MULTIPLE-ACTION SELF-HEALING COATINGS BASED ON REVERSIBLE POLYMER NETWORK SYSTEMS

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ABSTRACT

Research on self-healing materials has greatly expanded over the last several years, as a result of the increased interest in the development of alternative, sustainable and durable systems [1-3]. The concept of self-healing coatings on the basis of reversible polymer network systems is to actively heal a local damage by application of an external stimulus, breaking the reversible covalent bonds. Active corrosion inhibitors can be added to render the corrosion protection more autonomous. As the inhibitors diffuse to the local damage, the corrosion will be stopped immediately by the formation of a stable oxide layer. The polymer coating can then be healed via the application of an external stimulus, restoring the barrier properties. Combining the self-healing properties of a reversible polymer network with autonomous corrosion protection mechanisms yields a multiple-action corrosion resistance that can provide the needed protection in a wide range of applications, e.g. the automotive and transportation industry, but also in infrastructure, manufacturing and structural applications.

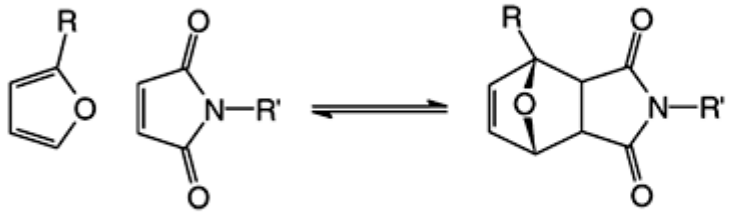

Figure 1: Diels-Alder equilibrium reaction for the furan-maleimide system

The self-healing polymer network system is based on the reversible Diels-Alder equilibrium reaction (Fig. 1). Dynamic covalent bonds are incorporated in the network structure by introducing furan and maleimide functional groups in the back-bone [4,5]. At room temperature the network structure is formed and exhibits properties comparable to irreversible thermosetting materials, such as superior mechanical and barrier properties. When the temperature is increased the equilibrium is shifted and the retro Diels-Alder reaction becomes more important. The network is gradually broken down, exhibiting flow behavior if the temperature is increased sufficiently, healing the sustained damage. Upon cooling, the network structure, and hence the mechanical and barrier properties, are restored. The reversible character of the network allows heating-used self-healing of sustained damage.

The structure of the polymer network was changed, altering the density of the reversible and irreversible cross-links and changing the length and the properties of the interlinking chains, to find the most desirable properties for self-healing applications. The influence of the changes in the network structure on the thermal reversibility of the polymer network was assessed in bulk by means of Modulated Temperature Differential Scanning Calorimetry (MTDSC) and rheology.

The reversible covalent network systems were applied to glass and Aluminum substrates. Local thermal analysis (LTA) measurements were performed to determine the thermal properties of the polymer coatings and to evaluate the uniformity and homogeneity of the coatings. Small defects were applied to the polymer coatings, exposing the substrate to a corrosive environment. The self-healing behavior of the coating was assessed using localized surface analysis techniques, including Atomic Force Microscopy (AFM), where the coating was allowed to heal by the in-situ application of heat, via a heating stage or a thermal micro-probe. The corrosion resistance of the polymer network was studied using Electrochemical Impedance Spectroscopy (EIS). The healed coatings were compared to the damaged coatings and the pristine coatings, showing the restoration of the barrier properties. For the corrosion study Aluminum 2024-T3 was used as a substrate. The Aluminum alloy is mainly used in aircraft applications for its superior mechanical properties, but it is very susceptible to corrosion.
Active corrosion inhibitors were added to the coating formulations to render the self-healing system autonomous. EIS measurements were performed on the coatings with the inhibitors to evaluate the corrosion protection of the metal substrate by the multiple-action self-healing system.

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