

Self-healing property characterization of reversible thermoset coatings

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Abstract A self-healing material for coating applications was synthesized using the Diels–Alder (DA) reaction as cross-linking reaction. The built-in reversibility allows local mobility and rearrangements in the polymeric network, which is composed of a furan functionalized epoxy-amine and a bismaleimide. The self-healing material was characterized by physical–chemical means using Fourier Transform Infrared spectroscopy, thermogravimetric analysis (TG) and rapid heat-cool differential scanning calorimetry. It has been shown that the reversibility, as a result of a change in DA/retro-DA equilibrium, occurs in a temperature window ranging from ca. 80 to 150 °C. The repeatability of the non-autonomous healing was checked by TG, showing no evaporation or degradation of the components involved in the temperature window of interest.

Keywords Self-healing · Reversible network · Thermoset coating · Diels–Alder

Introduction

Traditionally, densely cross-linked networks have superior barrier and mechanical properties compared to their linear analogues. Thermosetting materials are durable and can be

used in a wide variety of applications like composites [1, 2], adhesives [3, 4] and coatings [5, 6]. However, they exhibit severe limitations such as restricted processability and a lack of intrinsic repairability. As a result of their irreversible network architecture with a high network or cross-link density, thermosets do not possess the chain mobility of the thermoplastics so widely used in self-healing concepts. Therefore, the self-healing of thermosets has followed distinctly different approaches. The hollow fibre approach by Dry and Sottos [7] mimics nature by releasing healing agents stored in hollow fibres inside the thermoset to repair damage. A sort-like autonomous self-healing concept is the microencapsulation approach [8]. This technique involves a microencapsulated healing agent and a dispersed catalyst in a network. When a capsule is ruptured by cracking, the healing agent is released into the cracks due to capillary action. After this release, a subsequent reaction between the healing agent and the dispersed catalyst heals the material and prevents further crack growth.

A different approach is based on the incorporation of reversible cross-linking functionalities in the polymer backbone, such as Diels–Alder (DA) adducts. Wouters et al. [9] proposed the preparation of self-healing coatings which comprised an epoxy-amine curing between a diamine and a bifunctional epoxy containing reversible DA bonds. The built-in reversibility is non-autonomous and based on the use of heat as an external trigger. In this article, we report on a reversible cross-linked polymer network for coating applications, synthesized by the DA reaction between a furan functionalized epoxy-amine and a bismaleimide. The focus is on the thermal and physical–chemical characterization of local mobility and rearrangements in the polymer network, and on the temperature window of reversibility and repeatability.

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Experimental

Materials

Poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine D-400) with a number average molecular mass of approximately 400 ($M_n \sim 400$), furfuryl glycidyl ether (FGE; 96%) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (DPBM; 95%) were purchased from Sigma-Aldrich. All products were used as received.

Characterization

Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectroscopy was performed on a Perkin Elmer 2000 FTIR system equipped with a Perkin Elmer 1700X TG-IR heating stage. The IR samples were prepared by casting a thin film between two KBr discs from a chloroform solution. The solvent was evaporated under vacuum.

Thermogravimetric analysis (TG)

The TG measurements were performed on a TA instruments TGAQ5000 at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ using air as the purge gas at 25 mL min^{-1} .

Rapid heat-cool differential scanning calorimetry (RHC)

The RHC experiments were performed on a prototype RHC developed by TA instruments, particularly designed for operation at high scanning rates [10]. The system was equipped with a Liquid Nitrogen cooling device. Tzero calibration was performed at $500 \text{ }^\circ\text{C min}^{-1}$ with sapphire discs and temperature and enthalpy calibration were performed using an indium standard. Experiments in heating were conducted under a nitrogen atmosphere and neon is used as the purge gas (10 mL min^{-1}) for cooling. RHC crucibles of less than 2 mg were filled with sample masses in the range of 0.2–0.7 mg. Heating and cooling rates of $500 \text{ }^\circ\text{C min}^{-1}$ were used for all RHC experiments. A typical temperature profile applied to the reversible thermoset is shown in Fig. 1.

