

SELF-HEALING PROPERTY CHARACTERIZATION OF REVERSIBLE THERMOSET COATINGS

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Keywords: Self-healing, reversible network, thermoset coating, Diels Alder

ABSTRACT

Thermosets are irreversibly cross-linked polymer networks having superior mechanical properties and increased thermal and chemical resistance in comparison to their linear, un-cross-linked analogues. However, thermosets exhibit severe limitations such as restricted processability and certainly repairability. To overcome these drawbacks, the incorporation of reversible cross-linking functionalities in the polymer backbone, such as Diels-Alder (DA) adducts, has been explored. This built-in reversibility allows local mobility and rearrangements in the polymer network.

It is demonstrated that the network properties can be tailor-made by choosing the appropriate building blocks. Varying the chain length and the number of DA functionalities in the initial compounds, allows fine-tuning of the self-healing properties to the users desire. In a first step, the furan functional compound is synthesized by an epoxy-amine reaction between furfuryl glycidyl ether and an amine terminated compound. Afterwards, the furan functionalized product is mixed with a bismaleimide in order to synthesize the reversible thermoset.

The Diels-Alder/retro Diels-Alder equilibrium between FGE and DPBM is studied by FTIR. The Diels-Alder adduct, composed by the reversible linkage between FGE and DPBM, is favoured at room temperature. FTIR spectra were recorded as a function of increasing temperature and at each chosen temperature the system was allowed to evolve towards the new equilibrium condition [1].

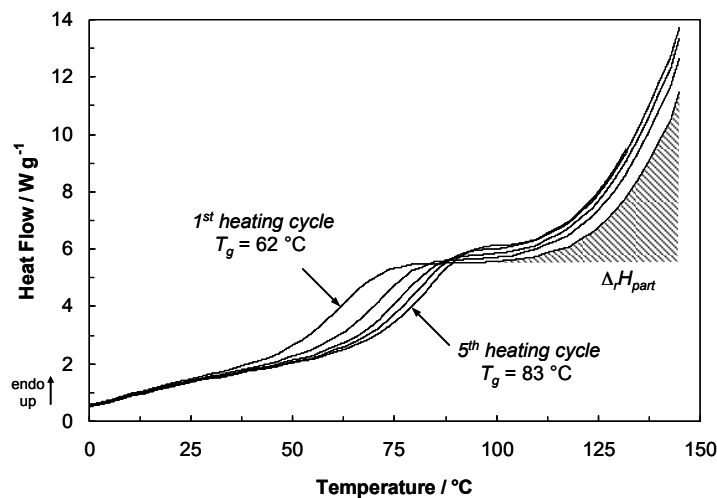


Figure 1: RHC analysis of the reversible network. Depicted are the 5 consecutive heating cycles, and after each isothermal segment at 80 °C (with different t_{iso}), the network is cooled to -100 °C and a successive heating cycle up to 150 °C is programmed.

Rapid heat-cool differential scanning calorimetry (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 [2]. 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.

Prior to the isothermal segment for DA reaction, in fig. 1 chosen at 80 °C, the network is heated to 150 °C to erase any thermal history and 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 minutes, figure 1 shows that the T_g of the network increases from 62 °C 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 ($\Delta_r H_{part}$). Figure 1 shows that an increase in T_g with increasing t_{iso} results in an increase in $\Delta_r H_{part}$. 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 $\Delta_r H_{part}$).

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 μm was manually scratched and healed upon heating. Figure 2 clearly shows that healing of the defects in the coating starts at temperatures around 90 °C (fig. 2 (B)), which is in agreement with FTIR and RHC experiments (see fig. 1). 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. 2 (D)) 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.

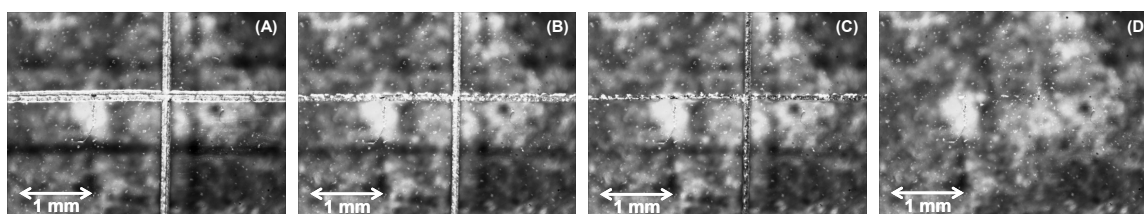


Figure 2: Non-isothermal healing at a heating rate of 30 °C min⁻¹ of a scratched reversible network coating composed of furan functionalized epoxy-amine FGE-Jeff400 and DPBM. Scratched coating at room temperature (A), at 90 °C (B), at 110 °C (C), and after 2 minutes at 130 °C (D).

The ‘Instituut ter bevordering van het Wetenschappelijk Onderzoek en de Innovatie van Brussel’ (IWOIB) is gratefully acknowledged for financial support in the framework of the ‘Impulse Programme-Environment 2008’.

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