REVERSIBLE THERMOSET SYSTEMS FOR COATING APPLICATIONS: SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION IN BULK AND AS A COATING

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ABSTRACT

Thermosets, irreversibly cross-linked polymer networks having superior mechanical properties and increased thermal and chemical resistance, are often used in composites and coating applications. For coatings, concerns about the environmental safety of chromium-based corrosion inhibitors and the current lack of equally efficient replacements, increased the interest in alternative, sustainable and durable coating systems. A major drawback of conventional thermoset systems is the irreversible character of the network bonds formed, thus not permitting healing of (micro-)cracks unless healing agents are incorporated, as discussed in, e.g., [1-3]. Incorporating reversible covalent bonds in the polymer network structure builds in self-healing capacity through the reversible character of the polymer network [4,5], while still retaining mechanical properties comparable to conventional thermoset systems. The reversible character of the network enhances the processability of the polymer network materials, and introduces reparability and ultimately recyclability of the network polymer. Thermally-induced self-healing is a property of interest for coating applications [6]. A reversible thermoset coating can be applied to a metal substrate to protect it from corrosion through its barrier properties and by healing sustained damage. As the healing relies on the thermally reversible reaction, the chemical potential for healing is in principle inexhaustible.

The reversible character of the polymer network system used in our work is based on the Diels-Alder chemistry, combining a conjugated diene and a substituted dienophile to form thermally reversible covalent bonds. At low temperatures the Diels-Alder adduct is stable and a network structure is attained. When the temperature is increased sufficiently, the Diels-Alder equilibrium is shifted towards the decomposition of the Diels-Alder adduct and the network is broken down. Upon cooling, the Diels-Alder links are reinstated and the network structure is recovered. The furan-maleimide Diels-Alder chemistry was used as a model for studying the reversible equilibrium (Figure 1). The Diels-

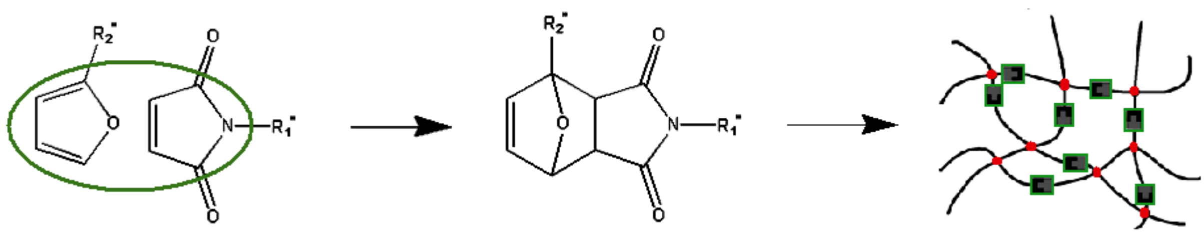

Figure 1. Reversible cross-linking based on the reversible Diels-Alder cyclo-addition of furan and maleimide functionalized building blocks forming a network with irreversible (red) and reversible (green) cross-links.

Alder kinetics and thermodynamics were investigated by spectroscopic and advanced thermal analysis techniques, including fast-scanning calorimetry [7]. Evaluating the temperature and concentration dependence of the Diels-Alder reaction facilitates adjusting the properties of the reversible polymer network system to the users' desire.

Polymer network materials with incorporated reversible covalent bonds were synthesized and their mechanical and chemorheological properties were studied. The mechanical properties and the network reversibility can be controlled by a suitable selection of furan and maleimide functionalized monomers, altering the density of reversible and irreversible cross-links and the properties of the interlinking chains. Bulk characterization indicated that the reversible polymer network materials are suitable for thermally induced self-healing in coating applications. A wide range of surface analysis techniques, including hotstage AFM and local electrochemical methods, was used to study different aspects of the healing behaviour (Figure 2). Combining the reversible thermosets with autonomous corrosion protection by incorporating corrosion inhibitors yields multiple-action corrosion resistance, providing the protection needed in automotive and aerospace applications.

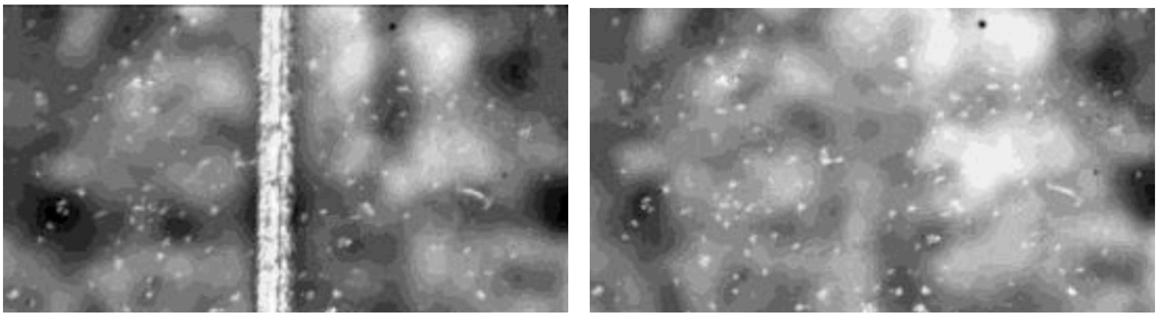

Figure 2. Reversible network coating after scratching (left) and subsequent healing (right). Image width ca. 2 mm.

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