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Biobased, thermoreversibly crosslinked polyesters

Beljaars, Martijn

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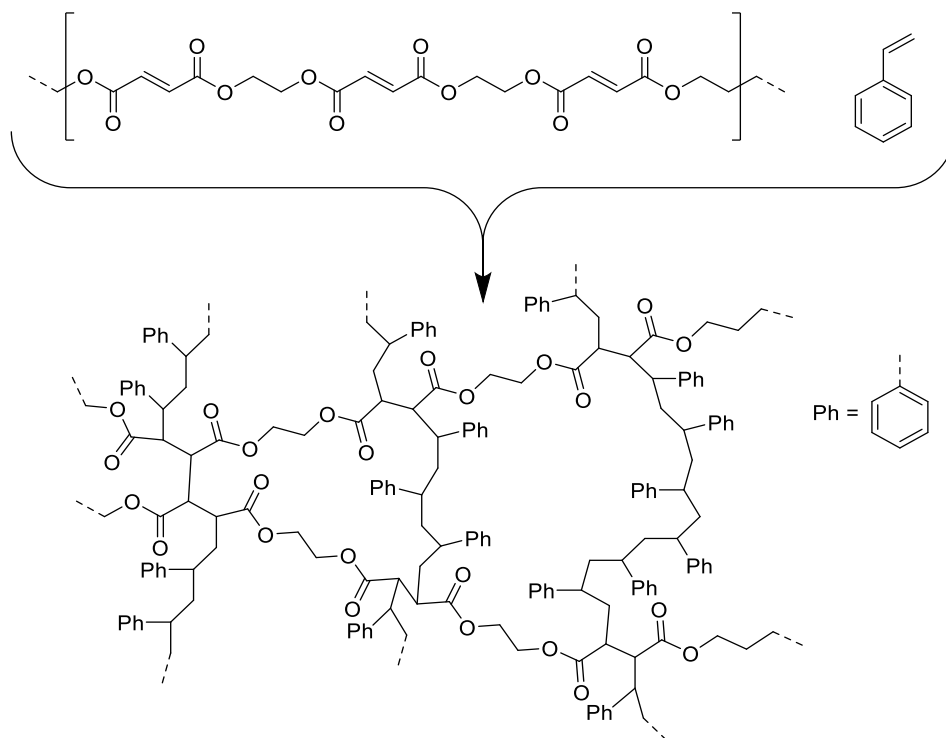
Chapter 1

Introduction

1.1 : Introduction

Crosslinked resins are usually employed in highly demanding applications where very specific properties are required of the resulting material: i.e. excellent chemical resistance, mechanical strength and dimensional stability¹. Unsaturated polyester (UP) resins neatly fit all these high demands; they possess the required mechanical properties due to the fact that they consist of polyester chains that are covalently crosslinked, essentially, the resulting material consists of one large network. Therefore, any significant deformation of this highly crosslinked material requires the breaking of chemical bonds. A testament to the success of UP resins is the volume at which they are produced: worldwide, an estimated 2.2 billion kg of UP resin are produced annually². Besides the superior (mechanical) properties of the final product, UP resins possess other qualities that render them highly desirable: the uncrosslinked material is stable and can be stored for a long time; the curing time can be adjusted by adding different amounts of curing agent and, finally, the uncrosslinked resin is a liquid, which makes it particularly well suited for embedding materials like fibers that can lend extra strength or reduce density. UP resins are liquids because they consist of (relatively short) unsaturated polyester chains that are dissolved in styrene (Scheme 1). The exact compositions of these resins depend on the application and producer, but on average they contain between 35 to 60 wt% of styrene, which acts as a reactive solvent. Indeed, styrene dissolves the polyester chains and, by a free radical polymerization mechanism, it then polymerizes *in situ*, thus resulting in the crosslinking of the final material (Scheme 1). Crosslinking is performed by addition of an initiator, usually methyl ethyl ketone peroxide is being used as radical initiator, combined with cobalt octoate as accelerator. The exact crosslinking mechanism is complex as it involves styrene homopolymerization, polyester homopolymerization utilizing the double bonds present in the unsaturated polyester and graft copolymerization of both³. The mechanism is further complicated by changes in the physical structure during the curing process: most importantly gelation and vitrification (i.e. the transition from amorphous liquid to a glass). Nevertheless, the resulting material is highly crosslinked.

Scheme 1: Representation of crosslinking in a styrene based UP resin



Unfortunately, despite its many merits, there are serious disadvantages to the use of styrene in this (or any other) polymers. Firstly, styrene is a volatile organic compound which has been classified as a “Group 2B, possibly carcinogenic to humans” by the International Agency for Research on Cancer (IARC)⁴. The metabolite of styrene, styrene oxide has been detected in workers exposed to styrene and IARC has classified this as a “Group 2A, probable human carcinogen”. The significance of this problem is illustrated by the loss percentages of styrene for various applications of UP resins (Table 1). Considering the styrene content of these resins (up to 60%, *vide supra*) it is evident that for any application other than closed processes special precautions have to be taken in order to prevent exposure to this dangerous chemical.

