BIOMAPS Guide to explore the structure and properties of vitrimeric biopolymer systems

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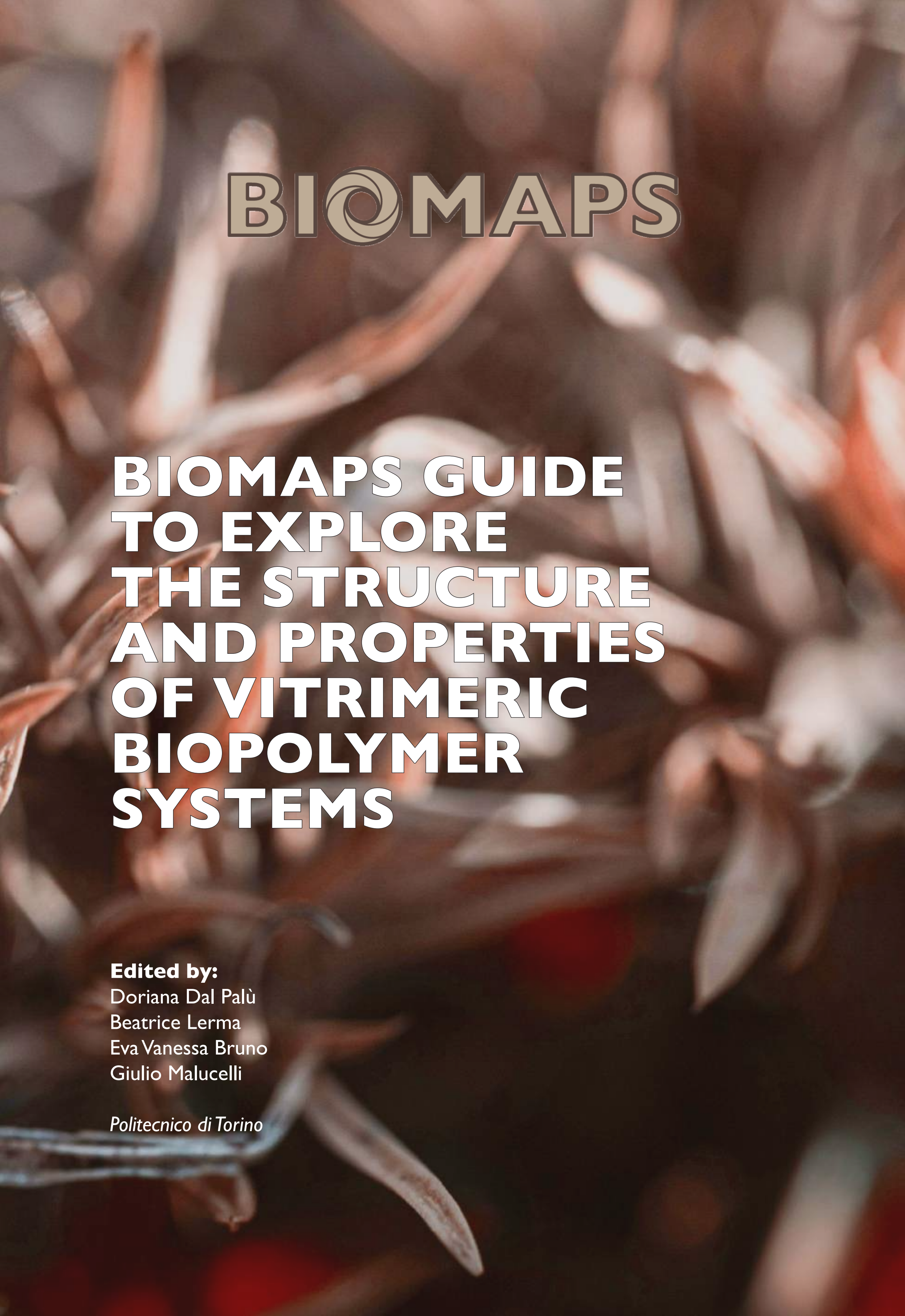

BIOMAPS

BIOMAPS GUIDE TO EXPLORE THE STRUCTURE AND PROPERTIES OF VITRIMERIC BIOPOLYMER SYSTEMS

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BIOMAPS Guide to explore the structure and properties of vitrimeric biopolymer systems

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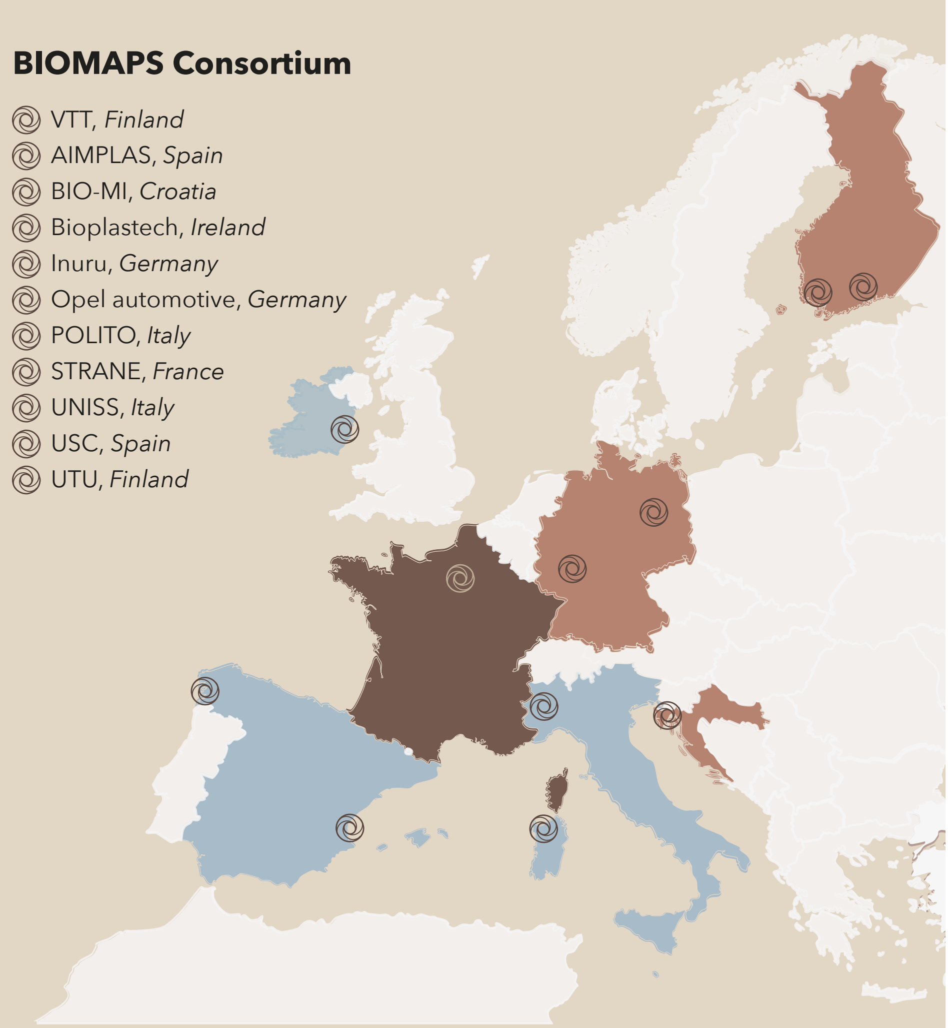
The BIOMAPS Project

