

Application of pyrrolidone building blocks in developing renewable 2-oxazolines based thermosets

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Summary

Polymers, both thermoplastics and thermosets, are of high importance in our daily life. However, the concern arising due to depletion of fossil feedstocks and traditional usage of plastics have forced both academia and industry to explore sustainable routes to develop polymers following biobased circular economy principles, i.e. through development of degradable, reusable, or recyclable polymers. To this end, biobased molecules synthesized from biobased/bio-sources or renewable feedstocks provide an alternative monomer source for polymers. One such interesting monomer is itaconic acid, with two functional dicarboxylic acids and one unsaturated bond, allowing it to undergo aza-Michael addition-cyclization (cascade) reaction, thereby generating a five membered heterocyclic pyrrolidone dicarboxylic acids functionality. Some of these pyrrolidone monomers have been recently used to develop fully renewable, degradable polymers like polyesters and poly amides, however the functional and reactive pyrrolidone monomer synthesis and its purifications are not yet optimized and explored. Traditional thermoset resins are non-recyclable, non-degradable which thereby end up as landfills or garbage thrown into oceans due to their permanent covalent crosslinking. Until now, epoxy resins have been extensively used to develop thermosets. However, there are several drawbacks of using epoxy resins, for example – its toxicity, brittleness, non-recyclability and poor mechanical performance. Retrospectively, bis(oxazolines) chemistry has proven its beneficial potential in developing linear and branched polymers over decades. Until now, these bis(oxazolines) are widely used as chain extenders, however, their potential in developing thermosetting resins is hardly explored. Furthermore, their curing kinetics, mechanical performances and their potential end-of-life has not been evaluated. Additionally, the green pathway for synthesis of these bis(oxazolines) makes them more interesting, while following the concepts of green chemistry and sustainability principles.

In this thesis, the potential of aza-Michael addition-cyclization (cascade) reaction is investigated with the aim to optimize the synthetic conditions and purification of various symmetric and multi-functional pyrrolidone dicarboxylic acids. They are further reacted with furan and phenyl based bis(oxazolines) to undergo ring opening polymerization, with the focus to understand their curing kinetics, mechanical properties under ambient and various controlled humidity conditions, and evaluating their potential end of life. Hence bis(oxazolines) chemistry is investigated thoroughly to develop both thermoplastics and thermosets, when reacted with the synthesized pyrrolidone dicarboxylic acids. The study also focuses on exploring the potential of renewable pyrrolidone dicarboxylic acids as new bio-based building blocks for generation of bio-based low viscous thermosetting resins, used as an adhesive. While performing this study the efforts are made to understand

1) the synthesis and purification steps following the requirements of green chemistry; 2) the curing kinetics of both linear chain formation and crosslinking density; 3) influence of ambient condition and relative humidity on the mechanical performances of the developed thermoplastic and thermoset; 4) potential end of life – recyclability, enzymatic depolymerization followed with recovery and reuse of the renewable monomers. This knowledge of understanding is relevant in developing a toolbox of novel renewable and recyclable thermoset resins/thermoplastics by using renewable bio-based building blocks.

The symmetrical (bis)pyrrolidone dicarboxylic acids synthesis and its purification obtained by using itaconic acid and various aliphatic diamines via aza-Michael addition reaction is performed and investigated using a combination of ^1H and 2D-NMR (structural analysis) and thermal analysis (DSC and TGA) (**Chapter 2**). Through NMR, GPC, and FTIR analysis it is demonstrated that these (bis)pyrrolidone dicarboxylic acids exhibit significantly enhanced curing rates in 2-oxazoline resins compared to resins containing aliphatic dicarboxylic acids such as sebacic acid. Overall, it is shown that the rate of 2-oxazoline ring opening addition with carboxylic acid functionalities is determined by the dicarboxylic acid, whereas the ring opening addition of the 2-oxazoline functionality with amide groups is determined by the bis(2-oxazoline) compound. The thermosets obtained after curing proved to be readily plasticized by water, thereby opening possibilities towards predicting its potential end of life via enzymatic degradation.