Process	Styrene loss (%)
Gelcoat spray	10-14
Spray-up, non-LSE resin	7-10
Gelcoat, brush	6-8
Filament winding	5-7
Hand Lay-up, non-LSE resin	4-6
Spray-up, LSE / LSC resin	4-6
Topcoat, spray	4-5
Topcoat, brush	3-4
Hand Lay-up, LSE / LSC resin	3-4
Pultrusion	1-3
Polymer concrete etc.	1-3
Continuous lamination	1-2
SMC/BMC manufacturing	1-2
SMC/BMC processing	1-2
Closed processes (RTM/RTM Light/Infusion)	<1

Table 1: Styrene loss for various processes⁵

LSE/C = Low styrene emission/content, SMC/BMC = Sheet/Bulk molding compound, RTM = Resin transfer molding

Besides the hazards of using styrene, there are other reasons to consider a replacement: the currently employed styrene is obtained from fossil fuels. Considering the prospect of declining oil reserves, a steady increase of global energy demands and environmental concerns⁶, a sustainable, bio-based alternative becomes more and more appealing. Given the availability of natural resources, the expected positive impact on carbon emissions and the scale of

styrene consumption, the potential merits of such a sustainable process are immediately evident. Fortunately, there are various options to increase the sustainability of a process in general, and a styrene based polymerization reaction in particular.

1.2 The first step: increasing sustainability or “going green”

The most straightforward way towards a sustainable process is by replacing styrene with itself, i.e. fossil based styrene with green, biobased styrene. This bio-based styrene would be identical in all aspects to the currently used one, save for its origin. The use of bio-based chemicals reduces the dependence on fossil fuels and, more importantly, their sustainable manufacturing will reduce the accompanying carbon emissions. Due to the scale of annual consumption of styrene, any minor improvement in sustainability is expected to have a major global effect. The direct substitution of chemicals by their bio-based alternatives is known as *drop-in replacement*, the viability of which is mainly dependent on the availability of the chemical to be replaced. Fortunately there is a large, ever expanding, library of biobased chemicals already commercially available, and with some minor chemical modifications this library can be exponentially expanded (Figure 1)⁷.

The commercial viability of drop-in replacements is demonstrated by various examples that include, besides the most famous green ethanol⁸, also green ethylene obtained from sugar⁹, lignin derived phenolics in wood glue formulations¹⁰ and benzene, toluene and xylene (BTX) obtained from wood chips¹¹. Using a drop-in replacement for styrene would be a step in the right direction towards increasing the green carbon content of UP resins. However, in order to obtain a fully biobased material all other involved chemicals (e.g. propylene glycol and maleic anhydride / maleic acid) used to make the polyester should be substituted as well. Unfortunately, despite the vast library of drop-in replacements, a green substitution is not always immediately available. In these cases an alternative solution may be found in the use of a comparable alternative chemical. Such a compound should have similar chemical and physical properties (e.g. reactivity and solubility) to make it a suitable substitute. Recent successful

examples of such functional replacements are the use of furane dicarboxylic acid as an alternative to terephthalic acid in order to produce PEF instead of PET¹² and high-impact polylactic acid, which should be able to replace the corresponding polystyrene grades¹³. The most well-known example is the use of ethanol as biobased fuel (additive)¹⁴. A green product will be obtained when all chemicals are replaced, either by drop-in alternatives or by functional substitutes and the production process is optimized. However, from a truly sustainable point of view “just” going green simply is not enough.