BIOMAPS is a Horizon Europe project concerning Bio-Intelligent Manufacturing of Multifunctional Bio-Based Polymer System.

The BIOMAPS project aims to develop a **fully circular manufacturing value chain** for bio-manufactured plastics (vitrimeric Polyhydroxyalkanoates - PHAs- a groundbreaking set of bio-based polyesters exhibiting mechanical recyclability, biodegradability, stability, and durability).
For this purpose, modelling and AI-based tools are developed in BIOMAPS to speed-up the adaptation of vitrimeric PHAs to replace their fossil-based counterparts in the European manufacturing industry.

The BIOMAPS project is funded by the **European Union** and will last three years, during which **11 academic and industrial partners** from **7** different **countries** will be involved.



BIOMAPS Consortium

- VTT, *Finland*
- AIMPLAS, *Spain*
- BIO-MI, *Croatia*
- Bioplastech, *Ireland*
- Inuru, *Germany*
- Opel automotive, *Germany*
- POLITO, *Italy*
- STRANE, *France*
- UNISS, *Italy*
- USC, *Spain*
- UTU, *Finland*

Project leader

VTT

Academic partners

Politecnico di Torino

USC Universidade de Santiago de Compostela

UNISS Università degli Studi di Sassari

University of Turku

Industrial partners

AIMPLAS Instituto Tecnológico del Plástico

bio-mi sustainable solutions

Bioplastech

inuru

OPEL

Strane Innovation

Why this Guide?

This Guide provides a clear and accessible **introduction to biobased vitrimers**, a rapidly emerging class of materials in polymer science. Like other emerging sustainable materials, vitrimers combine complex chemistry and real-world applications, which can be difficult to understand.

For this reason, this Guide aims to simplify these concepts by offering a narrative that is scientifically sound and easy to understand. Readers will learn how these **materials are designed**, why they are considered **sustainable**, and how they can **transform the future of plastics**.

Whether you are a student, researcher, or are simply curious about innovative materials, this Guide will help you understand why **biobased vitrimers are becoming increasingly important.**

Enjoy the read!

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Bioplastics: context and data

Bioplastics can exhibit properties comparable to those of conventional plastics and, in many cases, provide **additional benefits**. These include a lower carbon footprint and further waste management solutions, such as composting.

Bioplastics encompass a wide range of materials with different characteristics, which can be divided into three main categories:

- **non-biodegradable plastics** that are fully or partially biobased, as well as high-performance biobased technical polymers;
- plastics that are **both biobased and biodegradable**;
- **biodegradable** plastics derived from fossil-based resources.

Bioplastics are, therefore, a key component of the **bioeconomy** and represent a **rapidly growing** and **innovative sector** with the potential to decouple economic development from resource consumption and environmental impact.

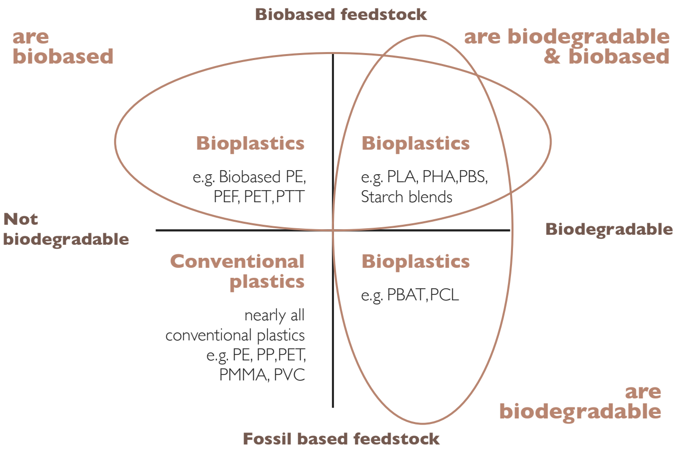

Figure 1: Material coordinate system for bioplastic. Retrieved May 18, 2026 from European Bioplastics & nova-Institute (2025), https://www.european-bioplastics.org/bioplastics/materials/