Followed with the understanding of their curing kinetics, several thermosets with varying crosslinking densities are prepared by mixing the desired ratio of (bis)pyrrolidone dicarboxylic acid with bis(oxazolines), followed by thermal curing at 180 °C (**Chapter 3**). The crosslink density of the thermosets is controlled by the usage of an excess of bis(2-oxazoline) and the achievement of full conversion is confirmed by Fourier transform infrared spectroscopy (FTIR). Retrospectively, the glass transition temperature of the thermosets increases with increasing crosslinking density. Nevertheless, all synthesized thermosets are prone to absorb water upon storage, resulting in a strong plasticizing effect and thus a suppression of the glass transition temperature. To assess the role of water on the thermo-mechanical properties, all thermosets are exposed to various relative humidity and their mechanical performance is evaluated. In general, we observe that the suppression in T_g under the influence of water facilitates a brittle-to-ductile transition as the T_g of the thermosets approaches room temperature, without significantly facilitating hydrolysis of the polymer backbone. Furthermore, it was observed that hydrolysis of the ester bonds can be enforced at elevated temperatures and high pressure in the presence of water, resulting in liberation of the used renewable (bis)pyrrolidone monomer in aqueous phase. Interestingly, the renewable (bis)pyrrolidone

dicarboxylic acids can readily be isolated by filtration as it crystallizes from water during cooling, thereby providing a promising route for its chemical recycling. Additionally, these renewable resins have better adhesive property to glass, metals and any polar surfaces having amide or ester bonds. Thus, the adhesion performance of these renewable thermoset resins is evaluated on aluminium and polylactide (PLA), both under ambient condition and after immersion in water that resulted in promising findings. Glass is excluded from the plan of experiment due to safety concerns.

Furthermore, the effect of additional functionality and reactive groups towards ring opening polymerization with bis(oxazolines) is studied while using the synthesized functional pyrrolidone dicarboxylic acids obtained by using itaconic acids and naturally occurring L-amino acids (**Chapter 4**). The developed monomers prove to be excellent candidates for thermal polymerization with bis(2-oxazolines), yielding thermally stable thermoplastic polymers and thermosets. Through GPC and NMR analysis, it is demonstrated that the aromatic alcohol group in the monomer derived from L-tyrosine is non-reactive towards thermal ring opening addition with 2-oxazolines under the employed reaction conditions. In other words, the thermal ring-opening addition polymerization of bis(2-oxazolines) can effectively be used to generate (co)polymers with pendant aromatic alcohol groups without requiring any protecting groups or solvents. Through evaluation of the visco-elastic response and stress relaxation tests, it can be proved that the relaxation behaviour of the developed polymers can be tailored by introduction of pendant functional groups, effectively increasing the secondary interactions.

As explained earlier in **Chapters 2 and 3** on the performance of 2-oxazoline based polymers, together with their potential for hydrolysis and consecutive recovery of the (bis)pyrrolidone dicarboxylic acids, the role of the residual diol of the ring-opened 2-oxazoline has been ignored. However, the presence of two hydroxyl groups combined with two amide moieties makes these organic compounds promising candidates as nucleating agents; because they exhibit high melting temperature due to strong hydrogen bonding and a strong ability to self-assemble/crystallize upon cooling. Thus, the potential of bis(2-hydroxyethyl)furan-2,5-dicarboxamide (BHEF) and N,N'-bis(2-hydroxyethyl)terephthalamide (BHET) are explored as additives for PLA (**Chapter 5**). Overall it demonstrates that the BHET compound, potentially isolated from chemical recycling of thermally cured polymers, based on terephthalic acid based bis(2-oxazoline), is a promising additive for PLA (acting both as a plasticizer and nucleating agent, depending on the amount used), whereas, BHEF, the product that can be isolated after hydrolysis of thermally cured polymers containing a 2,5-furandicarboxylic acid based bis(2-oxazoline) has, despite its renewable origin, no significant effect as additive for PLA. Hence this renewable monomer (BHEF) is

better suited for the development of bio-based and biodegradable polymers rather than for reuse as additive for PLA after chemical recycling.

