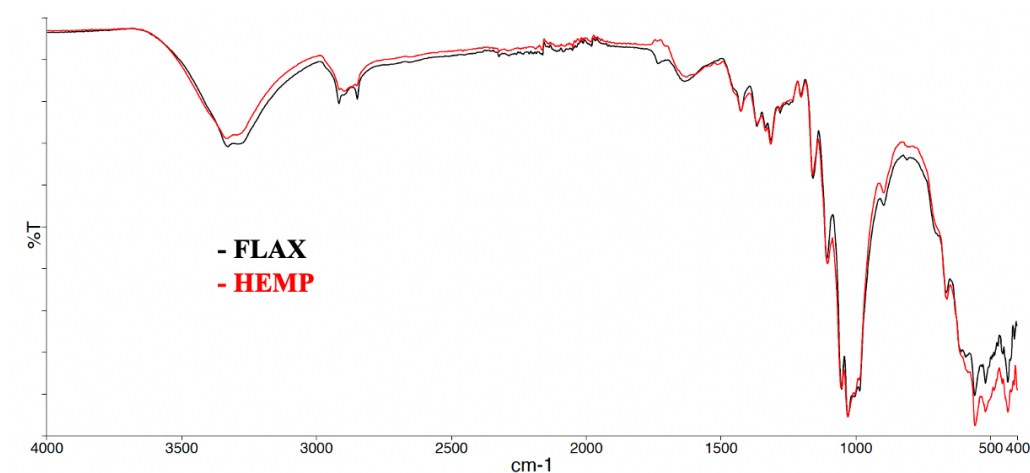


Figure 2.17. Overlay of the FT-IR spectra of pure flax and hemp fibers

2.8.2 Thermal stability analysis of natural fibers

The thermal degradation behavior of hemp and flax fibers was studied through TGA analysis and in Figure 2.18 are reported the thermogravimetric curves.

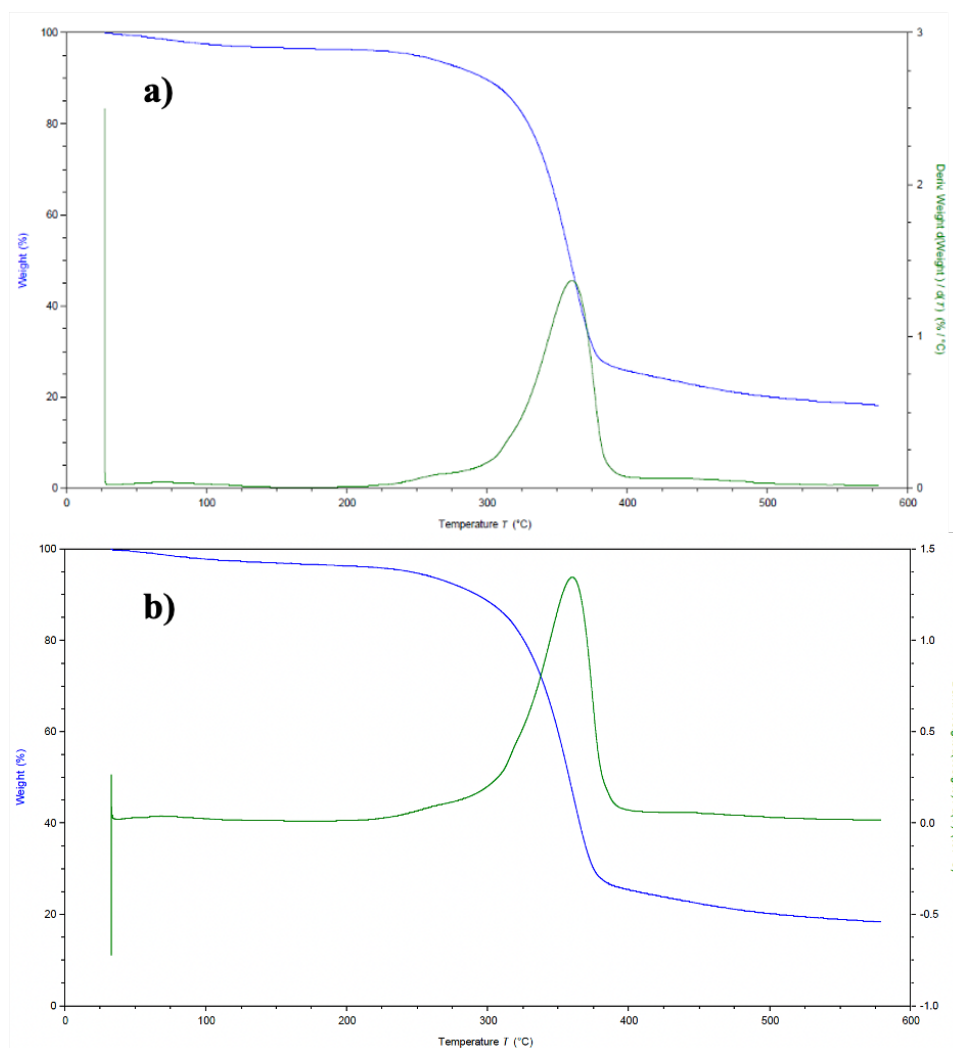


Figure 2.18. TGA curves of native flax (a) and hemp (b) fiber

The first decomposition step at T_{onset} around 55°C, found for both hemp and flax fibers, refers to the moisture evaporation and the loss in weight is approximately 3% for both (Table 2.6). The onset of the second thermal decomposition steps is at 326.4 °C for flax and at 324.9 °C for hemp fibers. The high-temperature tail present in both curves is due to the degradation of lignin, which resulted in a charred organic material residue around 25 wt.% for all lignocellulosic flours.¹⁴²

¹⁴² Yao, F.; Wu, Q.; Lei, Y.; Guo, W.; Xu, Y. *Polym. Degrad. Stab.* **2008**, 93(1), 90-98.

Table 2.6. TGA data of flax and hemp fibers

Sample	T _{onset} I (°C)	Mass loss I (%)	T _{onset} II (°C)	Mass loss II (%)
Flax	55.0	3.1	326.4	70.4
Hemp	54.3	2.7	324.9	71.2

2.8.3 Lignin and cellulose quantification of natural fibers

Hemp and flax fibers were characterized in their lignin and cellulose content. The organo-selective extraction was conducted, on grinded matrices, through DES method (Figure 2.19).¹⁴³ The deep eutectic solvent employed for the extraction is obtained by acetic acid and choline chloride, able to separate lignin liquor from the solid part made of cellulose.

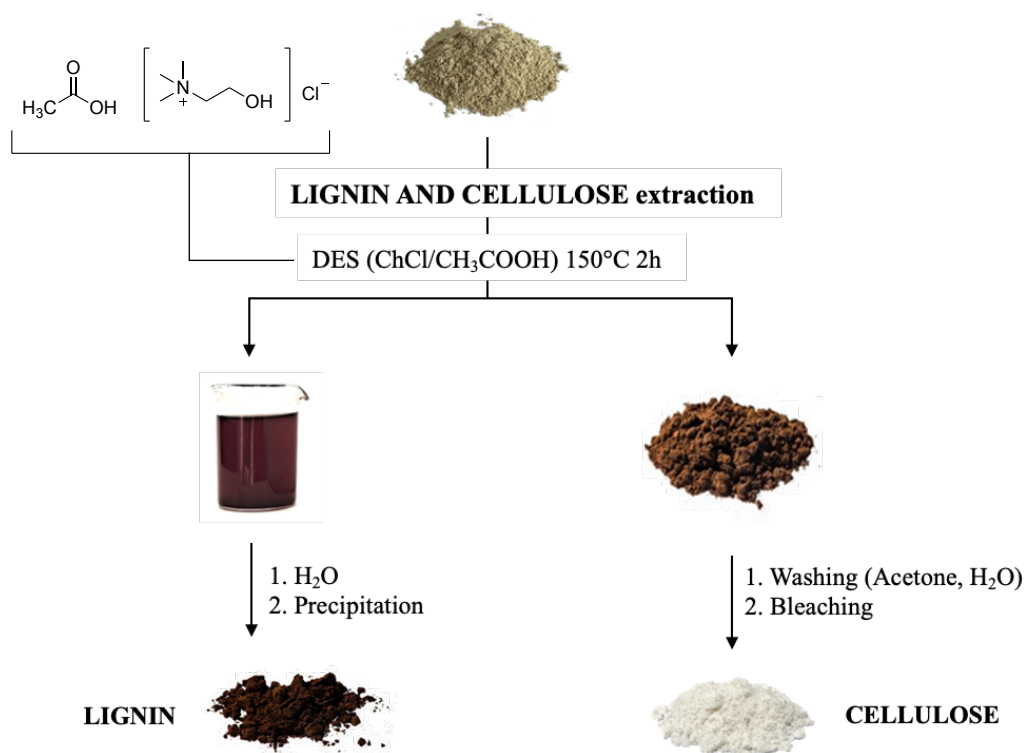


Figure 2.19. DES extraction of lignin and cellulose

¹⁴³ Chen, Y.; Zhang, L.; Yu, J.; Lu, Y.; Jiang, B.; Fan, Y.; Wang, Z. *R. Soc. Open Sci.* **2019**, 6(1), 181757.

Three tests were performed on each sample and their mean value was calculated (Table 2.7). The results of this quantification show as the major component of both hemp and flax fibers is represented by cellulose.

Table 2.7. Cellulose and lignin amount in hemp and flax fibers

Fiber	Cellulose	Lignin
Hemp	82%	3.4%
Flax	75%	2.6%

Lignin characterization

The extracted lignins were studied by FT-IR analysis, the spectrum related to hemp lignin is shown below (Figure 2.20).

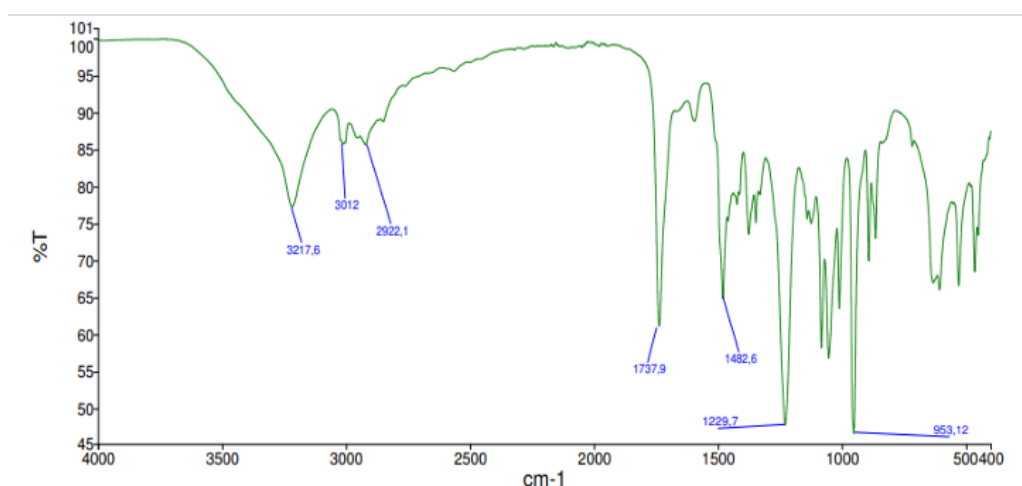


Figure 2.20. FT-IR spectrum of lignin of hemp fiber

The characteristic peaks of lignin depicted (for both the extracts) are:

- The broad absorption band at 3217 cm^{-1} is attributed to the hydroxyl group stretching of phenolic moiety.
- The region between $2800\text{--}3000\text{ cm}^{-1}$ is referred to the -CH , -CH_2 stretching vibration of fatty acid fractions of lignin.
- The stretching vibration of carbonylic and carboxylic functionality (-C=O and -COOH) is found at 1737 cm^{-1} .

- Peaks at 1482 cm^{-1} and at 1230 cm^{-1} were attributed to signals of syringyl units. These bands were found in both hemp and flax lignin samples, indicating that the syringyl unit was left intact after extraction by DES.¹⁴⁴

Cellulose characterization

In the same way, cellulose samples were chemically characterized through FT-IR analysis, the spectrum related to hemp cellulose is shown below (Figure 2.21).

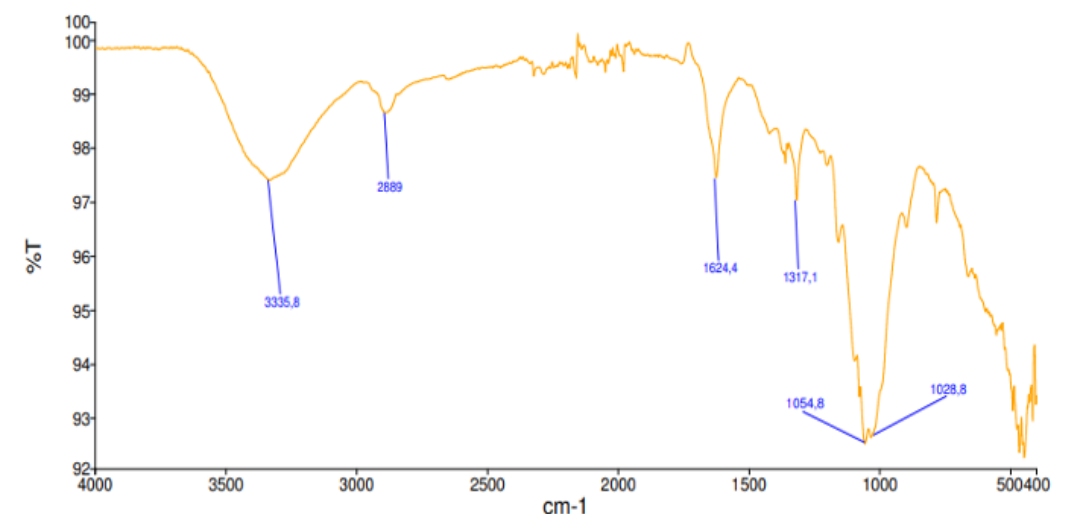


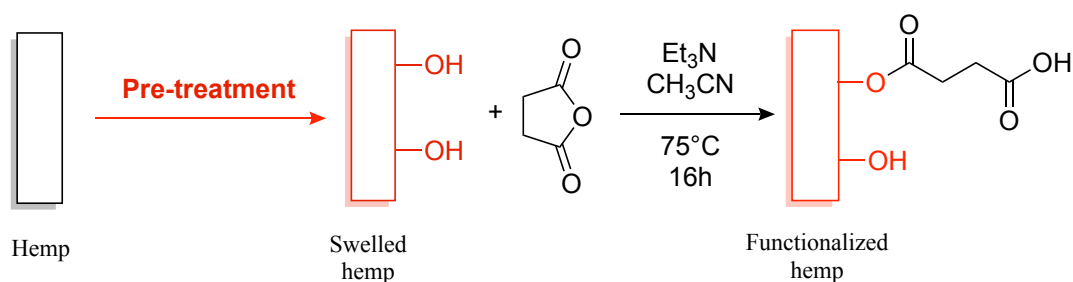
Figure 2.21. FT-IR spectrum of cellulose of hemp fiber

The peaks in the region of 3335, 2900, 1625 and 1050 cm^{-1} refer to -OH stretching, methyl and methylene -C-H stretching, -OH bending and -C-O- stretching vibration, respectively.

2.8.4 Pre-treatment of natural fibers

At this point, once the entire process on microcrystalline MCC was optimized, the reproducibility of this method applied to natural fibers, which are mainly composed of cellulose, has been verified. Different types of pre-treatments were tested and compared on the base of the degree of functionalization achieved (using the best conditions found for MCC) (Scheme 2.12).

¹⁴⁴ Liu, J.; Qi, L.; Yang, G.; Xue, Y.; He, M.; Lucia, L. A.; Chen, J. *Polymers* **2020**, *12*(7), 1599.



Scheme 2.12. Pre-treatment screening of natural fibers

Unlike microcrystalline cellulose, where the maximum value of the degree of substitution that can be obtained is three, due to the presence of three hydroxyl groups available in the monomeric unit, in case of natural fibers, it is not easy to determine a maximum and actual value. The matrix is in fact much more complex due to the presence of multiple elements (cellulose, lignin and hemicellulose) which contain -OH groups, and it is likely that the estimations of functionalization are less precise than those obtained with pure MCC.

The initial screening and optimization were evaluated on hemp fibers, stated that both matrices are characterized by similar chemical, thermal properties and composition in term of lignin and cellulose quantitative. To better understand the goodness of the whole pre-treatment and functionalization, the fibers were first processed in form of powder, grounded with MM500 nano mixer mill (Figure 2.22) and then used.



Figure 2.22. Grinding of hemp fibers with MM 500 nano mill

The native and pre-treated hemp powders were functionalized with succinic anhydride. Elemental analysis was used to get information about the total amount in carbon of each sample and compare them (Table 2.8). After the functionalization process, an increase

in carbon should be observed due to the presence of succinic anhydride linked to the hydroxyl groups of cellulosic phases.

Table 2.8. Elemental analysis of hemp samples

Entry	Sample	Carbon (%) (EA)
21	Hemp	44.81
22	Functionalized hemp (no pre-treatment)	47.46
23	Functionalized hemp (pre-treat. PEG 200)	46.98
24	Functionalized hemp (pre-treat. NaOH)	47.62
25	Functionalized hemp (pre-treat. Pyridine)	46.48

Considering elemental analysis strictly relates to the part of the sample taken, it's possible to say that an overall increase in the percentage of carbon was found in all samples. No significant differences were seen between different treatments.

FT-IR analysis of Entry 22 (Figure 2.23) confirms the effectiveness of functionalization. A decrease of the broad peak related to the hydroxyl groups (-OH) at 3300 cm^{-1} is observed in the functionalized sample, due to the decreased availability of these units after the chemical derivatization. The great increase of the peak around 1700 cm^{-1} characteristic of the carbonyl of the ester bond (-OC=O) is another corroboration of the successful reaction. The presence of both these factors confirms that the functionalization reaction has occurred.

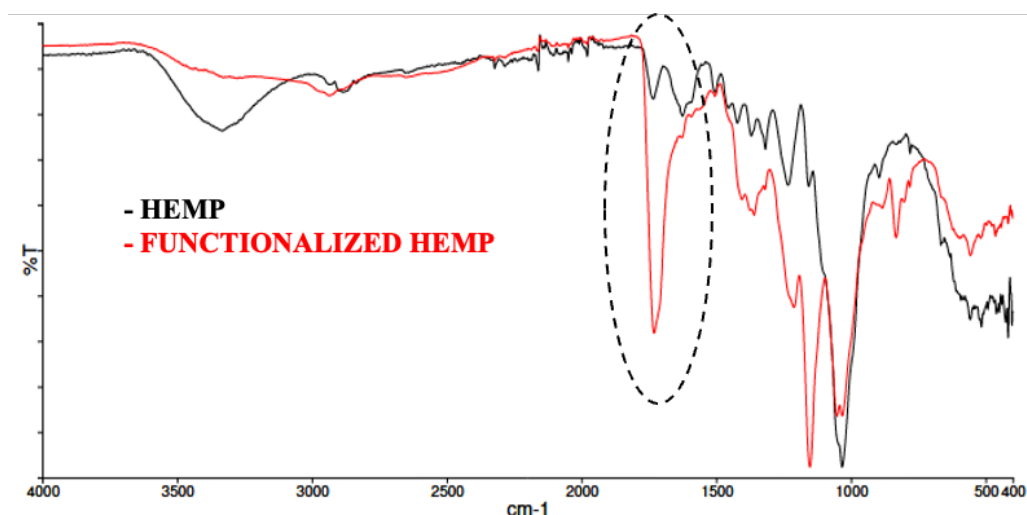


Figure 2.23. Overlay of the FT-IR spectra of pure hemp and functionalized hemp

The obtained results indicate that the pre-treatments applied to the fiber did not cause significant changes in carbon content, suggesting that the level of fiber functionalization remained unaffected. This is probably because PEG cannot easily penetrate inside the cellulose chains of lignocellulosic fiber, made up of elements that prevent its mobility and ability to expose -OH groups for a better derivatization. From this point on, the study therefore focused on using the pure fibers (without pre-treatment), functionalizing them with fatty acid derivatives for potential industrial applications. In fact, derivatization with these functional molecules has the aim of solving the problem related to the hygroscopicity of the fibers, thus increasing the adhesion with the polymeric matrices.

2.9 Natural fibers functionalization with fatty acids chlorides

Fatty acids are mostly known for their amphiphilic behavior due to the hydrophilic polar head and hydrophobic non-polar tail (Figure 2.24).

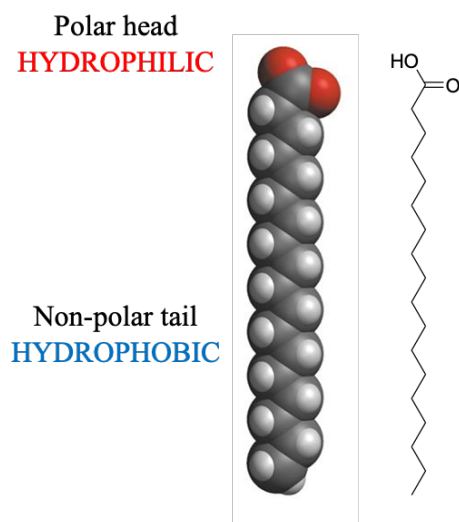


Figure 2.24. Typical structure of a fatty acid

Fatty acids on the surface of lignocellulosic matrix can create a hydrophobic barrier to water molecules and solve the problem of water absorption. Together with this, the functionalization can increase also the interaction with specific polymeric matrices (Figure 2.25).

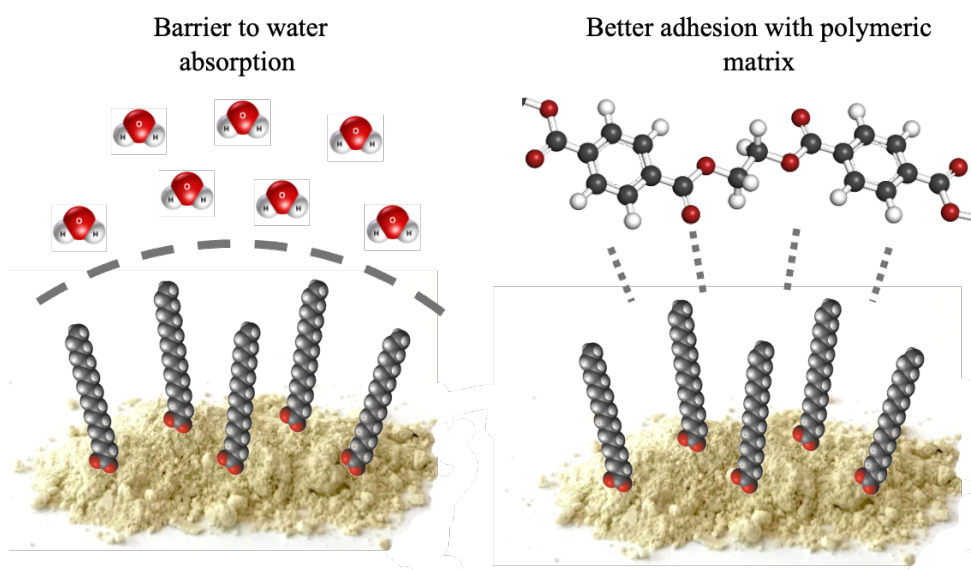
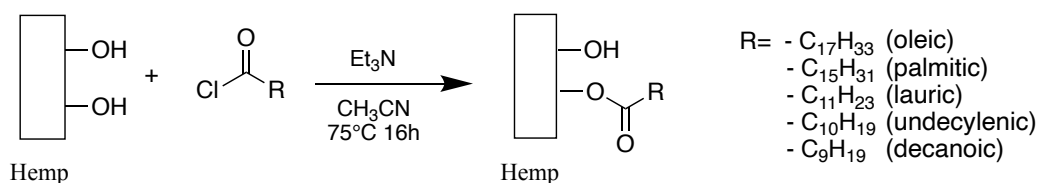


Figure 2.25. Effect of fiber derivatization with fatty acids

Different types of fatty acids chlorides, with variable aliphatic chain length and different saturation were analyzed. For this purpose, chlorides of the following fatty acids were used: oleic acid, palmitic acid, lauric acid, undecylenic acid and decanoic acid (Scheme 2.13).



Scheme 2.13. Fiber's functionalization with fatty acids chlorides

2.9.1 Characterization of functionalized hemp powder

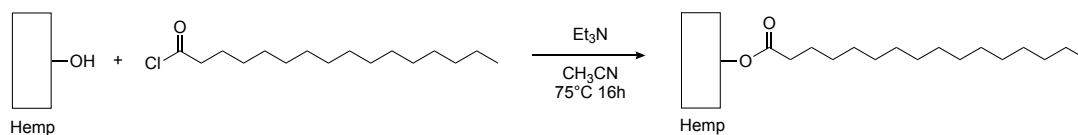
Analytical techniques such as EA, FT-IR and TGA were evaluated to confirm the functionalization with different fatty acid chlorides. In all the samples, an increase in carbon percentage was observed compared to the non-functionalized hemp, stating the goodness of the chemical derivatization (Table 2.9).

Table 2.9. Elemental analysis of hemp and functionalized hemp

Hemp	Carbon (%) (EA)
Non functionalized	44.72
Oleoyl chloride	69.55
Palmitoyl chloride	68.35
Lauroyl chloride	66.31
Undecenoyl chloride	65.42
Decanoyl chloride	63.57

FT-IR analysis shows for all chlorides employed, a reduction of the band around 3300 cm⁻¹ in pure hemp, characteristic of the hydroxyl groups (-OH) and an increase in the intensity of the peaks around 2900 cm⁻¹ and 2800 cm⁻¹ which refers to the aliphatic

chains (CH and CH₂) of fatty acid moiety. In addition, an increase of the peak at 1700 cm⁻¹ of carbonyl ester group (O-C=O) was observed.



Scheme 2.14. Fiber's functionalization with palmitoyl chloride

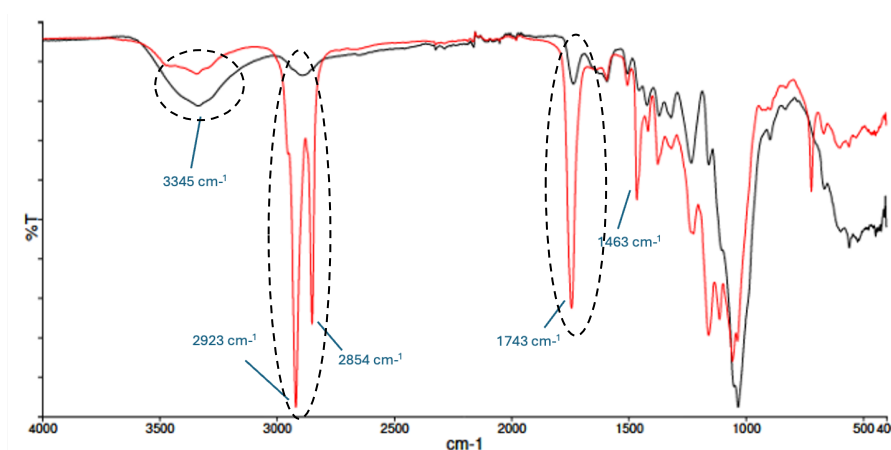
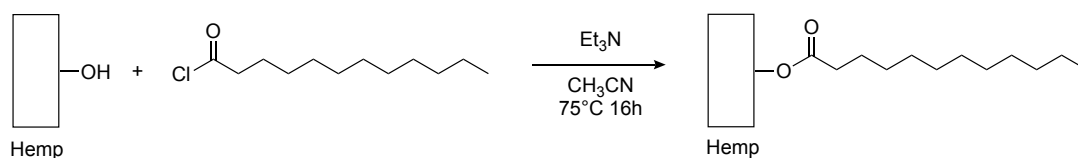


Figure 2.26. Overlay of the FT-IR spectra of pure hemp and hemp functionalized with palmitoyl chloride



Scheme 2.15. Fiber's functionalization with lauryl chloride

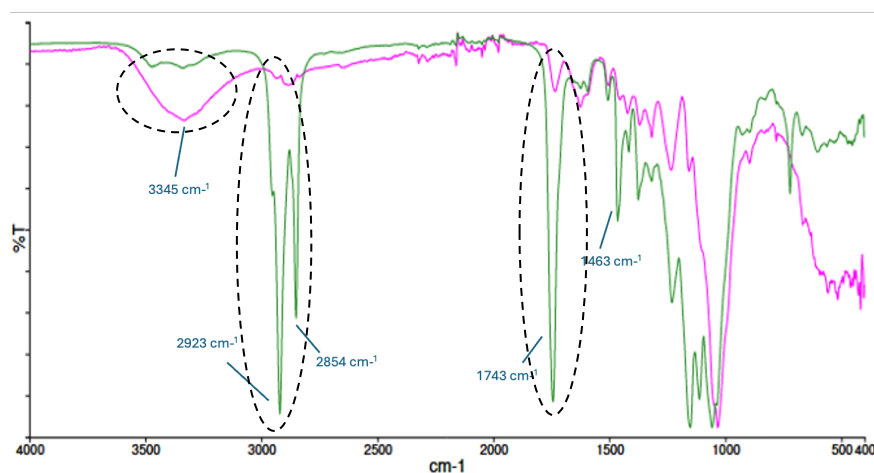
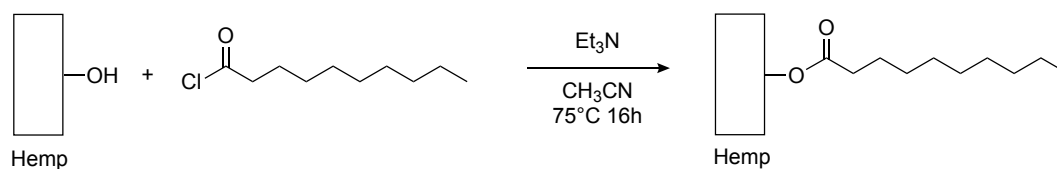


Figure 2.27. Overlay of the FT-IR spectra of pure hemp and hemp functionalized with lauryl chloride



Scheme 2.16. Fiber's functionalization with decanoyl chloride

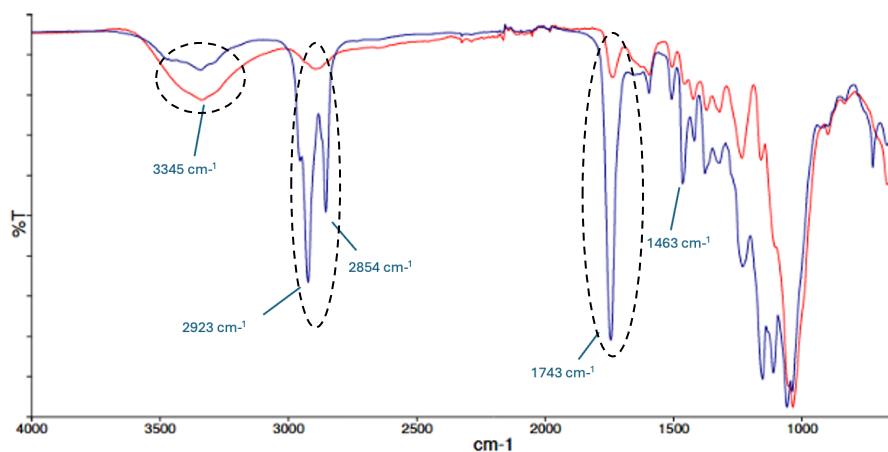
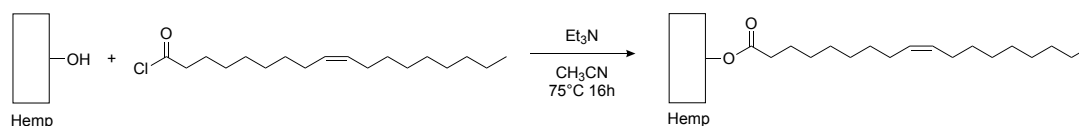


Figure 2.28. Overlay of the FT-IR spectra of pure hemp and hemp functionalized with decanoyl chloride

Furthermore, for fatty acids with a double bond in the aliphatic chain, a small peak around 3300 cm^{-1} is observed, characteristic of the -C=C- bond.



Scheme 2.17. Fiber's functionalization with oleoyl chloride

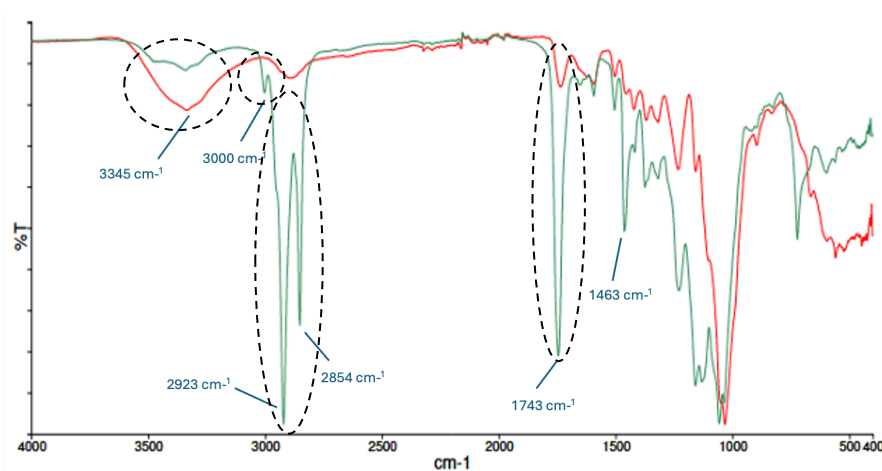
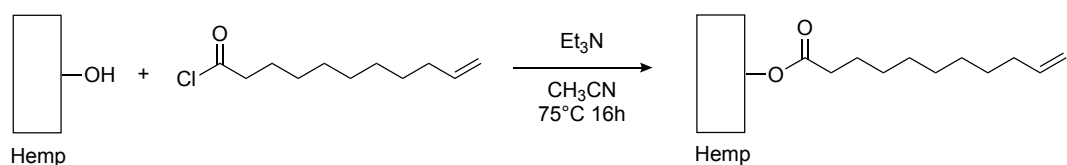


Figure 2.29. Overlay of the FT-IR spectra of pure hemp and hemp functionalized with oleoyl chloride



Scheme 2.18. Fiber's functionalization with undecenoyl chloride

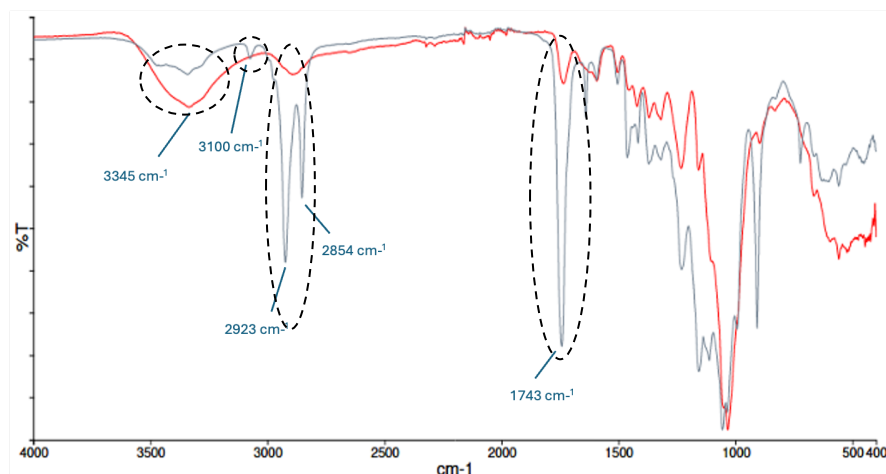


Figure 2.30. Overlay of the FT-IR spectra of pure hemp and hemp functionalized with undecenoyl chloride

Once the success of the reaction was verified, the functionalized hemp samples were analyzed by TGA analysis (Figure 2.31). The results show that, when functionalization with acyl chlorides were performed, the lignocellulosic matrix does not present the water weight loss, which is instead present in the native hemp. Furthermore, after the derivatization is observed a general increase in thermal stability.

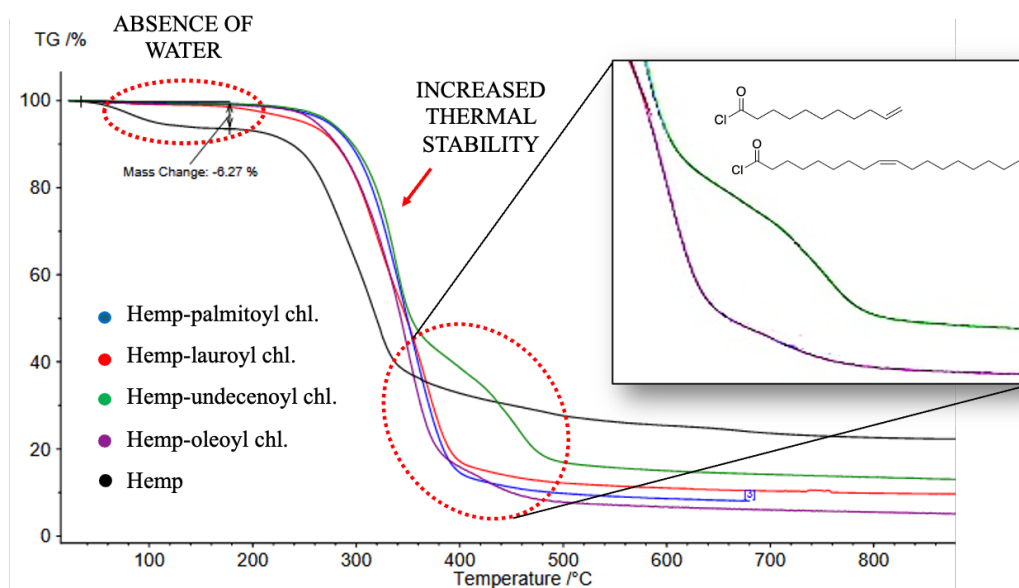


Figure 2.31. TGA thermograms of different functionalized hemp samples

Additionally, for hemp functionalized with chlorides of unsaturated fatty acids, such as oleic acid and undecylenic acid, a further weight loss is observed above 400°C. This thermal behavior is due to the formation of cross-linked zones, arisen from the interaction of unsaturated bonds, phenomenon known in many studies from literature. These cross-linking reactions have been observed to occur in esters with unsaturated side chains.¹⁴⁵

Finally, tests on moisture absorption were carried out exposing functionalized hemp, treated with undecenoyl chloride, to air for 3 and 6 weeks (Figure 2.32).