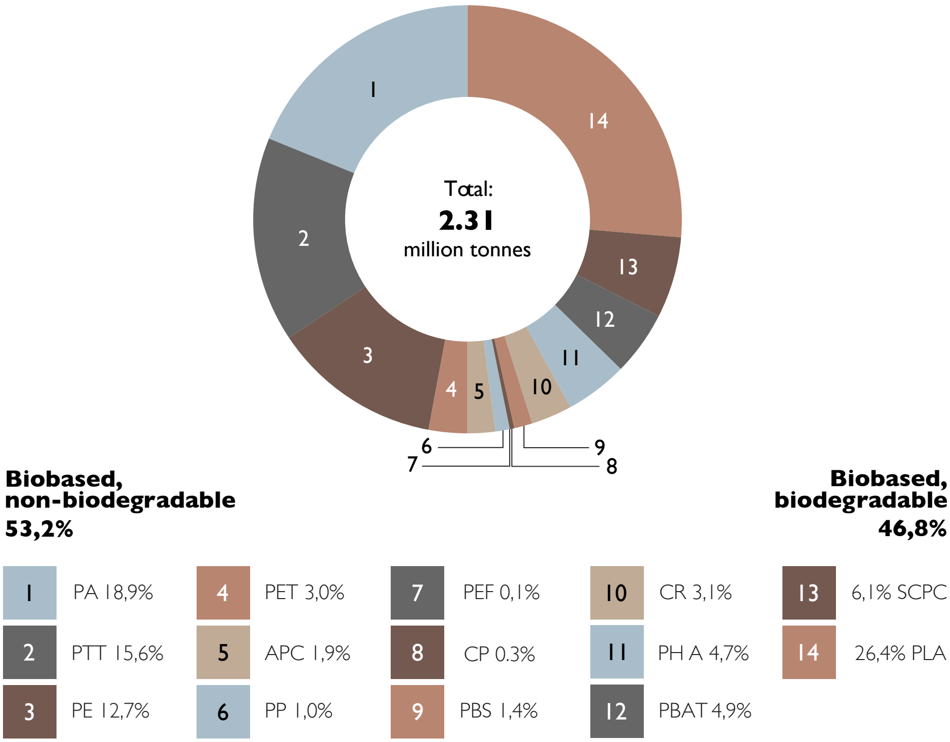

Figure 2: Global production capacities of biobased plastics 2025. Retrieved May 18, 2026 from European Bioplastics & nova-Institute (2025), https://www.european-bioplastics.org/bioplastics/materials/

Polymers and biopolymers

Before delving into the main focus of this Guide, vitrimers produced from PHAs (Polyhydroxyalkanoates), it is helpful to provide a more general **overview of polymers and biopolymers**.

Polymers are materials made of long chains of repeating molecular units, called **monomers**. They are **everywhere in our daily lives**: plastics, rubber, textiles, paints, packaging, and even DNA are all examples of polymers.

Thanks to their versatility, polymers can be lightweight, flexible, resistant, transparent, or biodegradable, making them **essential in modern technology and industry.**

Most conventional polymers are produced from **fossil resources** such as oil and natural gas.

Common examples include polyethylene, used in plastic packaging and bottles, and polypropylene, found in packaging and household objects. These materials are durable and cheap, but their widespread use has raised important environmental concerns, especially related to **waste accumulation and microplastic pollution.**

In response to these challenges, increasing attention is being given to **biopolymers**. These are

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INTRODUCTION

polymers derived from renewable biological sources such as plants, algae, bacteria, or agricultural waste. Some biopolymers are also biodegradable, meaning they can break down naturally under specific environmental conditions. Examples include cellulose, starch, poly(lactic acid) (PLA), and chitosan.

Biopolymers offer promising opportunities for **creating more sustainable materials** with lower environmental impact. They are being explored for applications in packaging, medicine, electronics, textiles, and advanced materials research. However, they are not a universal solution: their production, cost, performance, and disposal methods still present **technical and economic challenges**.

Today, research in polymer science focuses not only on improving material performance, but also on **designing smarter, safer, and more sustainable solutions**.
By combining chemistry, engineering, biology, and materials science, polymers and biopolymers are playing a key role in the transition toward a more circular and environmentally responsible economy.

Why a new biobased polymer?

Research on new bio-based polymers is becoming increasingly important in the seeking for more sustainable materials. Unlike traditional plastics derived from fossil resources, bio-based polymers are produced from renewable resources such as plants, algae, or agricultural waste.

Developing these materials can help reduce carbon emissions, decrease dependence on non-renewable resources, and limit environmental pollution. Scientists are also working to improve their properties, making them stronger, lighter, more durable, or biodegradable for specific applications.

New bio-based polymers are expected to **play a major role** in sectors such as **packaging, medicine, electronics, and transportation.**

By investing in this research, society moves closer to a circular economy where materials are designed to be safer, more efficient, and environmentally responsible.

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ADVANCING RESEARCH IN MATERIALS SCIENCE

Why biobased vitrimers?

In recent years, the environmental impact of plastics has become a major global concern. Most conventional polymers are derived from fossil resources and managing them at the end of their life cycle is often inefficient. Only a small fraction is effectively recycled.

In this context, biobased vitrimers emerge as a promising alternative. Designed using renewable resources such as vegetable oils, lignin, and other biomass-derived compounds, they reduce dependence on crude oil-based feedstocks. At the same time, they retain the dynamic behavior typical of vitrimers, enabling reshaping, repair, and recycling. **This combination aligns perfectly with the principles of sustainability and the current circular economy concept.**

Compared to traditional materials, biobased vitrimers have a smaller environmental footprint while maintaining comparable performance. **They represent a shift in perspective: materials are now designed for their entire life cycle, not just performance.**

Vitrimers: beyond standard polymers

For decades, polymers have been divided into two distinct categories: **thermoplastics**, which can be reshaped repeatedly when heated, and **thermosets**, which are stronger and more stable but cannot be easily recycled. This distinction has long represented a fundamental limitation in materials design.

Vitrimers were introduced to overcome this limitation by offering a unique combination of the two. They are a class of crosslinked polymers with dynamic covalent bonds that can undergo reversible chemical reactions, allowing them to **combine the permanent structure and strength of thermosets with the reprocessability and recyclability of thermoplastics.** These materials behave like traditional thermosets at low temperatures, maintaining their structural integrity and mechanical performance. However, when heated above a specific threshold, they can flow and be reshaped similarly to thermoplastics.

This unusual behavior is made possible by **dynamic covalent bonds** within their structure. Unlike conventional polymers, these bonds are not permanently fixed. Instead, they can rearrange over time without destroying the network.

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WHAT ARE VITRIMERS AND HOW ARE THEY PRODUCED?

As a consequence, the vitrimer can be repeatedly reshaped, reprocessed, and recycled, thus addressing the limitations of conventional thermosets. The ability to break and reform bonds also allows vitrimers to be self-healed and welded, similar to thermoplastics.

