



SPECIFIC POLYMERS

Recyclability purpose – Vitrimers strategy

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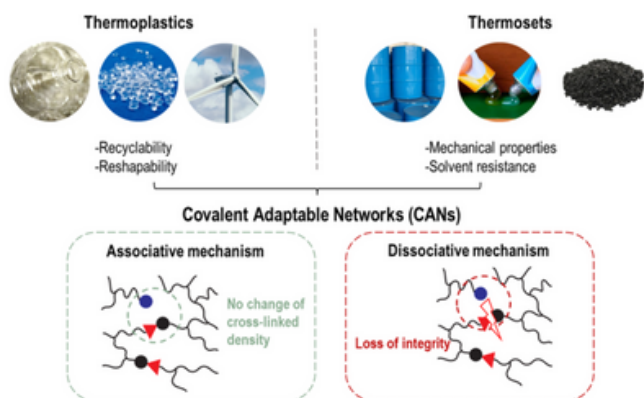
Since few decades, polymer materials are widely used in transportation vehicles, electronics, packaging materials, and many other industrial fields [1]. Unfortunately, these materials can be **damaged when exposed to daily life conditions** such as temperature and mechanical stress, causing irreversible cracks within their structure. These damages induce a **reduction of the materials performance** shortening their lifetime [1]. One attractive way to increase robustness of materials is to elevate the degree of connectivity into the polymeric network by increasing the crosslinking density. However, when considering highly crosslinked materials, such as thermosets, recyclability is profoundly limited. Hence, thermosets show promising properties regarding lifetime and resistance behavior but they remain a major challenge for plastic recycling concerns.



Today, synthetic polymers production reach 140 millions of tons every year with less than 10% being recycled [2]. Indeed, thermosets are **difficult to recycle** due to their irreversible three-dimensional structure. They are essentially destined to landfill and incinerated causing possible environmental pollution. The current recycling methods (chemical, mechanical) are often ineffective, expensive and require the use of aggressive chemicals with only partial material recovery. The most common recycling processes such as depolymerization, catalytic cracking or pyrolysis are performed with hazardous chemicals (methanolysis or aminolysis), additional catalysts (metals) or with high temperature conditions (above 400°C), respectively. Therefore, **important production costs** and **huge waste of resources** are becoming major threats to our ecosystem and our economy. **How can we deal with these problems ?**

Covalent Adaptable Networks

Because of the increasing demand for more sustainable materials, self-healable, thermosreversible and recyclable cross-linked polymer materials have recently received considerable attention. Among them, crosslinked polymers with dynamic covalent bonds are particularly interesting as they share both the advantages of thermoplastics with ease of reprocessing and mechanical resistance of thermosets. These reversible covalent materials pioneered by Bowman and co-workers [3], and so-called **covalent adaptable networks (CANs)**, are polymer materials that combine the strength of thermosetting materials with the processability, reparability, and recyclability of thermoplastics.



The emergence of covalent adaptable networks (CANs) offers a new alternative for the development of sustainable materials which remains a crucial challenge that needs to be addressed to limit environmental concerns. These types of thermosets have the ability to **reversibly rearrange their network structure** through exchange reactions of dynamic covalent bonds under external stimuli such as heat, pH, and UV light [4,5]. Owing to this topological rearrangement, CANs can be easily recycled, repaired and reprocessed. Generally, CANs are classified into two families depending on the mechanism of exchange: dissociative or associative mechanisms.

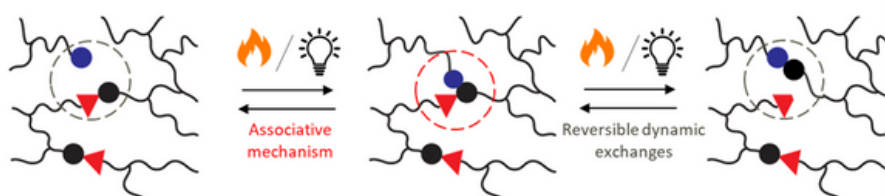
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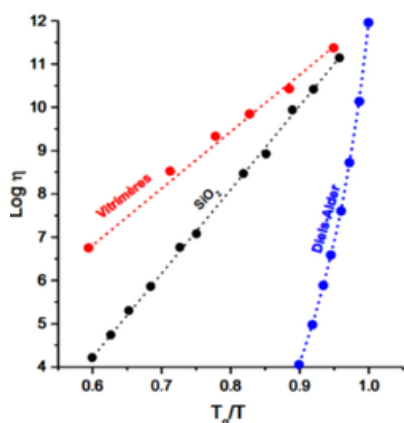
In **dissociative CANs**, the cross-linking bonds break upon heating and reform at lower temperature resulting in a decrease of network connectivity and modification of the cross-linking degree during network rearrangement. In contrast, associative CANs do not depolymerize and exhibit constant cross-link density when changing temperature. In fact, bond breaking only occurs when a new bond is formed conducting to a permanent degree of connectivity. This provides associative CANs with a very peculiar linear viscoelastic dependence. Because this behavior is common in inorganic materials and especially strong glasses, this dynamic polymer material was coined "vitrimer" by Leibler and coworkers [6].