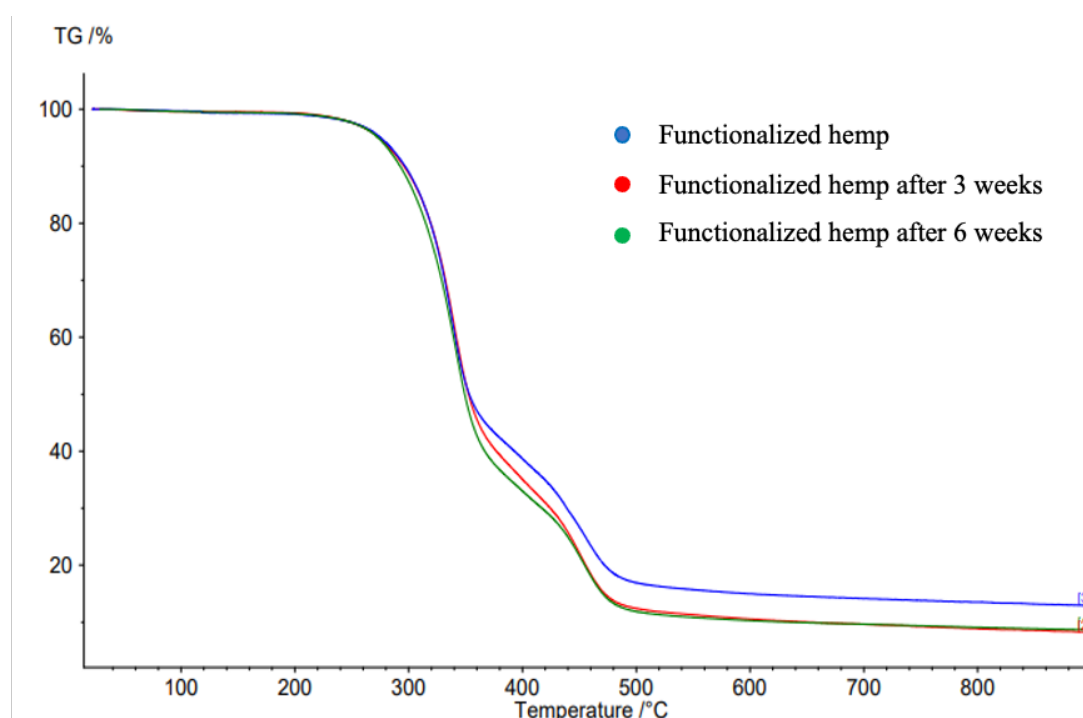


Figure 2.32. TGA thermograms of functionalized hemp at different times

No variations in thermal stability were observed at different times. This proves that the process makes the natural matrix hydrophobic and this keeps the hydrophobicity over time.

Next step will be focus on functionalization of more complex structures, the entire fabric and the fiber, instead of the powder, to study the scalability of the process at an industrial level.

¹⁴⁵ Lu, J.; Askeland, P.; Drzal, L. T. *Polymer*, **2008**, 49, 1285.

Fiber's functionalization

Lignocellulosic matrices in composite materials employed in automotive application are mostly used in form of fabric (Figure 2.33), able to give to the final product mechanical and physical properties required for high performances.



Figure 2.33. Flax fabric

The main objective now is to functionalize the fibers avoiding their deterioration, that would make difficult the subsequent step of manufacturing a unidirectional laminate in epoxy matrix. Different reaction conditions were tested on flax fabric, and the targets were evaluated on the base of increment in carbon percentage (obtained through elemental analysis) and water uptake (analyzed by TGA). The reaction was carried out with undecenoyl chloride, triethylamine to quench the hydrochloric acid produced, in acetonitrile medium. After the reaction, samples were washed three times with chloroform to eliminate traces of unreacted product.

Functionalization on fabric was performed in:

- Dynamic conditions → no functionalization observed in FT-IR analysis
- Static conditions → no functionalization observed in FT-IR analysis
- Ultrasound conditions → no functionalization observed in FT-IR analysis

The negative results are probably due to poor surface contact between the reagents, fiber and functionalizing agents. The fiber, ground into powder form is made of smaller particles, in which the surface area is greater. Consequently, the reaction speed and the possibility of reaction success increases in powder matrices. In addition, a good stirring that enhance a good dispersion of the reactants facilitates contact between the particles,

especially in multiphase systems (liquid-solid). Given the results obtained, it was therefore decided to act directly on the individual fibers (Figure 2.34), which will then be woven together to form the fabric.



Figure 2.34. Spool of flax fiber

The results shown in the Table 2.10 demonstrate that Entry 31 represents the best functionalization conditions in relation to increase in carbon percentage, water loss and water uptake with time (4 weeks). The reaction carried out with undecenoyl chloride, in these conditions, therefore leads to a surface modification of the fibers, creating a hydrophobic layer that limits the absorption of humidity.

Table 2.10. Functionalization conditions with undecenoyl chloride

Entry	Temp. (°C)	Time (h)	undecenoyl chloride (mmol)	Et ₃ N (mmol)	CH ₃ CN (ml)	C (%) increment	H ₂ O weight loss %	H ₂ O weight loss % after 4 weeks
30	75	16	5	5	8	4.49	1.23	3.4
31	75	16	10	10	8	8.95	1.26	1.2
32	75	24	10	10	8	6.79	0.96	2.3
33	75	8	10	10	8	4.40	0.55	1.3
34	50	16	10	10	8	3.67	0.84	1.4

Once the functionalization reaction with undecenoyl chloride was optimized, a scale-up of the reaction was performed (Figure 2.35) for both flax and hemp fibers aiming to produce a quantity of functionalized fiber sufficient to produce unidirectional epoxy resin laminates and evaluate thermal and mechanical properties of the reinforced composites.



Figure 2.35. Scale-up process of fibers functionalization

The scale-up effectiveness is confirmed by FTIR analysis; the appearance of peaks corresponding to the ester bond and the appearance of alkyl chain peaks of the fatty acid moiety confirm the goodness of the carried-out reaction.

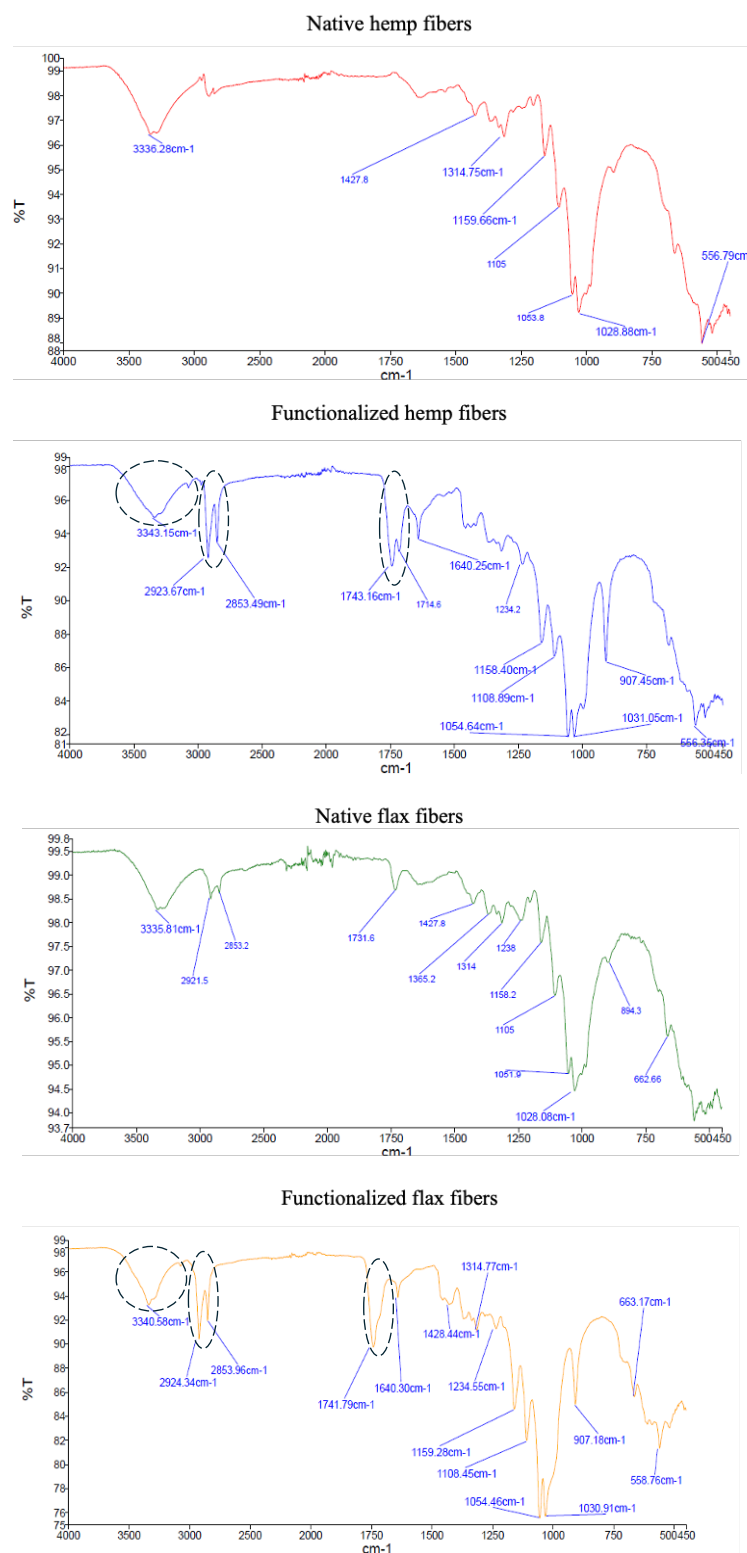


Figure 2.36 FT-IR spectra of native and functionalized hemp and flax fibers

2.9.2 Water content studies

Tests on water content of functionalized fibers were conducted (Figure 2.37). Hydro Tracer is a moisture analyzer specifically designed for measuring low concentrations of

water in solids. It is equipped with an increased sample volume, making it ideal for analyzing materials with low density or low water content. Due to its high accuracy and the ability to process large quantities of sample, this instrument can perform measurements with an accuracy of a few parts per million (ppm) of water. A distinctive aspect of this system is its ability to measure moisture only, excluding any volatiles from consideration.

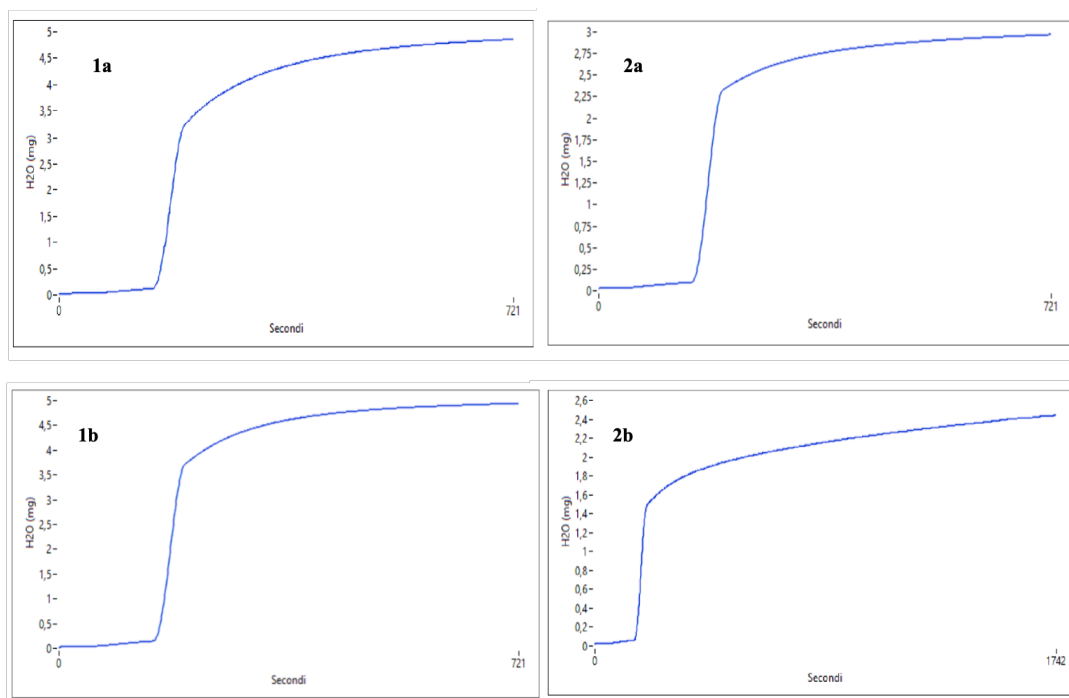


Figure 2.37. Hydro tracer curves of native (1a) and functionalized (2a) hemp fibers, native (1b) and functionalized (2b) flax fibers

For both fibers, the amount of water released by the functionalized fibers is significantly lower than that released from native fibers (Table 2.11). This is further evidence of the functionalization and achievement of the objective set by this research work.

Table 2.11. Hydro tracer data on water content of fibers

Sample	Water content (%)
Native hemp fibers	4.951
Functionalized hemp fibers	2.417
Native flax fibers	4.863
Functionalized flax fibers	1.892

2.9.3 Thermal stability studies

Undecenoyl chloride was chosen, not only because it was one of the reagents that, from the beginning, gave the best results in terms of carbon increase percentage and decreased moisture absorption but also because it brings an unsaturation which can generate cross-link bonds and create a more thermally stable zone at high temperatures (Figure 2.38).

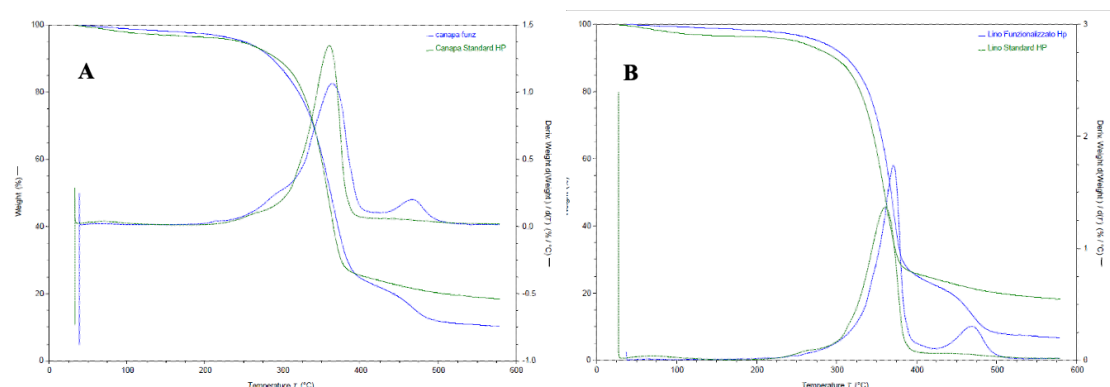


Figure 2.38. TGA thermograms of: A) native (green) and functionalized (blue) hemp fibers; B) native (green) and functionalized (blue) flax fibers

The decrease in the weight loss percentage occurring at the first decomposition step, observed for both fibers, confirms the functionalization of the fibers and the improved hydrophobicity obtained after the treatment (Table 2.12).

Table 2.12. TGA data of functionalized and native flax and hemp fibers

Sample	Decomposition step	T _{onset} (°C)	Weight loss (%)
Flax fibers	I	55.0	3.1
	II	326.4	70.4
Functionalized flax fibers	I	57.0	1.2
	II	342.1	72.3
	III	454.4	17.2
Hemp fibers	I	54.3	2.7
	II	324.9	71.2
Functionalized hemp fibers	I	60.0	1.5
	II	318.5	72.9
	III	457.3	12.7

The second decomposition peak, which occurs at an average of 330 °C for all fibers, shows similar weight loss percentages. This indicates that the functionalization treatment does not internally modify the fiber composition in terms of content of lignin, pectin, waxes and others. In both functionalized fibers, a further weight loss is observed at an average temperature of 455 °C, as previously reported, the latter is due precisely to unsaturated chains of fatty acids bound to the hydroxyl groups of fibers. The double bond led to a thermal cross-linking, which occurs in the initial phases of the degradation process and makes the fiber more thermally stable.

To further understand whether the weight loss at higher temperatures is actually due to the fatty acid bound to the fiber or to the fatty acid itself, thermogravimetric analyses were also performed on:

- undecenoyl chloride itself,
- native fiber with a drop of chloride,
- functionalized fiber (Figure 2.39).

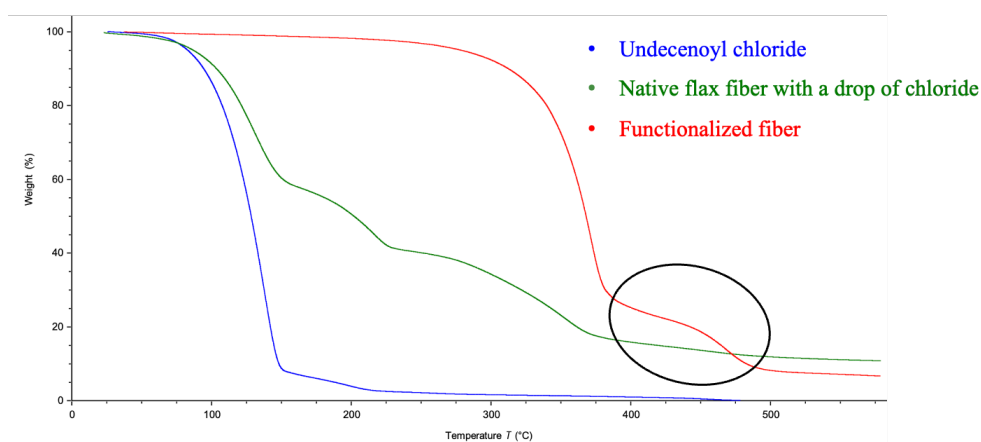


Figure 2.39. Thermogram curves of undecenoyl (blue), native fiber with a drop of chloride (green), functionalized fiber (red)

The results clearly show how the presence of unbound chloride not only decreases the thermal stability of the native fiber but also gives the latter different weight losses. The cross-link zone (black circle in Figure 2.39) that is formed is found only when the fatty acid is bound to the hydroxyls of the fiber, deducing an interaction between the new ester bonds created and the double bonds.¹⁴⁵ This study is crucial to confirm the effectiveness of the functionalization process on the fibers.

2.9.4 Morphological analysis

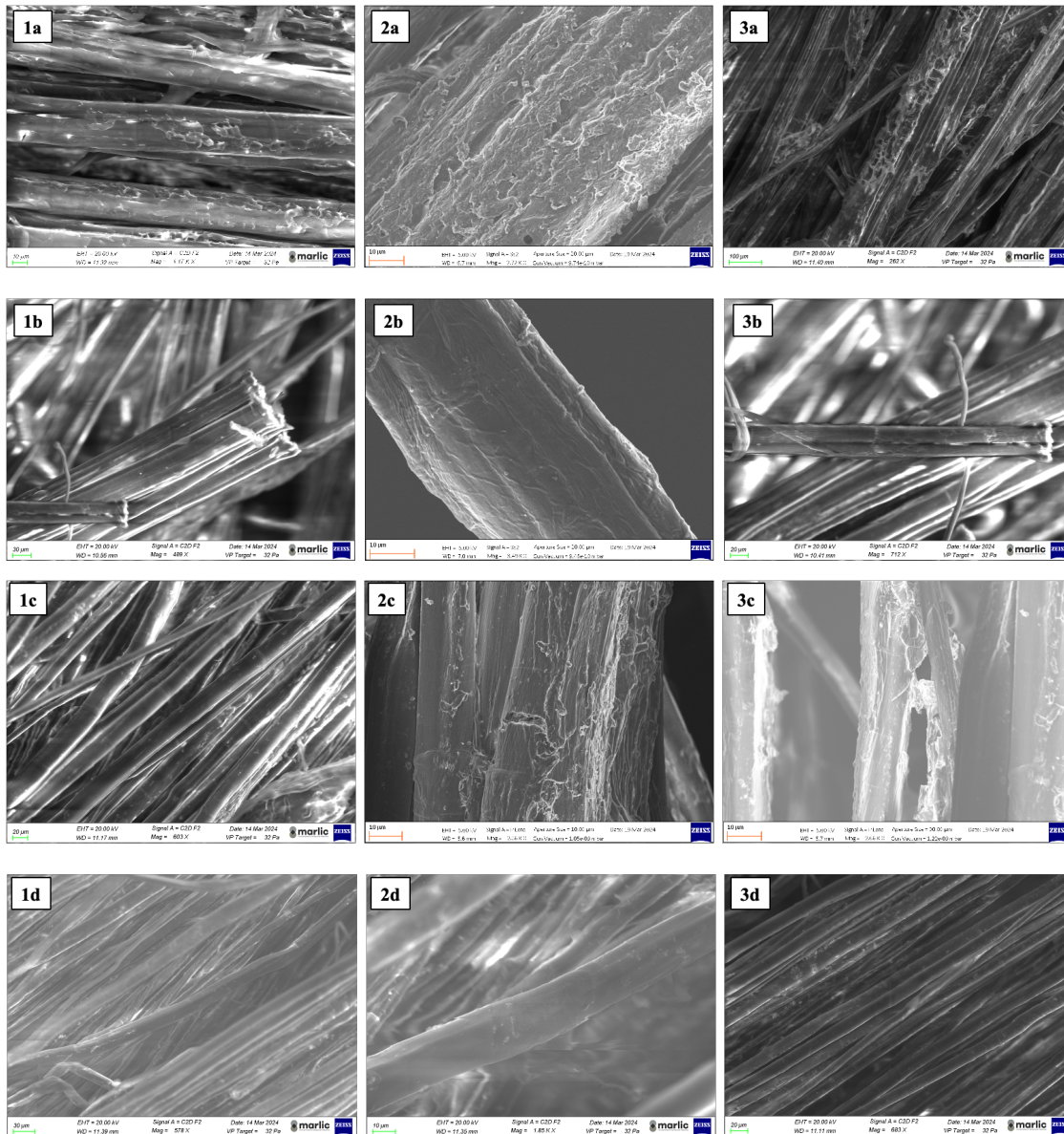


Figure 2.40. SEM images of functionalized hemp (1a -2a -3a) and native hemp (1b - 2b - 3b) fibers, functionalized flax (1c -2c -3c) and native flax (1d – 2d – 3d) fibers

SEM images (Figure 2.40) show that native fibers (1b – 2b – 3b, 1d – 2d – 3d) have a very smooth and regular surface, functionalized hemp (1a - 2a - 3a) and flax fibers (1c – 2c – 3c) have a much rougher and more irregular surface. Surface roughness and external deterioration of the fiber is a direct consequence of the functionalization process. The increased surface roughness of the fibers should improve the surface interactions with polymeric matrices and therefore the adhesion, between them and the matrix, increasing the mechanical performances of the composite.

The results of the EDX analysis in terms of percentage atomic composition were reported in Figure 2.41.

Native hemp						Functionalized hemp					
Element	Signal Type	Line	Wt%	Wt% Sigma	Atomic %	Element	Signal Type	Line	Wt%	Wt% Sigma	Atomic %
C	EDS	K series	55.08	0.43	62.16	C	EDS	K series	71.35	0.17	77.28
O	EDS	K series	44.40	0.43	37.62	O	EDS	K series	27.27	0.17	22.18
Na	EDS	K series	0.15	0.05	0.09	Na	EDS	K series	0.13	0.02	0.07
S	EDS	K series	0.14	0.03	0.06	Mg	EDS	K series	0.06	0.01	0.03
Ca	EDS	K series	0.23	0.04	0.08	Al	EDS	K series	0.11	0.01	0.05
Total			100.00		100.00	Si	EDS	K series	0.04	0.01	0.02
						Cl	EDS	K series	0.68	0.01	0.25
						Ca	EDS	K series	0.36	0.01	0.12
						Total			100.00		100.00

Native flax						Functionalized flax					
Element	Signal Type	Line	Wt%	Wt% Sigma	Atomic %	Element	Signal Type	Line	Wt%	Wt% Sigma	Atomic %
C	EDS	K series	50.95	0.24	58.14	C	EDS	K series	64.02	0.38	70.44
O	EDS	K series	48.71	0.24	41.73	O	EDS	K series	35.62	0.38	29.42
Si	EDS	K series	0.06	0.01	0.03	Si	EDS	K series	0.05	0.02	0.02
Ca	EDS	K series	0.28	0.02	0.10	Cl	EDS	K series	0.23	0.02	0.09
Total			100.00		100.00	Ca	EDS	K series	0.08	0.02	0.03
						Total			100.00		100.00

Figure 2.41. EDX analysis of samples native and functionalized fibers

In both comparisons between functionalized and native fibers, in terms of atomic percentages, the main differences are in terms of carbon and oxygen. In fact, in the functionalized fibers there is a decrease in the percentage of oxygen in favor of that of carbon. The change in the proportions of the two elements in the fibers makes sense considering the fatty acid chains attached to the fiber. These data further demonstrate that the functionalization has been successful. The other elements found in traces for functionalized hemp (Mg, Al, Si) are due to the type of storage (in aluminum foil) used or contamination during the washing process, as they were not subsequently found in the functionalized flax. The chloride ion, found in the functionalized fibers, derives from the functionalization process. Despite its presence, the percentages are attributable to very low traces.

2.9.5 Thermo-mechanical analysis of composites

The study, once the chemical treatment was optimized, and a functionalization scale up of one hundred grams hemp and flax fibers was carried out, was continued by HP Composites employees, which proceeded to create epoxy resin laminates using native and modified fibers arranged in a unidirectional way. Thermomechanical properties of reinforced composites were examined, using techniques such as DSC, DMA, tensile, flexural and interlaminar shear resistance tests.

- The results of DSC analyses showed that the composites with dried unfunctionalized flax and hemp fibers have a higher glass transition temperature (T_g) (88.53 °C) than the undried (83.89 °C) and functionalized (82.63 °C) ones. This reduction in T_g is attributable to the plasticizing effect of water and fatty acid residues, which lower the glass transition temperature of the functionalized composites.
- DMA analyses confirmed the results obtained by DSC, showing that the composites with functionalized fibers, both flax and hemp, have a lower T_g than the unfunctionalized ones, highlighting a greater plasticizing effect.
- Tensile tests highlighted significant differences in the properties of the composites, with the composites reinforced with unfunctionalized flax fiber presenting much higher tensile strength (up to 313.2 MPa) than the functionalized ones (32.6 MPa). Similar behavior was observed for hemp fiber composites, with functionalized composites showing a lower tensile strength (47.7 MPa) than non-functionalized-fiber composites (270.6 MPa). Furthermore, functionalized flax fiber composites have a significantly lower Young's modulus (5.01 GPa) than non-functionalized ones (up to 26.97 GPa), while functionalized hemp fiber composites (12.20 GPa) are stiffer than non-functionalized composites (19.88 GPa).
- Flexural tests confirmed that functionalized flax fiber composites withstand significantly lower flexural stresses than non-functionalized fiber composites.
- A similar effect was found in interlaminar shear strength tests, where the functionalized flax fiber composites showed a lower shear strength than the non-functionalized ones.

The composite with functionalized fibers is significantly more fragile than those made with the native fiber. This could be explained by the fact that the fiber, once functionalized, appears ruined, as stated by SEM images. The greater fragility is not caused by the loss of structural components of the fiber during the functionalization process or change in thermal stability since the TGA shows no changes after the functionalization process. The increase in fragility could however be explained by a possible decrease in the crystallinity of the cellulose contained on the surface of the fiber. The same effect has in fact been reported, by a recent paper on nanocellulose esterification with fatty acids. The study states that a moderate degree of substitution of cellulose, respect to a higher degree of substitution, presents higher mechanical properties when used as reinforcement in epoxy matrices. The fiber, due to the functionalization, could partially lose a portion of the intermolecular hydrogen bonds that hold the cellulose chains together, no longer allowing their organization in parallel planes, increasing the fraction of amorphous cellulose in the fiber and causing a decrease of specific mechanical properties.¹⁴⁶

¹⁴⁶ Ottesen, V.; Larsson, P. T.; Chinga-Carrasco, G.; Syverud, K.; Gregersen, Ø. W. *Cellulose* **2019**, *26*, 6615–6627.

2.10 Experimental protocols

2.10.1 Materials and methods

All reagent and solvent were purchased from commercial suppliers and used without further purification, unless mention otherwise. All glassware was oven dried at 100°C for more than two hours prior to use, when the reactions were performed under nitrogen atmosphere.

Lignin-cellulose extraction and isolation

In a 25 mL round-bottom flask 1 gr of hemp and 5 mL of DES (ChCl:CH₃COOH, 1:2) were added and heated at 155°C for 2 hours. The solution was centrifuged, and the solid residue was first washed three times with acetone and then with deionized water to obtain cellulose. The acetone-soluble fraction was added to the previously centrifuged solution and the solvent was subsequently removed under reduced pressure. The residue obtained is regenerated with distilled water and the mixture was cooled to 4°C for 24 h. The lignin was then recovered through filtration and was oven-dried at 80°C for 24 h.

Pretreatment of MCC/natural fibers

In a 50-mL one-neck flask, 1g of previously ground hemp fiber was placed, to which 10 mL of solvent was added for 24 h at room temperature. Afterwards, the fiber, was washed 3 times with distilled water, filtered and dried in an oven for at least 24 h at a temperature of 100°C. The whole procedure was conducted in an inert atmosphere and under stirring, thanks to a magnetic stir bar.

Functionalization of MCC/natural fibers

Functionalization was conducted in a 25 mL single-neck flask, into which, 0.5 g of fiber was placed and 6 mL of acetonitrile was added. The solution was stirred for 10 min. After this first step, 0.5 mL of triethylamine Et₃N and 10 mmol of functionalizing reagent were added to the reaction mixture. The reaction proceeds for 24h at 75°C. Then the fibers were washed with chloroform 3 times, filtered and then taken oven-dried for at least 24 h at 80°C.

Solvent and base distillation

To perform the distillation, the solvent/base is placed in a flask together with 0.5 g of CaH_2 for every 10 mL of their volume. The flask is then connected to a distillation condenser, with a calcium chloride stopper, and placed on a hot plate. The distilled liquid is stored in anhydrous conditions with molecular sieves of 4 Å

- Fourier-Transform Infrared Spectroscopy (FTIR-ATR)

FTIR spectra were recorded with a Perkin-Elmer FT-IR spectrometer Spectrum Two UATR, equipped with ZnSe crystal. The measurements were performed in a 400-4000 cm^{-1} range at a 2 cm^{-1} resolution, 4 scans and processed by a Perkin-Elmer data manager (Spectrum).

- Thermogravimetric analysis (TGA)

TGA analysis was carried out using a Perkin-Elmer STA 6000 thermal analyzer, equipped with Al_2O_3 crucibles.

- Scanning electron microscopy (SEM)

Samples were evaluated by an high-resolution scanning electron microscope with field emission gun (FE-SEM, Sigma Family, Zeiss, Oberkochen, Germany) operated at 15 keV, equipped with an energy-dispersive X-ray spectroscopy system (Quantax 200, EDS, Bruker) that enables elemental analysis. Samples were deposited on aluminium stabs using self-adhesive carbon conductive tabs and sputtered with a thin film of chromium (5 nm) by the sputter coater Quorum QT150 (Quorum, Laughton, UK).

- Elemental Analysis

The analysis was performed with a Fisons Instruments 1108 CHNS.

- Raman spectroscopy

Raman experiments were performed using a micro-Raman spectrometer (iHR320, Horiba, Kyoto, Japan) in backscattering geometry with a microscope (Olympus BXFM-ILHS, Olympus Corporation, Tokyo, Japan). A diode-pumped solid-state laser of 785 nm emission wave-length was used as the excitation

source while it has been used a 600 grooves mm^{-1} as diffraction grating. The scattered light has been collected using a CCD detector (Horiba Syncerity, Horiba, Japan).

- XRD analysis

The XRD patterns were collected using a Malvern Panalytical Empyrean system with theta-theta drive goniometer (Malvern Panalytical, Almelo, Netherlands). The diffraction patterns have been collected using a copper K-alpha X-ray source at a power of 45kV/40 mA ($\lambda=1.541$ Ångström). The diffractometer was used in reflection mode and the data was collected at 0.2° step size, from 4° to 100°.

- Hydro Tracer

In hydro tracer analysis, the sample is weighed and placed in the sample holder, which is part of the reactor. The heating plate increases the temperature of the sample, thus promoting the evaporation of the water. The vapor produced reacts with a reagent located in a lower temperature zone, generating hydrogen. The amount of hydrogen produced is proportional to the water content of the sample. A dedicated sensor measures the concentration of hydrogen present. In addition, another sensor detects the humidity of the environment, allowing to compensate the calculation of the humidity of the sample.

2.11 Conclusion

The tendency of natural fibers to absorb water from the environment is one of the main disadvantages of these materials. Water absorption accelerates degradation processes, compromising the durability and performance of the fiber-reinforced composites as well as decreasing the mechanical properties. In this work, the preliminary investigation on derivatization of microcrystalline cellulose (MCC) serves as a foundation for the study to improve the performances of natural fiber reinforced composites. In fact, the activation of cellulose by a non-dissolving method, and the subsequent functionalization, were studied in the first part of this chapter. This approach provided a solution to the hygroscopicity problem commonly associated with natural fibers, as demonstrated in the second part of the work, where functionalized flax and hemp fibers showed significantly improved resistance to water absorption. It has been demonstrated that functionalization treatment with fatty acids can create a hydrophobic barrier to water molecules on the surface of natural matrices solving the problem related to hygroscopicity, water absorption, and retention. On the other hand, however the treatment leads to a significant reduction in mechanical properties on the composites made with the functionalized fiber compared to those made with unprocessed native fiber. It is therefore necessary to consider a further the study in this direction. An evaluation of the functionalization in relation to the crystallinity of the fiber could be useful. At the same time, an additional treatment of the fiber through a silanization process, aimed at preserving the strength of the final material and improving its mechanical properties could provide a balanced solution, enhancing both the durability and the mechanical performance of the fiber-reinforced composites.

PART II. Reactive extrusion of hemp fibers-polyurea composites

2.12 General information of reactive extrusion process

The reactive extrusion process involves the mixing and compounding of polymers at elevated temperatures in a continuous flow that enables the production or modification of polymer properties.¹⁴⁷ This technique can be used to achieve different goals, the most important are:

- Synthesis of polymers
- Grafting and functionalization reactions
- Reactive compatibilization of polymer blends and compounds
- Mechanical and chemical recycling

The extruder consists of a hollow cylinder in which one or two screws rotate to move and plasticize the material through friction and external heating. The polymer, introduced as powders, granules or pellet through the hopper, can be mixed with additives and fillers depending on the required application. Once plasticized, the material is forced by the screw through the extruder and subsequently cooled to obtain a stable semi-finished product. Industrial plants can produce up to 1000 kg/h of materials and, for complex geometries, multiple feeding heads can be used to make multi-material components. The main types of extruders are¹⁴⁸:

- single screw
- twin screw, that can be co-rotating or counter-rotating, depending on the direction of rotation of the screws.

2.12.1 Single screw extruder

The single screw extruder, developed since the 1950s, is the most common device for processing polymers in the industrial sector.¹⁴⁹ The screw plays a crucial role in the movement of the polymer, in fact it has different functional zones (Figure 2.42):

- feed zone (with a constant core),
- compression zone (where the section progressively increases)

¹⁴⁷ Formela, K.; Zedler, Ł.; Hejna, A.; Tercjak, A. *Express Polym. Lett.* **2018**, 12 (1).

¹⁴⁸ Lawal, A.; Kalyon, D. M. *Polym. Eng. Sci.* **1995**, 35 (17), 1325-1338.

¹⁴⁹ Sakai, T. *Polimery* **2013**, 58 (11-12), 847-857.

- metering zone (where the core is thicker, and the section is constant).