Therefore, **vitrimers can be understood as a new class of materials that combine stability with adaptability.** The concept is straightforward: vitrimers are as strong as thermosets but can be reprocessed like thermoplastics!

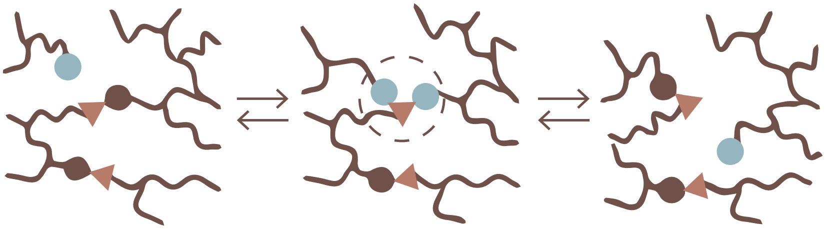


Figure 3: Associative bond exchange. Triangles and circles represent reaction sites on polymer chains that bond and de-bond resulting in a dynamic polymer crosslinking density. Blue circles represent reaction sites available to initiate a bond exchange reaction on existing bonds between the triangles and brown circles when new bonds are formed resulting a fixed crosslinking density. Adapted from (Denissen et al., 2016).

Vitrimers from PHAs

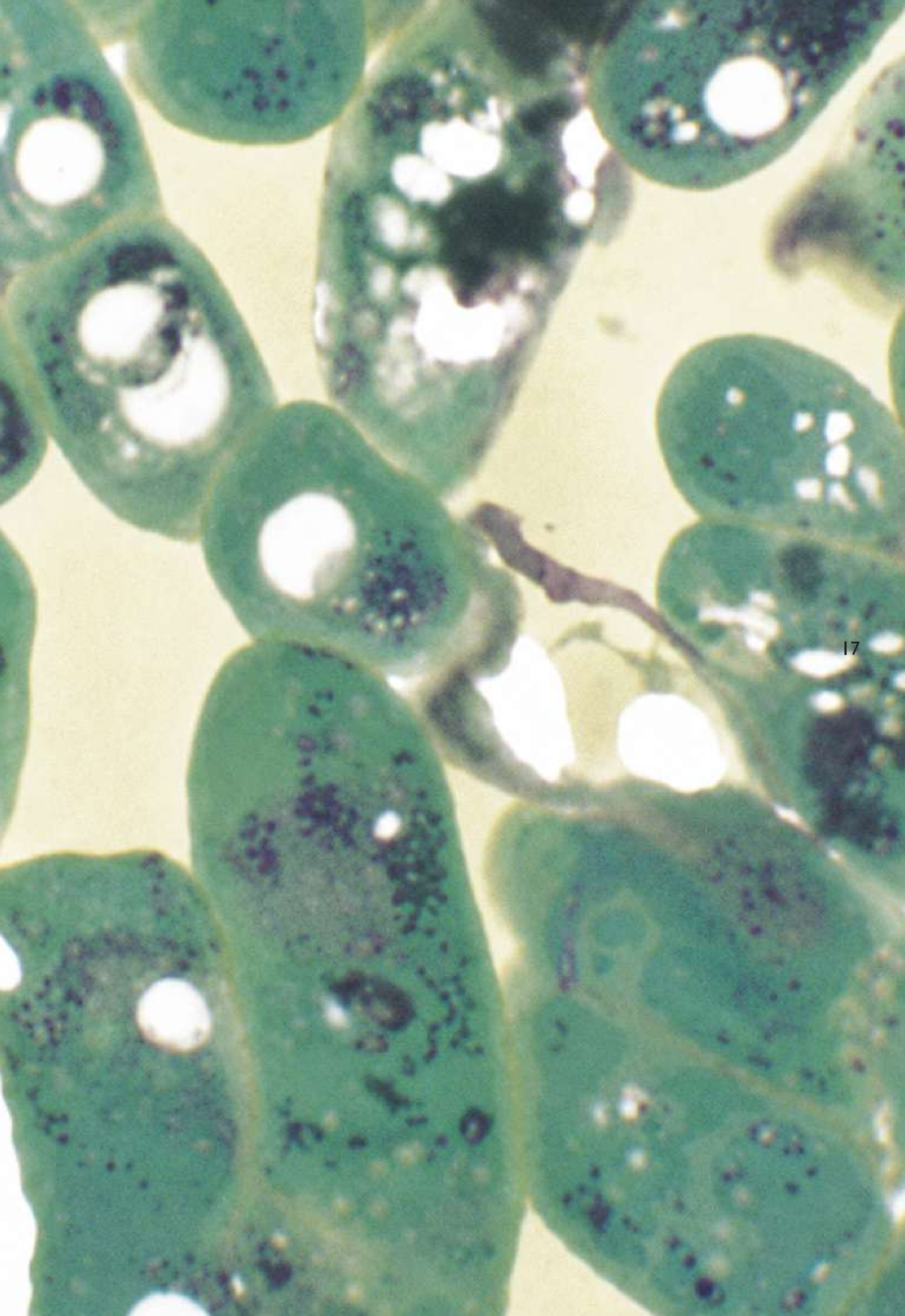
Polyhydroxyalkanoates (PHAs) are among the different renewable polymers that can be used to design biobased vitrimers and are attracting increasing attention. **PHAs are biodegradable polyesters produced naturally by microorganisms.**
They are considered **a promising alternative to conventional plastics due to their biological origin and environmental compatibility.**

When incorporated into vitrimeric systems, PHAs offer an appealing blend of sustainability and functionality. Their polyester structure makes them well-suited for dynamic exchange reactions, such as transesterification, which are commonly used in vitrimer chemistry. This allows the resulting materials to exhibit the adaptive behavior typical of vitrimers, including reprocessability and self-healing, while also being biodegradable.

However, using PHAs in vitrimer design introduces new challenges. Their relatively low thermal stability and processability compared to traditional polymers require careful control of the network structure and reaction conditions. Despite these limitations, **ongoing research aims to optimize PHA-based vitrimers by combining circularity, performance, and environmental compatibility in a single material system.**

Transesterification *is a chemical reaction that converts one ester into another by reacting with an alcohol.*

Photo by Giulio Malucelli.



