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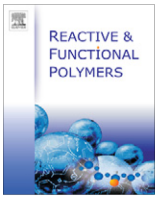

# A self-healing polymer network based on reversible covalent bonding

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ABSTRACT

A self-healing polymer network for potential coating applications was designed based on the concept of the reversible Diels–Alder (DA) reaction between a furan functionalized compound and a bismaleimide. The network allows local mobility in a temperature window from ca. 80 °C to 120 °C by shifting the DA equilibrium towards the initial building blocks. Changing the spacer length in the furan functionalized compound leads to tailor-made properties. Elastomeric model systems were chosen to evaluate the kinetic parameters by Fourier transform infrared spectroscopy. For the DA reaction a pre-exponential factor $\ln(A_{DA}$ in kg mol$^{-1}$ s$^{-1})$ equal to $13.1 \pm 0.8$ and an activation energy ($E_{DA}$) of $55.7 \pm 2.3$ kJ mol$^{-1}$ are found. For the retro-DA reaction, $\ln(A_{rDA})$ and $E_{rDA}$ are $25.8 \pm 1.8$ s$^{-1}$ and $94.2 \pm 4.8$ kJ mol$^{-1}$, respectively. The enthalpy and entropy of reaction are calculated as $-38.6$ kJ mol$^{-1}$ and $-105.3$ J mol$^{-1}$ K$^{-1}$. The kinetic results are validated by micro-calorimetry. Non-isothermal dynamic rheometry provides the gel-point temperature of the reversible network. The sealing capacity is evaluated by atomic force microscopy for micro-meter sized defects. Repeatability of the non-autonomous healing is checked by micro-calorimetry, ruling out side-reactions below 120 °C.

## 1. Introduction

In the field of organic coatings, thermosetting materials are widely used for corrosion prevention. These densely cross-linked structures possess advantageous barrier and mechanical properties compared to thermoplastics [1]. However, their life-time span is limited due to a number of factors, such as loss of adhesion, degradation by photo-initiated oxidation, and hydrolysis [2]. In addition, changes in temperature and humidity may result in cracking due to a difference in expansion coefficient between substrate and coating. When micro-cracks are formed through the brittle network coating, the underlying metal is left exposed, leading to an accelerated corrosion process [3].

Self-healing materials are promising systems to deal with this kind of coating failure. Over the last few years, strong research has been performed on this subject, giving rise to the development of numerous self-healing materials [4]. Two main groups can be identified based on their activation trigger: autonomic (or intrinsic) and non-autonomic (or extrinsic) self-healing systems [4,5]. In case of autonomic systems, the mobile phase responsible for healing is embedded in the coating matrix. This means no intervention is required as the material holds the substance that allows regeneration [6]. Therefore, the self-healing efficiency, and also repeatability, is limited to the amount of regenerating substance available.

For the non-autonomic self-healing systems, different external triggers are available, such as photo, mechanical, chemical and heat stimuli [7]. One specific type of a non-autonomic self-healing design is based on reversible cross-links using heat as an external trigger. This category comprises hydrogen bonds, ionomers, coordination bonds, and reversible covalent bonds [8]. The reversible [4 + 2] cyclo-addition, also known as the Diels–Alder (DA) reaction, has been introduced into thermosetting polymeric systems in order to synthesize thermo-remendable and recyclable materials [9–11]. In earlier work, we also demonstrated the feasibility of a reversible polymer network based on the DA chemistry between a bismaleimide and a furan functionalized compound (see Scheme 1). The reaction equilibrium is shifted from diene and dienophile towards cyclo-adduct (and backward) by decreasing (increasing) the temperature. Healing of macroscopic and microscopic defects takes place in a temperature window ranging from 80 to 130 °C [12,13]. The advantage of this particular self-healing system lies in its flexible network design by using spacers in the furan functionalized compound of different length. Networks with shorter spacers lead to a higher cross-link density and thermomechanical properties suited for coating applications. It was shown that higher concentrations of cross-links shift the thermo-reversibility towards higher temperatures [13].

The focus of this paper is on the thermal evaluation of the DA reaction between a bismaleimide and a 4-functional furan compound. Model systems with longer spacers (less suited for applications) are chosen based on their low glass transition temperature in order to avoid any vitrification during the kinetic evaluation.

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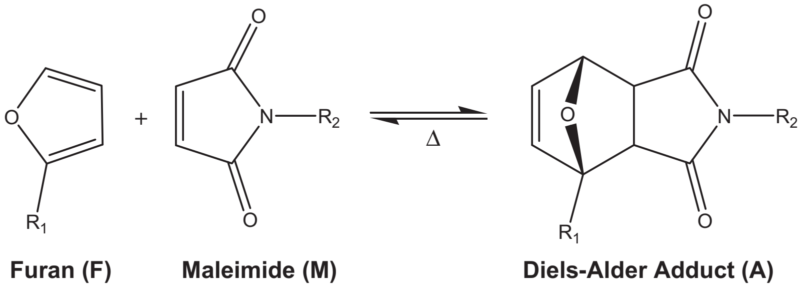


**Scheme 1.** Diels–Alder equilibrium reaction between furan and maleimide functional groups.

Furan and maleimide conversions as a function of time at different curing temperatures are obtained by temperature-controlled Fourier transform infrared (FTIR) spectroscopy. The kinetic model is validated through micro-calorimetry. The determination of pre-exponential factors, activation energies, molar heat of reaction and entropy of reaction will allow a controlled optimization of the healing procedure.