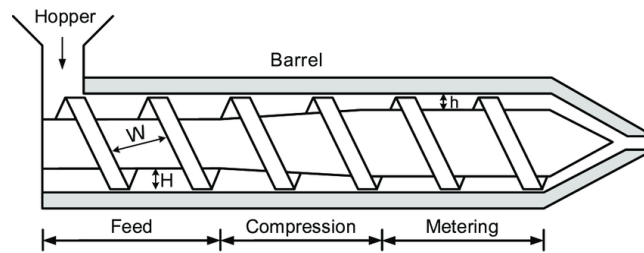


Figure 2.42. Schematic diagram of a single-screw extruder

During the process, the polymer is heated, it begins to melt and densify. The melting of the polymer is accelerated by a greater rotation of the screw or by heating the barrel. The molten material is pushed through the die with an adequate pressure to ensure a homogeneous output. The flow rate of the extruder depends on the rotation speed of the screw, the viscosity of the polymer and the geometry of the extruder itself. The extruder is designed to optimize the flow rate and the flow, keeping the temperature and pressure under control to avoid the degradation of the material. The geometric parameters of the screw and the type of the screw are chosen according to the material and the specific process.

2.12.2 Twin screw extruder

The twin screw extruder is chosen for applications that require higher performance than the single screw extruder, addressing issues such as low flow rate and limited mixing capacity. It consists of two screws rotating inside a single barrel that can be co-rotating or counter-rotating (Figure 2.43).

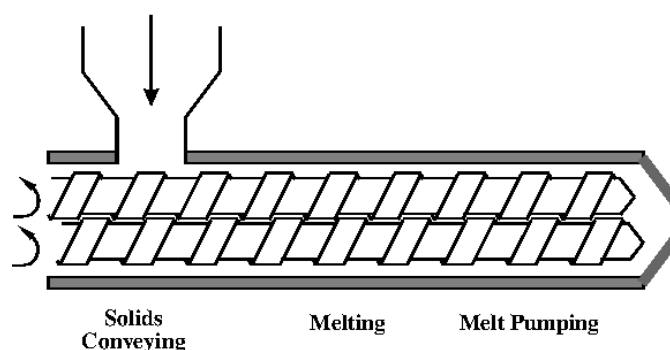


Figure 2.43. Schematic diagram of a twin-screw extruder

Co-rotating offers high precision, while counter-rotating is more suitable for compounding. The main advantages of the twin screw system include a reduction in processing time, a shorter residence time of the material in the barrel (limiting degradation) and a forced flow of material rather than by entrainment. In the melting process, unlike the single screw, there is no clear separation between solid and melt. The pellets start to plasticize on contact with the heated barrel, while the solids are suspended in the melt until they become completely viscous. This system is particularly useful in compounding, where the screw profile is modified with elements that improve the mixing and dispersion of the materials.

There are two types of mixing: distributive (which distributes the particles in the melt) and dispersive (which reduces the agglomerates into smaller particles). The latter increase the contact area thus improves the interaction between the particles and the composite matrix.¹⁵⁰ Finally, the twin-screw extruder can also be used as a chemical reactor, taking advantage of its flexibility and the ease of programming compared to traditional reactors.¹⁵¹

2.13 Micro compounder

Formulation development at the laboratory scale is conventionally performed using small-scale internal mixers and twin-roller mills (Figure 2.44).

¹⁵⁰ Gogos, C. G.; Liu, H.; Wang, P. Laminar dispersive and distributive mixing with dissolution and applications to hot-melt extrusion. In *Hot-Melt Extrusion: Pharmaceutical Applications*; 2012; pp 261-284.

¹⁵¹ Valle, G. D.; Colonna, P.; Tayeb, J. *Starch-Stärke* **1991**, 43(8), 300-307.



Figure 2.44. Micro-compounder

Laboratory-scale micro compounders offer advantages such as single-person operation, ease of use, less labor intensity, and rapid compound preparation (usually around 5 minutes). Furthermore, only small amounts of materials are required, beneficial to prepare compounds with expensive materials. The use of micro compounders is increasing in composite materials. For instance, formulation studies of ethylene propylene diene monomer (EPDM)/carbon black (CB) and EPDM/silica recipes have been performed, comparing a large-scale Banbury mixer and a laboratory-scale 15 mL high-torque twin-screw micro compounder.¹⁵² The use of the micro compounder improves significantly the silica dispersion allowing to a better quality of the composites in term of morphology, thermal behavior and mechanical properties. It has been demonstrated that this tool is useful for the mechanical recycling of degradable materials and how the implementation of an antioxidant in this type of sustainable extrusion is able to limit the thermomechanical degradation of PBS after repeated melt processing.¹⁵³ Another study showed that PET/FR compounds recycled with the micro-compounder exhibits reduced thermal degradation and improved homogeneity compared to those processed in traditional systems due to the micro compounder's more efficient mixing capabilities.¹⁵⁴ The high-torque twin-screw micro compounders at laboratory scale represent an innovative, sustainable and cost-effective tool for polymer preparation, processing and recycling.

¹⁵² YAZICI, N.; Kodal, M.; Özkoç, G. *Polymers* **2021**, 13 (24), 4391.

¹⁵³ Gammino, M.; Gioia, C.; Maio, A.; Scaffaro, R.; Lo Re, G. *ACS Appl. Polym. Mater.* **2024**, 6 (1), 1-12

¹⁵⁴ Bascucci, C.; Duretek, I.; Lehner, S.; Holzer, C.; Gaan, S.; Hufenus, R.; Gooneie, A. *Polym. Degrad. Stab.* **2022**, 195, 109783.

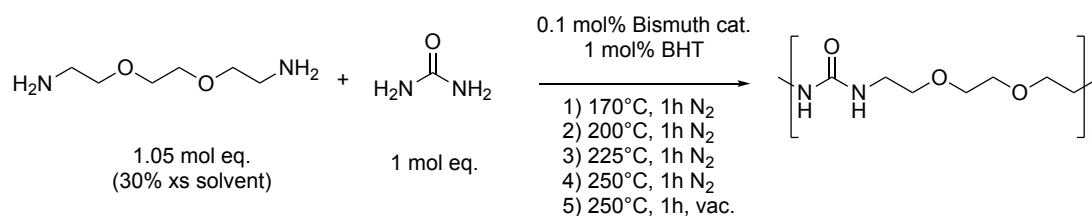
Experimental part

2.14 Aim of the work

This project is part of the work carried out in Arizona at the Biodesign Center for Sustainable Macromolecular Materials and Manufacturing, in the research group of Professor Timothy Long. The work focuses on the production of bio composites using hemp fibers as lignocellulosic reinforcements, and polyurea, as thermoplastic polymer matrix. The study aims to establish physico-chemical interactions between the reinforcement and the polymer matrix, through the reactive extrusion process, exploiting the functionality of a lab-scale micro compounder. Composite films with different weight percentages of hemp were extruded and the thermal and mechanical properties of the resulting film composites were evaluated. The ultimate goal is to develop a sustainable material, with a bio-based component that reduces the employment of polymers while maintaining high performances and properties comparable or greater to those of the virgin polymer.

2.15 Polyurea synthesis

Polyurea was synthesized through polycondensation of 2,2'-(ethylenedioxy)bis(ethylamine) (EDEA) with urea following a procedure known in literature (Scheme 2.19).¹⁵⁵ Urea, a bio-based monomer, provides a cheap and renewable feedstock to generate a non-isocyanate polyurea under melt polycondensation conditions with diamine in absence of solvent (Figure 2.45).



Scheme 2.19. Polyurea synthetic pathway

¹⁵⁵ Dennis, J. M.; Steinberg, L. I.; Pekkanen, A. M.; Maiz, J.; Hegde, M.; Müller, A. J.; Long, T. E. *Green Chem.* **2018**, 20 (1), 243–249.

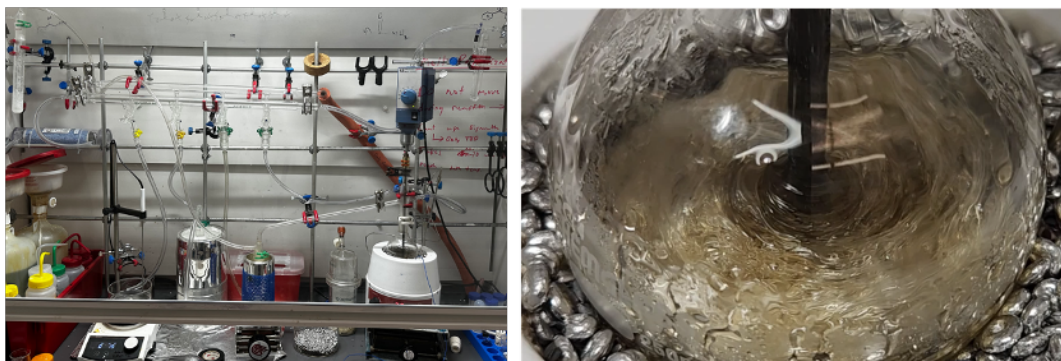


Figure 2.45. Melt-polycondensation synthesis of polyurea

To increase the processability of the obtained polyurea (Figure 2.46, image a) and allow a better interaction with the lignocellulosic matrix, the polyurea thus obtained was purified by dissolution in water and reprecipitation in acetone. The process was then followed by filtration (Figure 2.46, image c) and the obtained white granular powder was vacuum oven-dried at 80°C overnight.

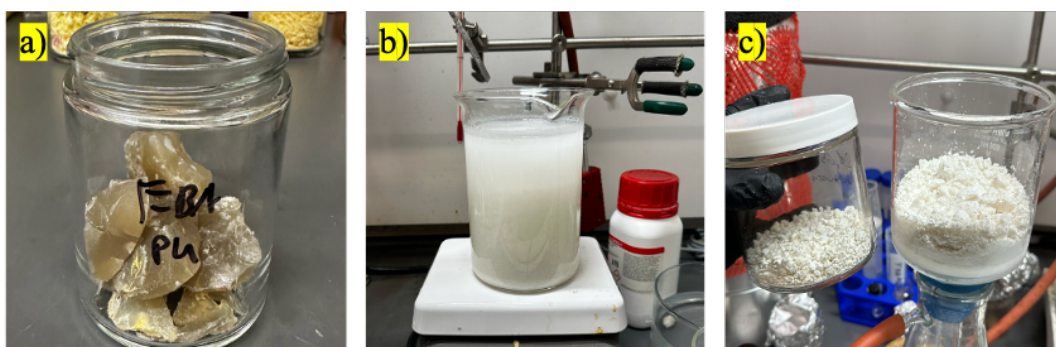


Figure 2.46. Purification process of polyurea

2.16 Hemp fiber treatment

Degummed hemp fibers (Figure 2.47, image a) were purchased from BIOPHIL Natural Fibers, a manufacturer of organic raw materials, operating in Lumberton, North Carolina. Degumming is a process for removal of phospholipids and other vegetable oils to improve physical stability and facilitate further processing.¹⁵⁶ The matrix was then used without further treatments. To facilitate processability during extrusion, the fibers were ground with a cryo-mill, CG-200 Freezer/Mill® 6775 (Figure 2.47, image b), and

¹⁵⁶ Chew, S. C.; Nyam, K. L. Kenaf (*Hibiscus cannabinus* L.) Seed Oil. In *Fruit Oils: Chemistry and Functionality*; Ramadan, M. F., Ed.; Springer: Cham, 2019; pp 451–494

reduced to microfibers with a variable length range from 40 to 80 μm (evaluated by SEM analysis).



Figure 2.47. Hemp fiber processing

2.17 Extrusion process

A lab-scale twin-screw micro-compounder (Xplore MC15 HT Micro Compounder) was used to prepare the hemp-based composites (Figure 2.48). The purified polyurea and grounded hemp were fed to the compounder. The mixing temperature parameter applied during the extrusion is 175°C, above the T_m of polyurea ($T_m = 131^\circ\text{C}$) and below degradation temperature of polyurea ($T_{d,5\%} = 332^\circ\text{C}$) and hemp ($T_{\text{Max}} = 217^\circ\text{C}$). The screw speed used is 250 rpm. The extruded films were then collected and annealed at 60°C before characterization.

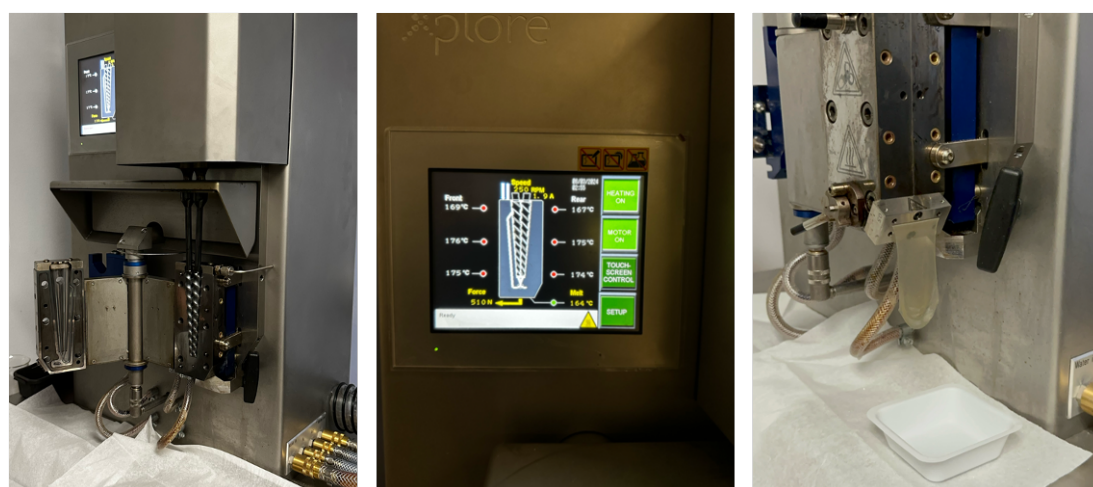


Figure 2.48. Reactive extrusion process of hemp-polyurea films

Polyurea composite films reinforced with hemp were produced at various content levels: 0 - 1 - 2.5 - 5 - 10 - 20 - 30 - 40 wt.%. The highest cellulosic reinforcement content used was 40 wt.%. A trial was also performed at 50 wt.% hemp, but the extruder became clogged due to the high percentage of lignocellulosic material. This block compromised the fluidity and proper mixing between the screws, preventing effective compounding.

2.18 Thermal studies of extruded composites

Thermal studies of composite samples were evaluated by TGA and DSC analyses using TGA 5500 and DSC25000 testing devices. The thermogravimetric analysis was conducted over a temperature range of 23 °C to 700 °C, with a heating rate of 10 °C/min, under a nitrogen flow of 50 ml/min (Figure 2.49).

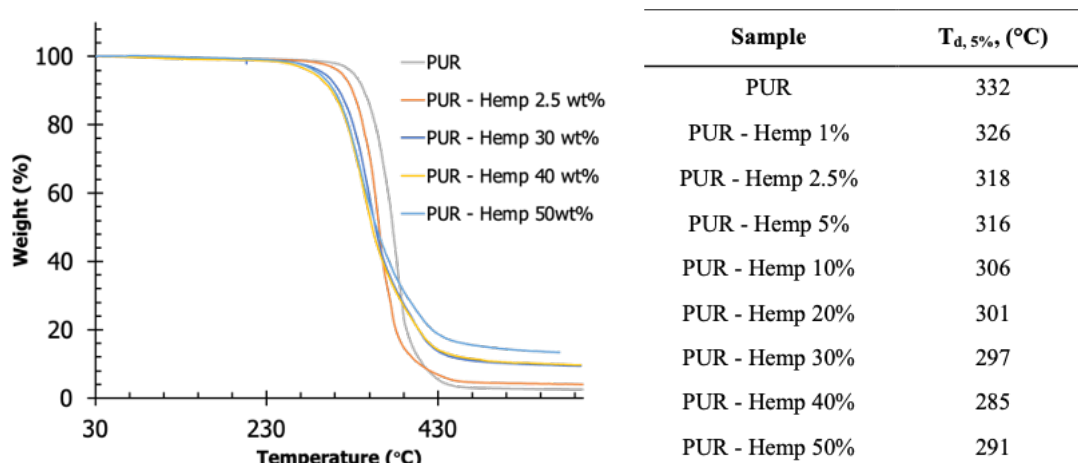


Figure 2.49. TGA thermograms and data of hemp composites

Degradation temperatures at 5 wt.% loss of hemp composites decrease with the increase of hemp loading. This can be due to the lower thermal degradation temperatures associated with the natural fiber, composed of cellulose, hemicellulose, and lignin which can negatively affect the thermal stability of the whole composite.¹⁵⁷ In addition, excessive fiber content can create non-uniform distribution within the matrix and poor interfacial adhesion which affects crystallinity and leads to a heterogeneous structure more susceptible to thermal degradation.¹⁵⁸

¹⁵⁷ Pradhan, D.; Jha, K.; Alagirusamy, R.; Zhang, J.; Dehghani-Sanij, A. *Polymers* **2022**, *14* (3), 481.

¹⁵⁸ Kumar, A.; Kumar, V.; Kumar, R.; Singh, S.; Sharma, D. *Polym. Eng. Sci.* **2022**, *62* (9), 2183-2200.

To better understand the implications of an increase in the fiber content and to provide a clear explanation of fiber-polymer interaction, DSC analysis was conducted. The differential scanning calorimetry analysis was performed through a heat cool heat program, with a heating rate of 10 °C/min, from -80 to 200°C (Figure 2.50) and the results are shown in Table 2.13.

Table 2.13. DSC data of hemp composites

Sample	T _g (°C)	T _c (°C)	T _m (°C)
PUR	15	99	131
PUR-Hemp 1%	13	97	128
PUR-Hemp 2.5%	11	96	128
PUR-Hemp 5%	13	97	129
PUR-Hemp 10%	16	89	122
PUR-Hemp 20%	17	89	122
PUR-Hemp 30%	22	101	120
PUR-Hemp 40%	13	88	119
PUR-Hemp 50%	13	-	118

Based on the DSC data of hemp composites, the melting temperature of polyurea was not affected by the addition of hemp for low concentrations whereas, a reduction in intensity and area of the endothermic peak was obtained for from PUR-Hemp 20% onwards which may stem from the decrease in polymer-reinforcement interaction.¹⁵⁹

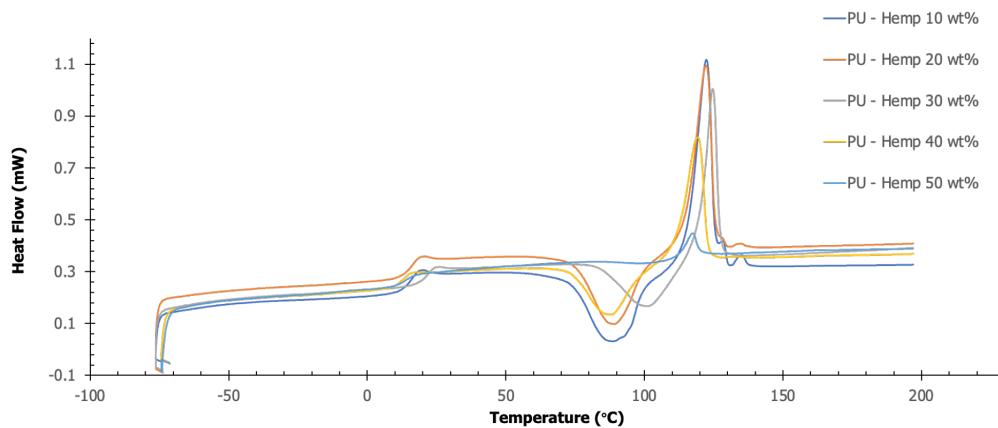


Figure 2.50. DSC curves of hemp composites

¹⁵⁹ Akar, A. Ö.; Yıldız, Ü. H.; Tayfun, Ü. *Conf. Proc.* **2023**, 2607 (1), 8.

The change in T_c shows no statistical changes in different hemp percentage composites, except for the PUR-Hemp 50% sample, for which no crystallization was detected. However, the increase in fiber reinforcement causes a certain increase in T_g (to 16, 17 and 22 for PUR-Hemp 10-20-30 wt% respectively) respect to T_g recorded for the pure polymer of 15 °C. The reason for increased T_g can be explained by the compatibility and interaction between the reinforcement and the polymer matrix which can restrict polymer chain mobility. Numerous studies have confirmed that polymers with high glass transition temperatures (T_g) have greater dimensional stability.¹⁶⁰

2.19 Mechanical studies of extruded composites

Tensile tests on dog bone samples, made with Exacta hand operated toggle press (Model JFP), of extruded polyurea composites were carried out, in accordance with ASTM standards, to investigate and compare the mechanical properties of the composites as a function of hemp percentage. Samples were annealed before testing, 60°C under vacuum for 2 hours. Tensile test parameters of composites are visualized by characteristic stress–elongation curves as displayed, and the relevant tensile test data are summarized in Table in Figure 2.51.

¹⁶⁰ Kumar, P.; Kumar, A.; Singh, S.; Sahu, A.; Gupta, P. K.; Kumar, V. *Sci. Rep.* **2023**, *13* (1), 5585

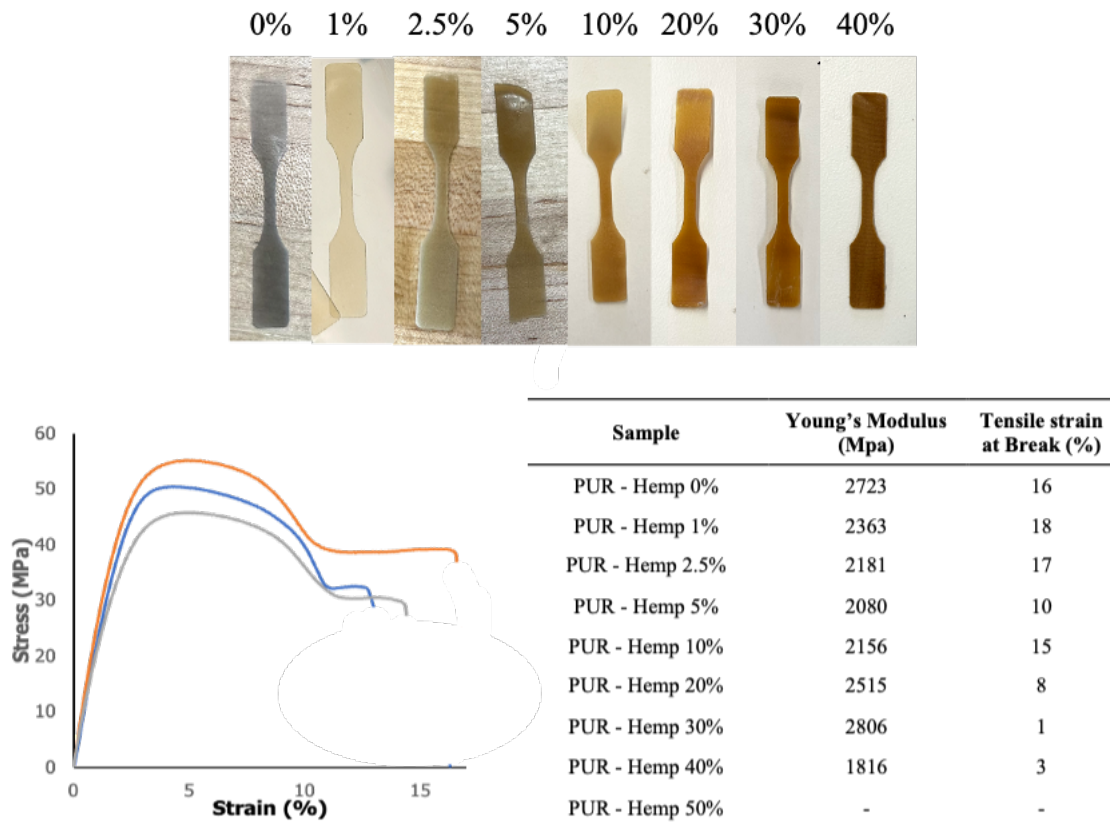


Figure 2.51. Tensile test samples, curves and data of hemp composites

Tensile test shows no statistical changes in different hemp percentage composites. The general trend shows a slight increase in tensile modulus as the percentage of hemp used increases. The highest Young's modulus depicted is that of the PUR - Hemp 30 wt. %, in which the value reached, of 2808 MPa, is comparable to the one of pure polyurea. Higher percentage of fibers leads to an overall increase in mechanical strength, but at the same time Tensile strain at the Break was affected negatively by hemp additions, sign its increase makes the polyurea stiffer and less ductile material.

2.20 Fracture surface morphology studies

Scanning electron microscopy (SEM) was used to examine the fracture surface of the tested specimens. SEM micrograph at 2000 x magnification of fractured surface of polyurea filled with 0-5-10-20-30-40 wt.% of hemp were shown in Figure 2.52.

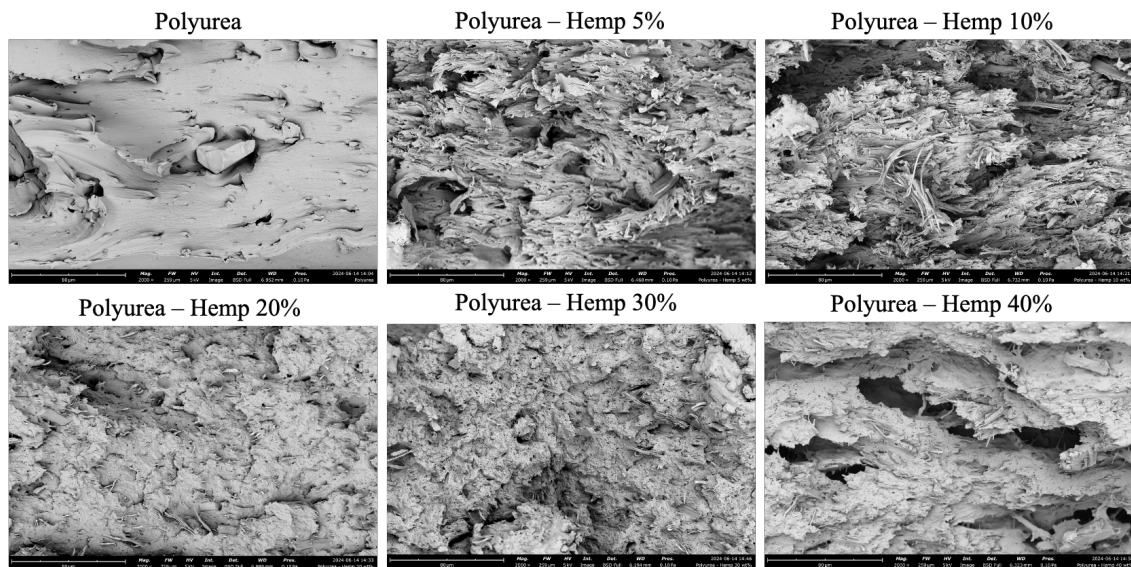


Figure 2.52. SEM images of fracture surfaces of hemp composites

The images of cross-sectional fracture morphology correlate with tensile test results. The breaking surfaces of the samples relating to 5-10 wt% of hemp appear not homogeneous and it is possible to distinguish the fibers from the polymer matrix, sign of poor interaction, which explains and confirms the low Young's modulus obtained for both samples. On the other hand, the samples at 20-30 wt% of hemp, present a more homogeneous cross-sectional surface. The fibers appear to have better wettability and interaction with the polymer, factors also evidenced by a higher Young's modulus. The last sample examined, PUR – Hemp 40 wt%, is characterized by a homogeneous surface in terms of fiber and matrix synergy but presents pores due to high content of hemp, which is easily correlated to the drastic decrease in Young's modulus in the tensile test analysis.

2.21 Conclusion

In summary, the study demonstrates that hemp can be successfully incorporated into polyurea composites, improving some mechanical properties such as stiffness, but also presenting challenges related to thermal stability. An optimal balance of the lignocellulosic content is crucial for a good fiber dispersion, which is required to preserve and enhance the properties of the composite. The composite with 30 wt.% hemp shows the best overall mechanical properties leading to a good compromise between performance and sustainability. An in-depth study on processing techniques and/or the use of a chemical functionalization treatment ad hoc for the natural fiber, could help to increase the compatibility with the polymer and enhance the properties of hemp-reinforced polyurea composites, leading to an ideal development of sustainable bio composite materials with unique performances.

3 Chapter 3: Synthetic polymers from bio-derived monomers

PART I: Bio-based Polyurethane acrylate

3.1 Polyurethane acrylate (PUA)

Polyurethanes (PUs) are a unique group of polymeric materials characterized by a wide variety of chemical composition and application. These materials are used in paints, coatings, elastomers, insulators, elastic fibers, and foams. The basic PU repetition unit is the urethane group (Figure 3.1) which is formed through the reaction between a diol or polyol which can be ether or ester based, with a diisocyanate (composed of a cyanate with two reactive groups -NCO) or with a polyfunctional isocyanate in the presence of catalysts.¹⁶¹

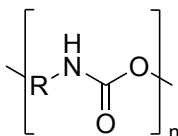


Figure 3.1. PU repeating unit

The versatility of these polymers mainly comes from the phase separation between hard and soft segments and the hydrogen bond between the urethane groups. First discovered by Bayer in 1937, PUs can be processed into a wide range of products, from thermoplastic polyurethanes to thermosetting resins, used in many industrial applications.¹⁶² Among different types of polyurethane, acrylated polyurethanes (PUAs) represent a particularly interesting class of materials. Those combine the properties of polyurethanes, such as elasticity and mechanical strength, with those of acrylates, known for their high reactivity and ability to form crosslinks under UV radiation. This combination makes them ideal for applications requiring rapid curing and chemical resistance, such as coatings, adhesives and sealants. Furthermore, the use of bio-based

¹⁶¹ Islam, M. R.; Beg, M. D. H.; Jamari, S. S. *J. Appl. Polym. Sci.* **2014**, 131.

¹⁶² Delebecq, E.; Pascault, J.-P.; Boutevin, B.; Ganachaud, F. *Chem. Rev.* **2013**, 113, 80-118.

3.1.1 General informations

- Step 1 - Polyaddition reaction between an excess of isocyanate and a polyol in presence of catalyst.
- Step 2 - Acrylation with an end-capping agent, such 2-hydroxyethyl methacrylate (HEMA).
- Step 3 - Radical polymerization by UV radiation of end-capped vinyl groups (Scheme 3.1)



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optimizing the synthesis and performance of polyurethane-acrylate by modulating the chemical structure. This includes considering the nature and concentration of the starting materials, the consequent hard/soft segment ratio, and the type of acrylate employed.

3.1.2 Polyols

Polyols are organic molecules that can be grouped into two important class: polyether and polyester polyols. Polyether can be obtained from the reaction between an epoxide and an active hydrogen-containing compound but also from the ring-opening polymerization of epoxy monomers.¹⁶³ These are characterized by low temperature properties, hydrolytic stability ad resistance to fungal attack. While polyesters can be obtained from the polycondensation of hydroxyl compounds and multifunctional carboxylic acids, and possess properties such as toughness, polarity to the resin, high tear strength, resistance to ozone and abrasion. Furthermore, polyols can be classified on base of their molecular weight. Polyols with molecular weights below 2000Da are used to make rigid PUs, while higher molecular weights (from 2000 to 10000Da) lead to the formation of more flexible polyurethanes.¹⁶⁴

Different types of polyols from non-renewable resources can be used as starting materials for PUA synthesis such as: polyethylene glycol (PEG) a non-toxic, inert, and non-volatile polymer as well as polypropylene glycol PPG more hydrophobic compared to polyethylene glycol, due to the presence of methyl groups in the propylene oxide units. (Figure 3.2).

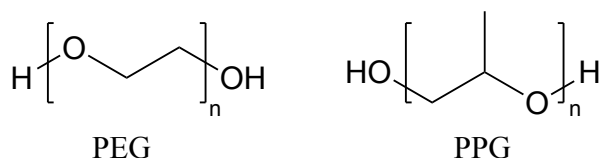


Figure 3.2. PEG and PPG structures

In the last years, the research has focused the attention on polyols obtained from natural and renewable sources, such as vegetable oils. Polyester polyols with linear structures

¹⁶³ Brocas, A.-L.; Mantzaridis, C.; Tunc, D.; Carlotti, S. *Progr. Polym. Sci.* **2013**, 38, 845-873.

¹⁶⁴ Tersac, G. *Polym. Int.* **2007**, 56, 820-820.

are usually produced by condensation polymerization of dicarboxylic acids, their esters or anhydrides with bio-based polyols or diols. Bio-based dicarboxylic acids can be easily obtained (Figure 3.3):

- From yeast fermentation of sugars, as succinic acid, **1**
- By oxidation of oleic acid, as azelaic acid, **2**
- From castor oil, as sebacic acid, **3**

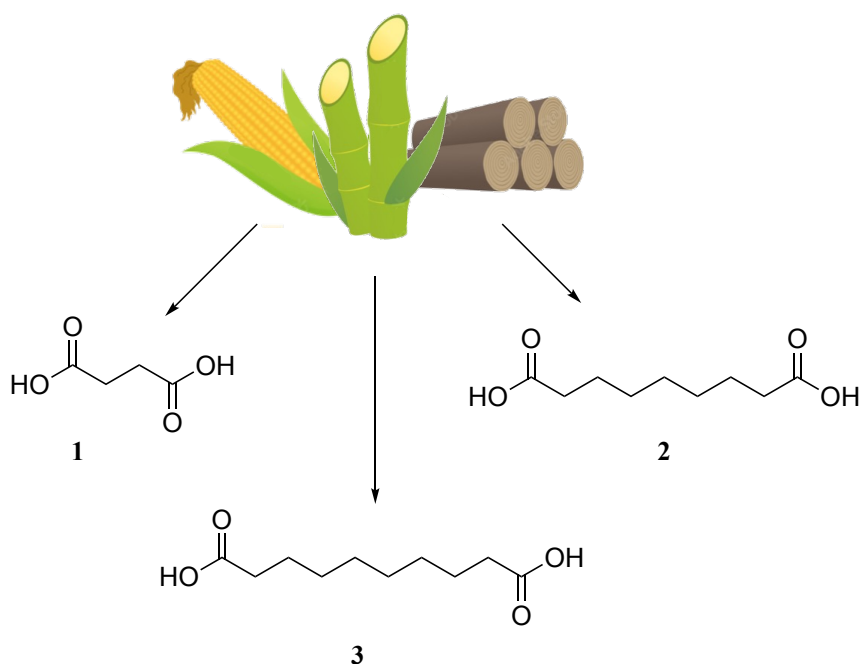


Figure 3.3. Bio-based dicarboxylic acids

The relative polyester polyols (Figure 3.4), obtained from polycondensation of dicarboxylic acids and bio-diols (such as diethylene glycol, 1,4-butanediol, etc.), are more sustainable and biodegradable than their synthetic counterparts.

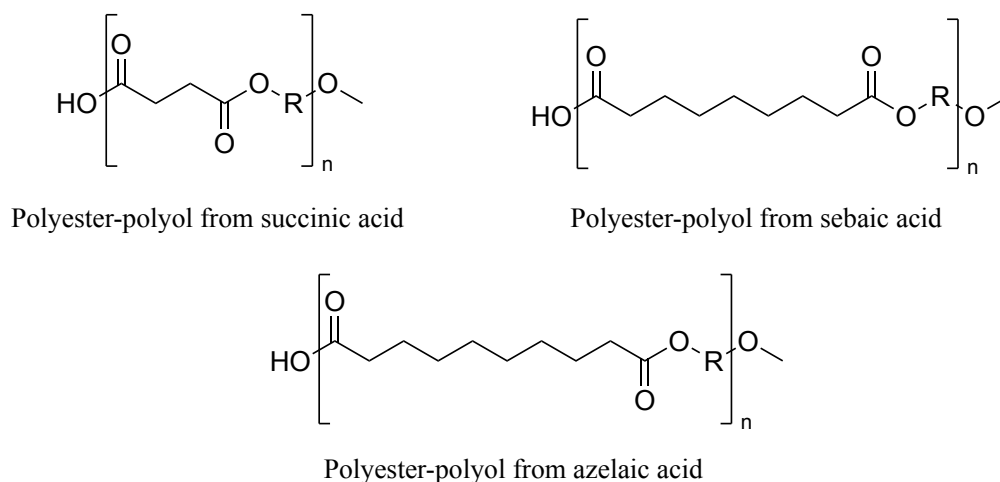


Figure 3.4. Bio-based polyester-polyols

Depending on the type of polyol structures, they can be classified into aliphatic and aromatic polyester polyols. The latter provide higher rigidity and are commonly used to produce flame-retardant rigid PU foams. While aliphatic polyester polyols are usually used to produce PU elastomers, flexible foams, and adhesives.

3.1.3 Isocyanates

Isocyanates are a class of compound fundamental for the preparation of polyurethane. They can be classified in relation to the number and type (aromatic or aliphatic) of functionalities. Among aromatic diisocyanates the most used are toluene diisocyanate (TDI) and methyl diphenyl diisocyanates (MDI) (Figure 3.5).