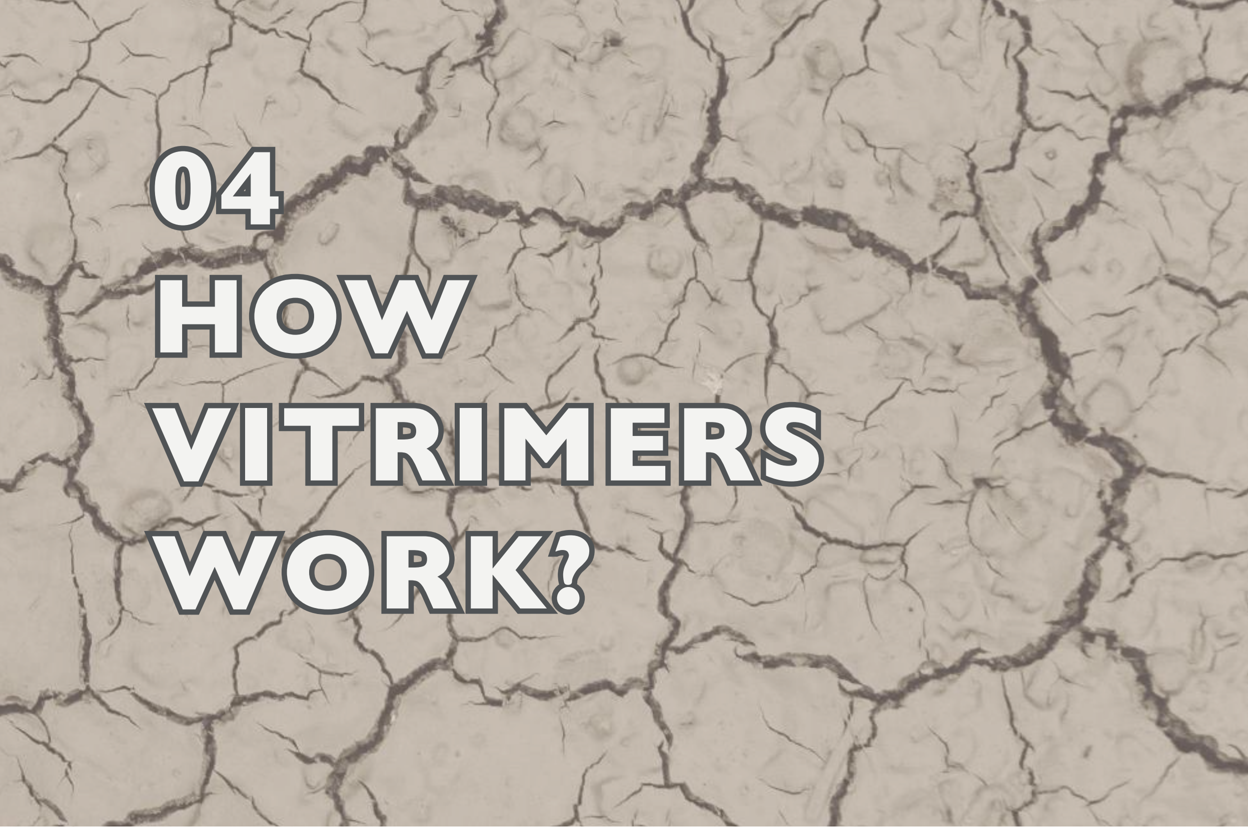
A glimpse into vitrimers

The concept of covalent adaptive networks lies at the core of vitrimer behavior. These networks consist of polymer chains that are interconnected by bonds that can exchange with one another under specific conditions.

Two characteristic temperatures define their behavior.
The first is the glass transition temperature, at which the material becomes softer and more flexible.
The second is the topology freezing temperature, at which the network begins to reorganize through bond exchange reactions.

Glass transition temperature (T_g)
is the specific temperature range where amorphous polymers transition from a hard, brittle, "glassy" state to a soft, flexible, rubbery state. It is a critical design parameter for determining if a material will act as a rigid solid or a flexible material at service temperatures.

Photo by Rishabh Mathew on Unsplash.



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HOW VITRIMERS WORK?

Topology-freezing temperature (T_v) *is a critical parameter for vitrimer materials, acting as the transition point between a rigid, viscoelastic solid and a malleable, flowing viscoelastic liquid.*

Below T_v, bond exchange is slow and the network behaves like a conventional thermoset, whereas above T_v, rapid bond exchange allows for self-healing and reprocessing.

When the material is heated beyond this second threshold, its internal structure reorganizes without breaking apart. Consequently, the vitrimer can flow, be reshaped, or be repaired while preserving its overall connectivity.

This behavior is fundamentally different from that of conventional polymers. Rather than melting or degrading, **the network continuously adapts.**

The material changes shape, but its identity remains the same!

The chemistry behind vitrimers

The unique properties of vitrimers stem from the chemistry of their dynamic bonds. **Various chemical reactions can be employed to design** these **adaptive networks, each offering distinct advantages**.

Transesterification, one of the most common mechanisms, plays a central role by enabling the exchange of ester bonds at **elevated temperatures**.

Disulfide bonds exhibit dynamic behavior at relatively low temperatures, contributing to **self-healing capabilities.**

Boronic esters introduce reversible interactions that can be adjusted based on environmental factors such as pH and temperature.

Imine bonds are widely used in biobased systems and are interesting because they can form and break reversibly under mild conditions, allowing for both **recyclability and adaptability.**

Additionally, Diels–Alder reactions provide a **thermally reversible pathway** that does not require catalysts.

Each of these chemistries defines how the material responds to external stimuli.