While working with BHET and BHEF as nucleating agents for PLA, it is observed that the cooling rate and the amount (wt%) of NA used plays a significant role in enhancing the nucleation efficiency of the matrix (PLA). Thus to further investigate the effect of supercooling, a series of oxalamide based organic compounds (OBOC) are synthesized and their capability to enhance the nucleation of polylactide is evaluated (**Chapter 6**). Interestingly, it is observed that the nucleation efficiency of the OBOCs increases at high cooling rates, making them more attractive for industrial processing conditions. It is observed that the nucleation efficiency of polylactide is significantly enhanced in the presence of OBOC crystals, as a transcrystalline PLA morphology grows from the OBOC crystal surface (at relatively low supercooling from the equilibrium melting temperature of PLA). However, such crystallization of PLA occurs only when the OBOC crystals are formed at or below 145 °C while cooling at 10 °C/min. In contrast, when the OBOC crystals are formed above 145 °C (i.e. from a lower supersaturated state), the nucleation efficiency is reduced. Thus these findings override the possibility of both epitaxy and soft-epitaxy as their only plausible nucleation mechanism. Supported with in-situ polarized optical microscopy, differential scanning calorimetry, plate-plate rheology and molecular modelling, it is confirmed that the enhanced nucleation results from local stresses imposed with crystal growth of the nucleating agent on the polylactide melt thereby invoking stress-enhanced nucleation. Thus the reasoning of nucleation efficiency is attributed to 1) The imposed local shear rates, facilitated by the rapid growth of the OBOC crystals, which are high enough to facilitate contour orientation of the high molecular weight PLA chains next to the growing OBOC crystals, confirming the possibility for stress-enhanced nucleation, and 2) surface roughness of OBOC crystals. OBOC crystallization at high supersaturation yields defected smaller/defected OBOC crystals, which provides higher surface area and surface roughness, in contrast to lowered supersaturation (> 150 °C), they undergo annealing thereby providing a smoother surface and lesser surface area – retrospectively exhibiting a decreased nucleation efficiency, irrespective of the PLA supercooling. Interestingly, both the surface roughness of OBOC crystals and the local stresses imposed on the PLA melt increase when the OBOC crystal growth proceeds from a highly supersaturated state, providing an explanation to the cause of the favored crystallization of PLA at high cooling rates in presence of the chosen oxalamides.

In this thesis, the potential of pyrrolidone based dicarboxylic acids is explored elaborately in developing renewable thermoplastics and thermosetting resins. The thesis conclusively demonstrates that the combination of renewable pyrrolidone dicarboxylic acids (both symmetrical and functional) together with potential biobased

bis(oxazolines) is a promising alternative in developing fast curable, biobased resins with controlled curing kinetics. The control over curing kinetics is highly desired in order to achieve optimal mechanical performance. Furthermore, the curing chemistry of bis(oxazolines) and pyrrolidone dicarboxylic acids proved to be also beneficial in developing functional and renewable biobased thermosetting resins with additional functionality as pendant groups, available for secondary interactions thereby enabling dynamic networks formation. Furthermore, these renewable resins have better adhesion performance with metal and PLA, both under ambient conditions and after immersion in water. Due to the presence of numerous polar groups, the developed renewable thermosets and thermoplastics are prone to moisture absorption and thus can undergo hydrolysis under extreme condition, enabling to predict its end of life via enzymatic depolymerization and recycling of the developed polymer. Furthermore, recovery and reuse of these renewable pyrrolidone monomer is a promising addition towards circularity, on the other hand the potential of the open diols, obtained from ring opened structure of used bis(oxazolines), is further used as an additive (nucleating agent) for PLA to enhance its nucleation efficiency. Thus this thesis demonstrates that the concept of biobased circularity can be achieved while using these renewable pyrrolidone monomers in developing 2-oxazoline based polymers. These scientific research findings, investigated with specific organic compounds or systems, are of general nature, thus can be also applied to develop other polymer systems.