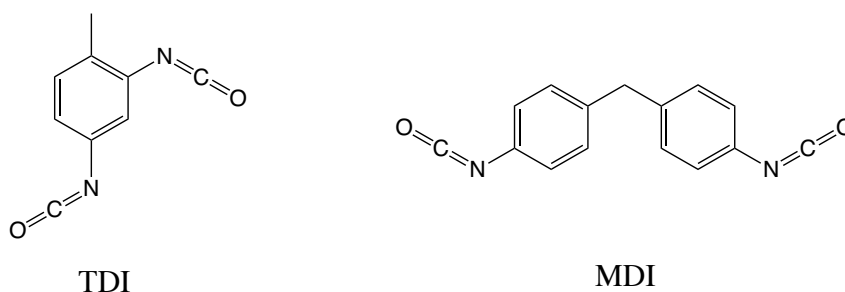


Figure 3.5. Structure of TDI and MDI

Aliphatic and cycloaliphatic isocyanates (Figure 3.6), such as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) are much less reactive than the

aromatic ones and they are more suitable for the synthesis of biodegradable polyurethanes finding application mostly in the sector of coating.¹⁶⁵

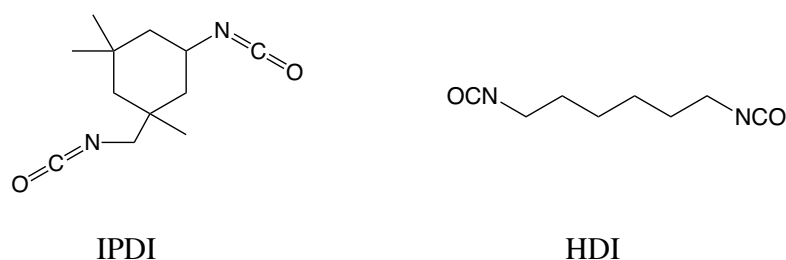


Figure 3.6. Structure of IPDI and HDI

It is possible to modify the isocyanates structure by incorporation of specific compounds to reduce their volatility and the toxicity. Currently, almost all bio-based PUs is produced from bio-based polyols and petroleum-based isocyanates with properties comparable to non-renewable ones. Only recently the research focused on the development of isocyanates from renewable resources, mostly in the synthesis of isocyanate based on fatty acid, lignin, and vegetable oil. For example, a dimer fatty acid isocyanate with 36 carbon atoms has been synthesized and commercialized for the development of UV curable coating. Also, oleic acid-based diisocyanates with and without carbon double bonds have been made by Curtius rearrangement showing good potential for producing PUs with comparable properties to those obtained from non-renewable sources.¹⁶⁶

Many efforts have been made in the production of bio-based diisocyanates for a sustainable synthesis of PUs with the aim of minimizing or eliminating the production of toxic degradation products. In this regard, esters of Lysine diisocyanate (Figure 3.7) in 50% of yield were synthesized from methyl or ethyl esters of Lysine, a natural amino acid.^{167,168}

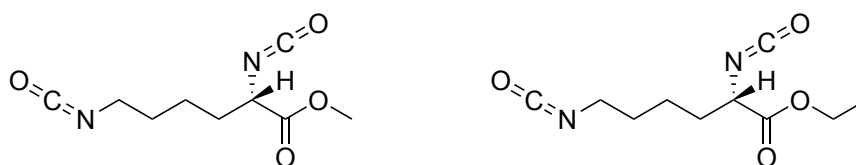


Figure 3.7. Structure of methyl and ethyl ester of Lysine diisocyanate

¹⁶⁵ Choe, H.; Kim, J. H. *J. Ind. Eng. Chem.* **2019**, *69*, 153-160.

¹⁶⁶ Hojabri, L.; Kong, X.; Narine, S. S. *Biomacromolecules* **2009**, *10*, 884-891.

¹⁶⁷ Jian H., Lin, Y., Ai-ying, Z., Jian, Z., Zeng-guo, F. *Front. Mater. Sci.* **2009**, *3*, 25-32.

¹⁶⁸ Zhang, J.-Y.; Beckman, E. J.; Hu, J.; Yang, G.-G.; Agarwal, S.; Hollinger, J. O. *Tissue Eng.* **2002**, *8*, 771-785.

3.1.4 End-capping agent

Once the NCO-terminated pre-polymer is formed, an end capping agent containing an hydroxyalkyl acrylate functionality is needed to form the urethane acrylate oligomer. Among them 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) are widely used in the production of PUA (Figure 3.8).

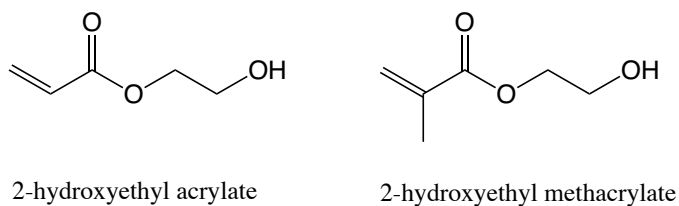


Figure 3.8. Structure of HEA and HEMA

The nature and ratio of the end-capping agent influence the properties of the PHA obtained, while always maintaining the biocompatible character. However, it should not be forgotten that the use of 2-hydroxyethyl acrylate requires strictly controlled conditions of use due to several risks it can bring to human health.¹⁶⁹

3.1.5 Reactive Diluents

Reactive diluents are generally used in PUA synthesis to control the progress of the polymerization reaction and to obtain the desired final properties. In this regard, they are useful to control the viscosity and the crosslink density, to improve processability, strength, shrinkage, and chemical resistance. It is important that diluents present characteristic such as good solvent power, low viscosity, low toxicity, desired physical properties after curing, low odor and low cost.

¹⁶⁹ Maurya, S. D.; Kurmvanshi, S. K.; Mohanty, S.; Nayak, S. K. *Polym. Plast. Tech. Eng.* **2018**, 57, 625-656.

3.2 Photo-polymerization, UV curing

UV-curing or photo-polymerization technique has received increasing attention over the years. It is a process in which ultraviolet light is used to initiate a photochemical reaction that generates a crosslinked polymer. Compared to other technologies, the UV-curing could be considered a green polymerization method that provides low-temperature (reduction of energy consumption), high-rate and solventless process because cure occurs via direct polymerization and not by evaporation.^{170,171}

UV-curing polymers consist of a three-dimensional network, due to the formation of cross-link bonds after exposure to light. The main components are monomers or oligomers (for example epoxy acrylates, urethane acrylates, polyether urethane acrylates, polyester acrylates, polyether acrylates and acrylate oils) and photo-initiators able to absorb light leading to the formation of reactive species (free radicals or ions) that start the polymerization reaction (Figure 3.9).¹⁷²

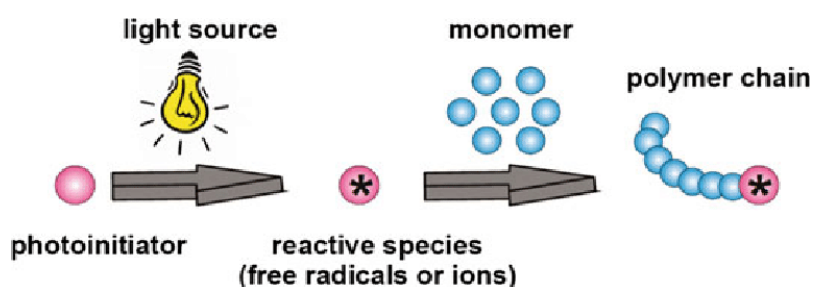


Figure 3.9. Photopolymerization process

There are two general ways for photoinitiation: free radical and ionic.

- Ionic polymerization

In ionic curing processes, an ionic photo-initiator is used to activate the functional groups of the oligomers that became suitable for UV-polymerization. Most ionic photo-initiators are cationic: onium salts, organometallic compounds and pyridinium salts (Figure 3.10).

¹⁷⁰ Carroll, G. T.; Devon Triplett, L.; Moscatelli, A.; Koberstein, J. T.; Turro, N. J., *J. Appl. Polym. Sci.* **2011**, 122, 168-174.

¹⁷¹ Stowe, R. *Int. Soc. Opt. Eng.* **1996**, 2831, 208-219.

¹⁷² Kunwong, D.; Sumanochitraporn, N.; Kaewpirom, S. *J. Sci. Technol.* **2011**, 33, 201-207.

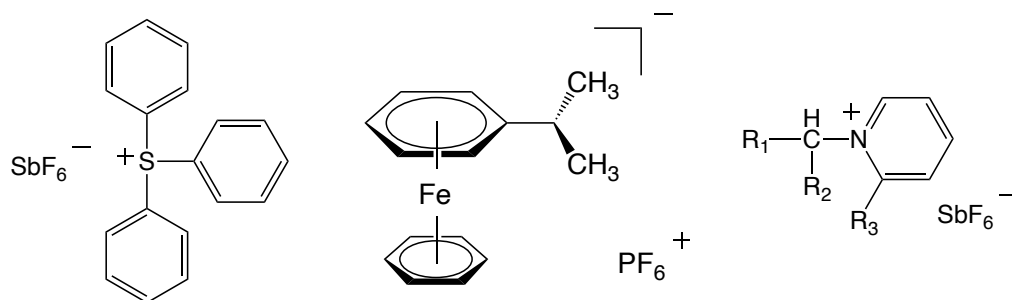


Figure 3.10. Examples of ionic photo-initiators

Several compounds are activated by cationic photo-initiators, the most employed in industry are epoxides, oxetanes, and vinyl ethers. The main advantage of cationic photopolymerization is that, once the polymerization initiated, it is no longer sensitive to oxygen and does not require an inert atmosphere.¹⁷³ Few studies have been done on anionic polymerization. Many of them are related to UV-curing of cyanoacrylates, in which isocyanate ions, generated through ligand exchange reaction upon photolysis, were the initiating species.¹⁷⁴

- Free-radical polymerization

The free radical polymerization process is a highly efficient method in which a polymer is formed through different mechanisms involving radical species. The process is divided into three stages: initiation, propagation, and termination steps. To start the polymerization, initiators must be added into the system containing the monomers. Radical photo-initiators can be classified depending on their reaction mechanism into different categories: bond α -cleavage type (*Norrish type I*) and hydrogen abstraction type (*Norrish type II*).

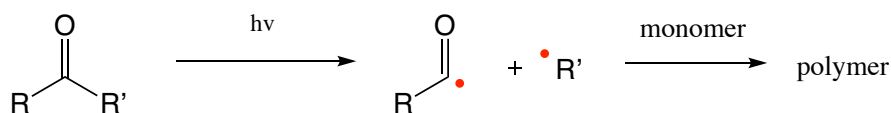
1. Bond α -cleavage type (*Norrish type I*)

The photochemical cleavage consists of the homolysis of photo-initiator, aldehyde or ketone, into two free radical intermediates which are highly reactive species. These radicals then initiate the polymerization (Scheme 3.2).¹⁷⁵

¹⁷³ Crivello, J. V.; Reichmanis, E. *Chem. Mater.* **2014**, 26, 533-548.

¹⁷⁴ Kutal, C.; Grutsch, P. A.; Yang, D. B. *Macromolecules* **1991**, 24, 6872-6873.

¹⁷⁵ Scaiano, J. C.; Stampeleskie, K. G.; Hallett-Tapley, G. L. *Chem. Commun.* **2012**, 48, 4798-4808.

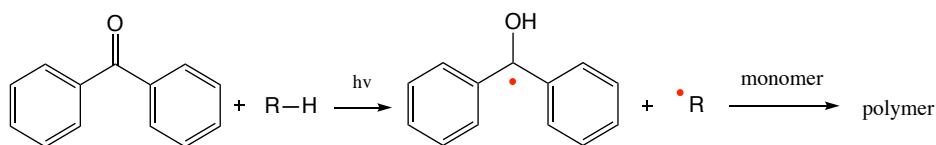


Scheme 3.2. Norrish type I mechanism

2. Hydrogen abstraction type (*Norrish type II*)

These types of initiators, when irradiated by UV-light, require the combination with hydrogen donor species. Under UV irradiation the Norrish II photo-initiator abstracts a hydrogen atom from the combine species, leading to the formation of two radicals that initiate the polymerization process (Scheme 3.3).

In Scheme 3.3, benzophenone, a Norrish type II initiator, leads to the formation of corresponding ketyl radical, relatively stable and typically not reactive towards vinyl monomers due to steric hindrance and delocalization of unpaired electron. In this case, co-initiators (hydrogen donors like methyl diethylamine) are used to rapidly produce reactive radical species capable of initiating the polymerization reaction.¹⁷⁶



Scheme 3.3. Norrish type II mechanism

In addition to benzophenone, other important photo-initiators are 4-benzoylbenzoic acid, 4,4'-bis(dimethylamino)-benzophenone, 1,4-dibenzoylbenzene, anthraquinone and many others (Figure 3.11).

¹⁷⁶ Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2010**, *43*, 6245-6260.

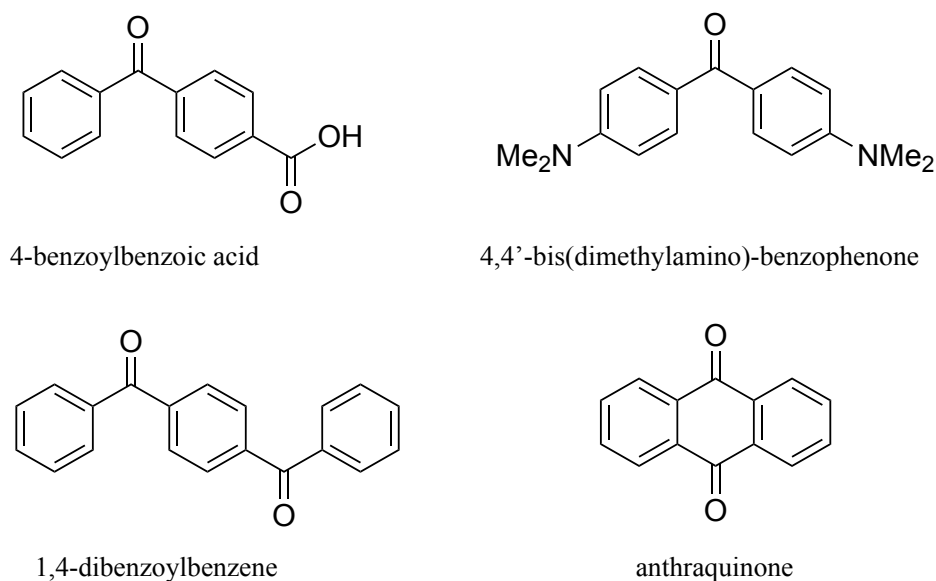
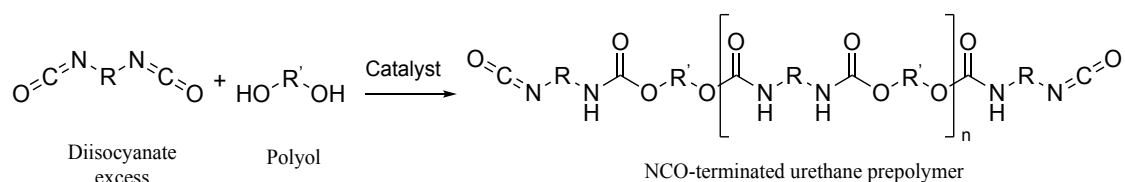


Figure 3.11. Examples of photo-radical initiators

3.3 Synthesis of UV-curable Polyurethane Acrylate (PUA)

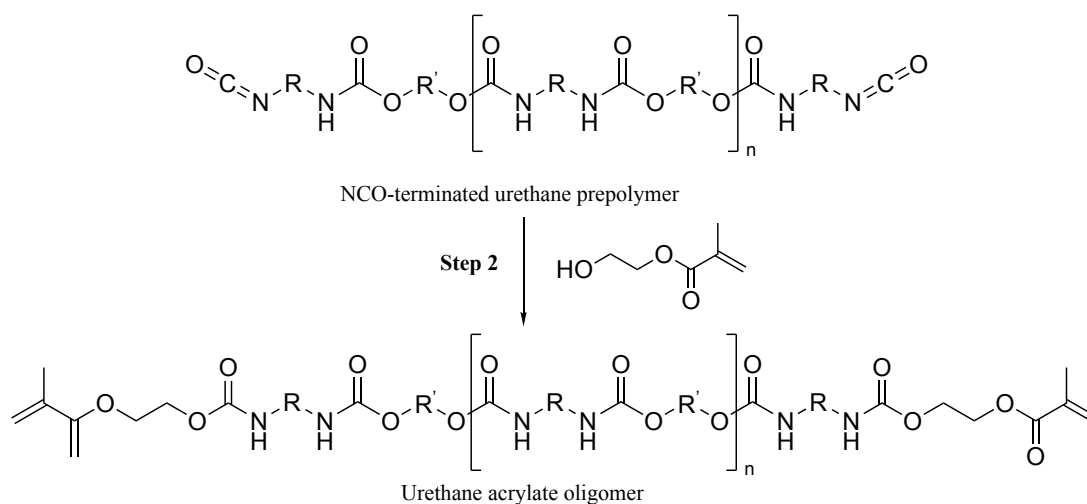
The starting building blocks of PUA are a polyether or polyester polyol that reacts with a diisocyanate in the presence of a catalyst, which allows to the formation of a pre-polymer with isocyanate end-groups. Then urethane acrylate oligomer (UAO) is obtained by adding an acrylate moiety.

The first step of the process is the reaction between the polyols with the diisocyanate molecules that leads to the formation of NCO-terminated urethane prepolymer (Scheme 3.4).



Scheme 3.4. NCO-terminated prepolymer formation

In the second step, an end-capping agent such as HEMA is added in order to obtain a urethane acrylate oligomer, UAO, (Scheme 3.5) suitable for the curing process.



Scheme 3.5. Urethane acrylate oligomer formation

The urethane acrylate oligomer is constituted by soft segments (SS) that include polyols with molecular weight between 550 Da and 4000 Da, and hard segment (HS) made up of diisocyanates and acrylates compounds. The soft part is responsible for the elasticity of the material, while the hard part acts as a reinforcer by regulating the degree of cross-linking. The chemical incompatibility between SS and HS leads to a phase separation into the polymer (Figure 3.12). However, by changing the nature, the molecular weight and the ratio between the soft and hard segments, the mechanical and physical properties of the final material can be controlled.

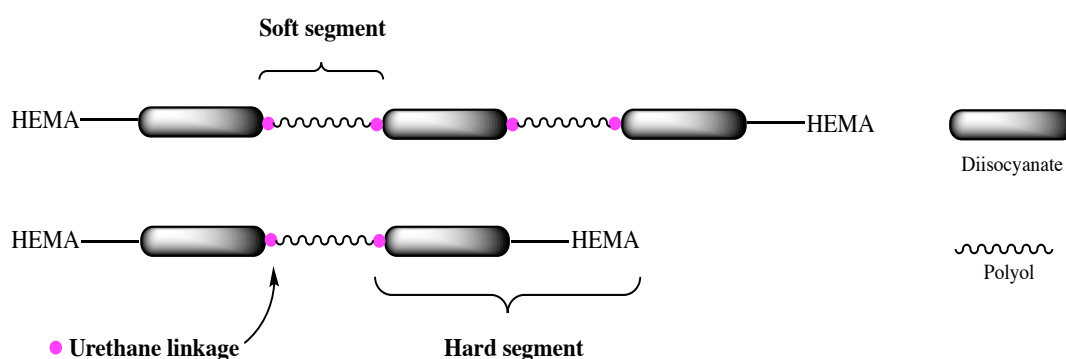
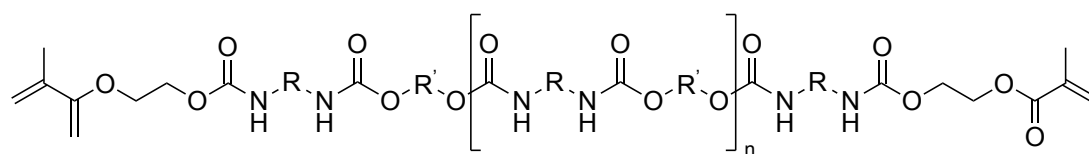


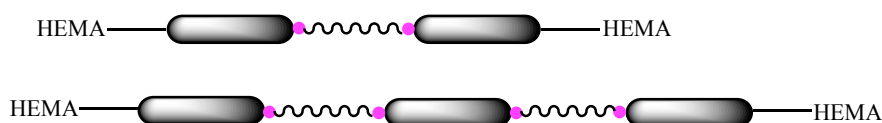
Figure 3.12. Hard/Soft segments in PUA

In the last step the radical polymerization occurs by exposing of the oligomer to UV radiation (Scheme 3.6). Thanks to the presence of the vinyl groups of the end-capping agent, UAO can be cross-linked in the presence of the initiators (such as benzophenone)

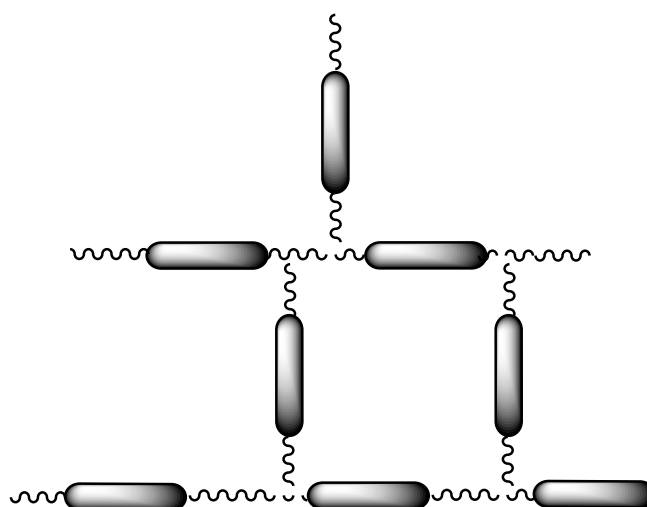
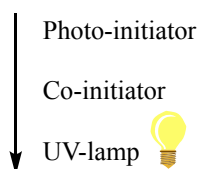
and co-initiators (such as methyl diethanolamine, triethylamine, or ethyl 4-dimethylamino benzoate).¹⁷⁷



Urethane acrylate oligomer



PUA oligomer



Scheme 3.6. UV-cured PUA synthesis

¹⁷⁷ Kowalska, A.; Sokolowski, J.; Bociong, K. *Polymers* **2021**, *13*, 1-17.

3.4 Catalysis

Catalysis refers to a process in which the rate of a chemical reaction is increased by the addition of a substance known as a catalyst. The latter is a substance used in a sub-stoichiometric amount and its role is to lower the activation energy of the reaction, increasing in this way the speed of product formation (Figure 3.13).

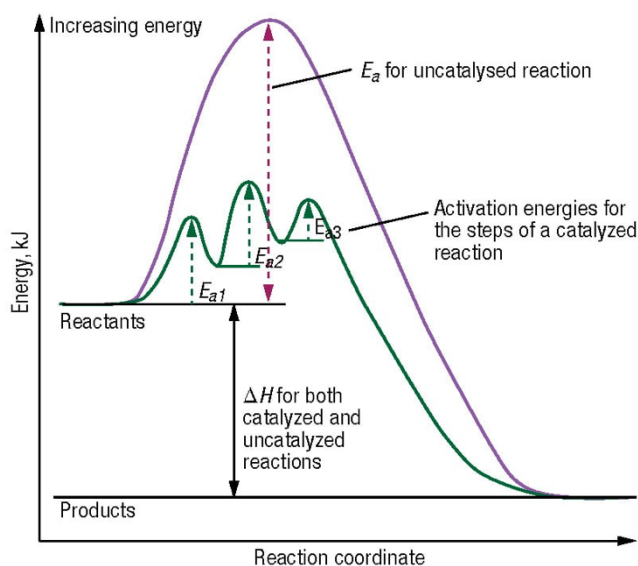


Figure 3.13. The activation energy graph

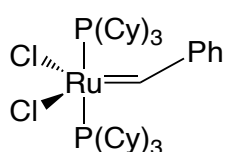
At the end of the reaction the catalyst remains unaltered unlike the reactants, which are consumed as it proceeds. However, the catalyst can progressively lose its effectiveness, expressed in terms of turnover number (TON) and turnover frequency (TOF).¹⁷⁸

Catalysis can be classified into three classes: *homogeneous*, where catalyst components are dispersed in the same phase of the reactants; *heterogeneous*, where catalyst components are not in the same phase of the reactants; *biocatalysts*, where catalyst components are represented by enzymes.

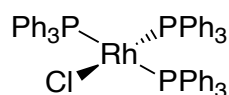
¹⁷⁸ Kozuch, S.; Martin, J. M. L. *ACS Catal.* **2012**, 2, 2787-2794.

3.4.1 Homogeneous catalysis

In homogeneous catalysis the catalyst is in the same phase of the reaction mixture. This type of catalysis involves the use of soluble metal complexes in which the transitional metal cation is stabilized by a ligand (usually an organic molecule) and changing the chemical nature of that ligand it is possible to obtain a catalyst with different properties. Organometallic complexes are the most used catalysts, and these are employed in both fine-bulk chemistry, as in the case of Grubbs catalyst and Wilkinson catalyst, useful for hydrogenation of olefin (Figure 3.14). This was true until a few decades ago, when organocatalysis began to develop, in which acceleration of chemical reactions with an organic small molecule that does not contain a metal. These organocatalytic reactions can represent important advantages over metal-catalyzed ones such as the danger that many metals are poisons and the characteristic that the metal-free reactions can typically be run under aerobic conditions.¹⁷⁹ However, much more work is needed for organocatalysis to achieve many other advantages that metal-catalyzed reactions exhibit. When the catalysts and reactants are in the same phase, it offers the advantage of improved contact between the two, leading to enhanced catalytic activity. However, this also presents a drawback, as separating and recovering the catalyst becomes significantly more challenging. This is why homogeneous catalysis is not widely used in industrial scale with exception of the chemicals and pharmaceuticals industries.¹⁸⁰



Grubbs I



Wilkinson's catalyst

Figure 3.14. Grubbs I and Wilkinson's catalysts

¹⁷⁹ García Mancheño, O.; Waser, M. *Eur. J. Org. Chem.* **2023**, 26(1), e202200950.

¹⁸⁰ Cornils, B.; Herrmann, W. A. *J. Catal.* **2003**, 216, 23-31.

3.4.2 Heterogeneous catalysis

Heterogeneous catalysis involves the use of a catalyst in a different phase than the substrates. Generally, the catalyst is fixed onto a support, inert or reactive, which keeps it fixed in a solid state, avoiding its dispersion in the reaction mixture. This setup allows for easy separation of the catalyst from the reactants and products through enabling its recycling for further applications.

Heterogeneous catalysis is a surface phenomenon. This means that the reaction occurs at reactant-catalyst interface, and involves few elementary steps (Figure 3.15):

- *diffusion* (**A**) of reactants from bulk phase to the active sites of catalyst surface
- *adsorption* (**B**) of reactants on active sites,
- surface reaction (**C**),
- *desorption* (**D**) of products from the active sites and catalyst.

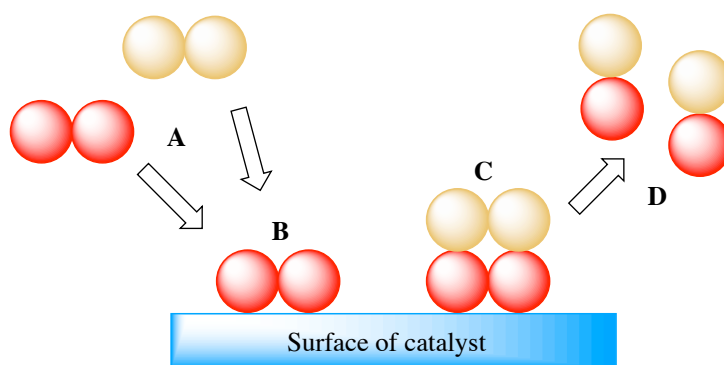


Figure 3.15. Heterogeneous catalysis

The most commonly used types of inorganics supports for heterogeneous catalyst includes amorphous support such as metal oxides, alumina, silica, and carbon; layered supports like clays, and macro or microporous supports, such as zeolites and polymers like Amberlyst and Amberlite.¹⁸¹

¹⁸¹ Ko, S.; Yao, C.F. *Tetrahedron Lett.* **2006**, 47, 8827-8829.

3.4.3 Bio-catalysis

Bio-catalysis refers to catalyzed chemical process in which is employed a biological system as catalyst. Natural catalysts, such as enzymes, perform chemical transformations through the interaction between the substrate and its active site, forming a complex. At the end of the reaction, the product can be separated from the catalyst which can be recovered and re-used for other catalytic cycles (Figure 3.16).

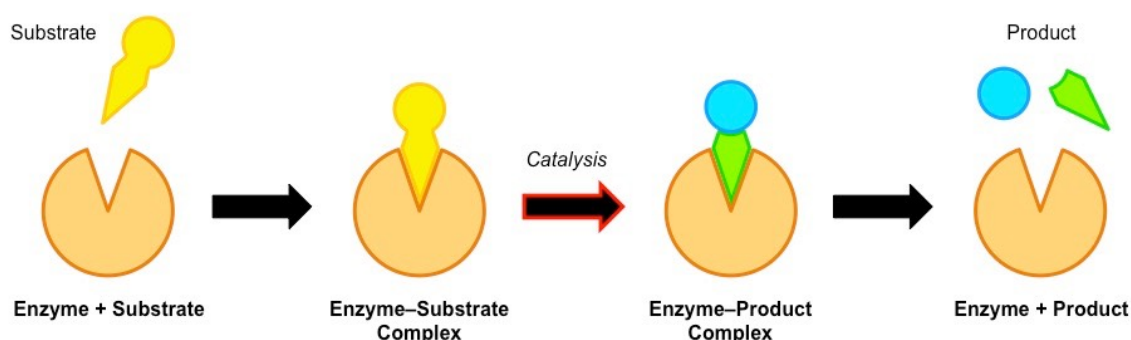


Figure 3.16. Mechanism of interaction between enzyme and substrate

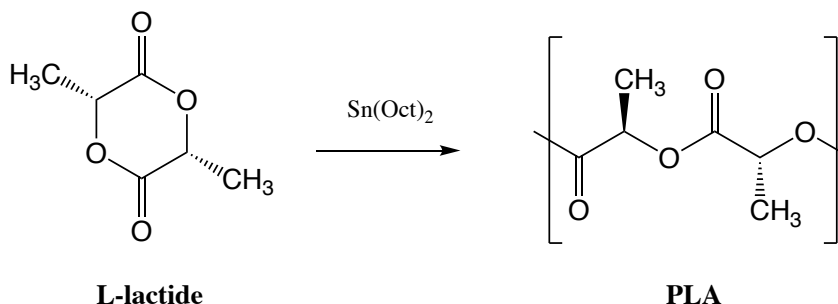
3.4.4 Lewis acid

Lewis acids catalysis play a fundamental role in organic reactions, and polymer synthesis. In this context, great interest has been devoted on exploring new generations of compounds. Among them, metal cations and covalent metal compounds are the most important. The latter acts as an electron pair acceptor in order to increase the reactivity of the formed adduct. Metal cations include:

- lithium (Li^+), sodium (Na^+), potassium (K^+), di- and trivalent ions such as magnesium (Mg^{2+}), calcium (Ca^{2+}), zinc (Zn^{2+}), indium (In^{3+}), scandium (Sc^{3+}) and bismuth (Bi^{3+}),
- transition metal cations and complexes,
- lanthanide cations, such as cerium (Ce^{3+}) and ytterbium (Yb^{3+}).

The most employed Lewis acid in polymerization reaction are tin-based catalyst. Several catalysts based on tin compounds (tin (II) acetate, tin (II) chloride, tin (II) 2-ethylhexanoate and tin (II) stearate) have been employed in transesterification and

esterification reaction to treat acid vegetable oils.¹⁸² The tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) is also used as catalyst in the ring-opening polymerization (ROP) of lactide in the synthesis of polylactic acid (Scheme 3.7).



Scheme 3.7. $\text{Sn}(\text{Oct})_2$ catalyst in ROP of lactide

The characteristics of this tin catalyst include high effectiveness, low costs, and stability during storage. However, $\text{Sn}(\text{Oct})_2$ shows a cytotoxic character, meaning it can be harmful to most living organisms (fungi, microbes, and animals) but its toxicity for humans is lower compared to other organotin compounds. Therefore, it has been approved as a food preservative by the American Food and Drug Administration.¹⁸³

Regarding the catalysis in the polyurethane synthesis process, one of the commonly used tin-based catalysts is the dibutyltin dilaurate (DBTDL) (Figure 3.17), active in the first step in which the polyol reacts with the diisocyanate to obtain the pre-polymer.¹⁸⁴

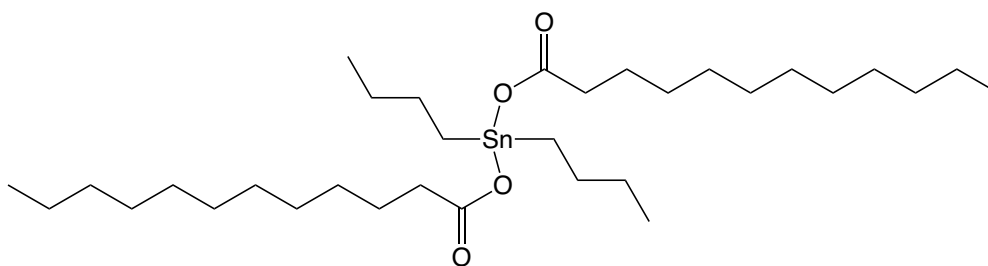


Figure 3.17. Structure of DBTDL

Even though tin-based catalysts are FDA-approved, studies on long-term liberation and physiological effects of tin ions from large tissue-embedded scaffold-matrices have not yet been conducted and which poses potential risks when used in the synthesis of

¹⁸² Casas, A.; Ramos, M. J.; Rodríguez, J. F.; Pérez, Á. *Fuel Process. Technol.* **2013**, 106, 321-325.

¹⁸³ Kricheldorf, H. R.; Weidner, S. M. *Polym. Chem.* **2020**, 11, 5249-5260.

¹⁸⁴ Xu, H.; Qiu, F.; Wang, Y.; Wu, W.; Yang, D.; Guo, Q. *Prog. Org. Coat.* **2012**, 73, 47-53.

compounds or polymers for biomedical applications. The possible adverse effects of tin catalysts stem from the fact that they remain trapped in the polymer matrix.¹⁸⁵ For this reason, research today is focused on finding eco-sustainable alternatives that can perform the same catalytic activity with less impact on humans and the environment. The interest is mainly focused on the development of cerium- and indium-catalysts.

- Cerium-based catalyst

Cerium is the most abundant element in the lanthanide's series, and it has been extensively used in its stable +3 and +4 oxidation states. Its potential derives from its strong biocidal and antibacterial properties, which have gained significant interest in the research field. Have been studied, in fact, the mechanisms of action underlying the use of CeO₂ nanoparticles for inducing oxidative death in bacterial cells have been studied, focusing on the direct contact between cerium oxide and the bacterial membranes (Figure 3.18).¹⁸⁶

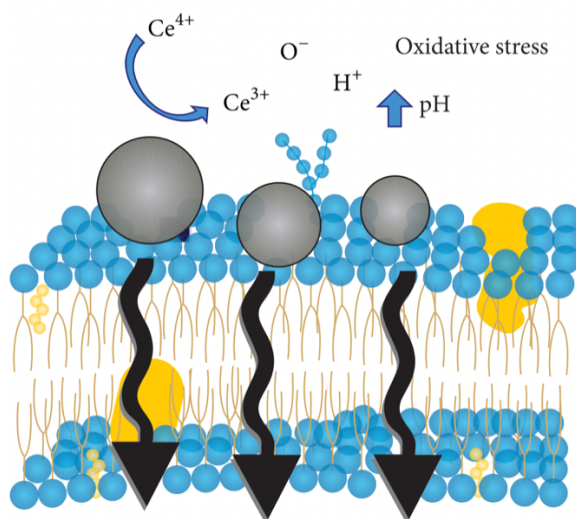


Figure 3.18. Antibacterial mechanism of CeO₂NPs

Cerium halides are effective Lewis acid catalysts, as they are water tolerant, non-toxic, easy to handle, inexpensive and can be reused without further purification. CeCl₃·7H₂O is an efficient catalyst for the synthesis of β -amino carbonyl

¹⁸⁵ Hege, C. S.; Schiller, S. M. *Green Chem.* **2014**, *16*, 1410-1416.

¹⁸⁶ Chatzimentor, I.; Tsamesidis, I.; Ioannou, M. E.; Pouroutzidou, G. K.; Beketova, A.; Giourieva, V.; Kontonasaki, E. *Pharmaceutics* **2023**, *15*(10), 2509.

compounds at room temperature through a one-pot reaction.¹⁸⁷ The latest research has shown that $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI is an effective catalytic system with non-toxic behavior toward PLLA synthesis, combined with its antibacterial activity, and this makes the compound a promising catalyst for bioengineering.¹⁸⁸

- Indium-based catalyst

Indium-based compounds have been used extensively as catalysts in recent years in their stable +3 oxidation state. Their free p orbital makes them Lewis acids, characterized by less reactivity than boron (III) or aluminum (III) but with higher chemoselectivity, and higher stability in water and air.

These advantages, together with the low toxicity and antimicrobial activity led to the increased use of indium as a catalyst in chemical processes.¹⁸⁹ In fact, it is used, as σ -Lewis acid (σ -acid), in a wide range of reactions such as Diels-Alder, Friedel-Craft, aldol, and allylation. However, recent studies have shown that In(III) is also an efficient π -Lewis acid that coordinates with unsaturated systems. In recent years, in fact, In(III) halides such as InCl_3 , InBr_3 , and InI_3 , and triflates have been used as π -Lewis acid catalysts in cycloisomerization, hydrofunctionalization and also for ring-opening polymerization reactions (Figure 3.19).