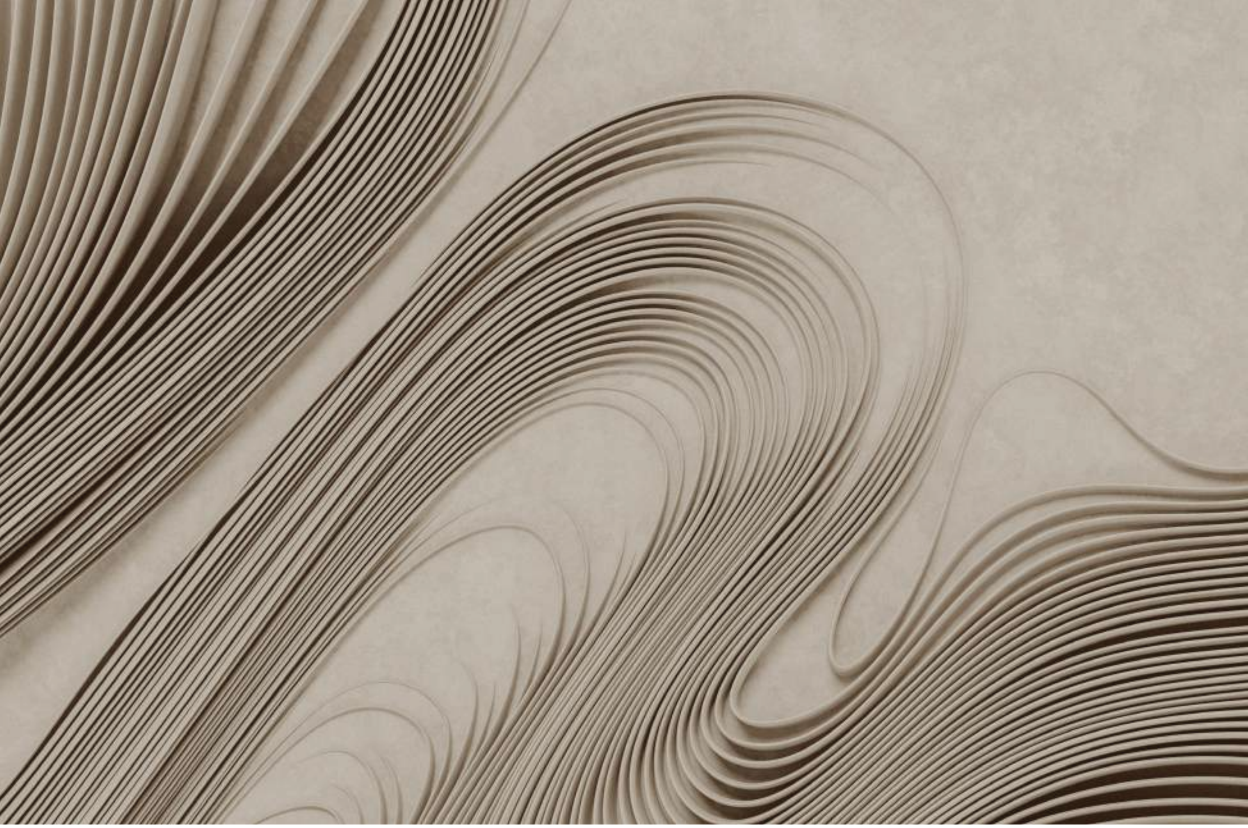
Selecting the appropriate mechanism allows one to tailor the properties of the vitrimer for specific applications.
In this sense, chemistry becomes a design tool!

Disulfide bonds *are strong, covalent linkages S-S formed by the oxidation of sulfhydryl groups on two cysteine residues within or between polypeptide chains.*
They are crucial for stabilizing the tertiary and quaternary structures of proteins, particularly in extracellular environments.

Boronic esters *(or boronated esters) are organoboron compounds formed by the reaction between a boronic acid and an alcohol.*
They are widely used in organic synthesis due to their stability in air and during chromatography compared to free boronic acids.

Imine bonds *are reversible chemical bonds containing a carbon–nitrogen double bond (C=N), formed by the reaction between amines and aldehydes or ketones. Because they can easily break and reform, they are widely used in self-healing and recyclable materials.*

Dies-Alder reactions *are chemical reactions in which two molecules combine to form a six-membered ring structure. They are widely used in polymer chemistry because the reaction can be reversible under heat, enabling the development of self-healing and recyclable materials.*



Mechanical properties

Biobased vitrimers exhibit a unique combination of properties rarely found in conventional polymers.

Below the topology freezing temperature (T_v), they have comparable mechanical performance (i.e., **strength**, **durability**, and **resistance to deformation**) to thermosets, as well as good chemical stability.

Conversely, above topology freezing temperature (T_v), the network topology can rearrange, enabling **reshaping**, **self-healing**, **recycling** or **reprocessing**.

Biobased vitrimers also demonstrate remarkable **viscoelastic behavior** due to the presence of dynamic covalent bonds within the network. These exchange reactions enable stress relaxation and creep resistance while maintaining structural integrity under mechanical load. Moreover, the **adaptable network architecture** contributes to improved toughness and damage tolerance, allowing the material to **recover or redistribute stress** when exposed to thermal or mechanical stimuli.

Photo by Pawel Czerwinski on Unsplash.

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PROPERTIES OF BIOBASED VITRIMERS

Stress relaxation *is the phenomenon by which the stress in a material decreases over time while the strain is held constant. It is a characteristic behavior of viscoelastic materials, such as polymers, elastomers, biological tissues, and some metals at elevated temperatures.*

Creep resistance *refers to the ability of a material to resist progressive, time-dependent deformation under a sustained load, particularly at elevated temperatures where creep mechanisms become significant.*

The self-healing and adhesive properties

These materials can repair themselves when damaged through bond exchange reactions activated by heat, restoring their original integrity. Their dynamic nature enables **reprocessing** and **reshaping**, significantly **improving their lifecycle**.

Another remarkable feature is their ability to form **strong adhesive interfaces**. When two vitrimer surfaces come into contact under the right conditions, new bonds form across the interface, effectively welding the materials together.