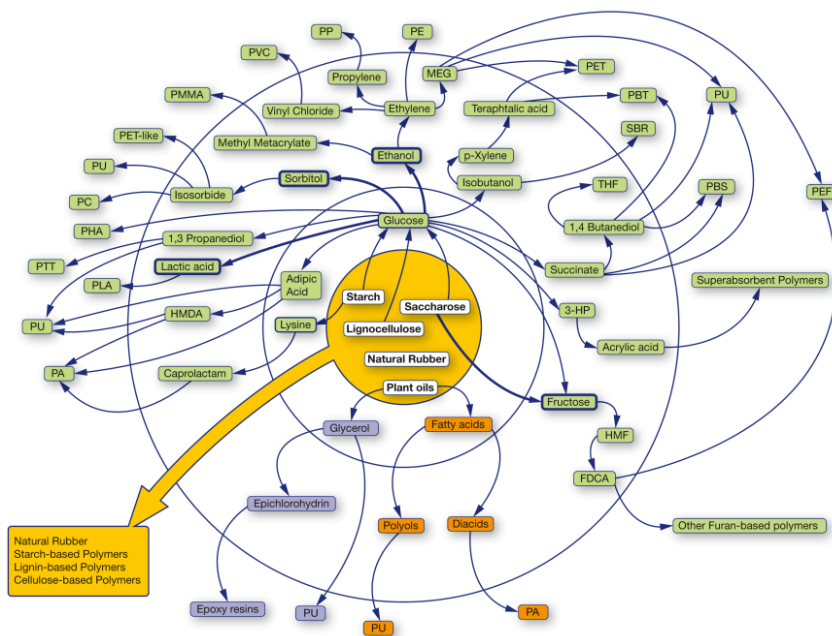


Figure 1: Overview of bio-based monomers and polymers with some of the currently available monomers and resulting polymers currently obtainable from sustainable resources.

1.3 The next step: addressing end-of-life

The strategies towards a green product outlined above (i.e. drop-in or functional replacement) can be effective in achieving a reduction in carbon emissions during production while at the same time lowering the toxicity of a given product (functional replacement). This potential reduction in toxicity is crucial for UPs where replacing the highly toxic styrene is of clear strategic importance. However, the product lifetime and end-of-use applications should be considered as well in 14

judging the importance of these approaches. A 2002 article describes the European waste policies by implementing a waste pyramid¹⁵ (Figure 2). In this waste pyramid the most favorable option (prevention) is listed at the top and the least favorable (disposal) at the bottom. The current best practice for UP resins consists of mechanical destruction (e.g. grinding) and subsequently using the resulting particles as filler material in new applications. This reduces the amount of virgin material needed (Material Recovery in Figure 2).

On the other hand characteristic applications of these ground resins are typically low cost and performance materials, e.g. roadside markers or asphalt bedding. This entails a significant decrease in value along the overall chain starting from highly valuable UP resins. This is even more evident when considering the fate of any other discarded UP resins not re-used in this manner: i.e. incineration (Energy Recovery) or dumping in landfills (Final Disposal).

Moving up one tier in the pyramid (i.e. to the Reuse option) exposes an intrinsic problem of UP resins and thermosets in general. As mentioned, the covalent bonds that form the crosslinks provide many beneficial mechanical properties, however they also severely limit any possibility for repairing or reclaiming spent material. During curing, a covalent network is formed; this network is so inert that it is factually impossible to reverse the curing reaction in order to obtain the starting materials once more. Moreover due to the inertness of the network, any damage sustained by the material (microfractures or cracking) cannot be repaired in a feasible way. This often means that in order to repair minor damages an entire piece has to be replaced. The inability for minor repairs combined with the rigidity of these resins renders them completely unsuitable for reuse in the same (or similarly valued) application (*cradle-to-cradle*¹⁶). To enable the reuse of these kinds of material, different crosslinking chemistry has to be considered altogether. If the bonds that make the network can be made in a reversible way, i.e. they can be broken and reformed on command by some external stimulus (e.g. temperature¹⁷, light, pH etc.), then a recyclable system should be obtained¹⁸. After opening the crosslinks, the starting materials would be (re)obtained, ready to be re-cured and used in a new application, or the same application without any concessions to mechanical properties. Furthermore, if the crosslinks can be broken by mild conditions (temperature rather than mechanical force); any embedded components could be reclaimed and potentially reused as well. Finally,

the implementation of reversible crosslinks should result in a material that can easily be repaired. Any broken crosslinks can be reformed under the same conditions as when the material was initially created. This potential for self-repair is known as *self-healing*, a concept closely related to the one of (thermo)reversible networks¹⁹.

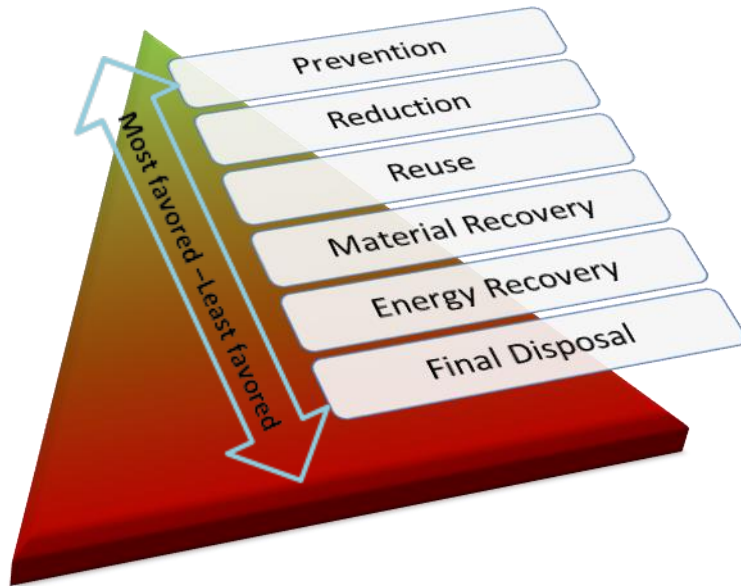


Figure 2: The hierarchy of waste management, listing the most favored solution at the top.

