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Intrinsic self-healing thermoset through covalent and hydrogen bonding interactions



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ABSTRACT

The intrinsic self-healing ability of polyketone (PK) chemically modified into furan and/or OH groups containing derivatives is presented. Polymers bearing different ratios of both functional groups were cross-linked via furan/bis-maleimide (Diels-Alder adducts) and hydrogen bonding interactions (aliphatic and aromatic OH groups). The resulting thermosets display tuneable softening points (peak of $\tan(\delta)$) from 90 to 137 °C as established by DMTA. It is found that the cross-linked system containing only furan groups shows the highest softening temperature. On the other hand, systems displaying the combination of Diels-Alder adducts and hydrogen bonding (up to 60 mol % of –OH groups) do not show any change in modulus between heating cycles (*i.e.* factually a quantitative recovery of the mechanical behaviour). It is believed that the novelty of these tuneable thermosets can offer significant advantages over conventional reversible covalent systems. The synergistic reinforcement of both interactions resists multiple heating/healing cycles without any loss of mechanical properties even for thermally healed broken samples.

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1. Introduction

Over the last few decades, researchers working on the design and optimization of plastic materials have reported considerable improvements (*e.g.* in mechanical properties of recycled materials) often stimulated by societal driven demands in terms of sustainability, enhancement of material quality and value-add services [1,2]. However, despite all the efforts, it is widely recognized that plastic recycling is still facing relevant problems regarding collection, separation, cleaning, processing chemistry and flow markets for recycled products [3–6].

As an attempt for improvements in this matter, the European Commission has categorized the waste treatment according to the most environmentally favourable strategies. The “waste hierarchy” establishes as priority the *prevention* followed by the *reuse* and *recycling* of waste, while the less favourable strategies are the *recovery* and *disposal* [7]. In the particular case of plastics, suitable materials for recycling are subjected to the availability of treatment technology and markets [8,9]. For instance, the most used procedures for thermoplastics recycling are the physical and chemical approaches. The physical recycling is realized by the grinding and re-melting of thermoplastics to produce a material with equal, similar or completely

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different properties compared to the original one. On the other hand, the chemical recycling turns thermoplastics into monomers or oligomers (by the addition of chemical additives and processing conditions) to be used as raw materials for the production of new polymers [10].

Thermosets unlike thermoplastics, cannot be recycled by using the above mentioned approaches (e.g. re-melted/re-shaped or chemical reduction to monomers) since they degrade or decompose. In this context, (thermally) reversible thermoset materials represent an accessible solution due to their remarkable ability of being mended and recycled (according to a “cradle to cradle” approach) in order to prolong their use after their first service life [11]. Several scientific articles have reported the ability of thermoset polymers to be repaired in different ways. These include the incorporation of low molecular weight additives in the form of capsules as healing agent after damage events (extrinsic self-repair) [12–16], but also the functionalization of raw non-reworkable polymers that can heal cracks as a consequence of an external stimuli like heat [17–20] and light [21–25] (intrinsic self-repair). The last approach relies on the chemical modification of the base polymer with functional groups able to undergo a reversible reaction as function of the presence/absence of the external stimulus. Diels-Alder or hydrogen bonding active groups are indeed often employed to prepare polymer networks with thermally reversible properties [26,27]. Therefore, in a fracture event, the healing process can be performed by the combination of covalent (Diels-Alder) and or non-covalent (H-bonds) reversible interactions. It is ideal as the intrinsic self-healing ability (i.e. bonds reconnection) of both functional groups plays a crucial role in supporting the recovery of the network (e.g. dimensional stability) at different levels of energy (i.e. complementary reinforcement of chemical and physical interactions). Therefore, the healing process can be achieved under different conditions (e.g. temperature) just by controlling the ratio between the introduced functional groups. These advantages have recently triggered the research on thermoset systems with tuneable chemical reversibility and mechanical properties (e.g. polymers containing reversible [20,26,28] and non-reversible [29–31] covalent interactions in combination with hydrogen bonding). However, the design of this kind of materials still faces problems in terms of lengthy, costly and cumbersome synthetic steps, thus hindering any application at industrial scale.

Against this drawback, we recently reported on the novel thermally self-healing properties of polymer networks containing reversible covalent and non-covalent interactions based on aliphatic polyketones [20,32]. In order to prepare the target materials, we started modifying alternating aliphatic polyketone (PK) into new polymers by using the Paal-Knorr reaction, i.e. the chemical modification of the di-carbonyl arrangement of PK into pyrrole groups bearing furan or amine active groups [20]. This synthetic pathway offers several advantages like high yield under relatively mild condition (100 °C) and fast reaction kinetics (4 h) even without any catalyst, with water as the only by-product. Subsequently, the modified PK was covalently cross-linked through the Diels-Alder (DA) reaction by using bis-maleimide. The simultaneous presence in the modified polymers of both interactions (H-bonding and DA adducts) resulted in networks with softening points from 100 to 185 °C. Remarkably, the materials retained quantitative modulus values after multi heating-healing cycles. However, they also displayed an increase in the softening point between cycles, which was ascribed to the formation of irreversible cross-linking points via the reaction of the pendant amine groups with the unreacted carbonyls along the backbone [20]. In order to overcome this drawback, this work is focused on preparing tuneable reversible thermosets through the synergistic cooperation of covalent and non-covalent interactions. These materials should then be able to display reversible properties after several heating/healing and recycling cycles. In principle, this can be achieved by using OH functional groups (instead of amino ones) as hydrogen bonding active moieties, thus avoiding any side reaction with the unreacted carbonyls along the backbone. In order to establish more clearly the role of the OH-groups, reference polymers displaying the same pyrrolic backbone of the target ones were functionalized with less reactive moieties without OH groups.

After modification, the polymers are covalently cross-linked via furan/maleimide Diels-Alder adducts and hydrogen bondings. The thermal and mechanical behaviour is then studied by differential scanning calorimetry DSC and dynamic mechanical thermal analysis (DMTA) to determine the reversibility, rework-ability and intrinsic self-healing ability of the thermoset polymers.

2. Experimental section

2.1. Reagents

The alternating aliphatic polyketone, terpolymer of carbon monoxide with 30% of ethylene and 70% of propylene per mol (PK30, Mw 2687 g/mol), on the basis of the total olefin content, was synthesized according to a reported procedure [33,34]. The resulting product presents a 43% of carbonyl content on the basis of the total molecular weight of polymer. Furfurylamine (**Fu**) was freshly distilled (Aldrich, ≥99%). 3-Amino-1-propanol (**Ap**) (Acros, The Netherlands), 2-(4-hydroxyphenyl) ethylamine (tyramine **Ty**) (Sigma Aldrich 99%), 2,5-hexanedione (Sigma Aldrich 98%), butylamine (**Ba**) (Sigma Aldrich 99%) benzylamine (**Bea**) (Sigma Aldrich 99%), 1-Propanol, Milli-Q water, (1,1-(methylenedi-4,1-phenylene) bis-maleimide (**b-Ma**) (Sigma Aldrich 95%), chloroform (CHCl₃ Laboratory-Scan, 99.5%), were purchased and used as received. Deuterated dimethylsulfoxide (DMSO-*d*₆, Sigma Aldrich, ≥99.9 atom%) was used as solvent for ¹H NMR measurements.

2.2. Model component reaction

Model reactions between stoichiometric amounts of 2,5-hexanedione (8.7 mmol) with either furfurylamine (previously reported by our group [35]), 3-amino-1-propanol (0.65 g) or tyramine (1.2 g) were carried out in order to identify the

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