STUDYING THE HEALING BEHAVIOR AT A MICROSCOPIC SCALE

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ABSTRACT

Research in the field of smart materials that exhibit self-repair mechanisms has greatly expanded over the last few years. This is especially true for polymers and polymer composite materials. One class of self-healing polymer materials is the reversible polymer network systems that use dynamic covalent bonds as a means to repair sustained damage. Currently a range of different dynamic covalent bonds is considered, of which the reversible Diels-Alder chemistry has drawn the most attention. Reversible covalent bonds have been incorporated into polymer network structures based on the Diels-Alder reaction between a furan and a maleimide [1-2]. Repair of sustained damage can be established by means of heating-used self-healing in bulk materials as well as in coating applications.

The aim of this research is to study the healing mechanism and healing kinetics at the microscopic scale and to compare this healing mechanism for different polymer network structures and chemistries. The self-healing behavior is studied with local and surface analysis techniques, including Atomic Force Microscopy as an important tool. A better understanding of the healing mechanism at the microscopic level will lead to a better understanding of the macroscopic healing phenomena and ultimately to the adaptation of the polymer network structure to obtain the desired material properties, such as mechanical properties, healing conditions and additional functional properties. The research can then be extended towards self-healing polymer composites, with e.g. a reversible polymer matrix, to evaluate the recovery of the composite material properties [3].

1. INTRODUCTION

Covalently cross-linked polymer network structures exhibit superior mechanical and barrier properties compared to their linear and physically cross-linked analogues. These exceptional properties find numerous applications in e.g. glues, adhesives, coatings, molded products,… The main disadvantage of these material systems is the irreversibility of the network formation reaction. The addition of dynamic covalent bonds to the polymer network structure has proven to render the network formation reaction reversible and gives rise to a new type of materials: reversible or dynamic polymer network systems. These dynamic covalent bonds originate from chemical reactions that are reversible or dynamic upon application of a certain stimulus. This stimulus can be light for photoreversible reactions, heat for thermoreversible reactions, force for mechanoreversible reactions or other. Through application of the corresponding stimulus to the dynamic material a healing action can be triggered and sustained damaged can be healed. When the external stimulus is removed the material will restore its initial properties and the material is considered to be repaired.

In this work heat will be considered as the stimulus to trigger a healing action in a reversibly cross-linked covalent polymer network based on the reversible Diels-Alder cycloaddition reaction between a furan and a maleimide. In previous work [2-4] it was demonstrated that polymer network materials based on these dynamic covalent bonds showed the required reversibility to establish a successful healing of sustained damage, both on a microscopic and a macroscopic scale.

At each temperature an equilibrium exists between the reactants (furan and maleimide functions) and the Diels-Alder cycloadduct. As the temperature is increased, the Diels-Alder reaction equilibrium is pushed towards the breaking of the dynamic bonds to form the reactants. By incorporating these dynamic covalent bonds as cross-links into a polymer network structure, reversible covalent polymer network structures with different mechanical and thermal properties can be created. As the temperature of the network is increased, the reversible bonds are broken and the material becomes softer as more bonds are broken. Above a certain temperature so many bonds are broken that the material starts to behave like a fluid. When the material has gained enough mobility to fill a sustained defect, healing of the material can be established. Upon decreasing the temperature the equilibrium shifts toward the formation of bonds and the initial properties of the network are restored.

2. MATERIALS AND METHODS

A series of Jeffamine D hardeners (Poly(propylene glycol) bis(2-aminopropyl ether)) are functionalized with furan functional groups by means an irreversible epoxy-amine reaction with furfuryl glycidyl ether (FGE). The reaction is allowed to go to completion yielding a 4-functional furan compound that is then reversibly reacted with 1,1'-(methylenedi-1,4-phenylene)bismaleimide (DPBM) to create a reversible polymer network structure. All products were purchased from Sigma-Aldrich and used as received.

Reversible covalent polymer network structures are created with a wide range of properties going from rubbery materials with glass transitions of -65 to -55 °C to more glassy materials with glass transition temperatures of 56 and 64 °C. The equilibrium gel point temperatures range from 49 °C to 83 °C.

The reversible polymer network systems are applied as coatings on pure aluminium substrates by means of spin coating from a 10 w% chloroform solution. The solvent is evaporated and the coatings are allowed to cure at temperatures slightly above room temperature (50 – 60 °C). Coatings with a thickness of around 1 µm were created. Changing the concentration of the coating formulation yields coatings of different thicknesses.

3. RESULTS AND DISCUSSION

3.1. Local Thermal Analysis

The thermomechanical behavior of the dynamic covalently cross-linked polymer network systems is analyzed by means of Local Thermal Analysis (LTA). This technique combines the conventional Atomic Force Microscopy (AFM) with the option to heat up the probe to a certain temperature while maintaining contact with the studied material, providing thermomechanical information about the material.