1.4 Enabling recyclability: Self-healing materials

Traditionally, there are several methods for repairing a damaged polymer resin: welding, patching or *in situ* curing. Not all methods are applicable to each material however. Welding enables the closing of cracks through rejoining the fractured surfaces or fusing new material to the damaged region. During the welding process, the material undergoes a number of transitions: surface rearrangement, surface approach, wetting and diffusion^{20,21}. It relies on chain entanglements between the contacting surfaces and it may be aided by the use of solvents and increased temperature²². Due to the requirement of chain entanglement, welding is mostly used in thermoplastic materials, as the chain ends in most thermosets

are usually not of sufficient length to enable entanglements. Furthermore, the entangled region will possess significantly different mechanical properties with respect to the crosslinked regions. Patching constitutes covering or replacing the damaged area with new material, either through mechanical fastening or through the use of adhesives. The success of patching is dependent on factors such as the interface between the patch and original material²³, the presence and orientation of reinforcing fibres^{24,25}, and the thickness of the patch^{26,27}. Due to the fact that extra material is added to patch the damage, this method is not always suited for a given application. The final method: *in situ* curing involves the application of new, uncured starting material, which will diffuse into the damaged region, increasing the contact area. The starting material can be used as an adhesive for any possible patches that are applied to the region as well²⁸. Most of these methods require the use of extra material and the properties obtained are usually inferior to those of the starting material. Self-healing eliminates the need for additional material while resulting in principle in no loss of mechanical properties. Self-healing has been achieved in two fundamentally different ways: extrinsic and intrinsic self-healing. Extrinsic self-healing is achieved via incorporation of capsules containing (low molecular weight) additives that can act as healing agents upon cracking, thus effectively performing *in situ* curing without the need of additional material²⁹⁻³⁴. Intrinsic self-healing involves the modification of the polymer to enable the healing of cracks in response to an external stimulus like heat^{17,35-37} or light³⁸⁻⁴¹. Ideally, in the near future a crack should be repairable merely by applying heat. As stated, in order to enable cradle-to-cradle recycling of these thermosets, as well as potential reclamation of embedded materials and possibly enabling self-healing, reversible crosslinking is the first requirement.

1.5 Thermally Reversible Networks: supramolecular crosslinking

There are various reversible crosslinking methods: hydrogen bonding, electrostatic interactions and (covalent) adaptive networks. Hydrogen bonding and electrostatic interactions can be classified as supramolecular bonds. When mechanical stress is applied to the material the weaker supramolecular bonds will fail first and, due to their reversible nature, these can later be reformed.

Hydrogen bonding is a non-covalent interaction between a hydrogen atom and a different one which is more electronegative. With a strength of 5-30 kJ/mol, a hydrogen bond is stronger than a van der Waals interaction, yet weaker than a covalent bond. Hydrogen bonds have been employed as crosslinking device in polymers for the first time by Klok et al⁴². However for this particular system, at increased temperatures (over 70 °C) the zero-shear viscosities increased sharply with temperature, indicating that most likely side reactions occurred. The hydrogen bonds are expected to break at elevated temperatures, leading to a lower viscosity.

The relatively weak bond strength is easily addressed by simply increasing the number of hydrogen bonds per crosslink as demonstrated by Chino and Ashiura⁴³ who described a rubber system crosslinked by using triazole rings. By using 3-amino 1,2,4-triazole, solidification of the normally liquid rubber was observed at room temperature. The mechanical properties of the resulting material are comparable to those of Sulphur vulcanized rubbers. There are some drawbacks to this method: the synthesis required is quite complex and has only been performed on lab-scale. More importantly, however: the obtained glass transition temperature of -60 °C is by far too low to be a competitor for styrene UP-resins and there is no mention of the effect of water on bond stability. Generally speaking, the presence of water has a devastating effect on hydrogen bonds. All this makes this particular system unsuitable for replacing styrene UP resins.

Another widely investigated method of reversible crosslinking is the use of ionomers^{44,45}. These materials are defined by the presence of ionic groups along the polymer backbone, or on pendant groups which can be present in many different forms e.g. sulfonate⁴⁶, carboxylic acid⁴⁷ or ammonium salt⁴⁸ groups. The counter-ion used is just as versatile; and is the main source of variability in material properties^{49,50} and mechanical behavior⁵¹⁻⁶³ of ionomers. These materials have generated a lot of scientific and industrial interest due to their many applications like fuel cells⁶⁴⁻⁶⁷, membranes^{65,68} and exfoliating aids during processing⁶⁹. Of particular interest for this work is the application of ionomeric bonds in thermoreversible crosslinking. The ionomeric crosslink is an electrostatic interaction that occurs by clustering of the ionic groups. These groups tend to associate in multiplets, which in turn organize themselves into clusters (Figure 3). The morphology of these clusters has been extensively studied and is shown to

have an established^{49,50} effect on the properties of the resulting material such as thermal and mechanical behaviour⁵¹.