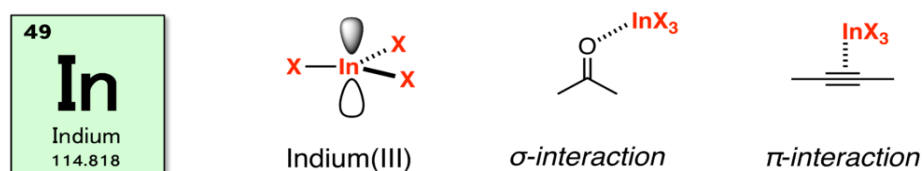


Figure 3.19. Types of interaction of InX_3

¹⁸⁷ Dai, Y.; Li, B. D.; Quan, H. D.; Lü, C. X. *Chin. Chem. Lett.* **2010**, 21, 31-34.

¹⁸⁸ Pastore, G.; Gabrielli, S.; Cecchi, T.; Giuliani, A.; Cimorelli, C.; Menchi, A.; Marcantoni, E. *RSC Adv.* **2021**, 11, 10592-10598.

¹⁸⁹ David, S.; Barros, V.; Cruz, C.; Delgado, R. *FEMS Microbiol. Lett.* **2005**, 251, 119-124.

3.5 Properties of UV-curable Polyurethane Acrylate, PUA

- Mechanical Properties

The nature of the backbone in PUA oligomer is responsible for the mechanical properties of the material, influenced by several factors, such as the ratio of NCO/OH and the hard and soft segment in PUA, the molecular weight and nature of polyol and diisocyanate, the concentration and nature of reactive diluent, and finally also the terminal double bond are determinants for the mechanical properties of PUA. In fact, it has been demonstrated that the tensile strength and the Young's modulus of the film increase with the rise in double bond content.¹⁹⁰ The latter determines also the level of cross-link and the hardness of the films once subjected to UV curing.

- Thermal properties

The thermal stability of PUA is determined by the chemical structure and functionality of the urethane acrylate oligomer, the concentration of reactive diluents and also the UV-polymerization process. These factors are strongly influenced by reaction conditions. In fact, at high temperatures, the thermal stability of the material can be seriously compromised, and this leading to thermal degradation of the polymer. The molecular weight of PUA influences the rate of depolymerization, high M_w values lead to a faster depolymerization reaction. However, the residual photo- initiator, the presence of oxygen and catalyst are several factors which can also influence the degradation of PUA and so compromise the final characteristic of the material.

- Physical properties

The physical properties, in particular the viscosity of the polyurethane acrylate oligomer, are determined by the structure and molecular weight of the NCO-terminated prepolymer as well as by the content of the reactive diluents. Even in this case the temperature is determinant, in fact the viscosity value decreases with increasing temperature due to the reduction of intermolecular hydrogen bonding within the polymer chain.

¹⁹⁰ Li, X.; Ye, F.; Wang, J.; Chen, Z.; Yang, X. *Polym. Chem.* **2021**, *12*, 1014-1022.

- Optical properties

The optical properties of polyurethane acrylate are defined by various factors, such as the nature of the terminal vinyl bonds, the structure of the backbone chain and the NCO/OH ratio. Through precise modification of these parameters, it is possible to obtain a PUA with a high degree of transparency.

3.6 Applications of PUA

The wide range of synthetic options that can be obtained by varying the hard/soft segments, the nature and content of starting materials, the chain extenders and reactive diluents allows to consider this polymer the ideal matrix for biological and not-biological purposes (Figure 3.20).

Polyurethane acrylate is one of the most suitable resins used for UV coatings because of its excellent properties of abrasion resistance, solvent resistance, flexibility and at the same time hardness.¹⁹¹ It is also an attractive material for biomedical applications (such as soft tissue repair, dental repairs and especially medicated plasters and tissue adhesives) thanks to the biocompatibility that characterizes it.



Figure 3.20. PUA applications

However, its use is somewhat limited by the fact that PUA is not always degradable, or its degradation products are toxic and not harmless. For this reason, efforts are being

¹⁹¹ Liao, F.; Zeng, X.; Li, H.; Lai, X.; Zhao, F. *J. Cent. South Univ.* **2012**, *19*, 911-917.

made to synthesize a bio-based PUA, derived from renewable resources that does not lead to the production of toxic substances after degradation and maintains the same properties as fossil-based PUA.

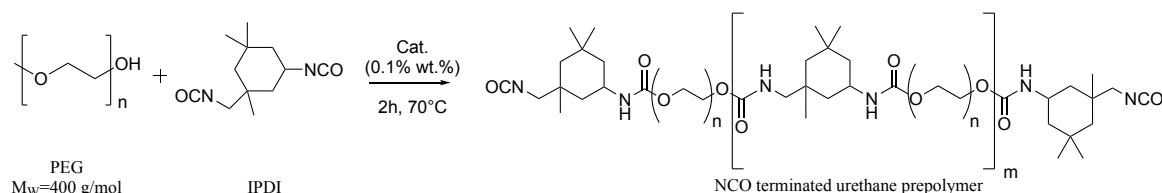
Experimental part

3.7 Aim of the work

Poly(urethane-acrylates) (PUAs) are UV-curable resins used for biomedical applications, skin adhesives, coatings and others. The synthesis of PUAs generally rely on fossil-based polyols and aromatic diisocyanates in the presence of tin-based catalysts. However, the well-known toxicity related to tin compounds, the release of carcinogenic degradation products of aromatic isocyanate and the problems due to the depletion of raw materials with the increase of the greenhouse gas emission have shifted the attention towards new sustainable solutions. In the present work, a sustainable and innovative synthesis of PUAs from renewable resources promoted by solid supported $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ - NaI/SiO_2 , heterogeneous catalytic system, was studied. This catalytic system was applied to bio-based polyols and diisocyanates and the target compounds were evaluated and compared to fossil-based PUAs in term of monomer conversion, molecular weights, chemical and thermal properties of the final materials.

3.8 NCO-terminated urethane prepolymer synthesis

In the first step, a urethane pre-polymer was synthesized starting from polyethylene glycol $M_w = 400$ g/mol (PEG400) and isophorone diisocyanate (IPDI) (Scheme 3.8).¹⁹²



Scheme 3.8. Synthesis of NCO-Terminated Urethane Prepolymer

¹⁹² Pastore, G.; Gabrielli, S.; Giacomantonio, R.; Lupidi, G.; Capodaglio, S.; Stella, F.; Leone, E.; Compagnucci, T.; Marcantoni, E. *Results Mater.* **2022**, *15*, 100294.

3.8.1 Catalysts screening

Different types of catalysts were studied in the initial phase of PUA synthesis and evaluated based on the molecular weight of the NCO prepolymer obtained (Table 3.1). From the screening performed, the catalytic system consisting of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NaI (Entry 6) produced remarkable results, generating oligomers with a molecular weight of $M_w = 1700$ Da and a monomer conversion of 94%, similar to that obtained with dibutyltin dilaurate (DBTDL). This cerium-based system acts as a highly active Lewis acid promoter, in which the oligomeric structure of cerium(III) trichloride is altered by the iodide ion, forming a more reactive monomeric structure.

Table 3.1. Catalysts screening

Entry	Catalyst ^a (wt%)	M_n^b (g/mol)	M_w^b (g/mol)	Conv. ^b (%)
1	-	600	700	60
2	DBLT	1500	1900	96
3	$\text{Ce}(\text{OAc})_3$	1000	1400	86
4	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$	1000	1300	89
5	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -KI	900	1300	87
6	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI	1100	1700	94
7	CeCl_3 -NaI	900	1300	91
8	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -CuI	900	1200	93
9	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI/ SiO_2	1200	1800	95
10	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI/ Al_2O_3	800	1100	90

^a Molecular weight has been determined by GPC analysis (detector RI, refractive index).

^b Percentage monomer conversion has been established by GPC peak area analysis.

Another positive aspect is the LD_{50} value of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, which is 2800 mg/kg, sixteen times higher than DBTDL (175 mg/kg). Thanks to its non-toxicity, low cost and ease of management, this system represents a significant alternative to produce PUA, helping to reduce the economic and environmental impact of the chemical process. To further investigate the potential of the eco-friendly catalytic system, the reactions with other iodine sources in combination with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were performed. The best result in terms of molecular weight was obtained using sodium iodide (Entry 6). Furthermore, to reduce costs and environmental impact, heterogeneous reaction conditions were tested,

allowing the recovery and recycling of the catalyst at the end of the reaction. The best performing systems led to a molecular weight of 1800 Da using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI/SiO₂ (Entry 9).

3.8.2 Catalyst recyclability

Additional tests were conducted to evaluate the recyclability of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI catalyst supported on SiO₂. This catalyst is filtered, washed, dried under vacuum and reused for seven cycles without showing any significant decrease in activity (Figure 3.21)

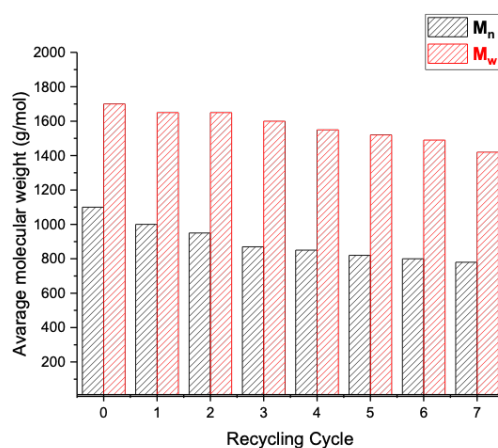


Figure 3.21. Catalyst recyclability screening

The stability and composition of the recycled catalyst were analyzed by SEM-EDX and FTIR. The results showed that the elements present in the fresh catalyst were still detectable after the seventh recycling (Figure 3.22) and no differences were observed in the FTIR spectra (Figure 3.23).

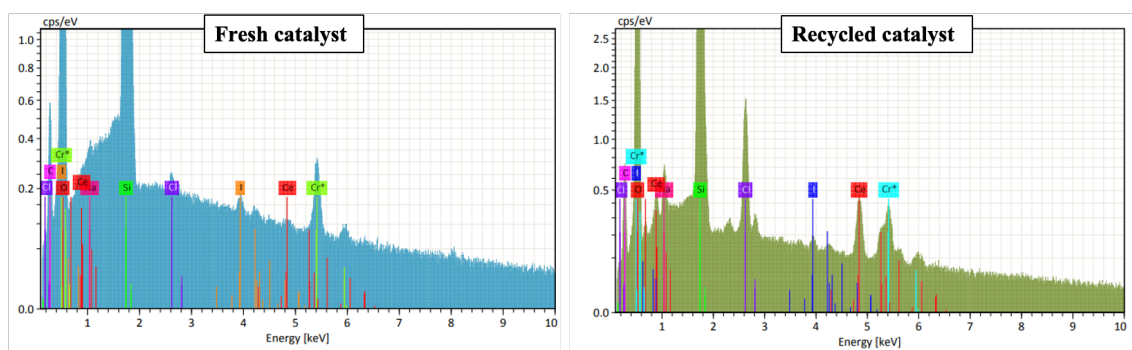


Figure 3.22. SEM-EDX analysis of fresh and recycled catalysts

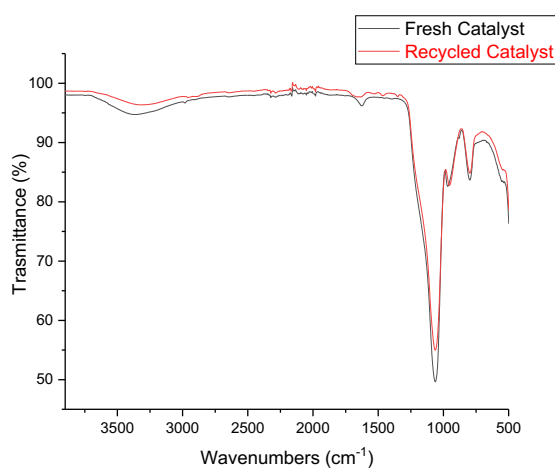


Figure 3.23. FTIR spectra of fresh catalyst and recycled catalyst

In particular, the peaks at 1080 and 800 cm^{-1} , associated with different O–Si–O or Si–O–Si vibration modes, were again identified in the recycled catalyst.

3.8.3 Optimization of the reaction conditions

After performing a catalyst screening and evaluating the promising results obtained with the solid-supported $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ – NaI/SiO_2 catalyst system, optimization of the reaction conditions was performed as reported in Table 3.2.

Table 3.2. Optimization of the reaction condition in pre-polymer synthesis

	CAT9 (wt%)	IPDI (eq.)	Temp. (°C)	M _n ^a (g/mol)	M _w ^a (g/mol)	Monomer Con. ^b (%)	Residual NCO ^c (%)
RC1	0.1	2.0	70	600	800	78	4.5
RC2	0.1	1.0	70	1000	1500	98	2.8
RC3	0.1	1.5	70	1200	1800	95	4.3
RC4	0.2	1.5	70	1000	1600	93	4.2
RC5	0.3	1.5	70	1200	1700	92	4.0
RC6	0.4	1.5	70	1100	1600	92	4.1
RC7	0.1	1.5	80	1100	1600	95	4.2
RC8	0.1	1.5	60	900	1400	96	4.0

^a Molecular weight has been determined by GPC analysis (detector RI, refractive index).

^b Percentage monomer conversion has been established by GPC peak area analysis.

^c The residual –NCO was determined by titration with DIN EN ISO

The highest molecular weight was achieved after 2 h at 70 °C using a solution containing 0.1 wt% CeCl₃·7H₂O–NaI/SiO₂ and 1.5 equiv of IPDI (Table 3.2, RC3).

In Table 3.2 is also reported the NCO content obtained by titration according to Equation 1:¹⁹³

$$\%NCO = \frac{(V_{mean\ blank} - V_{sample}) \times C_{HCl} \times M_{NCO}}{W_{sample}} \times 100$$

[Eq. 1]

Where:

V_{blank} = volumes of acid consumed for blank,

V_{sample} = volumes of acid consumed for samples,

C_{HCl} = the concentration of HCl,

M_{NCO} = molecular weight of NCO groups (42 g/mol),

W_{sample} = weight of the sample.

The lowest NCO percentage (2,8%) was obtained with 1 equivalent of isophorone diisocyanate (Table 3.2, RC2) After that, a kinetic study (Figure 3.24) of the reaction was performed, revealing that the highest molecular weight of 1800 Da was achieved after 2 hours. Increasing reaction times depolymerization reaction occurs.

¹⁹³ Marand, Å.; Dahlin, J.; Karlsson, D.; Skarping, G.; Dalene, M. *J. Environ. Monit.* **2004**, 6, 606–614.

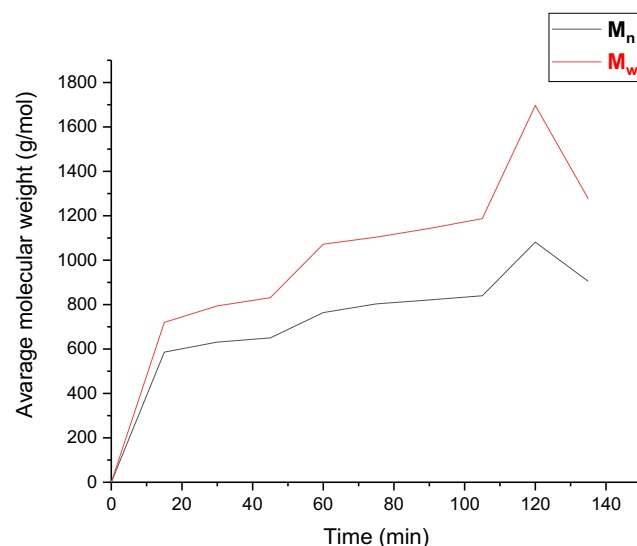


Figure 3.24. Kinetic study of 3a

3.8.4 NCO-terminated urethane prepolymer synthesis control

FTIR and NMR analyses were conducted to evaluate the formation of the urethane prepolymer. From the FTIR spectrum (Figure 3.25) it is possible to observe that the peak relative to NCO stretching (2254 cm^{-1}) decreases as the reaction time increases, while the characteristic peak of the urethane bond (1715 cm^{-1}) increases as the reaction proceeds. The broad peak at 3500 cm^{-1} which is related to the hydroxyl groups present in the polyol decreases and it is gradually replaced by a narrow peak at 3200 cm^{-1} which refers to the stretching of the -NHR functionality of the urethane group.

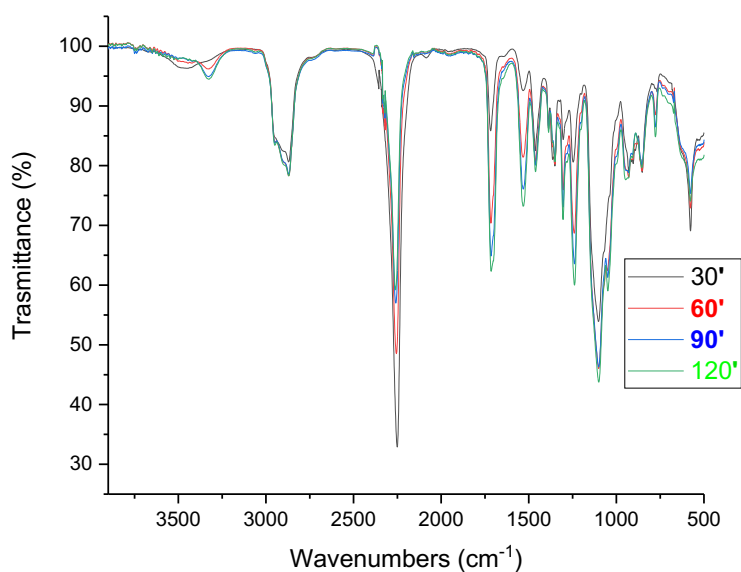


Figure 3.25. FTIR kinetic study of pre-polymer formation

The ^{13}C NMR spectrum also confirms the formation of the pre-polymers.

The spectra of the IPDI were analyzed before and after the addition of PEG. Basically, isophorone diisocyanate has a primary isocyanate group (peak **b**) at 122.2 ppm and a secondary isocyanate group (peak **a**) at 123.5 ppm (Figure 3.26).

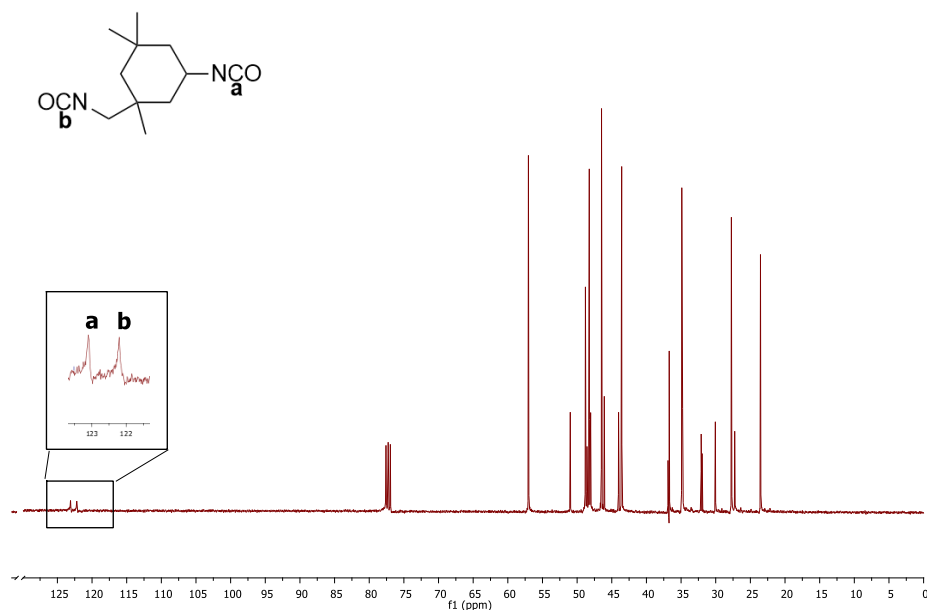


Figure 3.26. ^{13}C -NMR of IPDI

After the reaction with PEG 400, only the peak at 123.5 ppm disappears, suggesting that the secondary NCO group is more reactive than the primary one to be shielded by the β -

situated methyl substituents, the cyclohexane ring, and its neighbouring methyl group.¹⁹⁴ Therefore, it reacts with the hydroxyl groups of polyols to obtain a urethane bond, confirmed by the signal at 155.56 ppm (peak c) (Figure 3.27).

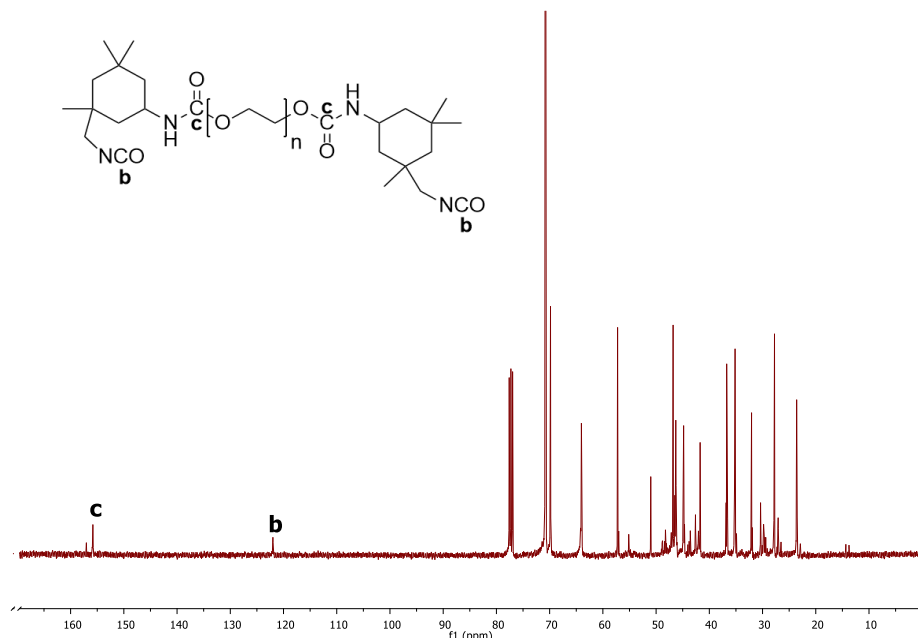


Figure 3.27. ^{13}C -NMR of pre-polymer

To demonstrate the effectiveness of the optimized catalytic procedure, different polyols in combination with various diisocyanate derivatives were investigated. Starting from the synthesis of bio-based NCO-terminated urethane prepolymers. Initially, the reaction between IPDI and different bio-diols, such as oligo(L-lactic acid) (OLLA) with a molecular weight of 400 g/mol and isosorbide, was performed with the aim of replacing PEG 400 (Figure 3.28). These reagents led to the formation of compounds with a molecular weight of 1300 Da (**3c** and **3e**, Table 3.3), results comparable to those obtained with fossil polyol (compound **3a**, Table 3.3). To obtain a fully bio-based NCO-terminated urethane prepolymer, OLLA and isosorbide were reacted with L-lysine diisocyanate. However, the latter showed lower reactivity than IPDI and the prepolymers **3d** and **3f** were obtained with a molecular weight of 1000–1100 Da.

¹⁹⁴ Hatada, K.; Ute, K.; Oka, K. I.; Pappas, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, 28, 3019–3027

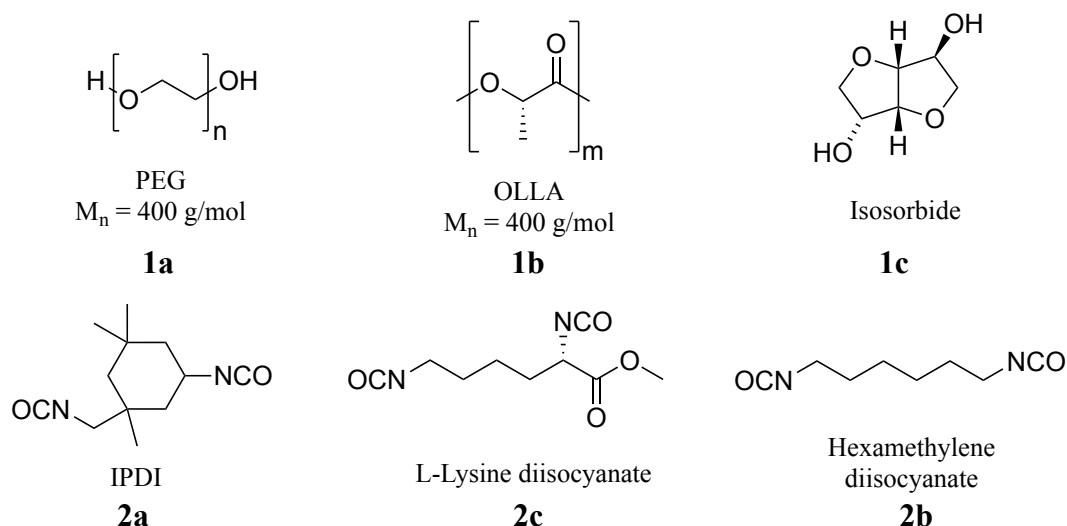


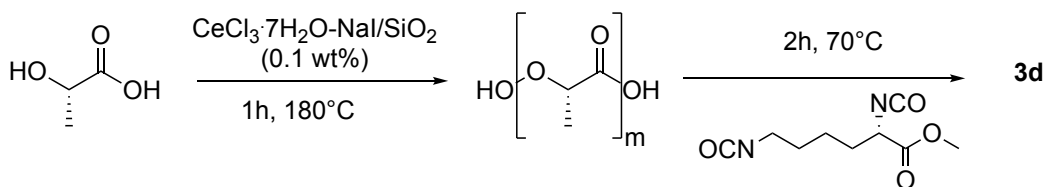
Figure 3.28. Polyols and diisocyanate employed in PUA synthesis

Table 3.3 Mw screening of pre-polymers

		Nco-terminated pre-polymer		
Compd. 1	Compd. 2	Compd. 3	Mn ^a (g/mol)	Mw ^a (g/mol)
1a^b	2a	3a	1200	1800
	2b	3b	2000	3400
1b	2a	3c	900	1300
	2c	3d	600	1000
1c	2a	3e	800	1300
	2c	3f	700	1100

^a Molecular weight has been determined by GPC analysis (detector RI, refractive index). ^b Reaction performed also on a 5 grams scale with comparable results.

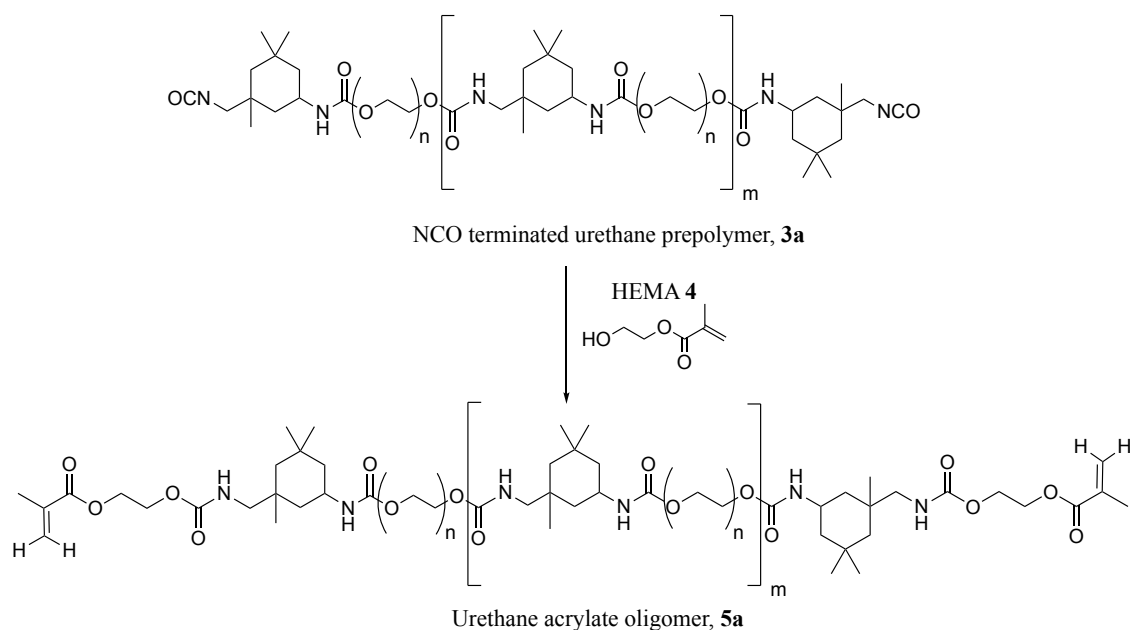
To demonstrate the effectiveness of the optimized catalytic procedure, a one-pot process for the synthesis of compound **3d** was developed. This process involves a first transformation of L-lactic acid (LLA) into OLLA, with a molecular weight of 400 Da, followed by the reaction with L-lysine diisocyanate (**2c**). It is important to specify that, for compound **3d**, the reaction occurs with a free carboxylic acid group, which can react with HEMA to form an ester functionality, thus ensuring the polymerization process (Scheme 3.9).



Scheme 3.9. One pot synthesis of 3d

3.9 Urethane acrylate oligomer synthesis

All the prepolymers were subsequently involved in the reaction with 2-hydroxyethyl methacrylate (HEMA, **4**) to obtain urethane acrylate oligomers. The synthesis of fossil-based urethane acrylate oligomers (Scheme 3.10). was compared to partially and fully bio-based approaches, focusing on the molecular weights achieved.



Scheme 3.10. Urethane acrylate oligomer (5a) synthesis

The obtained molecular weights were found to be comparable to those of compounds **3a-f** (Table 3.4).

Table 3.4. Mw screening of urethane acrylate oligomers

Urethane acrylate oligomer			Film
Compd. 5	Mn ^a (g/mol)	Mw ^a (g/mol)	Compd. 8
5a	1400	1900	8a
5b	2100	3600	8b
5c	1000	1400	8c
5d	800	1100	8d
5e	1100	1500	8e
5f	900	1100	8f

^a Molecular weight has been determined by GPC analysis (detector RI, refractive index).

The formation of compound **5** was monitored using FT-IR (Figure 3.29). The disappearance of the isocyanate peak at 2254 cm⁻¹ after four hours confirms the production of urethane acrylate oligomers due to the reaction between NCO groups and HEMA.

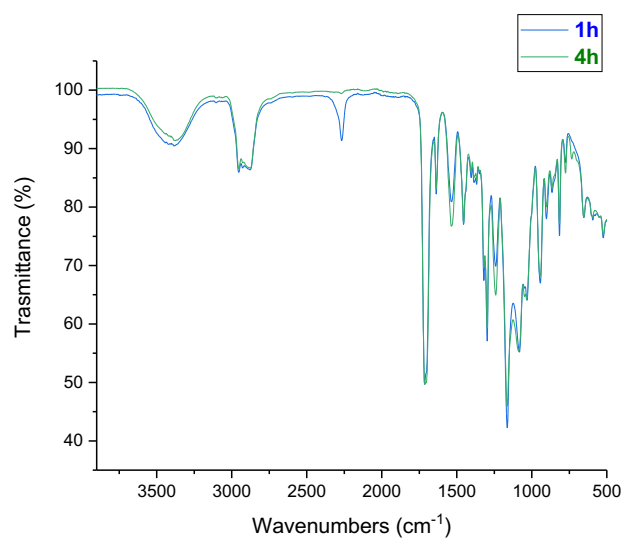
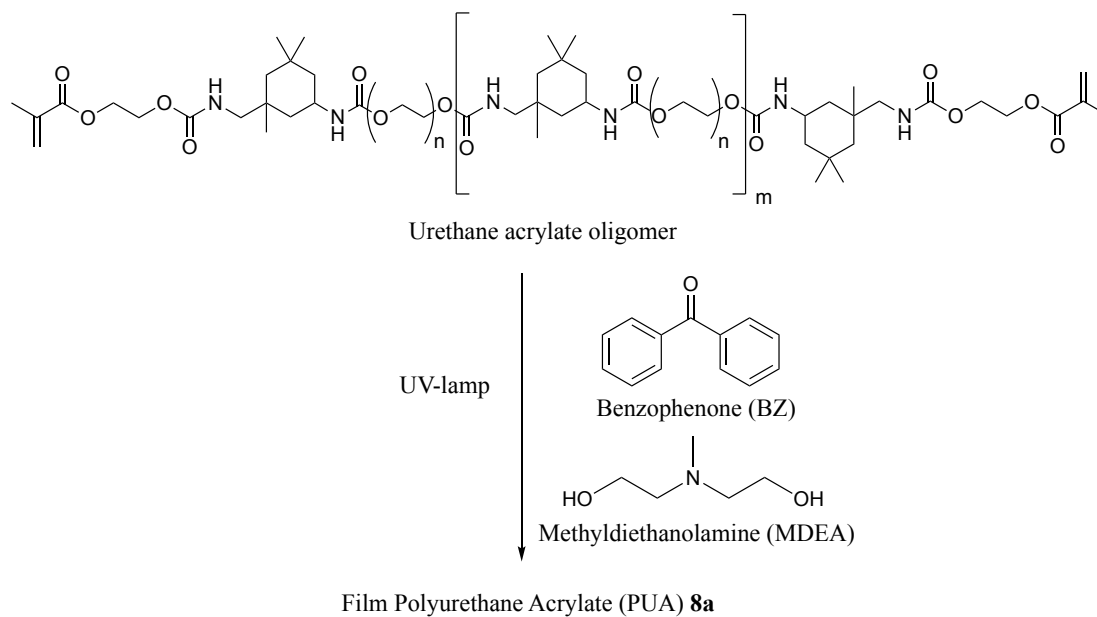


Figure 3.29. FT-IR check of pre-urethane oligomer synthesis

3.10 UV-cured PUA synthesis

Photopolymerization of **5a-f** was performed in presence of benzophenone as photo-initiator and N-methyl diethanolamine as co-initiator (**8a** synthesis in the Scheme 3.11).



Scheme 3.11. UV-cured PUA (8a) synthesis

The final poly(urethane-acrylates) **8a-f** were chemically characterized, and their thermal properties were determined.

3.11 Chemical and thermal characterization of PUA

The formation of PUA was verified by FT-IR (Figure 3.30). and further characterized by TGA, DSC, and SEM analyses.

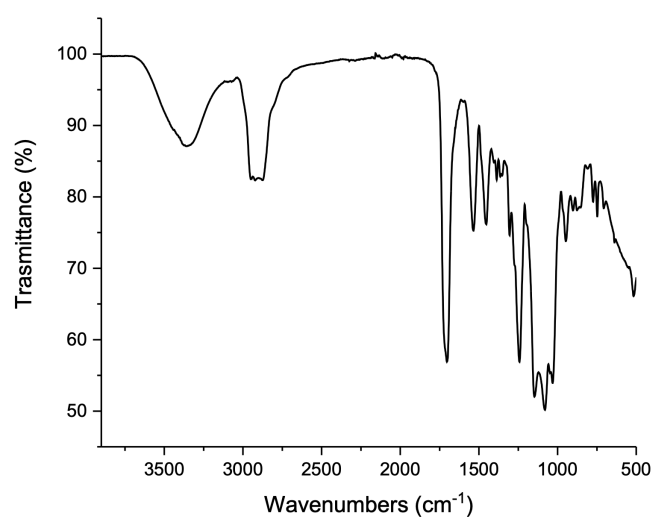


Figure 3.30. FT-IR of PUA of 8a

No characteristic peaks were observed for acrylic double bonds (1634 cm^{-1} and 814 cm^{-1}) in the FT-IR spectrum, indicating that carbon–carbon double bonds are involved in the formation of new chemical bonds via photopolymerization. TGA analysis of the UV-cured polymer films reveals two distinct weight loss stages (Figure 3.31). The first decomposition stage occurs between $120\text{ }^{\circ}\text{C}$ and $350\text{ }^{\circ}\text{C}$ and is attributed to the thermal degradation of the hard segments, leading to the cleavage of the urethane bond. The second stage corresponds to the degradation of the soft segments, which exhibit higher thermal stability and start to decompose between $350\text{ }^{\circ}\text{C}$ and $470\text{ }^{\circ}\text{C}$. The initial mass loss up to $120\text{ }^{\circ}\text{C}$ is associated with moisture evaporation.

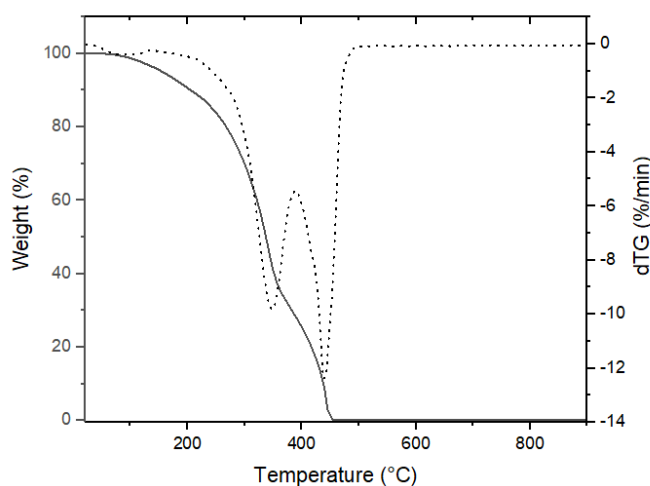


Figure 3.31. TGA profile of UV-cured PUA film

Both weight loss and T_{onset} (initial degradation temperature) remain constant when PUA is synthesized from renewable resources (Table 3.5). The glass transition temperature (T_g) of the polymerized samples **8a–f** was analyzed by DSC. Only compound **8e** showed a positive T_g of $68\text{ }^{\circ}\text{C}$ due to the cyclic structure of both starting materials, isosorbide and IPDI.