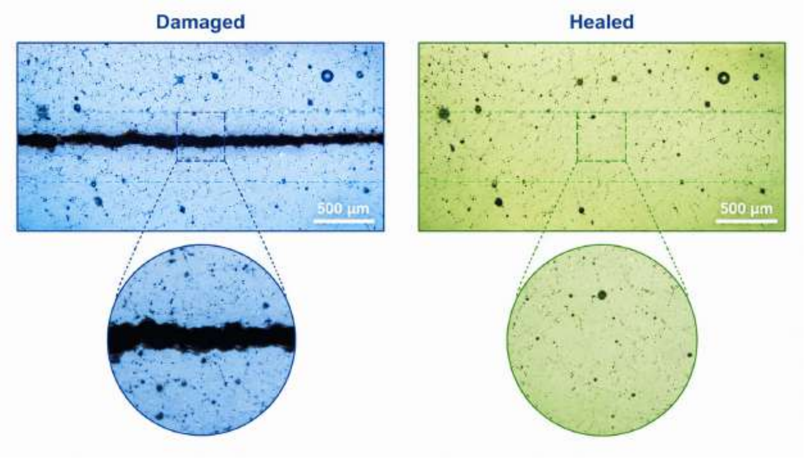


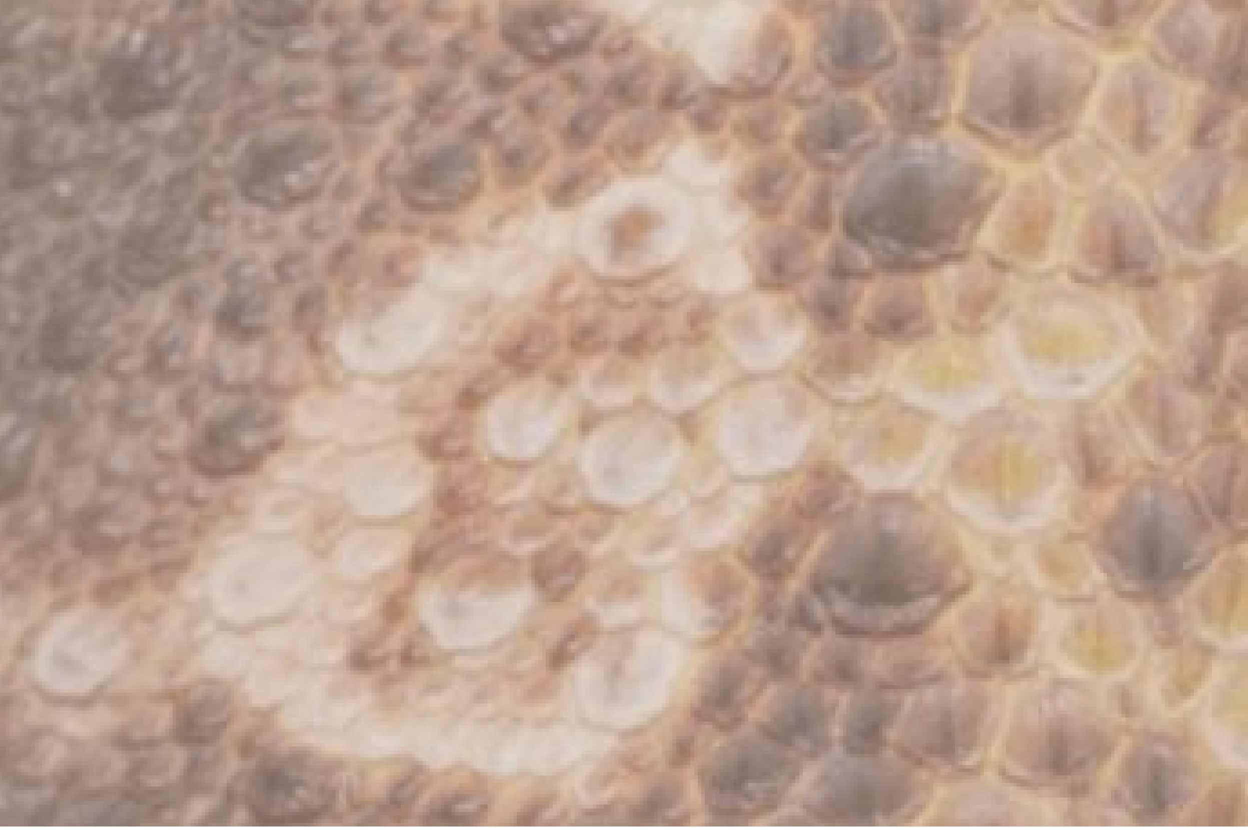
Figure 4: Self-healing properties observable under a microscope. By Giulio Malucelli

Figure 5: Self-healing properties observable under lab condition. By Daniele Nuvoli.

The environmental properties

From an environmental perspective, using **renewable resources** enhances their sustainability even more. Modern formulations rely on green chemistry by utilizing bio-based feedstocks like plant oils instead of petroleum, and advanced variants are engineered to degrade safely at the end of their lifecycle. Compared to fossil-based polymers, biobased vitrimers contribute to **lower emissions** and **improved resource efficiency**.

From above: Photo by Marc Newberry on Unsplash; Photo by NicoElNino on iStock .



Possible uses of biobased vitrimers

The versatility of biobased vitrimers allows them to be used in a **wide range of advanced applications**.

Their self-healing capability makes them ideal for **coatings and protective materials** where durability is paramount.

Their adhesive properties allow for the design of reversible bonding systems, which are useful for **electronics and structural components**.

In the field of recycling, vitrimers can be reprocessed by applying heat or chemical treatments that recover their building blocks. This opens the possibility of **closed-loop material cycles** where waste is minimized and materials are efficiently reused.

Their shape-memory behavior enables the development of smart materials that can change shape in response to temperature. These systems are particularly relevant for **robotics, aerospace**, and **biomedical devices**.

Additionally, emerging research explores their potential applications in **energy-related sectors**, such as materials for **batteries** and **flexible electronic components**.