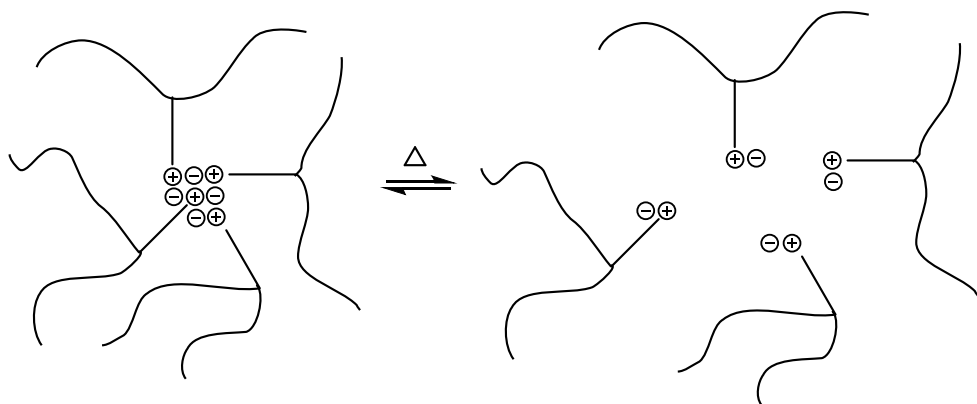


Figure 3: Association and dissociation of ionic groups in an ionomer

For example, the crystallization rate for sulfonated syndiotactic polystyrene was found⁷⁰ to be inversely proportional to the ionic radius of the counter-ion. Other factors that influence the mechanical properties of these materials are the position of the ionomeric group along the chain, and its distance from the polymer backbone⁷¹ as well as the type of ionomeric group employed (e.g. ionomers bearing sulfonic groups are reported to display higher tensile strength than those bearing carboxylic groups⁷²). Unfortunately, though the properties of these materials can be influenced by the type of counter-ion, the fact remains that a metal is needed in all of the systems described. From an environmental and sustainable point of view this makes these materials less appealing. Furthermore, for most applications of ionomers (especially membranes, and in particular those used in fuel cells) water uptake is considered a crucial factor, since it influences the stability of the membrane⁷³. When considering an alternative for UP-resins, water uptake is disastrous for most of the applications. This also renders ionomeric materials unsuitable candidates for replacing styrene UP resins.

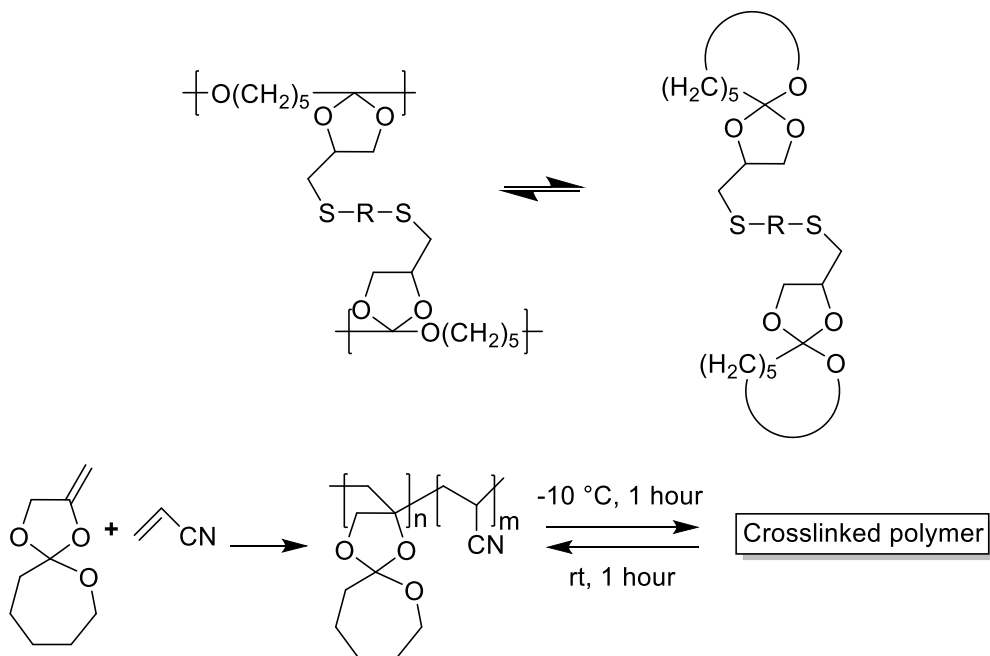
There is an intrinsic problem when considering supramolecular crosslinking methods: by definition, in order to achieve self-healing, the crosslinking bonds have to be weaker than the bonds in the polymer matrix. In this way, when force is applied to the material the weaker bonds will fail first, which can later be reformed. Seeing as toughness is one of the main appeals of UP-resins, a proper

replacement should preferably be based on covalent crosslinking. Covalently crosslinked materials in general possess better creep resistance, high modulus, high fraction strength and excellent solvent resistance. Some options in this respect are discussed in the following.