Table 3.5. TGA and DSC data of PUA films

Specimen	TGA Analysis		DSC Analysis
	T _{on} I °C (Weight loss %) ^a	T _{on} II °C (Weight loss %) ^a	T _g (°C) ^b
8a	310 (48)	431 (46)	-1
8b	315 (47)	432 (47)	-28
8c	298 (49)	430 (45)	-4
8d	310 (49)	430 (45)	-30
8e	297 (50)	433 (44)	68
8f	300 (48)	428 (46)	-42

^a Determined by TGA analysis. ^b Determined by DSC analysis

SEM images (Figure 3.32) reveal that the surfaces of both bio- and fossil-derived poly(urethane acrylates) are smooth and homogeneous, without visible cracks or phase separation, confirming the effectiveness of the polymerization process.

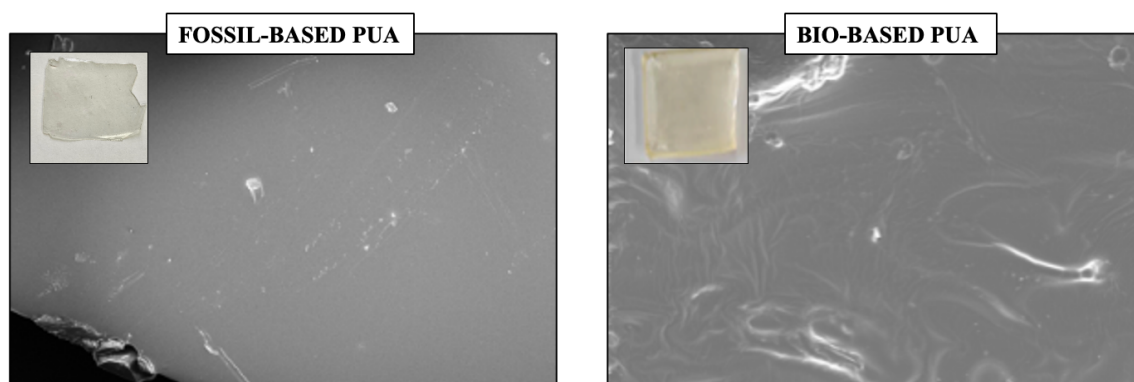


Figure 3.32. SEM images of fossil-based PUA (8a) and bio-based PUA (8d)

3.12 Experimental protocols

3.12.1 Materials and methods

All reagent and solvent were purchased from commercial suppliers and used without further purification, unless mention otherwise. All glassware was oven dried at 100°C for more than two hours prior to use, when the reactions were performed under nitrogen atmosphere.

Synthesis of polyurethane acrylate, PUA

In a 25 mL two-necked round-bottom flask, 1 g of polyol is reacted with an appropriate amount of diisocyanate at 70 °C for a specific time. At the end of this initial step, the oligomer is cooled to 50 °C and subsequently end-capped with HEMA (50 wt%) by adding it dropwise to the reaction mixture. The synthesis of urethane acrylate oligomers (UAO) is conducted at 50 °C for 4 hours. Following this, the reaction mixture is cooled to room temperature, and benzophenone and methyl diethanolamine are added. The resulting mixture is then deposited in a small teflon plate and exposed to UV light to form a film of polyurethane acrylate.

- Fourier-Transform Infrared Spectroscopy (FTIR-ATR)

FTIR spectra were recorded with a Perkin-Elmer FT-IR spectrometer Spectrum Two UATR, equipped with ZnSe crystal. The measurements were performed in a 400-4000 cm⁻¹ range at a 2 cm⁻¹ resolution, 4 scans and processed by a Perkin-Elmer data manager (Spectrum).

- Thermogravimetric analysis (TGA)

TGA analysis was carried out using a Perkin-Elmer STA 6000 thermal analyzer, equipped with Al₂O₃ crucibles.

- Differential scanning calorimetry (DSC)

Samples (5–6 mg in an aluminum concave pan with pierced lid) were analyzed with DSC 250 TA, according to the following thermal program: heating from

–90 °C to 100 °C (2 min hold), cooling to – 90 °C (2 min hold) and heating to 100 °C, all steps at 10 °C/min.

- Nuclear magnetic resonance (NMR)

¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury 400 (400 MHz or 100 MHz respectively). Chemical shifts are quoted in ppm and are referenced to residual protons in the deuterated solvent as the internal standard such as CDCl₃ (7.26 ppm for ¹H and 77.0 ppm for ¹³C) or dimethyl sulfoxide-d₆ (DMSO-d₆, 2.50ppm for ¹H and 39.5 ppm for ¹³C). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

- Gel permeation chromatography (GPC)

The GPC measurements were carried out with an Agilent 1260 Infinity II Multi Detector Suite (MDS) device. In this device, there was an Agilent 1260 Infinity Quaternary Pump (G7111B), containing a 4-channel vacuum degasser to pump the eluent into the system. The auto sampler was G7129A and the thermostatic column compartment G7116A. The used device consisted of three different detectors (G7800A): a dual light scattering detector (measuring in the angles of 15° and 90°), an RI detector, and a VS-detector. The THF mobile phase contained 250 ppm of BHT (butylhydroxytoluene) and the flow rate was fixed at 1.0 ml/min. In the measurements and data analysis, an Agilent GPC/SEC Software, was used. GPC system was equipped with two columns in series (PLgel MIXED-C and PLgel MIXED-D) and before the columns there was also a guard column (Agilent GPC/SEC Guard Column). The standards used in the measurements for column calibration were PSs with different Mp values in the range of 580-283800 g/mol.

- Scanning electron microscopy (SEM)

Samples were evaluated by an high-resolution scanning electron microscope with field emission gun (FE-SEM, Sigma Family, Zeiss, Oberkochen, Germany) operated at 15 keV, equipped with an energy-dispersive X-ray spectroscopy system (Quantax 200, EDS, Bruker) that enables elemental analysis. Samples were deposited on aluminium stabs using self-adhesive carbon conductive tabs

and sputtered with a thin film of chromium (5 nm) by the sputter coater Quorum QT150 (Quorum, Laughton, UK).

3.13 Characterization

Compound 3a.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 4.19-4.17, 3.63, 3.00, 1.74-1.67, 1.23-1.20, 1.09-1.01, 0.94-0.89. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 155.81, 122.00, 70.77, 69.84, 64.03, 57.23, 46.80, 46.30, 44.83, 41.73, 36.74, 35.16, 32.07, 27.76, 23.59. *FT-IR* (neat, cm^{-1}): 3327, 2922, 2254, 1715, 1531, 1461, 1304, 1237, 1102, 1050, 855, 777, 578.

Compound 3b.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 4.19, 3.63, 3.30-3.28, 3.16-3.12, 1.61-1.58, 1.51-1.30. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 155.44, 69.56, 68.68, 41.88, 39.85, 25.33, 25.23. *FT-IR* (neat, cm^{-1}): 3337, 2942, 2253, 1714, 1550, 1430, 1300, 1250, 1100, 1040, 870, 740, 550.

Compound 3c.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 5.14-5.03, 4.35-4.33, 2.99, 1.64-1.45, 1.07-0.90. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 169.41, 154.82, 121.76, 69.14, 66.74, 57.07, 46.66, 44.91, 41.43, 36.68, 35.16, 31.88, 27.72, 23.46, 16.79. *FT-IR* (neat, cm^{-1}): 3386, 2952, 2253, 1715, 1536, 1453, 1383, 1364, 1185, 1128, 1088, 1044, 863, 740, 577.

Compound 3d.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 5.15-5.03, 3.47, 3.01, 1.71-1.54, 1.05-0.91. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 169.60, 152.33, 126.99, 69.36, 66.92, 57.31, 54.20, 48.35, 40.96, 33.42, 29.39, 28.53, 26.84, 22.75, 16.90. *FT-IR* (neat, cm^{-1}): 3376, 2944, 2250, 1739, 1524, 1450, 1358, 1189, 1128, 1083, 1051, 865, 736, 581.

Compound 3e.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 4.98, 4.68, 4.37, 4.19, 3.87-3.81, 3.58-3.55, 2.96, 1.75-1.65, 1.15-0.85. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 154.95, 122.04, 86.06, 81.25, 74.42, 74.07, 70.21, 57.19, 46.73, 46.24, 45.04, 41.64, 36.74, 35.13, 32.08, 27.74, 23.60. *FT-*

IR (neat, cm^{-1}): 3330, 2954, 2261, 1704, 1525, 1462, 1363, 1305, 1232, 1046, 1018, 772, 735, 578.

Compound 3f.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 5.12, 4.80, 4.48, 4.32, 4.05-3.92, 3.81, 3.18, 1.84-1.73, 1.53-1.42. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 171.95, 155.77, 126.99, 86.05, 81.28, 74.51, 74.03, 70.20, 57.45, 54.21, 48.35, 40.95, 33.56, 29.42, 28.54, 22.83. *FT-IR* (neat, cm^{-1}): 3330, 2954, 2261, 1704, 1525, 1462, 1363, 1305, 1232, 1046, 1018, 772, 735, 578.

Compound 5a.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 6.14, 5.59, 4.30-4.28, 4.18, 3.88-3.85, 3.64, 2.91, 1.95, 1.85-1.69, 1.24-1.17, 1.05, 0.92-0.87. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 167.79, 136.23, 126.26, 70.76, 69.84, 66.63, 63.97, 61.55, 55.12, 46.49, 44.85, 42.05, 36.58, 35.27, 32.05, 27.84, 23.42, 18.54. *FT-IR* (neat, cm^{-1}): 3346, 2923, 1715, 1634, 1534, 1365, 1298, 1239, 1165, 1098, 944, 815, 484.

Compound 5b.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 6.14, 5.59, 4.30-4.27, 4.19, 3.88-3.85, 3.63, 3.14, 1.95, 1.47, 1.31. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 167.95, 156.69, 136.22, 126.28, 70.76, 69.88, 66.64, 61.57, 41.07, 30.07, 26.53, 18.56. *FT-IR* (neat, cm^{-1}): 3355, 2930, 2867, 1706, 1637, 1532, 1455, 1318, 1295, 1246, 1162, 1095, 944, 816, 779.

Compound 5c.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 5.14-5.03, 4.35-4.33, 2.99, 1.64-1.45, 1.07-0.90. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 169.57, 167.41, 155.56, 136.18, 126.27, 69.34, 63.15, 55.05, 46.48, 45.00, 41.92, 36.60, 35.24, 32.06, 27.82, 23.43, 18.53, 16.95. *FT-IR* (neat, cm^{-1}): 3356, 2955, 1709, 1637, 1527, 1439, 1405, 1364, 1319, 1296, 1221, 1163, 1081, 947, 896, 815, 776, 654.

Compound 5d.

$^1\text{H NMR}$: (400 MHz, CDCl_3) δ_{H} = 6.13, 5.60, 5.16, 4.32-4.28, 3.89-3.74, 3.16, 1.96-1.94, 1.59-1.42. $^{13}\text{C NMR}$: (100 MHz, CDCl_3) δ_{C} = 173.07, 169.61, 155.51, 136.21, 126.33, 125.74, 69.33, 66.62, 63.01, 61.58, 53.83, 52.70, 40.76, 32.37, 30.53, 29.53, 27.00,

22.44, 18.55, 16.93. *FT-IR* (neat, cm^{-1}): 3351, 2952, 1746, 1720, 1637, 1527, 1453, 1297, 1190, 1131, 1093, 1049, 950, 866, 816, 654.

Compound 5e.

^1H NMR: (400 MHz, CDCl_3) δ_{H} = 6.10, 5.56, 5.06, 4.70, 4.45, 4.29-4.28, 3.95, 3.72-3.69, 2.90-2.87, 1.83-1.81, 1.70-1.67, 1.03-0.90. ^{13}C NMR: (100 MHz, CDCl_3) δ_{C} = 167.11, 156.60, 135.97, 125.91, 85.86, 81.01, 74.09, 73.74, 66.34, 62.57, 60.94, 54.84, 46.95, 46.10, 44.74, 41.59, 36.38, 34.98, 31.78, 27.55, 23.17, 18.23. *FT-IR* (neat, cm^{-1}): 3321, 2954, 2871, 1717, 1638, 1531, 1460, 1365, 1300, 1235, 1166, 1102, 1057, 900, 733, 654, 475.

Compound 5f.

^1H NMR: (400 MHz, CDCl_3) δ_{H} = 6.14, 5.60, 5.09, 4.83, 4.32-4.28, 3.88-3.73, 3.16, 1.95, 1.53-1.24. ^{13}C NMR: (100 MHz, CDCl_3) δ_{C} = 136.23, 126.28, 66.63, 64.41, 63.15, 62.13, 61.95, 52.88, 40.74, 32.39, 29.53, 22.44, 18.51. *FT-IR* (neat, cm^{-1}): 3356, 2955, 2869, 1709, 1637, 1527, 1439, 1405, 1364, 1319, 1296, 1221, 1163, 1018, 947, 896, 815, 654, 479.

Compound 8a.

FT-IR (neat, cm^{-1}): 3330, 2869, 1689, 1536, 1460, 1303, 1238, 1099, 1040, 949, 865, 638.

Compound 8b.

FT-IR (neat, cm^{-1}): 3330, 2925, 2865, 1700, 1532, 1448, 1303, 1238, 1099, 1040, 949, 865, 638.

Compound 8c.

FT-IR (neat, cm^{-1}): 3356, 2951, 1720, 1585, 1450, 1383, 1241, 1184, 1130, 1086, 867, 749, 702, 514.

Compound 8d.

FT-IR (neat, cm^{-1}): 3317, 2942, 1725, 1602, 1530, 1449, 1381, 1191, 1131, 1077, 896, 750, 705, 512.

Compound 8e.

FT-IR (neat, cm^{-1}): 3320, 2926, 1699, 1530, 1456, 1305, 1237, 1140, 1031, 771, 702, 639.

Compound 8f.

FT-IR (neat, cm^{-1}): 3299, 2933, 1655, 1447, 1275, 1071, 698, 581.

3.14 Conclusion

An efficient and environmentally friendly method for the synthesis of fully bio-based poly(urethane-acrylate) (PUA) catalyzed by a sustainable $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI system supported on SiO_2 has been successfully investigated. This catalytic system, which is recyclable up to seven times without any loss of activity, enables the production of a prepolymer with a molecular weight of 1800 Da. Chemical characterization also confirmed the successful bio-based PUA synthesis and thermal properties were evaluated using DSC, TGA and SEM, demonstrating that both bio-based and fossil-based PUAs share similar chemical characteristics and performances.

PART II: 3D-printing of itaconic anhydride-based polysalts

3.15 Additive manufacturing

A recent advance in the to design materials is the process known as additive manufacturing (AM) or 3D printing, which allows to fabricate complex and precise computer-designed objects. 3D models, created using computer-aided design or advanced structure algorithms, are composed of layers, which are deposited in sequence. Unlike subtractive methods, which define the shape of the part by removing material from an initially monolithic form, or formative methods, which define the shape of the part by injecting it into a reusable cavity, AM is suited to the production of materials with complex geometries with rapid and sustainable prototyping. This technology was first developed by Charles Hull in 1986 in a process known as stereolithography, which was followed by later developments such as powder bed fusion, fused deposition modeling, inkjet printing, and contour machining.¹⁹⁵ The growing interest in using 3D manufacturing system over traditional techniques is attributed to several advantages, including the fabrication of complex geometries with high precision, maximum material savings, flexibility in design, and personal customization. Polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) are the main polymers used in composite 3D printing together with other type of polymers, metals and ceramics.¹⁹⁶ The accuracy of printed parts depends on the accuracy of the method employed and the optimization of printing parameters are factors that could limit the potential of large-scale printing. On the other hand, the limited materials available for 3D printing pose challenges in using this technology in various industries.¹⁹⁷ Therefore, there is a need to develop suitable materials that can be used for 3D printing and provide high performance.

¹⁹⁵ Hull, C. W. *Res. Technol. Manage.* **2015**, 58(6), 25–30.

¹⁹⁶ Wang, X.; Jiang, M.; Zhou, Z.; Gou, J.; Hui, D. *Composites Part B: Eng.* **2017**, 110, 442–458.

¹⁹⁷ Ngo, T. D.; Kashani, A.; Imbalzano, G.; Nguyen, K. T.; Hui, D. *Composites Part B: Eng.* **2018**, 143, 172–196.

3.16 3D-printing techniques

Additive manufacturing is a methodology which consists of layer-by-layer printing. The ISO/ASTM 52900:2015 states that there are 7 main categories of AM/3DP techniques.¹⁹⁸

3.16.1 Material extrusion

In this technique a heated thermoplastic material is selectively dispensed through a nozzle at a constant rate to form the 3D part.¹⁹⁹ The head of the extruder is based on a plotting system able to move in a horizontal plane. Extrusion based methods are the most used 3D printing methods for bio-composites.²⁰⁰ However, different types of processes can be distinguished. Fused Deposition Modeling (FDM) is the common low-budged 3D printer based on extrusion process. It is characterized by low dimensional accuracy (Figure 3.33).

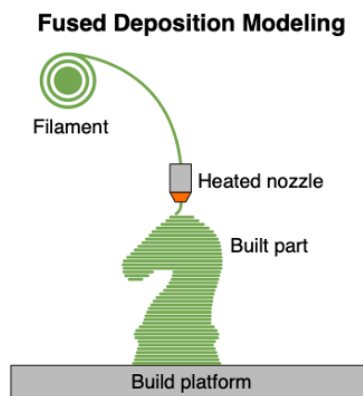


Figure 3.33. FDM printing

In Direct Ink Writing (DIW) the extruded material comes from a viscoelastic ink instead of a filament. First patented by Cesarano and Calvert at Sandia National Laboratory in 1997, DIW has emerged as a printing technique for complex ceramic structures (Figure 3.34).²⁰¹

¹⁹⁸ Pontes, A. J. Designing for Additive Manufacturing. In *Design and Manufacturing of Plastics Products*; Elsevier: Amsterdam, The Netherlands, 2021; pp 249–292.

¹⁹⁹ Chen, Z.; He, Y.; Pan, Z.; Sun, L. *Sci. China Technol. Sci.* **2020**, *63* (7), 1247–1270.

²⁰⁰ Song, Y.; Jiang, Y.; Zhang, X.; Zhang, R.; Deng, H.; Lin, L.; Ni, Y. *Mater. Rep. Energy* **2021**, *1* (2), 100008.

²⁰¹ Jiang, Y.; Cui, C.; Li, X.; Shao, Z.; Zhang, M.; Sun, J.; Yang, J.; Hu, S.; Lin, Y.; Gong, W.; Yao, Y.; Zhao, C.; Shen, Z.; Xie, T. *Adv. Mater.* **2022**, *34* (4), 2108855.

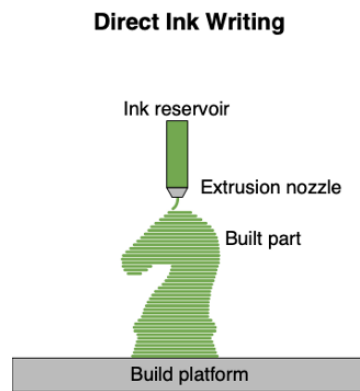


Figure 3.34. DIW printing

3.16.2 Material/Binder jetting

Material Jetting (MJ) selectively cures liquid photopolymer to build 3D-printed parts.²⁰² MJ technology provides higher resolution than FDM and the printed parts are characterized by a smoother surface than the ones based on FDM process due to lower layer thickness values (MJ: 0.016 mm, FDM: 0.330 mm).²⁰³ On the other hand, Binder Jet printing dispenses a liquid binding agent on another substrate that is a powder precursor of the target material (Figure 3.35).²⁰⁴

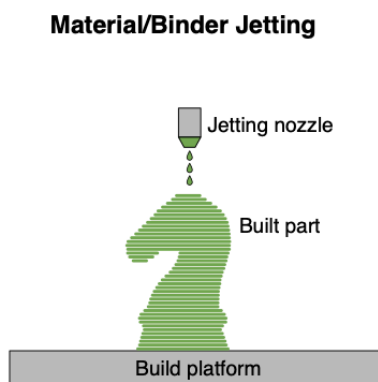


Figure 3.35. Material/Binder Jetting printing

²⁰² Zhang, H.; Zhang, Y.; Wang, X.; Liu, Y.; Zhang, Y.; Wang, C. *Polymers* **2021**, *13*(16), 2829.

²⁰³ Lee, K.Y.; Cho, J.W.; Chang, N.Y.; Chae, J.M.; Kang, K.H.; Kim, S.C.; Cho, J.H. *Korean J. Orthod.* **2015**, *45*, 217–225.

²⁰⁴ Ziaee, M.; Crane, N. B. *Addit. Manuf.* **2019**, *28*, 781–801.

3.16.3 VAT-polymerization (VP)

VP process exploits an ultraviolet (UV) light source to cure a of liquid photopolymer placed inside a moveable vat, crosslinking and solidifying the resin layer by layer. It possesses many attractive features, including high dimensional accuracy, excellent printing resolution, high dimensional accuracy, low-cost manufacturing, and the ability to control the material properties (Figure 3.36).²⁰⁵

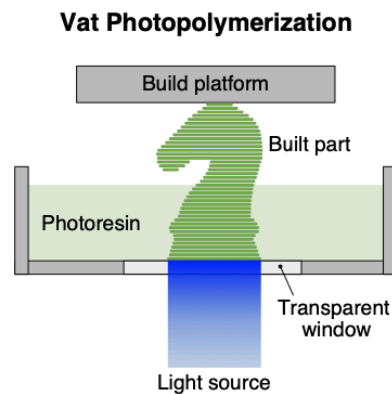


Figure 3.36. VP printing

3.16.4 Powder bed fusion (PBF)

Powder bed fusion process use a laser or an electron beam source to melt and fuse material powders together. Electron beam melting (EBM), selective laser sintering (SLS) and selective laser melting (SLM) fall into this category (Figure 3.37).²⁰⁶

²⁰⁵ Shaukat, U.; Rossegger, E.; Schlögl, S. *Polymers* **2022**, *14*(12), 2449.

²⁰⁶ Sefene, E. M. *J. Manuf. Syst.* **2022**, *63*, 250–274.

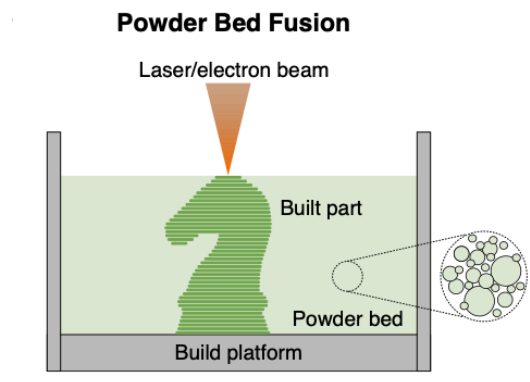


Figure 3.37. PBF printing

3.16.5 Directed energy deposition (DED)

Directed energy deposition process is similar to material extrusion process. The 3D printer is based on a nozzle mounted on a multiaxis appendage, from which the melted material is deposited onto a specific surface. This technique has attracted significant attention due to its ability to print metals and metal-alloy system, in form of either powder or wire (Figure 3.38).²⁰⁷

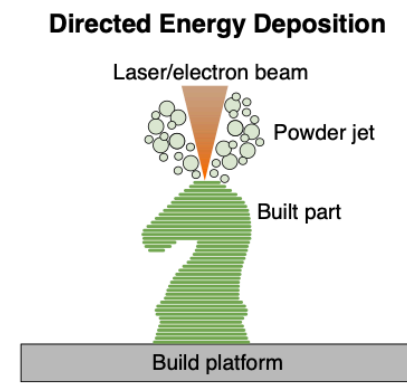


Figure 3.38. DED printing

3.16.6 Sheet lamination

Sheet lamination process create net shape 3D printed parts from bonded stacked layers of thin sheets using multiple methods, like ultrasonic additive manufacturing (UAM),

²⁰⁷ Dass, A.; Moridi, A. *Coatings* **2019**, *9*(7), 418

very high power ultrasonic additive manufacturing (VHP UAM), laminated object manufacturing (LOM), and friction stir additive manufacturing (FSAM).²⁰⁸

3.17 VAT-polymerization

3.17.1 History of VAT-polymerization

In 1981, Hideo Kodama reported the development of systems for 3D-printing of liquid photocurable resin.²⁰⁹ Kodama demonstrated that 2D images of light source could be projected to cure an entire layer of photo resin placed in a vat or alternatively a laser/point light could be scanned over the photo resin to form the printed part. These techniques are now known as digital light processing (DLP), and stereolithography (SLA) respectively (Figure 3.39).

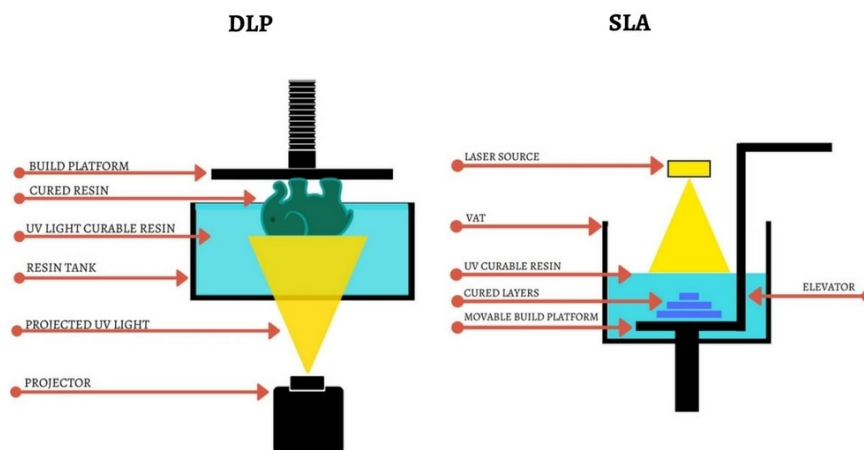


Figure 3.39. DLP and SLA printing process

While Kodama's innovation represents the first discover of what is now called stereolithography, this word was not defined until Charles Hull coined the term stereolithography in a 1984 patent application named "apparatus for production of three-dimensional objects by stereolithography".²¹⁰ Hull's patent was significant, as it

²⁰⁸ Haddad, M.; Nixon, K. B.; Wolff, S. Sheet Lamination. In *Springer Handbook of Additive Manufacturing*; Pei, E., Bernard, A., Gu, D., Klahn, C., Monzón, M., Petersen, M., Sun, T., Eds.; Springer International Publishing: Cham, 2023; pp 407-423.

²⁰⁹ Harris, T. A.; Dyer, A. L.; McCarthy, K. J. *Rev. Sci. Instrum.* **1981**, 52(11), 1770-1774.

²¹⁰ Hull, C. W. Apparatus for Production of Three-Dimensional Objects By Stereolithography. Patent 1984, 16.

supported the founding of the first commercial AM company, 3D Systems.²¹¹ Since then, the field of vat photopolymerization has received always more interest in academic field, with a rapidly increasing number of publications since the development of the technology.

3.17.2 VAT-polymerization operation and parameters

The VP process is based on the curing of liquid photo-sensitive polymer by the action of a certain wavelength of light, which supplies the energy to initiate the photo polymerization reactions to form a 3D object. The wavelength and intensity of the laser source and exposure time are the key factors to induce an appropriate photopolymerization. Additionally, some key important printing parameters for VAT polymerization printing include laser scanning speed, layer thickness, Z compensation and part orientation. These printing parameters are highly inter-dependent, and the selection of appropriate printing parameters is critical towards the fabrication of objects with good accuracy.²¹² The relationship between the various printing parameters implies that the printing parameters should be carefully studied and optimized, in relation to the resin type, to achieve high resolution structures with strong interface bonding between adjacent layers. Although VP has been developed mostly for use with polymers, it has also been demonstrated for organogels, hydrogels, glasses and ceramics. However, material selection is still limited due to challenges with resin stability, processability and synthetic accessibility of photo resins either as a suspension or as an inorganic-organic mixture.

There are two essential components to consider with VP printing: photoinitiators and monomers. Photo-initiators are the species that absorb UV light and generate a reactive species that initiates the polymerization of the monomers, usually via radical or cationic polymerization mechanisms. Monomers, that gives rise to the formation of polymer, should have reactive functional groups, such as epoxides or acrylate functionalities, able to form cross-linking bonds. Most materials used in VP printing cure through radical photopolymerization which is based on three phases: initiation, propagation and termination. A radical photo-initiator, present in the resin, absorbs light and generates a

²¹¹ Gibson, I.; Rosen, D.; Stucker, B. *Additive Manufacturing Technologies*; Springer New York: New York, NY, 2015; pp 63–106

²¹² Ng, W. L.; Lee, J. M.; Zhou, M.; Yeong, W. Y.; Naing, M. W. *Biofabrication* **2020**, 12(2), 022001

reactive radical species that initiates the radical polymerization. The two main types of radical photo-initiators are: Norrish Type I and Type II. As explained previously, in PART I (paragraph 3.2 “Photo-polymerization, UV curing”), Type I initiators comprise single molecules that are cleaved into radical species, while Type II initiators require two molecules: a photo-initiator and a co-initiator that forms the radical species following the donation of a hydrogen atom to the photo-initiator. The most used photo-initiators for VP printing are: TPO, Irgacure 2959 and Irgacure 819 (Figure 3.40).^{213,214,215}

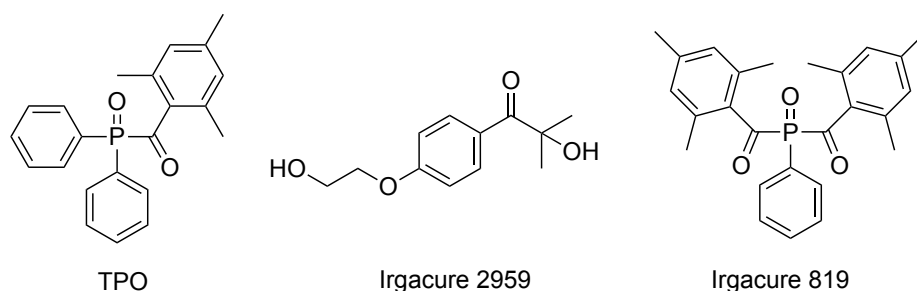


Figure 3.40. Radical polymerization photo-initiators

Acrylate or methacrylate are the most used cross-linkers in vat polymerization photo-resins. Additives such as absorbers, fillers, diluents and others are often used to reduce light scattering, improve printability or add functionality. For all printing techniques, understanding light penetration and the behavior of the reactive species is important as it affects the amount of light absorbed and penetrated through the curable resin. The light penetration depth is expressed by the Beer-Lambert equation:

$$C_d = D_p \ln \left(\frac{E_{max}}{E_c} \right)$$

where C_d is the polymerization depth, D_p is the light penetration depth into the photo-resin, E_{max} is the light exposure dose and E_c is the critical exposure dose or gel point.²¹⁶ Varying light intensity on a specific resin is known to affect the degree of polymerization and result in differences in print efficiency and goodness. Therefore, rheology studies on the resin may be necessary before proceeding to the actual printing process.

²¹³ Moore, D. G.; Barbera, L.; Masania, K.; Studart, A. R. *Nat. Mater.* **2020**, *19*, 212–217.

²¹⁴ Han, D.; Lu, Z.; Chester, S. A.; Lee, H. *Sci. Rep.* **2018**, *8*, 1–10.

²¹⁵ Chan, V.; Zorlutuna, P.; Jeong, J. H.; Kong, H.; Bashir, R. *Lab Chip* **2010**, *10*, 2062–2070.

²¹⁶ Hofstetter, C.; Orman, S.; Baudis, S.; Stampfl, J. *Addit. Manuf.* **2018**, *24*, 166–172.

3.18 Characterization techniques for VP printing

Knowing the rheological properties of resins is fundamental for VAT-polymerization process, as a specific range of viscosity is required in order to produce successful prints. Resin viscosity can be adjusted with reactive or nonreactive diluents to ensure a target range.²¹⁷ Diluents, like propoxylated neopentyl glycol diacrylate, are used to reach the target low viscosity needed for the specific system.²¹⁸ On the other hand, precursors of high viscosities limit diffusion of radicals which can affect resolution and prevent object sedimentation.²¹⁹ A crucial step, in this regard, is photo rheology technique, which is used to determine the viscosity of the resin, to detect the gel point and to determine the appropriate light intensity for the resin under test. Furthermore, it is used to determine the reaction kinetics and the effect of the photo-initiator, understating the way it interacts with the resin and its optimal dose. This tool allows to measure the time needed for the storage modulus of the resin to increase at different light intensities; it is also possible to determine the gel point of the resins thanks to the crossover that occurs when the storage modulus, under illumination, exceeds the loss modulus, providing the ideal time needed for good curing during 3D-printing.²²⁰

Additionally, FT-IR technique is often used to evaluate the presence of functional groups in the resin, such as carbon-carbon double bonds, or C-O-C bonds, to ensure and confirm the polymerization of acrylate, vinyl or epoxide monomers. The degree of cure can be determined and studied by monitoring the change in C=C peak area or intensity. The infrared technique allows to confirm the photopolymerization by checking the disappearance of the acrylic functionality due to the formation of cross-linking bonds. SEM can be further used to evaluate the morphology of the printed part, to study the spatial distribution of multiple materials and the cohesion between the interconnected printed layers.

²¹⁷ Choi, J. W.; Kim, H. C.; Wicker, R. *J. Mater. Process. Technol.* **2011**, *211*, 318–328.

²¹⁸ Choi, J. W.; MacDonald, E.; Wicker, R. *J. Adv. Manuf. Technol.* **2010**, *49*, 543–551.

²¹⁹ Kelly, B. E.; Bhattacharya, I.; Heidari, H.; Shusteff, M.; Spadaccini, C. M.; Taylor, H. K. *Science* **2019**, *363*, 1075–1079.

²²⁰ Mishra, A.; Wallin, T. J.; Pan, W.; Xu, P.; Wang, K.; Giannelis, E. P.; Mazzolai, B.; Shepherd, R. F. *Sci. Adv.* **2020**, *5*, 3918.

3.19 VP printing of biopolymers

Although VP technique is relatively new and has only recently gained more interest, progress is being made in the area of bioprinting and the in-depth development of engineering aimed at sustainability, biocompatibility, and at the same time high performances. Some bio-based resins are often derived from the use of bio-based monomers or diluents including polyethylene glycol acrylate (PEGDA) or gelatin methacrylate (GelMA).²²¹ Studies shown as biopolymers of natural origin such as hyaluronic acid or alginate have been modified with methacrylate groups to form photopolymerizable bio-resins that can be used for 3D printing.^{222,223} A thorough understanding of the type of bio-resin suitable for additive manufacturing, the way in which how the components, including monomers, diluents and photoinitiators interact with each other will help to develop a bio-resin that has potential in terms of resolution, performance, biocompatibility and applicability.

Biologically derived monomers could enable the 3D printing of novel cured polymers. In this regard, unsaturated vegetable oils, for instance, with conjugated carbon–carbon double bonds, can undergo radical polymerization, originating alternatives to fossil-based building-blocks suitable for AM such as polyesters, polyurethanes, polyolefins.

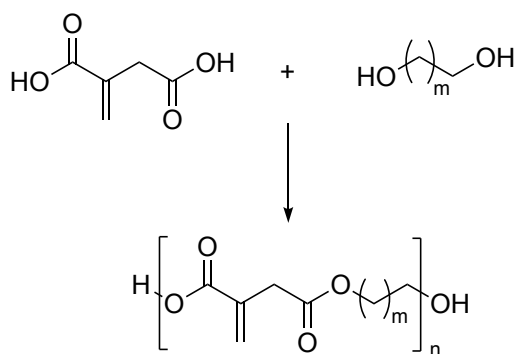
3.20 Itaconic acid-based polymers for bio 3D-printing

Itaconic acid-based polyesters, obtained through polycondensation process between itaconic acid and diol/polyol (Scheme 3.12), have been identified as potential bio-based resins for 3D-printing materials, due to the presence of α,β -unsaturation that enable the easy UV-curing and the possibility of tuning the thermomechanical properties based on the type of diol or polyol used.

²²¹ Grigoryan, B.; Paulsen, S. J.; Corbett, D. C.; Sazer, D. W.; Fortin, C. L.; Zaita, A. J.; Greenfield, P. T.; Calafat, N. J.; Gounley, J. P.; Ta, A. H.; Johansson, F.; Randles, A.; Rosenkrantz, J. E.; Louis-Rosenberg, J. D.; Galie, P. A.; Stevens, K. R.; Miller, J. S. *Science* **2019**, *364* (6439), 458–464.