Vitrimers : The third generation of polymeric materials

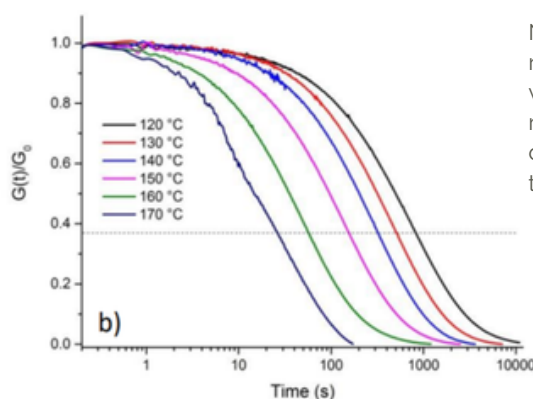
Vitrimers are a class of **associative dynamic covalent networks** in which exchange reactions allow direct reprocessing of materials without depolymerization leading to materials with unaltered properties and cross-linking density [7]. These attributes have gained interest to enhance thermomechanical and solvent resistance properties of conventional thermoplastics while keeping the recyclability unaffected. Indeed, at high temperatures, vitrimers behave as **viscoelastic liquids** and can be reshaped like traditional glass materials. While at low temperatures, the network structure is comparable to that of **traditional thermosets** with good network integrity [8,9].



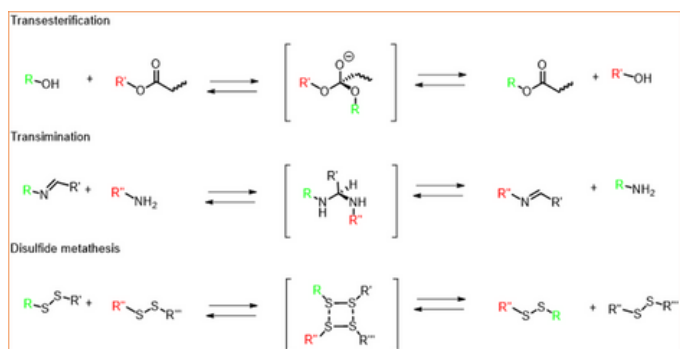
Indeed, compared to processable plastics, cross-linked polymers show linear-like gradual viscosity variations (red line) like those of silica (black line). This new class of materials is characterized by a complete stress relaxation at high temperature thus, the material is able to flow, while upon cooling, the exchange reactions kinetics decrease and the materials structure is fixed, showing a permanent topology like a solid. These properties allow unique advantages over classical thermosets.



Angell fragility plot showing viscosity as a function of inverse temperature normalized to 1 at the glass transition temperature (T_g) for Vitrimer (red), silica (black) and dissociative CANs (blue)



Normalized stress relaxation of vitrimers-like materials at different temperatures [10]



To achieve this molecular network rearrangement, it is necessary to introduce specific dynamic covalent bonds. Therefore, various dynamic covalent chemistries were reported such as **transesterification, imine amine exchange, vinylogous transamination, olefin metathesis, disulfide exchange and hindered urea exchanges**. In contrast to some of the traditional exchange reactions, these associative mechanisms don't require high temperature treatments, petro-based additional monomer, special processing (e.g., sonication), and/or metal catalysts to allow recycling process.