1.6 Thermally Reversible Networks: covalent crosslinking

There are various thermoreversible systems known involving covalent bonds, for instance ester bond rupture which employs a dithiol as crosslinker. The system described by Endo *et al* in the original publication⁷⁴ can be better described as a reversible polymerization reaction (Scheme 2, top). A later publication describes⁷⁵ a system where the technique is employed as a true reversible crosslinker: an acrylonitrile matrix is reversibly crosslinked by pendant spiro orthoester groups (Scheme 2, bottom).

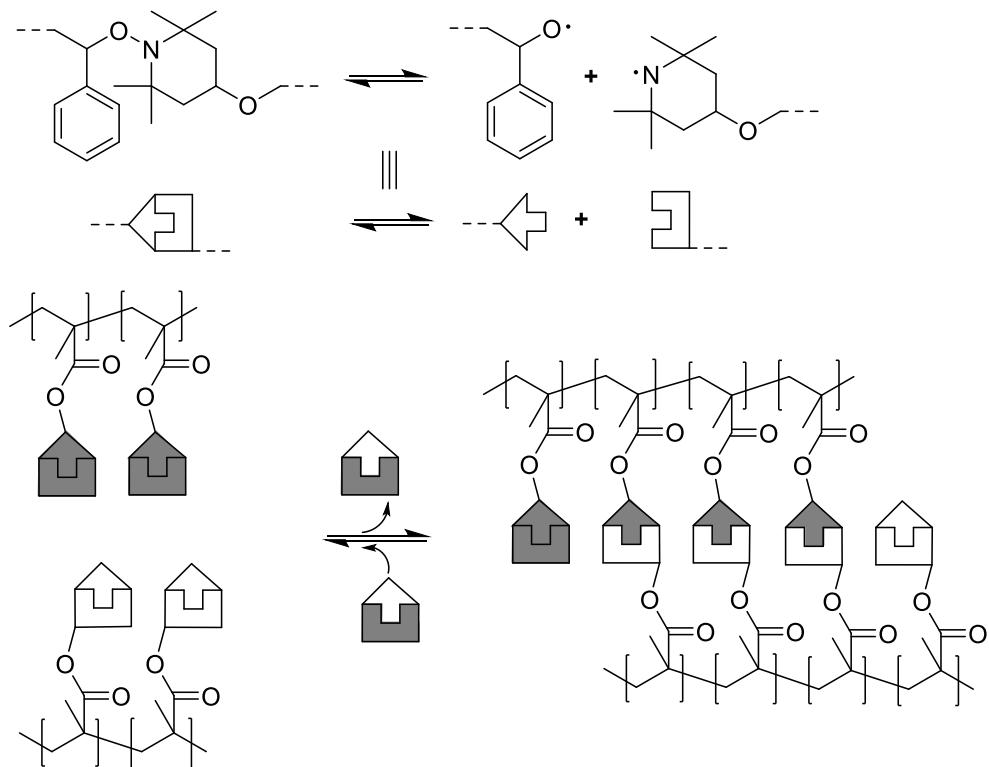
Scheme 2: ester amide bond rupture (top), employed as reversible crosslinker (bottom).



Unfortunately, this method cannot be applied to polyesters as these will depolymerize as well under the de-crosslinking reaction conditions.

Another possible method of reversible covalent crosslinking is the use of a radical exchange reaction. Higaki *et al* described⁷⁶ a polymer containing a pendant alkoxamine group based on 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO). This alkoxamine is able to undergo reversible C-O bond cleavage yielding two radicals (Scheme 3). These radicals can reconnect to yield the original alkoxamine unit. Inter- and intramolecular C-C coupling is not observed due to fast capping of the formed carbon radical by a nitroxide radical. Unfortunately, the decoupling temperature of 100 °C is somewhat low for the considered application as UP-resin substitute. Furthermore, the need to add or remove an external compound in order to obtain the desired configuration (e.g. adding extra alkoxamine in order to obtain the decrosslinked material, and removing the alkoxamine to obtain the crosslinked material) severely limits the potential applications of this method.