Results and discussion

Reversible thermoset synthesis

In the first step, the Jeffamine D-400 is furan functionalized through an irreversible epoxy-amine reaction with FGE. This reaction was performed at $56 \text{ }^\circ\text{C}$ until completion. In the second step, this furan functionalized epoxy-amine

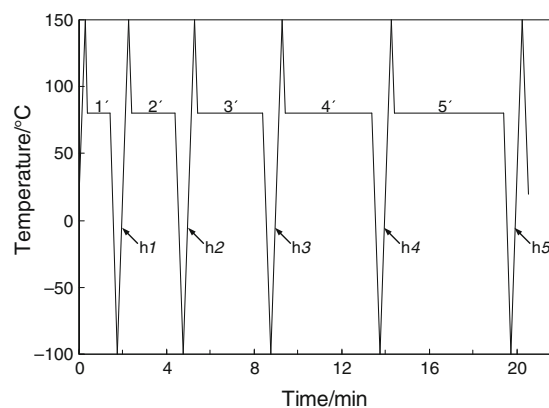
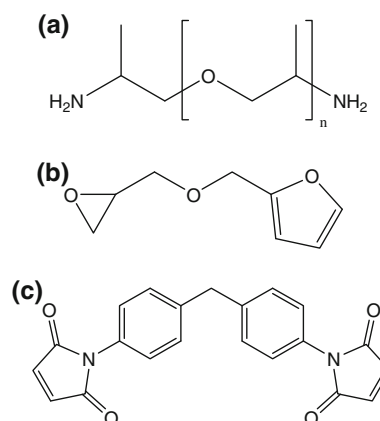


Fig. 1 Temperature profile of the RHC experiment, with $\beta = \pm 500 \text{ }^\circ\text{C min}^{-1}$. After each isothermal segment at $80 \text{ }^\circ\text{C}$ (with different t_{iso}), the network is cooled to $-100 \text{ }^\circ\text{C}$ and a successive heating cycle (h) up to $150 \text{ }^\circ\text{C}$ is programmed

(FGE-Jeff400) is added to DPBM in a stoichiometric amount to create the reversible thermoset through DA reaction. Before the DA reaction, the DPBM was dissolved in chloroform to obtain a homogeneous reversible network. The DA reaction between FGE-Jeff400 and DPBM was carried out at $25 \text{ }^\circ\text{C}$. The remaining chloroform was removed under vacuum at $80 \text{ }^\circ\text{C}$ (Scheme 1).

Thermally reversible network

The DA/retro DA equilibrium between FGE and DPBM is studied by FTIR. The DA adduct, composed by the reversible linkage between FGE and DPBM, is favoured at room temperature. FTIR spectra (see Fig. 2) were recorded as a function of increasing temperature and at each chosen temperature the system was allowed to evolve towards the new equilibrium condition before the acquisition of the spectrum.



Scheme 1 Components used for the synthesis of the reversible network: **a** Jeffamine D-400 ($n \sim 6.1$), **b** FGE and **c** DPBM

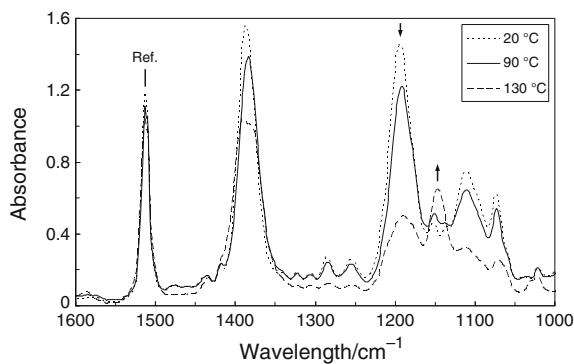


Fig. 2 FTIR spectra of FGE (diene) and DPBM (dienophile) at different temperatures. The peaks at 1513 cm^{-1} (ref.); 1194 cm^{-1} (DA-adduct) and 1146 cm^{-1} (DPBM) are indicated

The reference peak at 1513 cm^{-1} represents a C–C stretch in the phenyl groups of DPBM [11]. The absorbance of the reference signal remains constant with a change in reaction equilibrium. The IR absorbance at 1146 cm^{-1} corresponds to an asymmetric C–N–C stretch in DPBM [11]. Regarding Fig. 2, it is clear that the IR absorbance, corresponding to the asymmetric C–N–C stretch, shifts from 1194 cm^{-1} (representing DPBM linked to FGE) to 1146 cm^{-1} (representing DPBM) with increasing temperature.