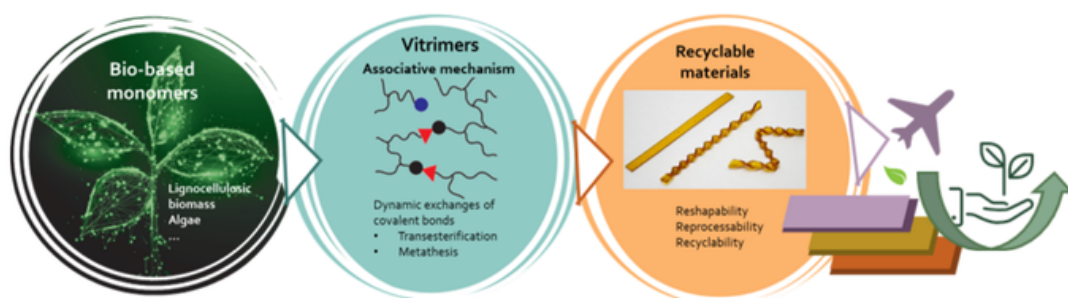
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Further vitrimer investigations

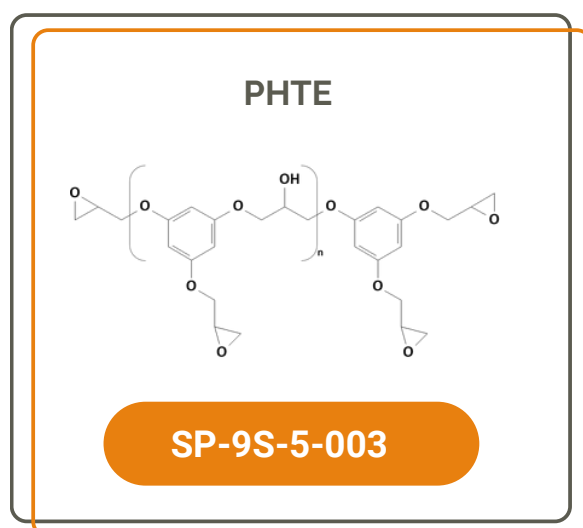
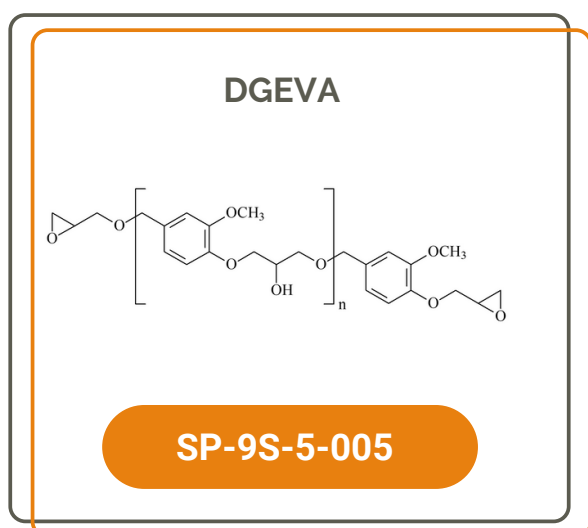
Recent attention has been paid to explore new recycling strategies **reducing additional treatments** to convert the rigid networks into viscoelastic liquids. For example, as described by K. Fukuda and coworkers [11], imine dynamic exchanges can combine both associative (transimination) and dissociative mechanisms (imine hydrolysis and reformation). The resulting vitrimers can be recycled through acidic hydrolysis. Besides, disulfide bonds, studied by T.N Tran and coworkers [12], showed promising dynamic properties at moderated temperature without any catalyst. Same recent investigations highlighted **innovative vitrimers** that could exhibit promising degradable characteristics under mild conditions by preparing, for example, polyschiff-based vitrimers with self-healing properties or by investigating novel imine chemistry [13,14].

In recent years, increasing attention emerged regarding **vitrimers issued from renewable materials and eco-friendly recycling strategies** [14,15]. Thus, the integration of vitrimer properties within bio-based materials appears to be innovative and represents a major issue for the development of a circular economy for materials.



For this purpose, the synthesis of vitrimer-like thermosets materials is becoming an important topic in SPECIFIC POLYMERS research activities. For instance, the company's is working on the integration of reversible moieties into thermoset materials prepared from sustainable epoxy building blocks (BPA-free or biobased). These building-blocks are of great interest since they can replace the commonly used, petro-based, bisphenol-A diglycidyl ether (DGEBA). For instance, **SPECIFIC POLYMERS** supplies **diglycidyl ether of vanillyl alcohol (DGEVA)** made from vanillyl alcohol and **phloroglucinol triglycidyl ether (PHTE)** made from phloroglucinol. Even if petro-based precursors' grade are currently used at the moment to validate proof of concept, both these phenolic precursor are of high interest since they are (i) BPA-free products and since (ii) a biobased supply chain is on the rise since both molecules (vanillin alcohol can be extracted from lignin and phloroglucinol can be extracted from algae).

Related R&D products



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