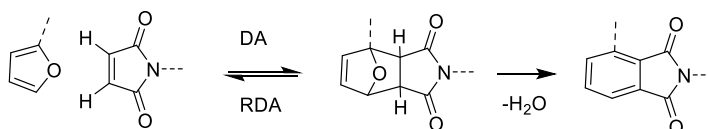
Scheme 3: reversible crosslinking via radical exchange reaction. Top: schematic representation of the radical pair, bottom: the coupling and decoupling reaction influenced by the addition or removal of alkoxamine.



Finally, in the field of adaptive covalent networks, the most commonly employed reaction is the 2+4 cycloaddition reported by, and named after, Diels and Alder⁷⁷. It is a thermoreversible 2+4 cycloaddition which can be performed by various combinations of functional groups e.g. furan and maleimide, anthracene and maleimide, cyclopentadiene and fulvene. This variance in possible pairs ultimately results in precise control over the properties of the resulting material: The Diels-Alder (DA) addition reaction is in fact an equilibrium that at lower (application) temperatures favors the adduct, yet above a certain temperature shifts towards the dissociated compounds. The association and dissociation temperatures are dependent on the specific groups utilized (Table 2). From these options, the furan-maleimide pair stands out: its crosslinking temperature is sufficiently low to allow for the formation of a network by using a relatively low amount of energy.

Furthermore, the decrosslinking temperature is sufficiently high as to not hamper its use in most applications, yet not so high as to risk decomposition of the polymer matrix during decrosslinking. Finally, various furanics can also be obtained from sugars, making them an interesting candidate from a sustainability point of view. The furan-maleimide reaction has been widely and extensively studied⁹⁶⁻⁹⁸ and the first reported polymer based on this pair was already reported in 1986^{99,100}. However, while this research did employ the Diels-Alder reaction to make linear polymers of difuranes and dimaleimides, the authors then proceeded to aromatize the product in order to obtain the desired polymer, preventing any retro-Diels-Alder reactions taking place (Scheme 4).

Scheme 4: Diels-Alder equilibrium and aromatization



The first mention of a thermoreversible linear polymer was in 1994 when Kuramoto *et al* described¹⁰¹ an A-A B-B type polymer obtained by combining a difuran and bismaleimide. It then took until 2002 when Chen *et al* reported^{102,103} the first thermoreversibly crosslinked system by combining a tetra-furan with bis- and tris-maleimides. All the systems described so far are polymers obtained from coupling furanic and maleimide-containing monomers. A different strategy involves the implementation of the Diels-alder reaction only as a crosslinking tool between existing polymers. In order to achieve this, a polymer containing furane or maleimide groups in the backbone or as pendant groups needs to be synthesized. In 1979 Stevens *et al* reported¹⁰⁴ the crosslinking reaction of styrene containing pendant maleimide groups. The reversibility was not discussed until 1992, when the reversible gelation of the system was finally reported¹⁰⁵. Since then many systems have been described that incorporate the Diels-Alder reaction as crosslinking tool^{37,106}. Judging by the variance of polymer matrices employed, it seems that Diels-Alder crosslinking is a perfect fit for replacing styrene based UP-resins.

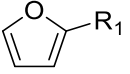
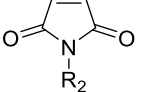
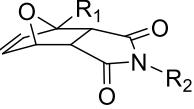
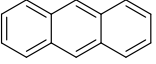
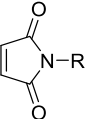
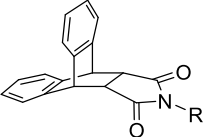


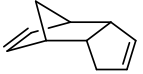
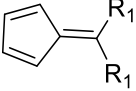
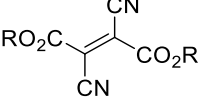
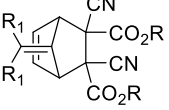
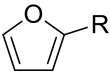

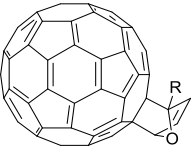

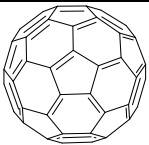
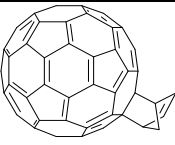
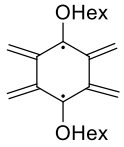

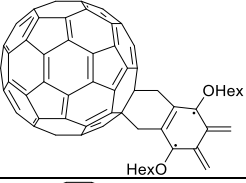
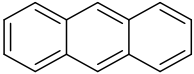