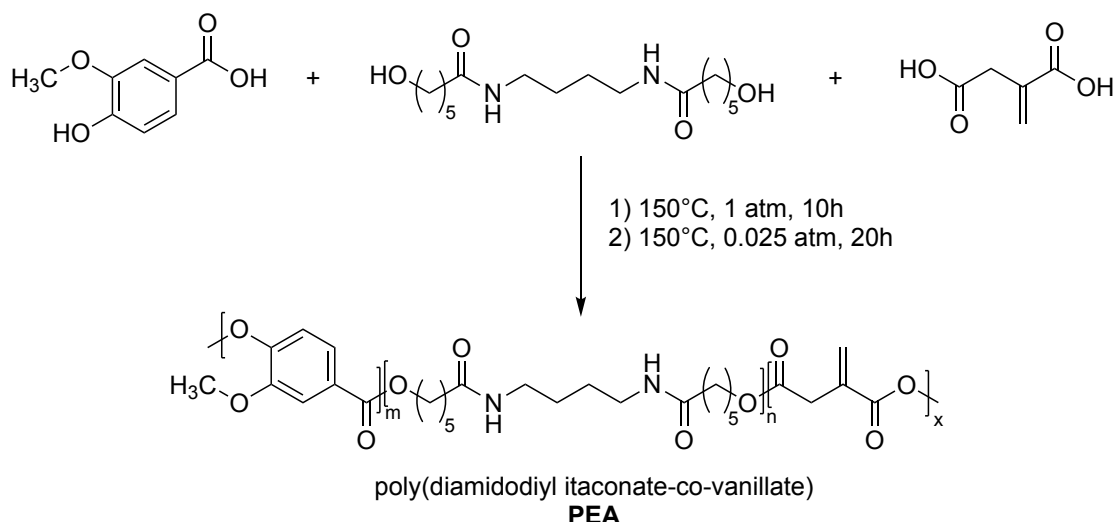
²²² Poldervaart, M. T.; Goversen, B.; De Ruijter, M.; Abbadessa, A.; Melchels, F. P.; Öner, F. C.; Dhert, W. J. A.; Alblas, J. *PLoS One* **2017**, *12*(6), e0177628.

²²³ Mishbak, H.; Cooper, G.; Bartolo, P. *Int. J. Bioprint.* **2019**, *5* (2), 189



Scheme 3.12. Itaconic acid-based polyesters synthesis

A study demonstrated the potential of unsaturated poly(ester amide) (PEA), synthesized through polycondensation (Scheme 3.13), in additive manufacturing, displaying great results in term of elongation (30%) at the break of the 3D-printed parts and showing no intrinsic cytotoxicity.²²⁴



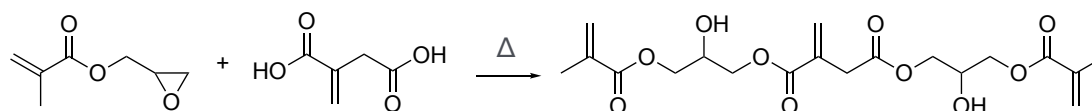
Scheme 3.13. Unsaturated poly(ester amide) synthesis

Another study reported the combination between bio-based polyester itaconates with crosslinkers to produce phosphorescent inks characterized by good elongation at the break (18%) and a transition temperature of 8°C. Although these resins still need further investigation as they show a post-production yellowing process.²²⁵

²²⁴ Vetri Buratti, V.; Sanz de Leon, A.; Maturi, M.; Sambri, L.; Molina, S. I.; Comes Franchini, M. *Macromolecules* **2022**, 55 (8), 3087–3095.

²²⁵ Maturi, M.; Pulignani, C.; Locatelli, E.; Buratti, V. V.; Tortorella, S.; Sambri, L.; Franchini, M. C. *Green Chem.* **2020**, 22 (18), 6212–6224.

Recently, itaconic based acrylates are generating growing interest since almost the majority of photoactive acrylates commercially available are fossil-based derived.²²⁶ Glycidyl methacrylate (GMA), a bio-based material, and itaconic acid have been combined to synthesize photoactive acrylic monomers, via a solventless reaction (Scheme 3.14).²²⁷



Scheme 3.14. Photoactive acrylic monomers synthesis

In another study, three different types of reactive diluents derived from itaconic acid were synthesized with sustainable processes and high yields. Here, the use of the itaconic reactive diluents improved the final conversion of double bonds (evaluated by photo-DSC) and the gel content compared to the neat resin employed.²²⁸

Further modifications of itaconic acid-derived monomers with bio-based alcohols and epoxides are currently under investigation to further increase the bio-based content. This will lead to acrylic acid-free photoactive compound and completely bio-based UV-curable materials that can be applied not only in additive manufacturing processes.

3.21 Itaconic anhydride as bio-based building block

Itaconic anhydride (IAN) is considered one of the most important building blocks of renewable origin and it is usually obtained from pyrolysis of citric acid, or it can be produced through dehydration reaction of itaconic acid. Itaconic anhydride is characterized by two main functional groups, an acid anhydride ring group and a vinylidene group that contribute to its reactivity (Figure 3.41).

²²⁶ Zhang, B.; Kowsari, K.; Serjouei, A.; Dunn, M. L.; Ge, Q. *Nat. Commun.* **2018**, 9 (1), 1831.

²²⁷ Wang, S.; Wu, Y.; Dai, J.; Teng, N.; Peng, Y.; Cao, L.; Liu, X. *Eur. Polym. J.* **2020**, 123, 109439.

²²⁸ Pérocheau Arnaud, S.; Malitowski, N. M.; Meza Casamayor, K.; Robert, T. *ACS Sustainable Chem. Eng.* **2021**, 9 (50), 17142–17151.

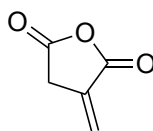


Figure 3.41. Itaconic anhydride structure

This renewable anhydride has been widely used as a compatibilizer molecule for composite materials as it shows great potential for improving the interfacial adhesion between natural fibers and polymer matrices.^{229,230} It has also been used for antimicrobial polymers suitable for biomedical applications and drug delivery system.²³¹

Furthermore, itaconic anhydride is beneficial for derivatizing amino groups in collagen, a biopolymer, in basic condition, to prepare itaconic anhydride-modified collagen (CITA) (Figure 3.42).

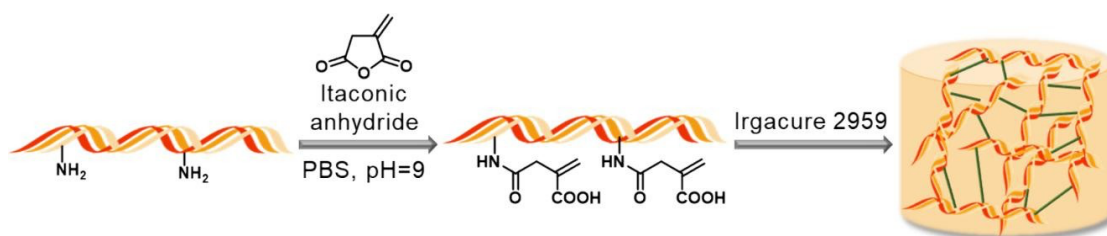


Figure 3.42. Collagen derivatization with itaconic anhydride

The hydrogel obtained is characterized by antibacterial properties and good biocompatibility and the itaconic anhydride modification allows in the gelation of modified collagen via free radical polymerization, making CITA a promising bio-based resin for 3D-printing.²³²

Itaconic anhydride, due to its bio-based nature, is gaining increasing interest in polycondensation polymerization to produce polyesters, through ring opening mechanisms catalyzed by enzymes such as lipases. The ring-opening addition condensation polymerization (ROACP) obtained by reacting cyclic anhydrides (succinic, glutaric and itaconic) and different diol has been studied. The regioselectivity of the ROP reaction with itaconic acid and octanol has been analyzed in presence and

²²⁹ Conti Silva, J. A.; Walton, H.; Dever, S.; Kardel, K.; Martins Lacerda, T.; Lopes Quirino, R. *Coatings* **2022**, *13* (1), 25.

²³⁰ Silva, J. A. C.; Dever, S.; Siccardi, A.; Snelling, D.; Al Qabani, I.; Thompson, S.; Anastasopoulou, K.; Piera, E.; de Carvalho, A. J. F.; Lopes Quirino, R. L. *Coatings* **2023**, *13* (7), 1188.

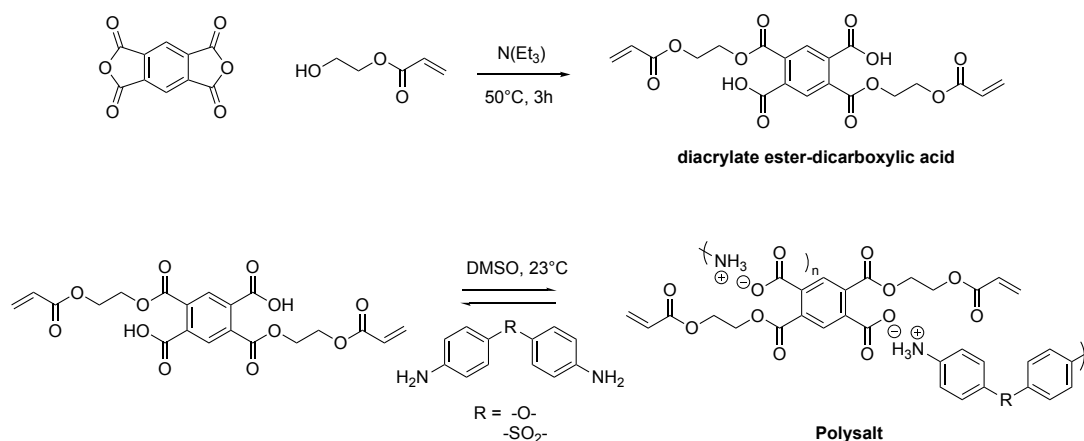
²³¹ Boschert, D.; Schneider-Chaabane, A.; Himmelsbach, A.; Eickenscheidt, A.; Lienkamp, K. *Chem. Eur. J.* **2018**, *24* (32), 8217–8227.

²³² Zhang, J.; Liu, Y.; Xu, H.; Sui, P.; Wei, B.; Xu, C.; Lin, Z.; Zhang, L.; Wang, H. *Eur. Polym. J.* **2024**, 113240.

absence of lipase catalyst, confirming the preferred formation of the β -adduct, being the β -carbonyl sterically more available than the α -carbonyl adjacent to the vinylidene group.²³³

3.22 VAT-polymerization of polysalts

Polysalts are polymers that exist as dissolved salts in solution in which each monomer contains two electronic charges. When heated, the solvent of organogel-polysalts evaporates and the monomers react to form a high molecular weight polymer. 3D printing of polysalts is made possible by co-dissolving a scaffold or through the nature of the polysalt itself. There is a growing interest in the use of polysalt resins in additive manufacturing, thanks to the ability of those to first form crosslink bonds by VAT-polymerization, and then to undergo thermal polymerization once heated to reach high molecular weight polymers. In a recent study is demonstrated that the ring-opening of dianhydrides with acrylate molecules containing nucleophiles produces diacrylate dicarboxylic acids which enables the printing of organogel upon neutralization with an aromatic diamine in DMSO solution (Scheme 3.15).



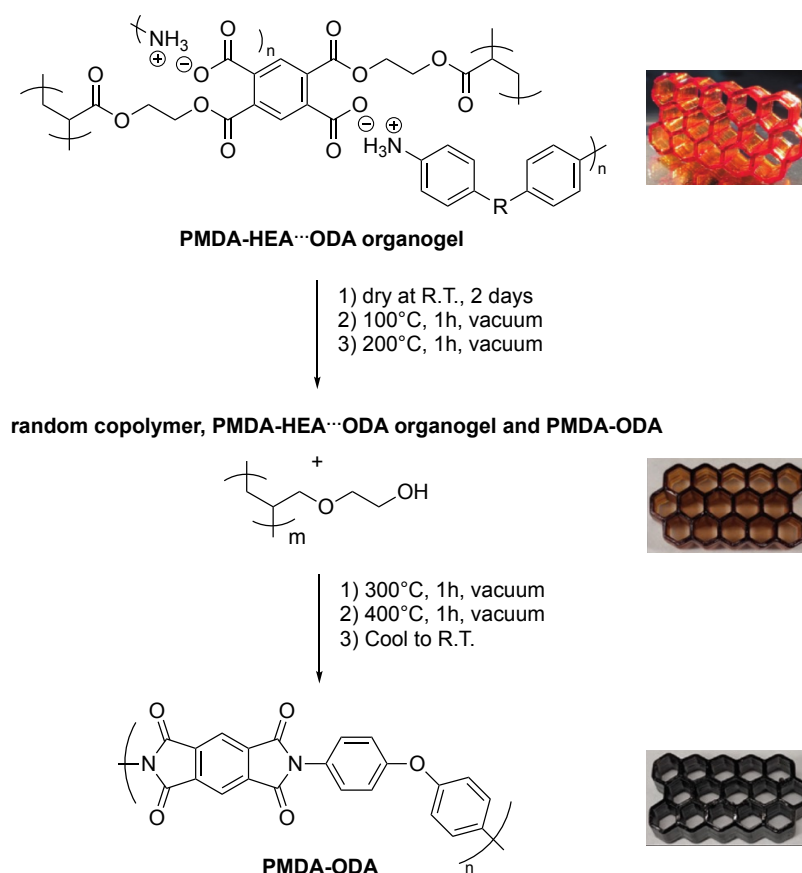
Scheme 3.15. Dicarboxylic acid synthesis and subsequent polysalt formation

In this study the effect on polysalt stability of the R group of the aromatic diamine and its impact in driving Michael reaction at the double bond of the diacrylate dicarboxylic acid were investigated by *in situ* FT-IR and photo-rheology. An electron-withdrawing R group, such as SO₂, can limit this unwanted reaction and therefore allow the formation

²³³ Yamaguchi, S.; Tanha, M.; Hult, A.; Okuda, T.; Ohara, H.; Kobayashi, S. *Polym. J.* **2014**, 46(1), 2–13.

of the polysalt enabling the reproducible VP printing of polyimide organogel intermediates. This represents a valid approach to fully exploit VAT-polymerization techniques for aromatic polyimides.²³⁴

Additional studies show how supramolecular polysalts are characterized by a reduced solution viscosities compared to traditional-synthesized organogel, which facilitates a higher wt% polymer loading during VP-printing allowing to a lower level of isotropic shrinkage during the imidation process (Scheme 3.16).²³⁵



Scheme 3.16. Conversion of polysalt to polyimide strategy of the reported literature

Furthermore, in the same study, the thermal process of 3D parts was compared with the thermal process coupled with the PMR method (Polymerizable Monomeric Reagents) and it was seen how this produced highly consolidated objects maintaining the fidelity of printing in the 3D structures. It can therefore be concluded that the ease of synthesis

²³⁴ Weyhrich, C. W.; Will, J. W.; Nayyar, G.; Westover, C. C.; Patterson, S.; Arrington, C. B.; Long, T. E. *Small* **2023**, 19 (32), 1-12.

²³⁵ Arrington, C. B.; Hegde, M.; Meenakshisundaram, V.; Dennis, J. M.; Williams, C. B.; Long, T. E. *ACS Appl. Mater. Interfaces* **2021**, 13 (40), 48061–48070.

and processability of polysalts provide a versatile platform for future studies on 3D structures of high-performance polyimides and polyamides.

3.23 Experimental part

3.24 Aim of the work

This project is the second part of the work carried out in Arizona at the Biodesign Center for Sustainable Macromolecular Materials and Manufacturing, in the research group of Professor Timothy Long. The work aims to synthesize photocurable and 3D printable polysalts obtained from bio-derived monomers. The use of itaconic anhydride as a monomer of biological origin, characterized by an acrylic functionality will enable the 3D printing of new polymers (Figure 3.43).

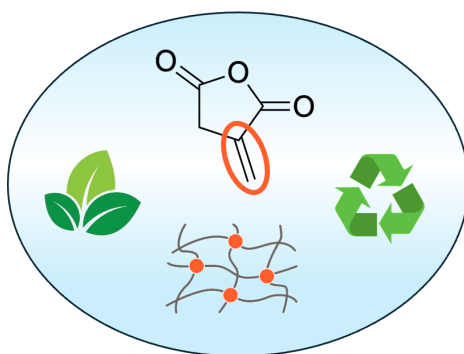
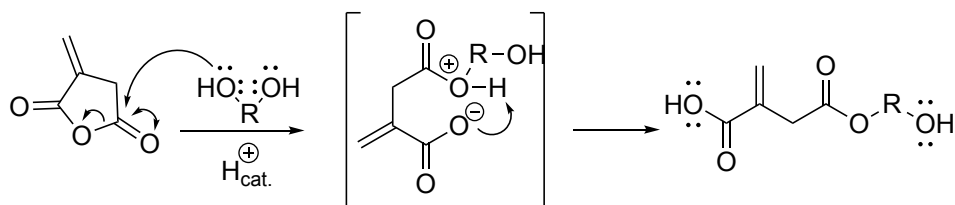


Figure 3.43. Itaconic anhydride functionalities

Specifically, the ring opening of this anhydride mediated by an alcohol, also of biological origin, gives rise to the formation of new fully biological photoactive acrylate dicarboxylic acid. The reactivity in terms of rheological properties of these dicarboxylic acids will be studied. Based on the results obtained, a study on the synthesis of new polysalts with diamines of different basicity will be reported. The final goal consists in the printing of a new bio-derived polysalt with a sustainable and advanced technique based on VAT-polymerization.

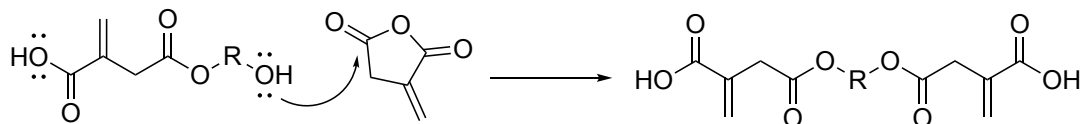
3.25 Dicarboxylic acid synthesis from IAn ring opening

The ring opening of anhydride took place selectively towards the unconjugated carbonyl group in presence of acid catalyst. Brønsted acids like p-toluenesulfonic acid (pTSA) are commonly used for this type of reaction (Scheme 3.17).



Scheme 3.17. Ring opening of itaconic anhydride in presence of an alcohol

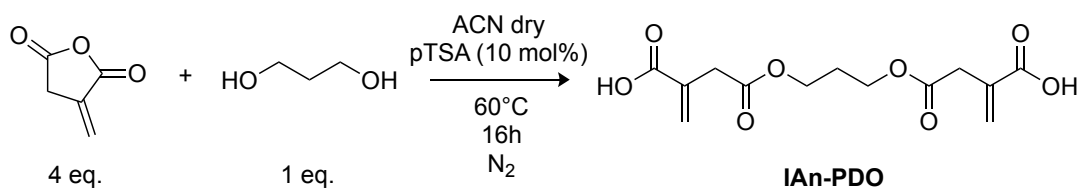
The lone pairs in the oxygen of the carboxylic moiety are delocalized into the C=O π bond via resonance. This decreases the nucleophilicity of the oxygen atoms compared to alcohols moiety where the lone pairs are more available and more likely to attack the β -carbon of another anhydride molecule (Scheme 3.18).



Scheme 3.18. Dicarboxylic acid synthesis from RO of itaconic anhydride

3.26 Synthesis of IAn-PDO with 1,3-propanediol

A mixture of IAn (4 eq.), 1,3-propanediol (PDO) (1 eq.) and pTSA (10 mol%) in 50 ml of anhydrous ACN was placed in a three-neck round-bottom flask and stirred at 60°C under nitrogen flow. An excess of itaconic anhydride was used to ensure the end capping of the diol (Scheme 3.19).



Scheme 3.19. Small dicarboxylic acid (IAn-PDO) synthesis by RO of itaconic anhydride with 1,3-propanediol

In situ FT-IR (Figure 3.46) was used to control the reaction progress and check the dicarboxylic acid (IAn-PDO) synthesis through the evaluation of the intensity related to the anhydride functional group (1851 cm^{-1}) and the new ester functionality (1734 cm^{-1}). The reaction was ended once the anhydride signal intensity goes from 0.3 to 0.15, a decrease that correspond to the half of the whole amount of IAn.

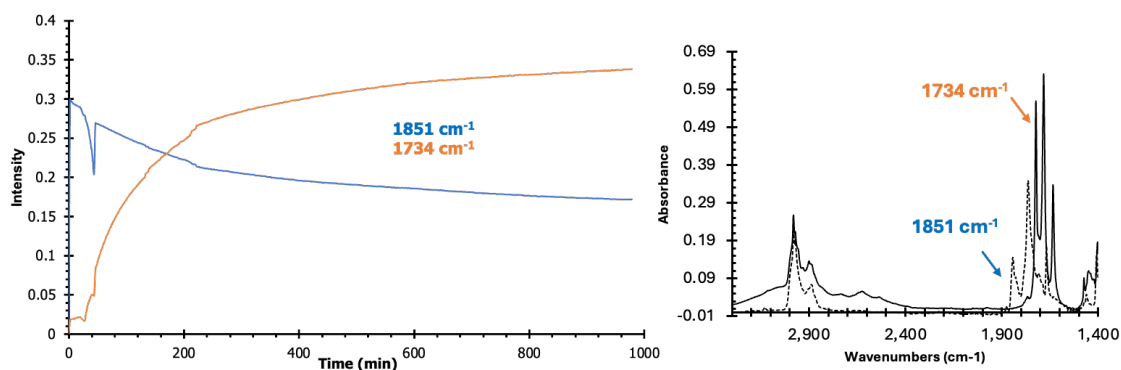


Figure 3.44. *In situ* FT-IR and FT-IR spectrum analysis of IAn-PDO synthesis

The dicarboxylic acid was then isolated by precipitation in toluene without further purification. After the filtration, the obtained product, a white powder, was then dried overnight in a vacuum oven at 80°C (Figure 3.47) yielding the desired compound in quantitative yield.

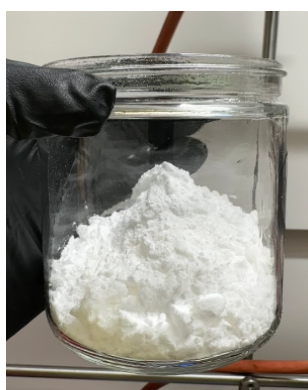


Figure 3.45. Purified IAn-PDO

It was then further analyzed by ^1H NMR, in deuterated DMSO (analysis conducted with 500 MHz, 128 scans, 5 s relaxation). The analysis confirms the product purity (Figure 3.48).

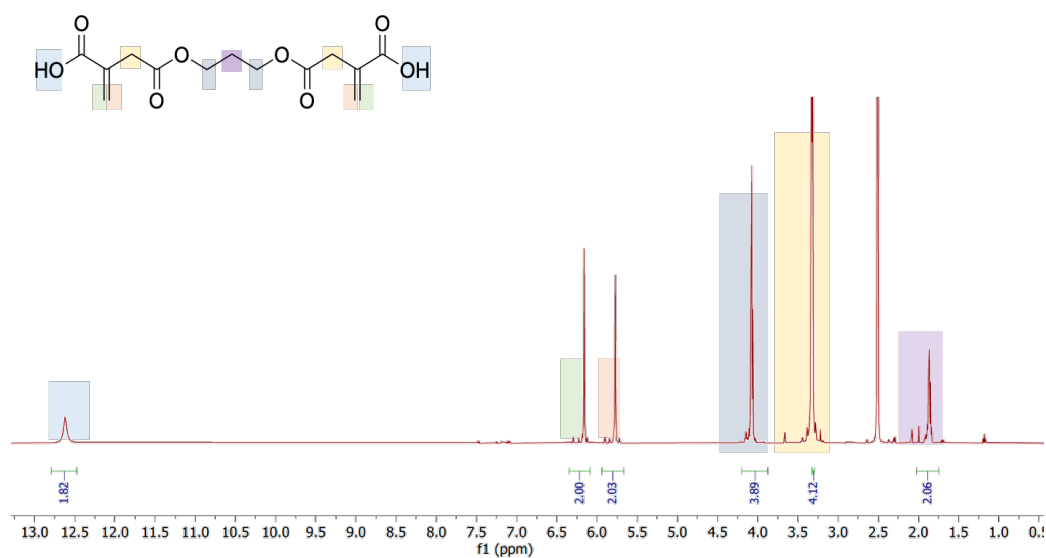


Figure 3.46. ^1H NMR of IAn-PDO

Also ^{13}C NMR (DMSO- d_6 125 MHz, 128 scans, 5 s relaxation) confirms the goodness of the reaction synthesis and the purity of the product (Figure 3.49).

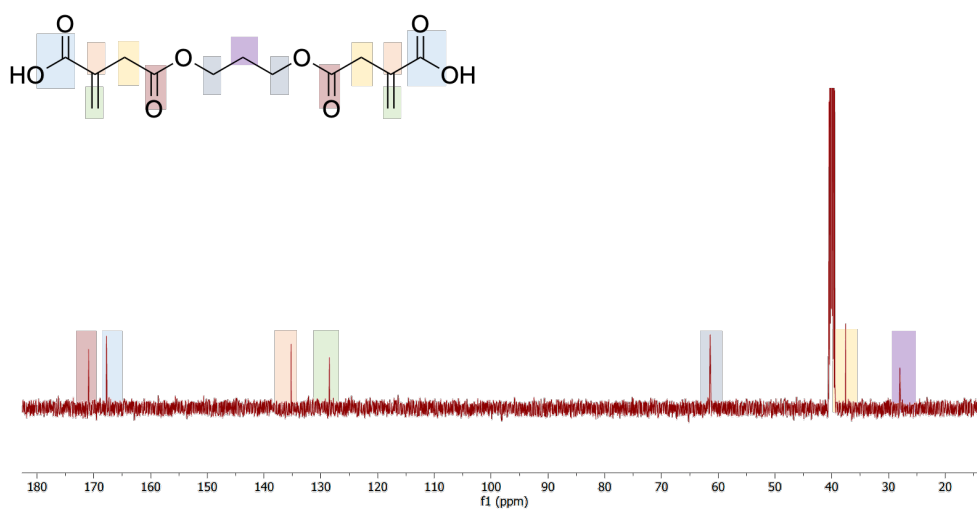


Figure 3.47. ^{13}C NMR of IAn-PDO

To establish and confirm the expected reaction regioselectivity HMBC (Heteronuclear Multiple Bond Correlation) analysis was studied (Figure 3.50). The analysis confirms that the alkene peaks are nearer to the carboxyl group, as they relate to the peak at 168

ppm, instead of 171.4 referred to the ester carbonyl, in accordance with literature regarding unsaturated ester carboxylic acid.^{236,237}

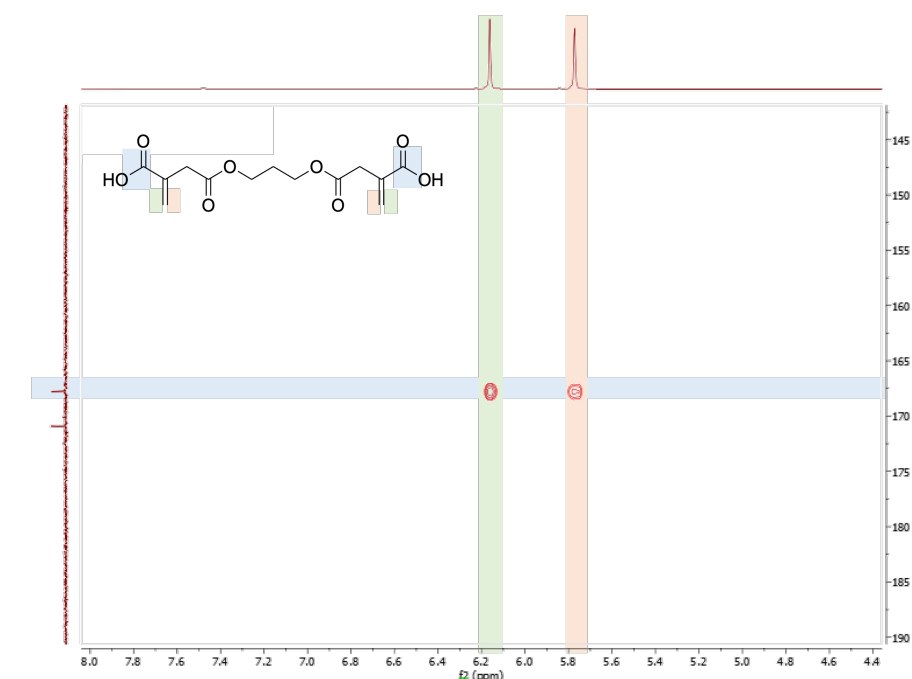


Figure 3.48. HMBC analysis of IAn-PDO

The new synthesized photoactive bio-dicarboxylic acid, IAn-PDO, has also been thermally characterized by TGA analysis (Figure 3.51). The thermogravimetric analysis shows two losses in weight. The first decomposition step occurs between at $T_{\text{onset}} = 217.57$, showing a greater thermal stability respect to the majority of photoreactive

²³⁶ Rajabi, F.; Wilhelm, C.; Thiel, W. R. A. *Green Chem.* **2020**, 22 (14), 4438–4444.

²³⁷ Kurmasheva, N.; Said, A.; Wong, B.; Kinderman, P.; Han, X.; Rahimic, A. H.; Olagnier, D. *Nat. Commun.* **2024**, 15 (1), 4096

dicarboxylic acid, and itaconic acid itself. The second temperature region, between 250 and 450 °C indicates decarboxylation and carbonization processes.²³⁸

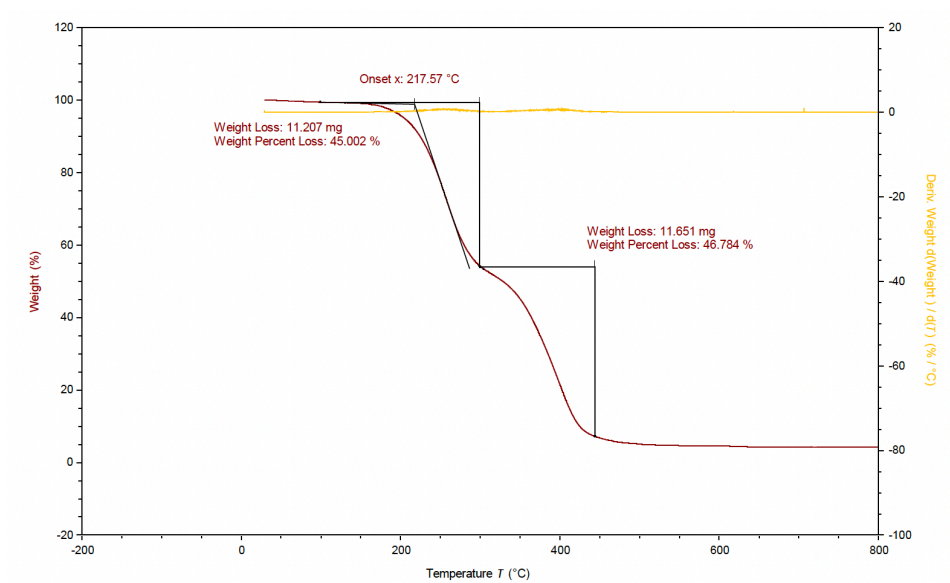


Figure 3.49. TGA analysis of IAn-PDO

Also, a further characterization was given by DSC analysis (Figure 3.52), from which is possible to notice that the melting point of the synthesized dicarboxylic acid is 112.60°C.

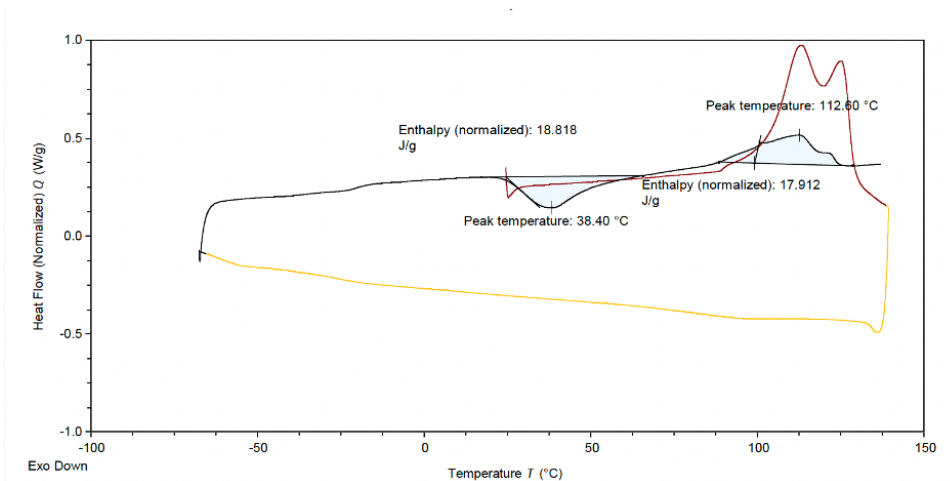


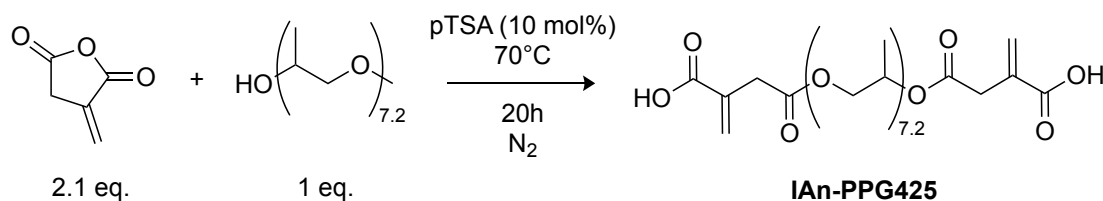
Figure 3.50. DSC analysis of IAn-PDO

After fully characterizing the new molecule, the same synthetic approach was applied to produce a second photoreactive dicarboxylic acid with a longer chain, achieved through the ring opening of itaconic anhydride using a macro-diol.

²³⁸ Coşkun, R.; Soykan, C.; Delibaş, A. *Eur. Polym. J.* **2006**, 42 (3), 625–637.

3.27 Synthesis of IAn-PPG425 with PPG425

Propylene glycol with $M_w = 425$ g/mol (PPG425) (1 eq.) and IAn (2.1 eq.) were mixed, in presence of pTSA (10 mol%), under nitrogen at 60°C for 20 h (Scheme 3.20).



Scheme 3.20. Synthesis of macro dicarboxylic acid with PPG425 (IAn-PPG425)

The reaction was stopped when no further increase in the -COOH peak was detected in according with the disappearance of anhydride functionality (Figure 3.53).

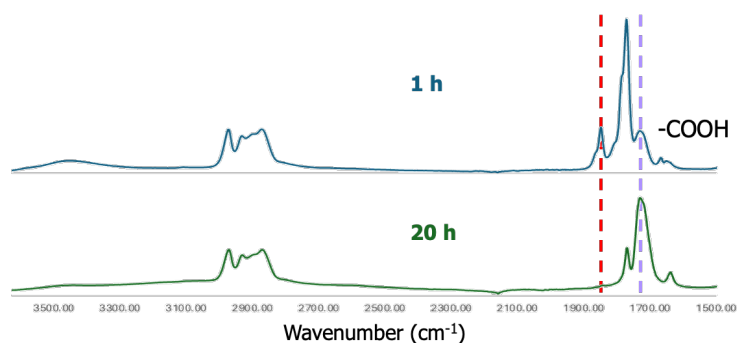


Figure 3.51. FT-IR check analysis of reaction synthesis of macro dicarboxylic acid with PPG425

The product came out as honey-like yellow liquid (Figure 3.54). Due to purification issues given by the macro-diol, the product was utilized with no further treatments.

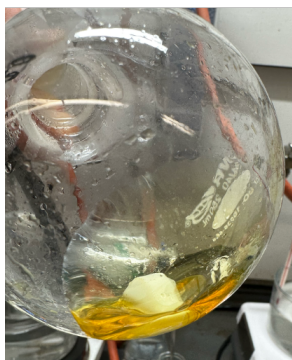


Figure 3.52. IAn-PPG425

3.27.1 Photorheology studies of dicarboxylic acids

Photo-rheology, as mentioned before, is one of the most common techniques used to depict the crosslinking ability of photocurable resins at a controlled UV exposure time, irradiance, and wavelength. IAn-PDO with 20 wt.% of DMSO and 2.5 wt.% of TPO and IAn-PPG425 (solventless) with 2.5 wt.% of TPO were analyzed with Discovery Series HR3 (w/ Photo-accessory, 100mW/cm² 20mm parallel plate, 200 μ m gap, 1 Hz, 0.1% strain) (Figure 3.55).