For clarity, the absorbance ratio (AR) of both the DA-adduct (at 1194 cm^{-1}) and DPBM (at 1146 cm^{-1}) is presented in Fig. 3 relative to the absorbance of the reference peak at 1513 cm^{-1} .

The bottom graph in Fig. 3 shows the release of DPBM at elevated temperatures. The upper part of Fig. 3 shows the evolution of the DA-adduct formed by the reversible linkage between DPBM and FGE. The general conclusion is that as the temperature increases above $80\text{ }^{\circ}\text{C}$, the retro DA reaction becomes more prominent, shifting the equilibrium from the DA-adduct towards the diene (FGE) and dienophile (DPBM).

Thermal analysis

When the reversible cross-linked network is subjected to temperatures above $80\text{ }^{\circ}\text{C}$, the equilibrium of the DA/retro-DA reaction shifts significantly towards the initial diene and dienophile components: the furan functionalized epoxy-amine and DPBM. In order to preserve a reversible self-healing coating system, it is required that these components are thermally stable at the required healing temperatures, i.e., do not degrade and/or evaporate out of the coating in healing conditions. In Fig. 4, the TG analysis of all relevant components (DPBM, FGE, and the reversible network) is plotted. It can be concluded that the DPBM (Fig. 4, line 1) is not a critical component, since degradation occurs at temperatures above $500\text{ }^{\circ}\text{C}$ under the applied

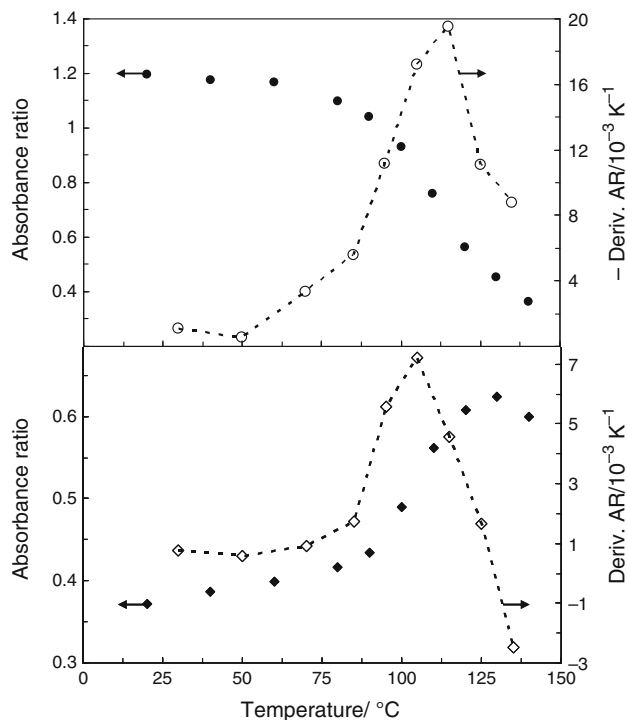


Fig. 3 Temperature dependence of the DA/retro-DA equilibrium between FGE (diene) and DPBM (dienophile). *Top*: AR representative for the DA-adduct (filled circle), and its temperature derivative (open circle). *Bottom*: AR representative for DPBM (filled diamond), and its temperature derivative (open diamond)

conditions. However, long healing periods of the reversible network above $150\text{ }^{\circ}\text{C}$ must be avoided, as the DPBM will homopolymerize as demonstrated by Hopewell et al. [12]. More critical is the loss of furan functionalities throughout healing experiments. However, evaporation of FGE (Fig. 4, line 3) in this self-healing system (Fig. 4, line 2) is excluded, because FGE is irreversibly linked to the Jeffamine D-400. Out of the TG experiment the conclusion is made that a maximum temperature of $150\text{ }^{\circ}\text{C}$ is acceptable throughout other thermal analysis or healing experiments to avoid any thermal degradation of the reversible network.