In addition to kinetic modelling, rheological information is essential to take into account the thermo-mechanical behavior during healing. The self-healing mechanism under study is based on a temporary increase in local mobility due to a decrease in viscosity upon heating. The change in viscosity and viscoelastic behavior should be limited in order to maintain the mechanical integrity of the coating on the substrate. The flow behavior of the model network is studied by dynamic rheometry and allows determination of a gel-point temperature. In addition, sealing of microscopic scratches through viscous flow is determined by atomic force microscopy at elevated temperatures.

After sealing any damage at higher temperature in the thermo-reversible temperature window, the recovery of initial properties takes place in a subsequent cooling with reformation of covalent bonds by DA cyclo-addition. An important concern is the repeatability of the reversible DA reaction. In order to ensure repeatable healing, the concentration of reactive groups must be maintained. No leaching of reactive component should occur and no irreversible side-reaction should take place during the healing procedure. Repeatability of the exothermic DA reaction of the model system is studied by micro-calorimetry at ambient temperature to rule out any side-reaction in the thermo-reversible temperature window used in this study.

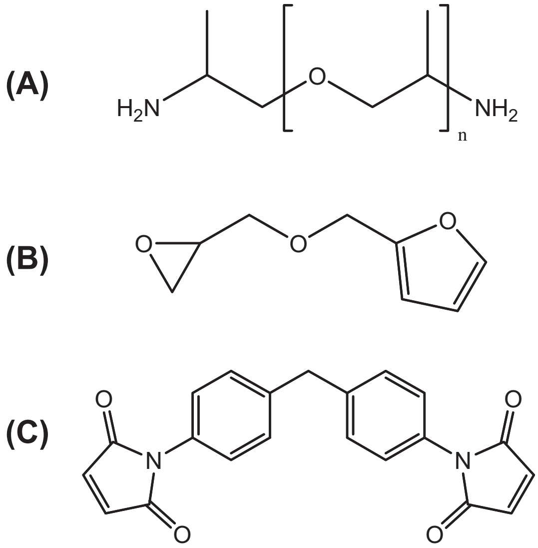
## 2. Experimental

### 2.1. Materials

Poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine D-series) with average degree of polymerization *n* (determined by nuclear magnetic resonance spectroscopy) of 2.9 (trade name Jeffamine D-230 or abbreviated J230, $\overline{M}_n = 240\ \mathrm{g\,mol^{-1}}$), 7.0 (J400, $\overline{M}_n = 478\ \mathrm{g\,mol^{-1}}$), 39.2 (J2000, $\overline{M}_n = 2345\ \mathrm{g\,mol^{-1}}$), 99.4 (J4000, $\overline{M}_n = 5839\ \mathrm{g\,mol^{-1}}$), furfuryl glycidyl ether (FGE, 96%), 1,1′-(methylenedi-1,4-phenylene)bismaleimide (DPBM, 95%), and triethylamine were purchased from Sigma–Aldrich. All products were used as received (see Scheme 2).

### 2.2. Remendable polymer network synthesis

The synthesis of the remendable network was performed in two steps. In a first step, FGE was irreversibly bonded to Jx (x = 230, 400, 2000, and 4000) through an epoxy–amine reaction, yielding a furan functionalized compound. This reaction was performed at 80 °C without any solvent until completion. In a second step, the furan functionalized compound (FGE-Jx) was mixed with DPBM in a stoichiometric ratio to obtain the reversible polymer network through DA reaction. Prior to the DA reaction, the DPBM was dissolved in chloroform to obtain a homogeneous reversible network. In order to create bulk samples, the DA curing reaction between FGE-Jx and DPBM was carried out at 25 °C by solvent casting, and traces of chloroform were removed under vacuum.



**Scheme 2.** Monomers used for the synthesis of the reversible network system: (A) Jeffamine D-series Jx (*x* = 230, 400, 2000, 4000), (B) FGE, and (C) DPBM.

### 2.3. Thermal analysis techniques

#### 2.3.1. Differential scanning calorimetry (DSC)

DSC experiments were performed on a Q2000 from TA instruments, equipped with a liquid nitrogen cooling device. Tzero calibration was performed at 2.5 °C min$^{-1}$ and 20 °C min$^{-1}$ with sapphire disks and temperature and enthalpy calibration were performed using an indium standard. A heating rate of 20 °C min$^{-1}$ was applied to evaluate initial building blocks, Jx and FGE-Jx. In order to characterize the synthesized remendable polymer networks, modulated temperature DSC experiments (MTDSC) were performed at 2.5 °C min$^{-1}$.

#### 2.3.2. Micro-calorimetry

The micro-calorimeter used was a thermal activity monitor TAMIII from TA instruments, with a precision of 200 nW. In a glass ampoule of 4 ml a bulk sample was heated to a maximum temperature of 150 °C for 15 min. Immediately after heating, the material was quenched in liquid nitrogen. In the micro-calorimeter, the formation of covalent bonds by the exothermic DA reaction was stud-