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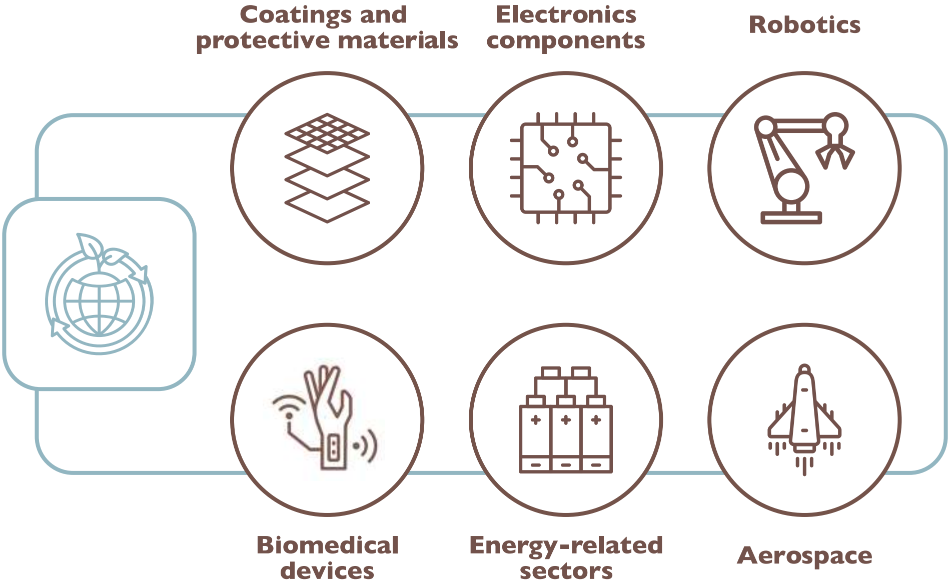
THE POTENTIAL APPLICATIONS



Coatings and protective materials

Electronics components

Robotics

Biomedical devices

Energy-related sectors

Aerospace

Biobased vitrimers are more than just a new type of polymer. They are emerging as a new paradigm in materials science, offering an innovative approach to designing sustainable polymeric materials that integrate renewable feedstocks, dynamic covalent chemistry, recyclability, self-healing capabilities, and long-term performance.

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FUTURE PERSPECTIVES

What can we expect from vitrimers in the future?

The field of **biobased vitrimers is still evolving**, but its potential is already evident. Current research focuses on enhancing mechanical performance, optimizing processing techniques, and increasing production scale.

One of the main challenges is striking a balance between performance and sustainability. However, advances in chemistry and materials design continuously push this boundary forward.

Biobased vitrimers are expected to play a pivotal role in transitioning to a more sustainable material economy, where products are designed to be repaired, reused, and recycled, thus contributing to the circular economy.

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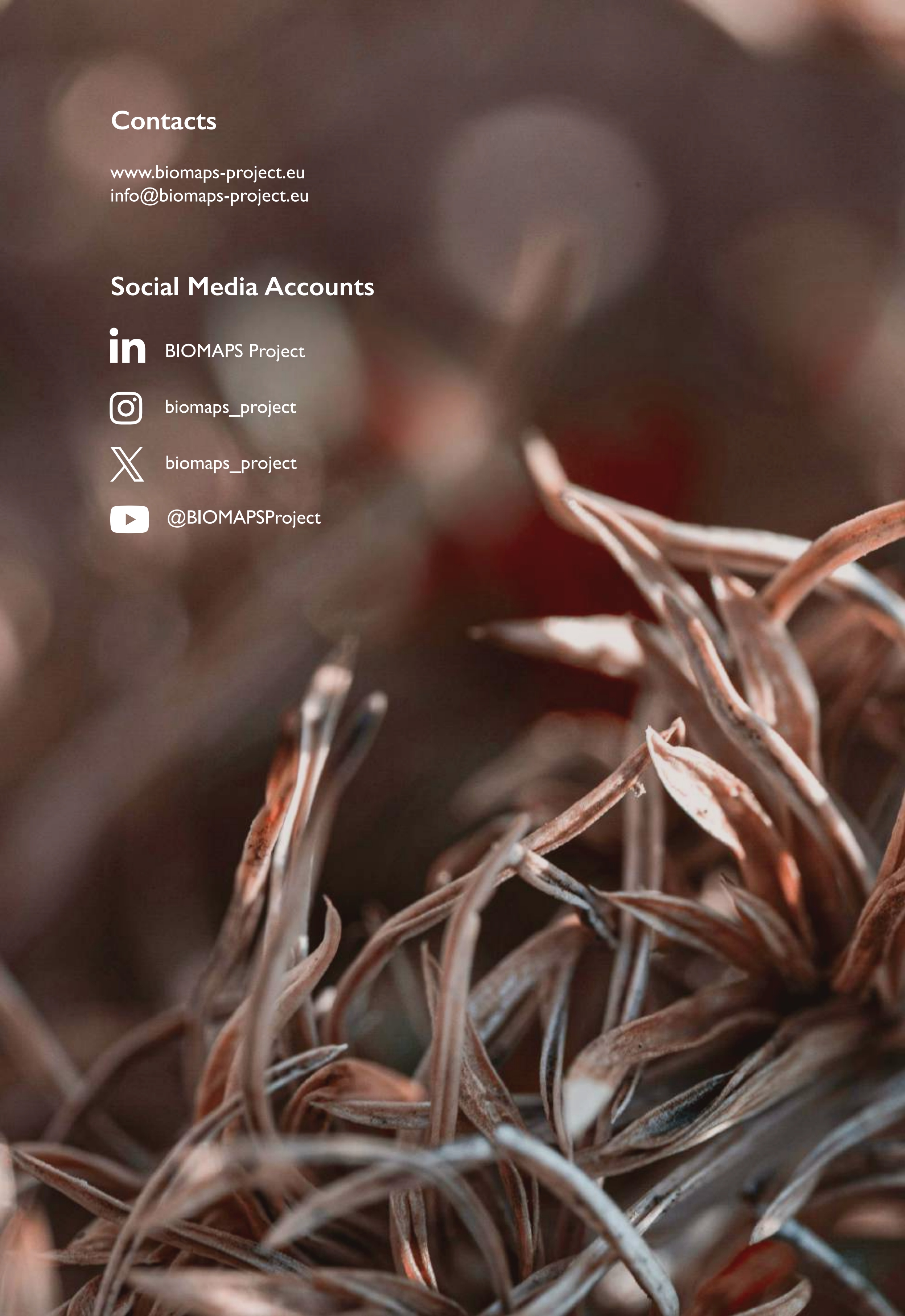

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