The RHC enables us to perform thermal analysis with higher heating and cooling rates compared to conventional differential scanning calorimetry (DSC), an essential feature to study in situ the DA/retro-DA equilibrium with temperature and as such the non-autonomous healing capacity of the reversible thermoset. The equilibrium shift with temperature will cause the reversible thermoset to depolymerise at higher temperatures leading to a lowered value of T_g together with an increased mobility and ability to flow, and oppositely, to cross-link again at lower temperatures leading to an increased value of T_g and re-established mechanical properties. The temperature profile of Fig. 1 was applied to study the reversible thermoset with

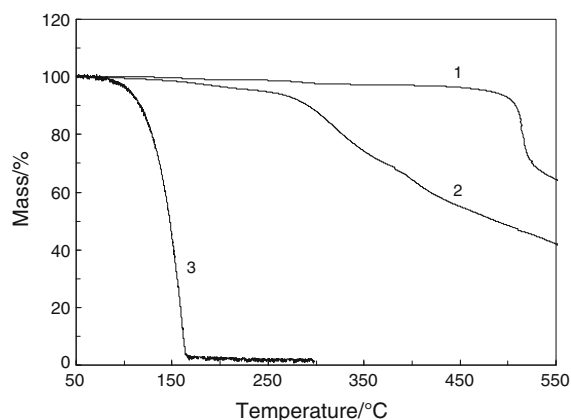


Fig. 4 TG analysis of DPBM (line 1), reversible network (line 2) and FGE (line 3)

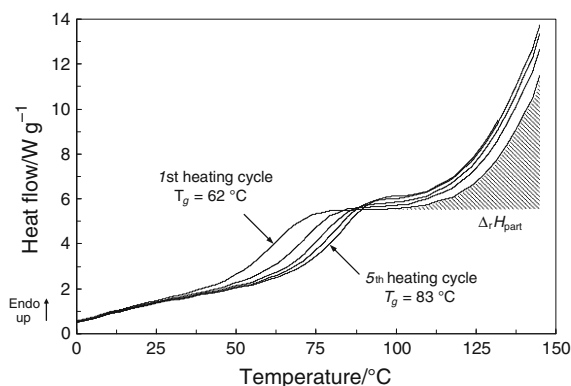
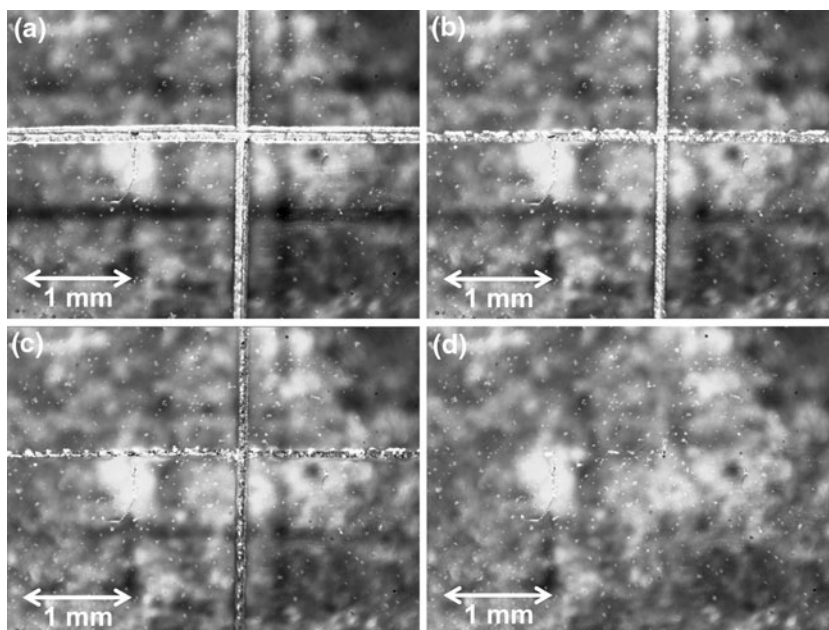