Increasing the cross-link density of the network by altering the building blocks for the formation of the network structure, increases the toughness of the network and the glass transition temperature. Consequently the density or concentration of the Diels-Alder functional groups is also increased, influencing the equilibrium of the forward and reverse Diels-Alder reactions. The lower the cross-link density, the lower the equilibrium conversion becomes for the Diels-Alder reaction and the softer and more rubber-like the material becomes. In contrast, the higher the cross-link density, the harder and more glass-like the material becomes and the higher the equilibrium conversion becomes. Higher temperatures will be needed for the more cross-linked networks to break down a sufficient amount of bonds in the network structure to obtain efficient healing of sustained damage. It has been demonstrated that when the temperature is increased sufficiently and enough bonds are broken, a reversible gel transition is observed due to the reversible polymerization reaction. Above the gel point temperature the material behaves like a liquid.

3.2. Self-healing behavior

In order to create defects in a controlled and reproducible manner, the nano-lithograpy option on an Asylum Research MFP-3D^{TM} Atomic Force Microscope (AFM) was used. Exerting a well-defined force on a rigid AFM probe allows the creation of defects such as scratches with very controllable and reproducible depth and width. In the case of nano-indentation elastic recovery of the material may interfere with the studied healing mechanism. Scratches and indentations can be made with varying width and depth to evaluate the effect of these parameters on the healing mechanism and its efficiency. The materials are heated in-situ in the AFM by means of a polymer heating stage. Damage was healed at different temperatures for different times to reveal the healing mechanism.

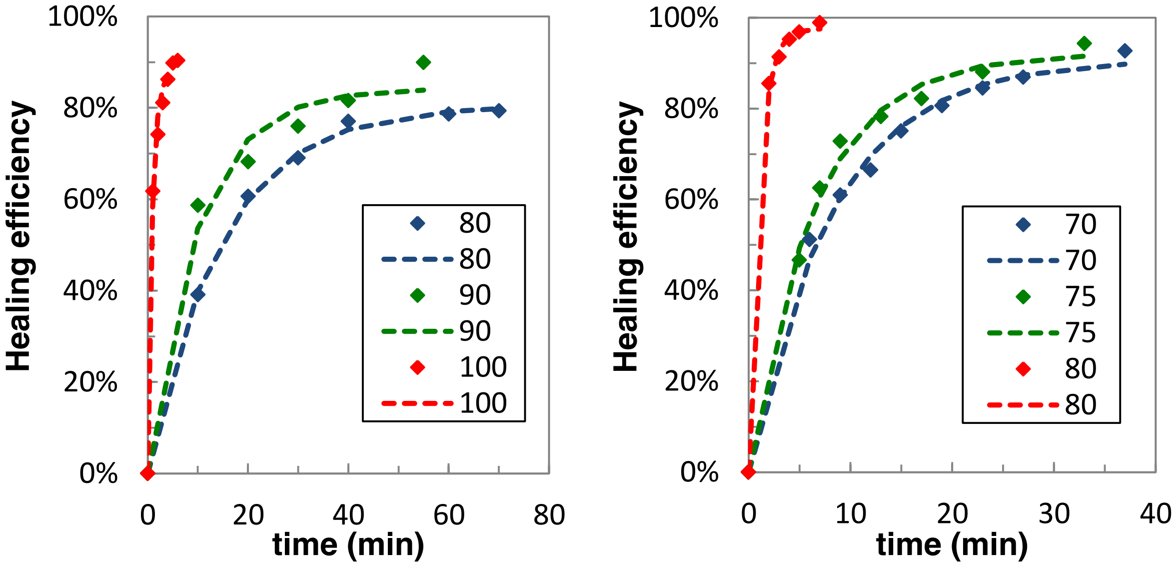

Figure 1: Local healing of defects in DPBM-FGE-J400 (left) and DPBM-FGE-J2000 (right) reversible covalent polymer network coating on pure a aluminum substrate.

As the temperature is increased the equilibrium shifts towards the breaking of dynamic bonds and the reaction conversion decreases. The mobility in the material is increased and the healing action is facilitated. For both the rubbery and glassy material systems the self-healing can only take place at temperature well above the glass transition temperature. The higher the healing temperature, the more mobility is created inside the material, hence the shorter the healing times and the more efficient the healing will be (Figure 1). Yet it was proven that healing of damage can be obtained at temperatures little below the gel point temperature, though very slowly and only to a certain extent. The size and geometry of the defect dictate the degree of mobility that is needed to efficiently heal the defect. To cover a microscopic defect the flexibility of the chains can be sufficient below the gel transition temperature. In this case the network structure can be retained and the material remains solid-like. For macroscopic defects a higher degree of mobility is needed and the network will need to be broken down to a higher extent to cover the bigger defects. For recycling purposes it may be even more interesting to go to even higher temperatures and lower conversions to obtain a liquid material, which then can be given a new shape.

4. CONCLUSIONS

Healing of sustained damage was achieved in different reversible polymer networks systems based on dynamic covalent bonds from the reversible Diels-Alder reaction between a furan and a maleimide functional group. Local thermal analysis was used to study the thermomechanical properties of the self-healing materials. It was demonstrated that not only the mechanical properties, but also the temperature window in which the healing of sustained damage can be established can be tailored by changing the building blocks in the reversible polymer networks structure.
Other reversible chemistries will be considered to optimize the healing circumstances and building blocks will be changed to alter the mechanical and thermal properties of the self-healing materials with regard to the intended applications.

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