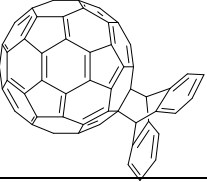

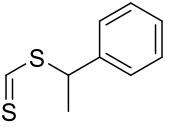
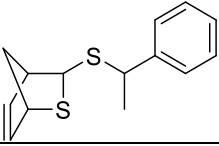
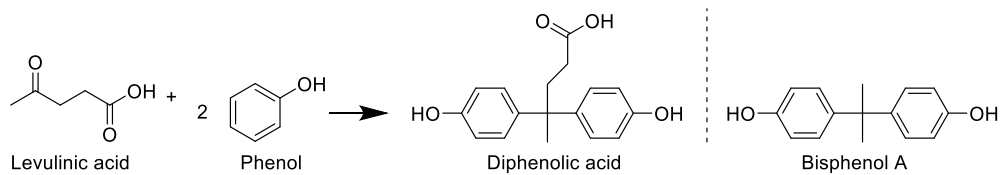
Diene	Dienophile	Adduct	T _{DA}	T _{RDA}	Ref
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			125	250	82-84
			25-120	150-215	85-87
			RT	50-100	86,88,89
			RT	180	90
			RT	95	91
			214	n.a.	92
			RT	60-82	93
			RT	80-95	94,95

Table 2: Coupling (T_{DA}) and decoupling (T_{RDA}) temperatures of various Diels-Alder couples

1.7 Monomer selection

Having established the merits of reversible crosslinking, and determined that the current systems are unsuited for such an approach, the use of a different monomer should be considered. Considering all of the above, there are three requirements that can be formulated for this monomer: it must be able to be incorporated in a polyester, it must be obtainable via a sustainable route and finally, it must possess a furanic or maleimide functionality, or sufficient extra functionality to incorporate one. The first, most obvious candidate is furandicarboxylic acid (FDCA). Although this monomer is readily incorporated in a polyester matrix¹⁰⁷ and obtainable in sustainable fashion¹⁰⁸, proof-of-principle experiments have demonstrated that the methoxyester of FDCA is not active in the (DA) reaction with maleimide. The next option would be employing a furanediol. However, recently a polyester was reported¹⁰⁹ including the furanediol which is able to undergo reversible (DA) crosslinking. The material obtained is too flexible to fulfill most of the requirements defined for UP-resins. An excellent candidate is levulinic acid, which is produced commercially from cellulose in a large scale (10000 megaton in 2017 up to 50000 megaton in 2019 from a single plant)¹¹⁰ and is relatively easily converted into diphenolic acid by condensation with phenol (Scheme 5). Diphenolic acid possesses a diol functionality, making it suitable to be incorporated in a polyester. Furthermore, it possesses an additional pendant acid group that can be converted to accommodate a DA moiety. Furfurylamine seems an excellent candidate for this as it contains an amine group, which can be converted into an amide, which in turn reduces the risk of any transesterification occurring in the final polyester, and it is a bio-based chemical typically obtained from furfural. Due to its structural similarity to bisphenol A (see Scheme 5), which allegedly possesses estrogenic properties, diphenolic acid has been placed on a watch list for expected toxicity. However, as the research described herein entails a proof-of-principle study this concern has been preliminarily discarded in order to investigate the potential possibilities before optimizing the system before implementation.

Scheme 5: Levulinic acid and its conversion to diphenolic acid, a structural analogue to bisphenol A



1.8 Contents of this thesis

The aim of this work was to devise a “human friendly” alternative to currently employed unsaturated polyester resins. In order to be able to compete, the resulting material should have the mechanical properties commonly ascribed to thermoset materials. At the same time the material should aim for maximum sustainability, using as many bio-based chemicals as possible. Already realizing at the early stages of the research that sustainability should not only come from the resources employed, but also the application and disposal of the material, the goal of this research was: the development of a biobased polymer able to undergo reversible crosslinking in order to enable recycling of the material at end of life.

Chapter 2 describes the search for a proper monomer: one that is both biobased and suitable for polymerization and functionalization. After settling on diphenolic acid, its modification, incorporation into a polymer and testing of the resulting material are discussed.

Chapter 3 describes the further modification of the polymer obtained in chapter 2. This modification is carried out in order to enable milder processing conditions. This chapter describes the modification, the effects on the processing conditions and the resulting material.

After obtaining the desired polymer with the processing conditions outlined in chapter 3, the properties of the resulting crosslinked product were improved by blending with a rubber. This was necessary in order to overcome the brittle nature of the prepared polymer. Chapter 4 describes the resulting change in properties upon incorporation of the functionalized rubber in the UP resin matrix.

In order to better understand the crosslinked material on a chemical level and to find the possible ways of tuning its mechanical properties, a range of different crosslinkers has been investigated. The effect of the type of crosslinker as well as the amount has been investigated, and the results are presented in chapter 5.

The final chapter attempts to complete the value chain by providing a technological assessment of the initial reaction: the formation of diphenolic acid as well as the final stage of the material: implementation. An attempt is made to improve upon the former by employing a different process. While the latter is

emulated by tests performed on samples reinforced with fibrous materials. In keeping with the sustainability mindset natural fibers are employed.

1.9 References

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