Fig. 5 RHC analysis of the reversible network. Depicted are the five consecutive heating cycles as described in Fig. 1

Fig. 6 Non-isothermal healing experiment with a heating rate of 30 °C min^{-1} of a scratched reversible network coating composed of furan functionalized epoxy-amine FGE-Jeff400 and DPBM. Scratched coating at room temperature (a), at 90 °C (b), at 110 °C (c) and after 2 min at 130 °C (d)



RHC. Before the isothermal segment for DA reaction, in this setup chosen at 80 °C , the network is heated to 150 °C to erase any thermal history and to shift the equilibrium towards the diene and dienophile components. High cooling rates ($\beta = 500\text{ °C min}^{-1}$) are necessary for freezing in the attained condition at 80 °C , avoiding any further reconstruction of the network in the cooling. During the isothermal segment at 80 °C , the DA reaction occurs, forming covalent cross-links between the furan (diene) and maleimide (dienophile) functionalities. As the isothermal time (t_{iso}) increases from 1 to 5 min, Fig. 5 shows that the T_g of the network increases from 62 to 83 °C . It illustrates the progress of the cross-linking process at 80 °C with increasing t_{iso} .

Note that above T_g , around 100 °C , the endothermic contribution of the retro-DA reaction is always observed, illustrating the concept of reversible bonding. Evaluating the area of the retro-DA reaction gives a measure for the partial heat of reaction ($\Delta_r H_{\text{part}}$). Figure 5 shows that an increase in T_g with increasing t_{iso} results in an increase in $\Delta_r H_{\text{part}}$. This can be explained by the fact that a more cross-linked structure at 80 °C (and thus a higher T_g) will result in more bonds that can be rebroken upon heating (and thus a higher $\Delta_r H_{\text{part}}$).

Self-healing ability of reversible thermoset coating

In order to check the feasibility of the DA chemistry between a furan functionalized compound and a bismaleimide to create a self-healing material, a solvent-cast coating with a thickness of approximately $200\text{ }\mu\text{m}$ was manually scratched

and healed upon heating. Figure 6 clearly shows that healing of the defects in the coating starts at temperatures around 90 °C (Fig. 6b), which is in agreement with FTIR (see Fig. 3) and RHC experiments (see Fig. 5). Heating the reversible network higher than 90 °C shifts the equilibrium further towards the diene and dienophile, resulting in a decreasing viscosity, allowing more mobility and flow of the coating. The healed coating (Fig. 6d) will regain its mechanical properties in a subsequent cooling. The overall healing process in the coating is accomplished by the combined action of local mobility and reversible covalent bonding.

Conclusions

In this study, the feasibility of using the DA reaction as cross-linking reaction to create a non-autonomous self-healing material is studied. A furan functionalized epoxy-amine is reacted with a bismaleimide through the DA reaction to synthesize the studied reversible thermoset. FTIR experiments were performed on the reversible network as a function of increasing temperature. They showed that the retro-DA reaction occurs in a temperature window of ca. 80–150 °C, making its reversibility useful for practical applications.

The repeatability of the self-healing system was verified by TG, indicating that no evaporation or degradation of functional groups occurs in the temperature window of interest. Thermal analysis by rapid heat-cool DSC revealed a clear relationship between the T_g of the cross-linked material and the partial heat of reaction ($\Delta_r H_{\text{part}}$) due to the endothermic retro-DA reaction. A more cross-linked structure at 80 °C (and thus higher T_g) results in a higher concentration of bonds to be rebroken upon heating (and thus a higher $\Delta_r H_{\text{part}}$).

Based on a healing experiment performed on a solvent-cast reversible network, it can be concluded that the

reversible DA chemistry leads to a decreasing viscosity at elevated temperatures. Above 90 °C there is an important gain in mobility, leading to the healing of the material, making this system a good candidate for practical self-healing coating applications.

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