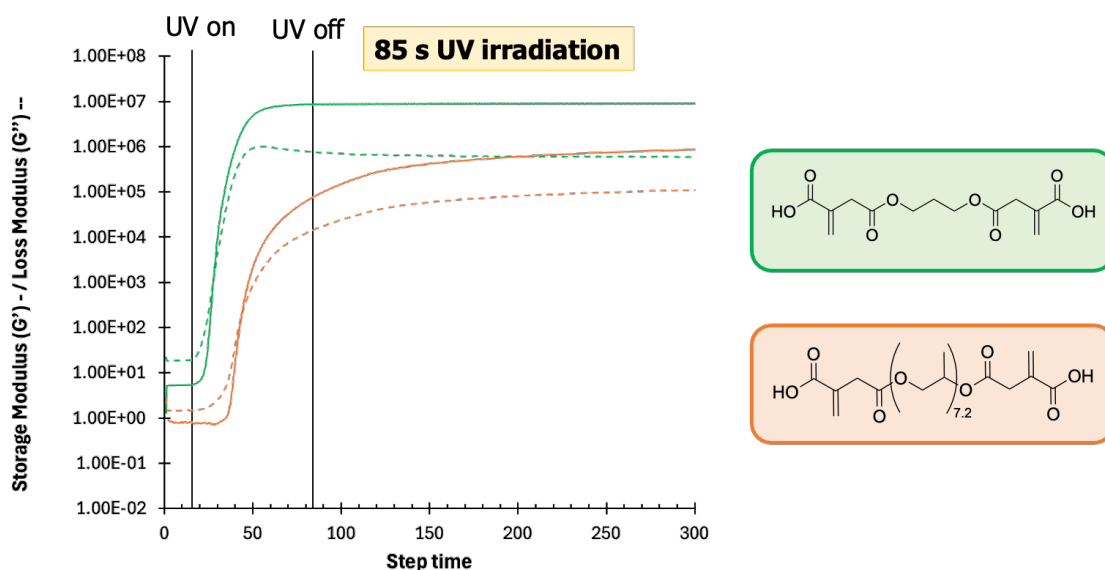


Figure 3.53. Photo-rheology of IAn-PPG425 (green curve) and IAn-PDO (orange curve)

With UV irradiation time of 85 seconds both the synthesized dicarboxylic acid has proven to be curable. The best results are given for the IAn-PDO, which reach a higher storage modulus (10⁷ Pa) right after the crossover time (11 sec from the beginning of UV irradiation). IAn-PPG425 instead presents a higher crossover time, as an indication of slower radical polymerization process, under the same test conditions, due to the presence of an extended backbone chain between the acrylic functionalities. It can also be observed that this resin continues to form crosslink bonds even after exposure to UV light, factor that can pose a problem for 3D printing. In order to see if the photoactive resins are chemically crosslinked and not subject to a physical or incomplete crosslink, gel fraction tests were performed on the discs extracted from the photo rheology analysis (Figure 3.56).

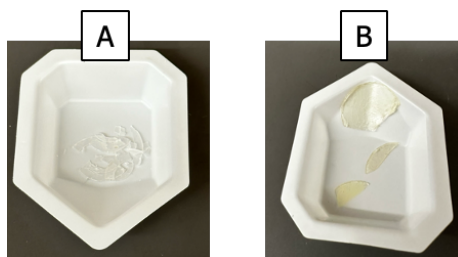


Figure 3.54. Photo rheology discs of small (A) and macro (B) dicarboxylic acids

DMSO was used as a solvent able to dissolve the non-crosslinked part. The samples were left in solution overnight, they were then extracted and dried in a vacuum oven. The calculated weight of the samples thus recovered was compared with the initial weight and gel fraction was calculated with the following formula:²³⁹

$$\text{Gel fraction (\%)} = \frac{W_2}{W_1} \times 100$$

Where W_1 is the initial mass of the resin and W_2 is the mass of the resin after the drying. Gel fraction percentage obtained for IAn-PDO is 80% indicating a good chemical crosslinking confirmed by disappearance of carbon-carbon double bond from FT-IR analysis. The value obtained for IAn-PPG425 is 47% revealing an incomplete curing in confirmation of what was observed in photo rheology test. A longer UV exposure time would be optimal to enhance the gel fraction percentages.

²³⁹ Karásek, L.; Meissner, B. *J. Appl. Polym. Sci.* **1998**, 69 (1), 95–107.

3.27.2 Photo-DSC studies of dicarboxylic acids

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by DSC-Q2000 equipped with Photo-accessory, at 30 s exposure, 80 mW/cm², 25 °C with N₂ as purge gas. The dicarboxylic acid solutions (the same fraction solutions used for photo-rheology) were exposed to UV radiation and the heat flow versus time profiles was studied under isothermal mode (Figure 3.57).

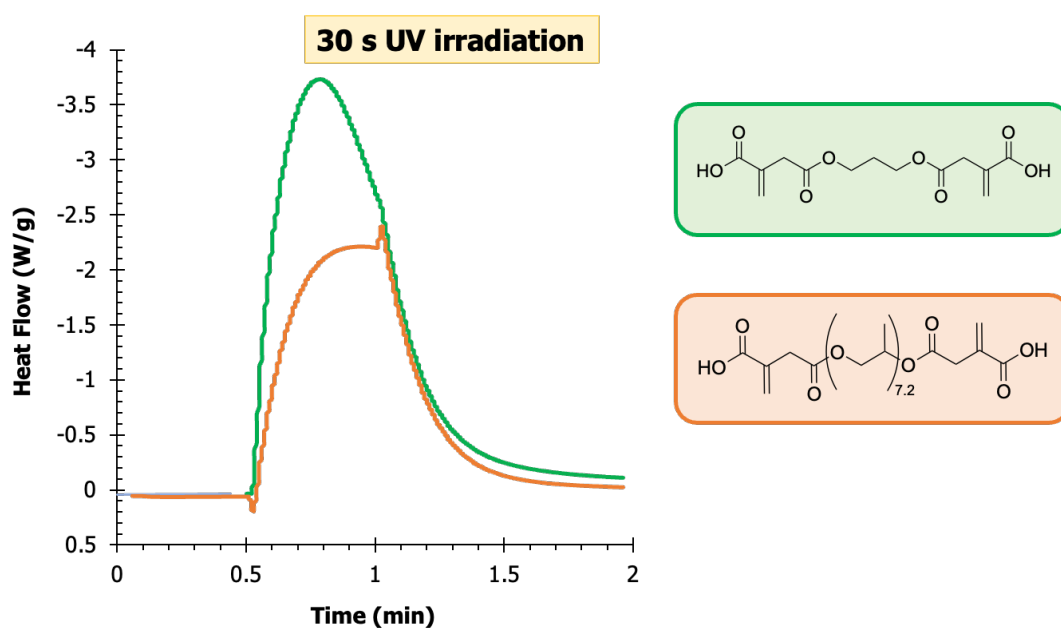


Figure 3.55. Photo-DSC of small (green curve) and macro (orange curve) dicarboxylic acids

Photo-DSC reveals kinetics of C=C conversion in dicarboxylic acids. The reaction heat liberated in the radical polymerization is directly proportional to the number of vinyl groups reacted in the system. It is therefore possible to calculate the conversion of vinyl double bonds by integrating the area under the exothermic peak according to the following equation²⁴⁰:

$$\text{Double bond conversion (\%)} = \frac{\Delta H_t}{\Delta H_0^{(theor)}}$$

where ΔH_t is the heat liberated at time t and $\Delta H_0^{(theor)}$ is the theoretical heat for complete conversion.²⁴¹ The heat liberated for the small dicarboxylic acid dissolved in DMSO (80

²⁴⁰ Palanisamy, A.; Rao, B. S. *Prog. Org. Coat.* **2007**, 60 (3), 161–169

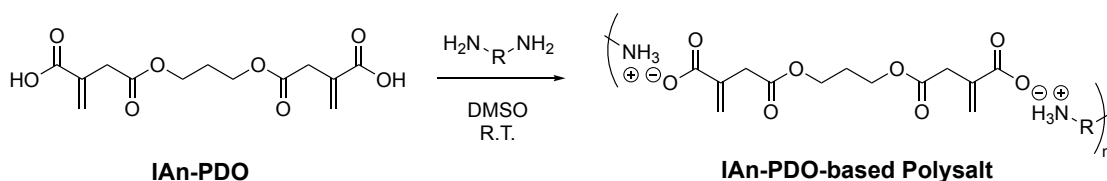
²⁴¹ Roy, S. *Polym. Bull.* **1999**, 42, 229–236.

wt.% of IAn-PDO, 20 wt.% of DMSO) is $\Delta H_t = 109.69$ J/g allowing to a complete C=C conversion in 30s. The heat liberated for IAn-PPG425 is $\Delta H_t = 76.965$ J/g allowing to a C=C conversion of 34%. The photo-DSC further confirms the better propensity of IAn-PDO to undergo radical polymerization and its greater ability to convert carbon-carbon double bonds compared to the PPG425-based dicarboxylic acid which requires longer cure times for high acrylate conversion.

Based on the obtained results, the study will focus now on the 1,3-propanediol-based dicarboxylic acid, which represents a promising photoreactive building block, fully bio-based, for the synthesis of bio-derived polymers in additive manufacturing techniques. Its potential and its distinct properties will therefore be exploited in the synthesis of novel polysalts polymers.

3.28 Synthesis of polysalts

A stoichiometric mixture of IAn-PDO with the corresponding diamine in DMSO (50 wt.%) yielded the desired polysalt (Scheme 3.21). The dicarboxylic acid and the diamine were mixed at room temperature until the complete dissolution (≈ 1 h).



Scheme 3.21. IAn-PDO-based Polysalt synthesis

The different diamine explored for the polysalt synthesis are 4,4'-oxydianiline (ODA), 4,4'-diaminodiphenyl sulfone (DDS) and 2,2'-(ethylenedioxy)bis(ethylamine) (EDEA). Once synthesized each polysalt were characterized by ^1H NMR.

3.28.1 Polysalts chemical characterization

^1H NMR confirms the formation of the polysalt with ODA (Figure 3.58).

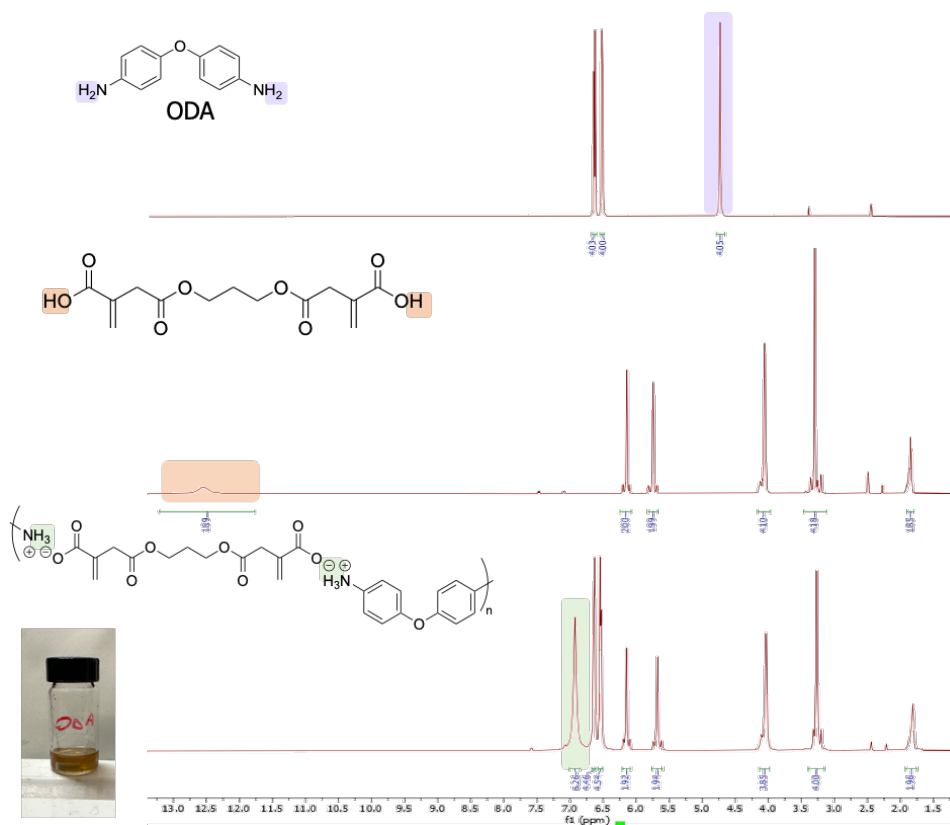


Figure 3.56. ^1H NMR spectra of ODA, IAn-PDO and polysalt (IAn-PDO-ODA)

From the comparison between the NMR spectra of ODA, IAn-PDO and polysalt it is possible to confirm the formation of the polysalt by the disappearance of the peak at 4.77 ppm referred to the amine protons of ODA and the appearance of the peak 6.9 ppm which integrates 6H, as the protons of the salt $-\text{OH}_3\text{N}-$ in the obtained monomer. Furthermore, it's evident that the reaction with the diamine does not give rise to undesirable side reactions as the Michael addition, verified by the presence of the protons of the double bond related to the dicarboxylic acid functionality.

^1H NMR confirms the formation of the polysalt with DDS (Figure 3.59).

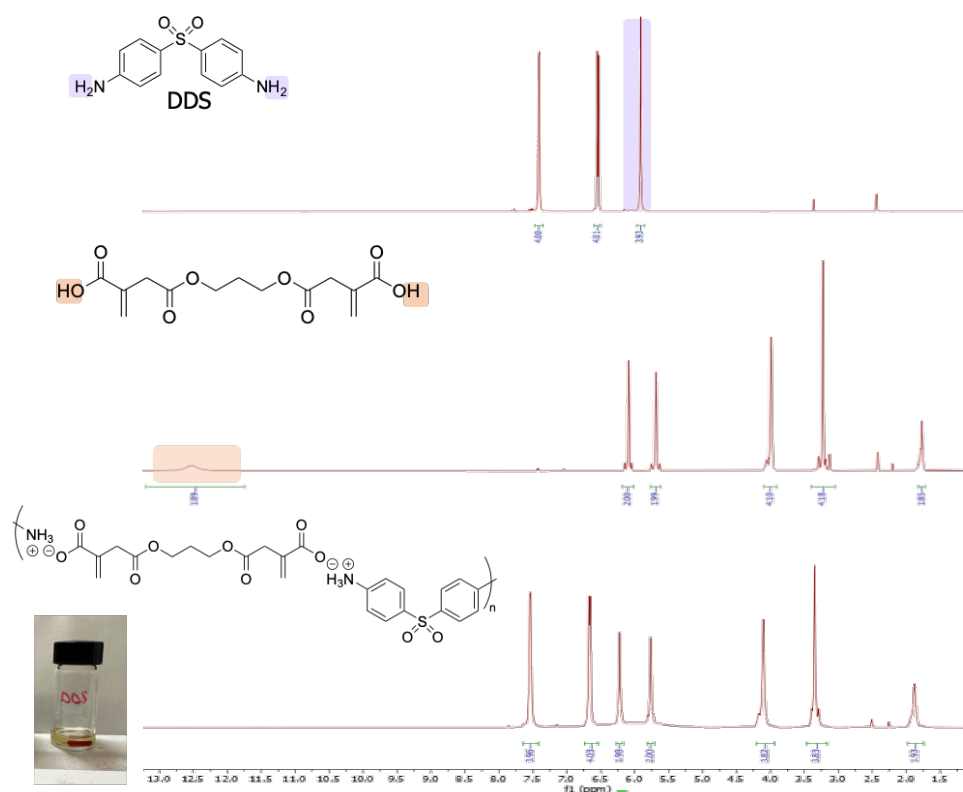


Figure 3.57. ^1H NMR spectra of DDS, IAn-PDO and polysalt (IAn-PDO- $\cdots$ DDS)

Also in this case, the polysalt formation was confirmed by the disappearance of the amine protons of DDA at 5.9 ppm. It's not possible to notice the appearance of the peak related to the salt protons due to the presence of the electron withdrawing group SO_2 in DDS. In any case the polysalt formation can be further established by the disappearance of the hydroxyl protons relative to the dicarboxylic acid and by the persistence of the protons of the double bonds.

Finally, also IAn-PDO $\cdots$ EDEA polysalt formation was confirmed by ^1H NMR analysis with the same explanations (Figure 3.60).

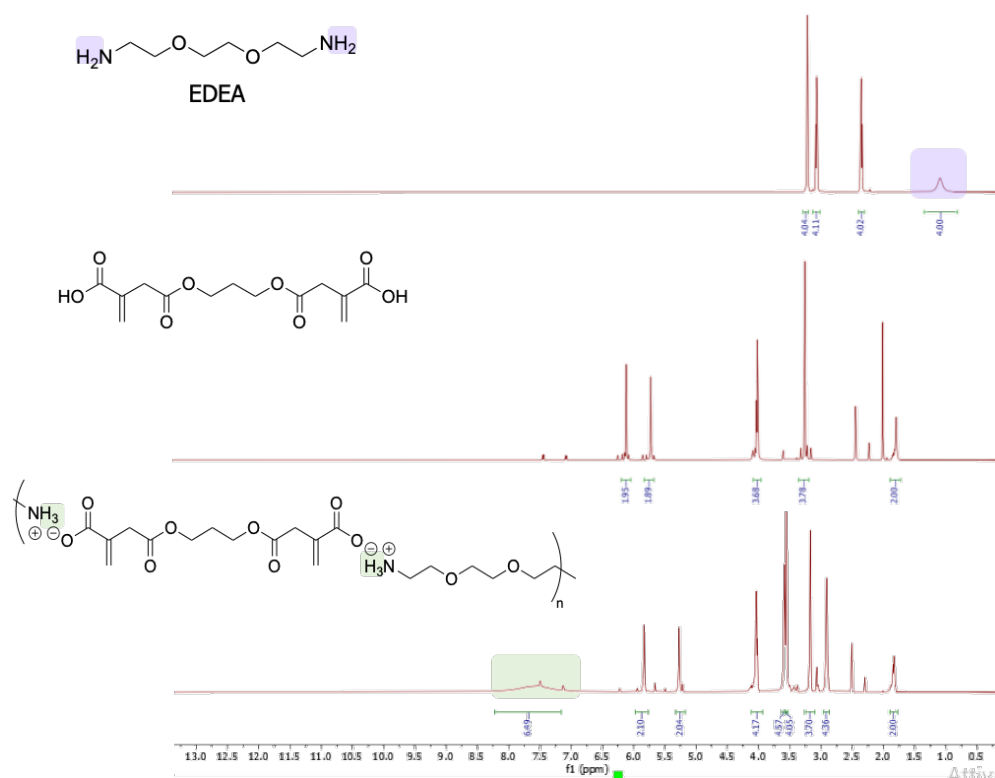


Figure 3.58. ^1H NMR spectra of EDEA, IAn-PDO and polysalt (IAn-PDO···EDEA)

3.28.2 Photorheological studies of polysalts

Photorheological studies on polysalts were performed using solutions made of diacid: diamine 1:1 (50 wt.% NMP, 2.5 wt.% TPO) (Figure 3.61).

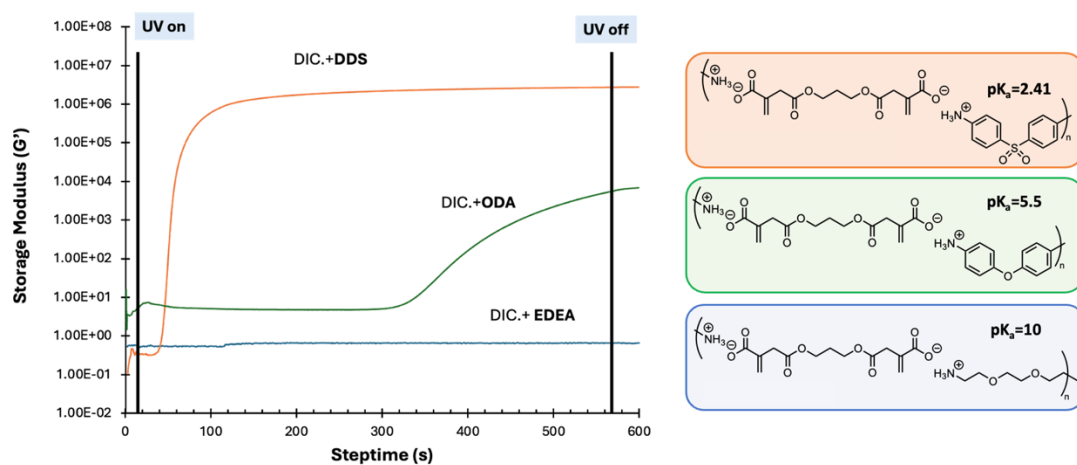


Figure 3.59. IAn-PDO···DDS, IAn-PDO···ODA, IAn-PDO···EDEA photo rheology

The depicted crossover times for relative polysalts are:

- IAn-PDO...DDS (50 wt% NMP, 2.5 wt% TPO) → 27,5 sec.
- IAn-PDO...ODA (50 wt% NMP, 2.5 wt% TPO) → 372,3 sec.
- IAn-PDO...EDEA (50 wt% NMP, 2.5 wt% TPO) → no crossover

It's evident that the basicity of the diamine and the proximity of the these to the double bond affect the radical polymerization process of photocurable polysalts. With the increase of the basicity of the diamine was observed an increase in the crossover time. This could be due to the diamine's ability to extract hydrogen atoms from the dicarboxylic acid, terminating the radical propagation steps. Additionally, the electron-withdrawing substituent in DDS decreases the electron density in the double bond of the dicarboxylic acid, making it more electrophilic thus increasing the propagation rate of the radical polymerization process (Figure 3.62).^{242,243}

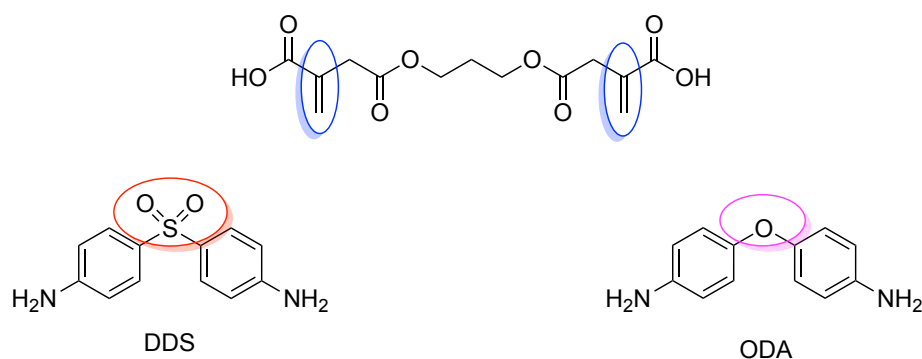


Figure 3.60. IAn-PDO, DDS, ODA structures

Consequently, the electron-donating substituent in ODA increases the electron density in the double bond of IAn-PDO, making it less electrophilic and reducing its reactivity towards the addition of the propagating radical. No crossover was observed for the IAn-PDO...EDEA polysalt, since due to the inductive effect of the aliphatic groups in EDEA, the aliphatic diamine increases the electron density at the double bond more than ODA does, thus hindering the radical polymerization.²⁴⁴

²⁴² Colombani, D. *Prog. Polym. Sci.* **1999**, 24(3), 425–480

²⁴³ Rzaev, Z. M. O. *Prog. Polym. Sci.* **2000**, 25(2), 163–217.

²⁴⁴ Burget, D.; Jacques, P.; Vauthey, E.; Suppan, P.; Haselbach, E. *J. Chem. Soc., Faraday Trans.* **1994**, 90 (17), 2481–2487.

3.29 3D-printing of polysalt

Based on the rheological results of the analyzed polysalts, the scale up of IAn-PDO $\cdots$ DDS in NMP (50 wt.%) and TPO (2.5 wt.%) was performed. It is important to note that the polysalt in solution is quite stable with polar aprotic solvents such as DMSO and NMP. But a better retention of the supramolecular structure and ionic interactions was observed using NMP as solvent, which avoids the crash out of the freshly photocured reagents.

The first tests of polysalt printing with Asiga Max X27 DLP printer coupled with 385 nm UV source (Figure 3.63), have shown that the polymer is not able to cure properly, even changing parameters like layer thickness, exposure time, and UV intensity.

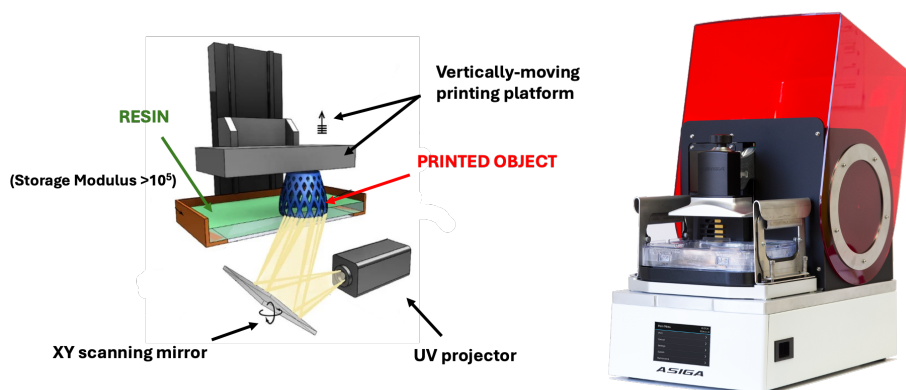


Figure 3.61. 3D-printer parts and Asiga Max X27 DLP printer

Thus, to solve printing issues, a non-volatile reactive diluent such as trimethylolpropane triacrylate (TMPTA) was used to better increase the C=C diffusion (Figure 3.64).

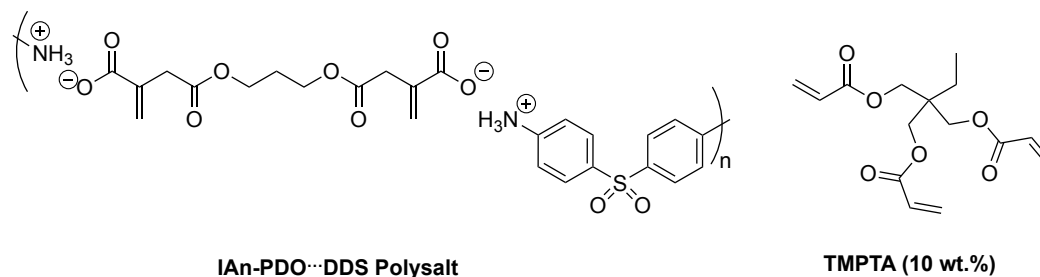


Figure 3.62. IAn-PDO $\cdots$ DDS and TMPTA structures

A solution of IAn-PDO $\cdots$ DDS, 50 wt.% solid in DMSO, 2.5wt.% of TPO and 10 wt.% of TMPTA was made for the printing. Photo rheology was performed as a preliminary analysis to verify the effect of the reactive diluent on the crossover time and how it can affect the storage modulus (Figure 3.65).

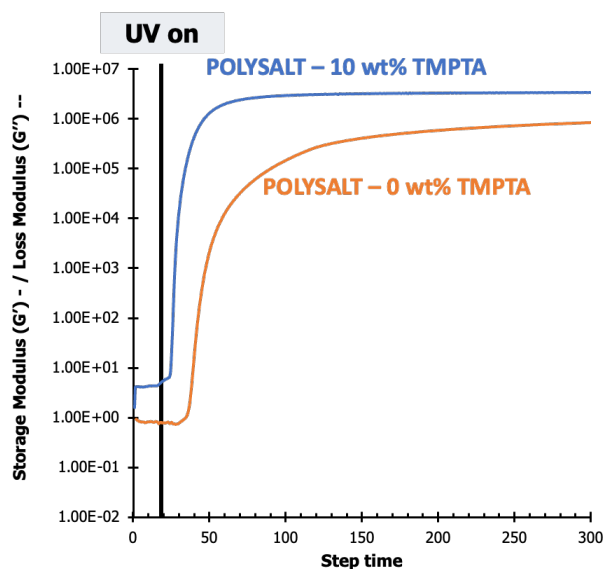


Figure 3.63. Photo rheology of IAn-PDO $\cdots$ DDS (orange) and IAn-PDO $\cdots$ DDS with TMPTA (10 wt.%)

The results show a decreased crossover time (less than 10 seconds are needed for the crosslinking) and an improvement of the storage modulus, which is comprised between 10^6 and 10^7 Pa, the optimal value for VAT-polymerization.

TMPTA enable the 3D printing of honeycomb geometry (Figure 3.66).

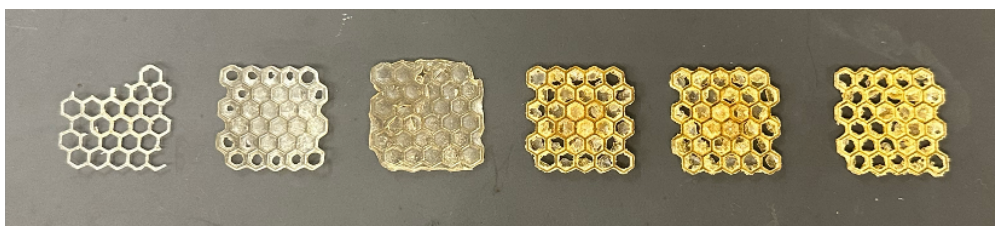
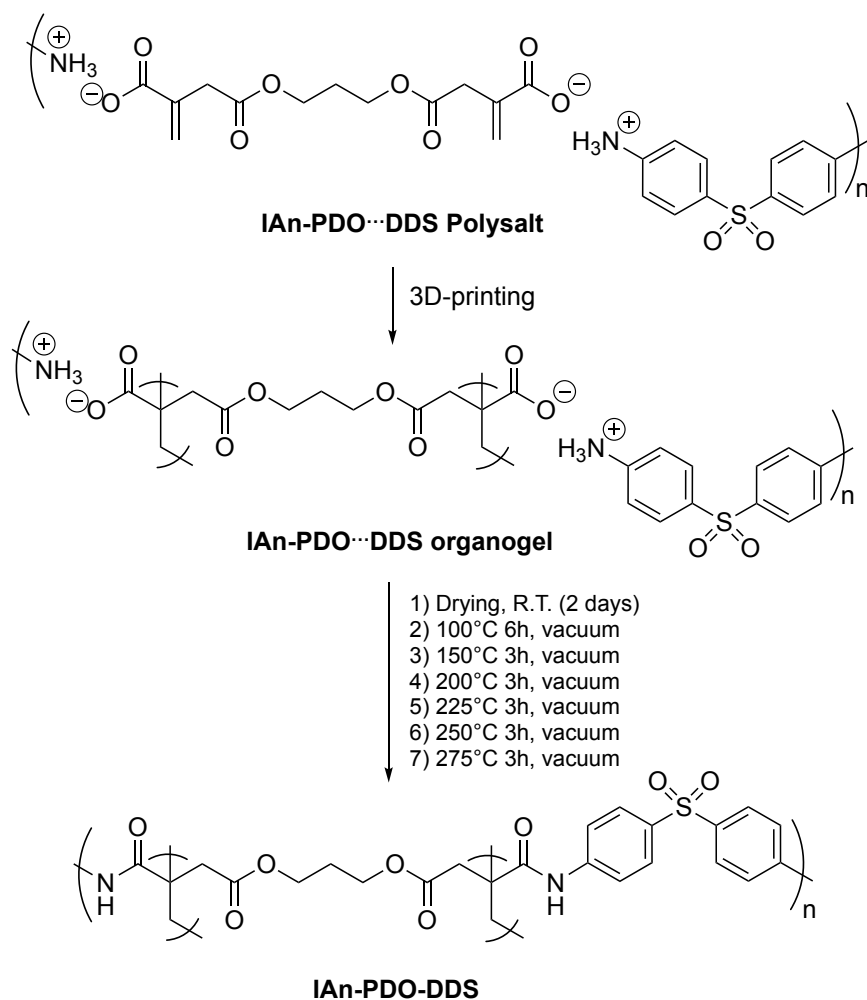


Figure 3.64. 3D-printing of IAn-PDO $\cdots$ DDS with TMPTA

The printing process needs to be further optimized, and the 3D-parts are not characterized by an optimal resolution; the setting of the printing parameters requires an in-depth and targeted study of the employed resin.

3.30 Thermal treatment of polysalt

Once the polysalt organogel was synthesized, the printed parts were thermally treated to enable the thermal amidation process (Scheme 3.22).



Scheme 3.22. 3D printing and thermal amidation

The samples were heated under vacuum at different set temperatures for varying amounts of time. At each specific temperature range the thermal stability of the material was evaluated by TGA 5500, with a heating program of 10°C per min., from 30 to 800°C under N₂ atmosphere (Figure 3.67).

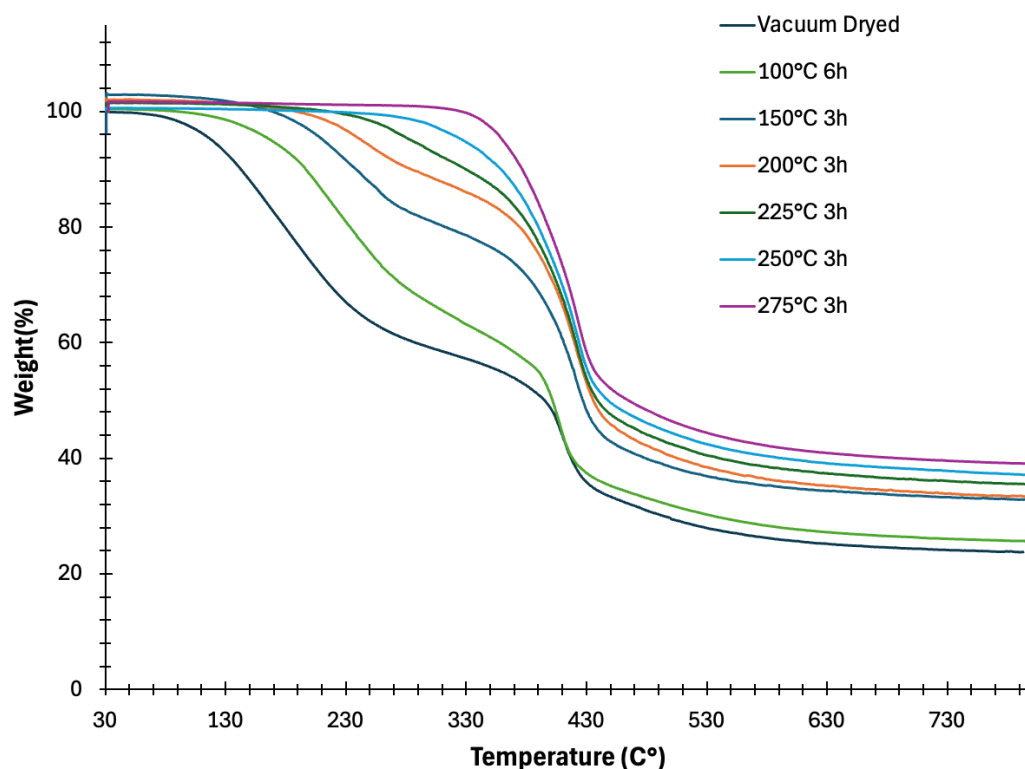


Figure 3.65 Thermal analysis of heated IAn-PDO-DDS (TMPTA) organogel

The results of the TGA analyses show a gradual increase in thermal stability at higher temperatures, factor that suggests the successful thermal amidation process. The amidation is known to occur at temperatures ranging from 120°C to 160°C, but it can also take place at higher temperatures, such as 230°C, depending on the chemical structure of the monomer.^{245,246}

²⁴⁵ Lanigan, R. M.; Sheppard, T. D. *Eur. J. Org. Chem.* **2013**, 2013 (33), 7453–7465.

²⁴⁶ Goossen, L. J.; Ohlmann, D. M.; Lange, P. P. *Synthesis* **2009**, 2009 (01), 160–164

3.31 Conclusion

The unique properties of bio-based itaconic anhydride, endowed with an external acrylic functionality, enabled the facile synthesis, through ring opening reaction, of a novel 1,3-propanediol-based dicarboxylic acid. IAn-PDO constitutes a promising renewable cross-linking reagent and building block for applications in supramolecular intermediates such as polysalts. Its chemistry, thermal properties, and reactivity were fully exploited in the present work highlighting the practical applicability of this molecule. Different types of polysalts have been synthesized with diamines with distinct characteristics. It has been observed, through rheological studies, how the presence of electron withdrawing or donating groups, vicinal to the double bond in beta of the dicarboxylic acid, affects the radical polymerization process. It has indeed been confirmed that the optimal photo-reactive properties were provided using 4,4'-diaminodiphenyl sulfone, which thanks to the electron-donating group, increases the electronic density at the double bond, favoring the radical polymerization reaction and promoting a faster curing process.

In the context of VAT-polymerization, the present work serves as an initial step toward exploiting the full potential of this novel resin. However, optimization of printing parameters for the specific polysalt, crucial for the synthesis of high molecular weight polyamides, requires deeper investigation. Additional chemical and mechanical analyses of the printed samples are necessary to fully assess their properties and performance. However, the whole study represents a significant and innovative advance as it demonstrates the successful synthesis of a sustainable, fully bio-based dicarboxylic acid. This novel bio-based building block enables the production of materials useful for VAT-polymerization, demonstrating a great potential for efficient and environmentally friendly processes for additive manufacturing and contributing to a more sustainable future in materials science.

General conclusions and future perspectives

This thesis has explored innovative approaches for the development of bio-based polymers and composites, addressing key challenges related to their durability, processability, and performance. Through a combination of organic functionalization strategies, advanced processing techniques, and novel synthetic pathways, this work has demonstrated that bio-based materials can achieve competitive properties while reducing environmental impact.

The main achievements of this research include:

- The successful functionalization of natural fibers, enhancing their hydrophobicity and moisture absorption resistance.
- The optimization of reactive extrusion techniques, leading to successfully recycle polymers reinforced with hemp fibers.
- The development of new synthetic biopolymers using environmentally friendly catalytic systems and selected bio-based precursors.

Despite these achievements, further research is necessary to fully exploit the potential of bio-based materials. Future directions will focus on:

- Exploring additional functionalization solutions to enhance fiber-matrix interactions and extend the applicability of fibers for bio-composites.
- Expanding the development and application of bio-based materials, particularly in fields such as biomedical research and in additive manufacturing.

Based on these findings, future studies will contribute to the continuous advancement of sustainable polymer science, encouraging the transition towards a biocircular economy.