Characterization of Healable Polymers

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ABSTRACT

Materials with an internal mechanism for damage repair would be valuable in isolated environments where access is difficult or impossible. Current work is focused on characterizing neat polymers with reformable cross-linking bonds. These bonds are thermally reversible, the result of a Diels-Alder cycloaddition between furan and maleimide monomers. Candidate polymers are examined using modulated differential scanning calorimetry (DSC) to confirm the presence of reversible bonding. One polymer, 2MEP3FT, was expected to have these bonds, but none were observed. A second polymer, 2MEP4FS, with a modified furan monomer does exhibit reversible bonding. Further DSC testing and dynamic mechanical thermal analyses (DMA) are conducted to determine material properties such as glass transition temperature, storage modulus and quality of the polymerization. Healing efficiency is established using the double cleavage drilled compression (DCDC) fracture test. A column of material with a central hole is subjected to axial compression, driving cracks up and down the sample. After unloading, the cracks are healed, and the sample is retested. Comparing the results gives a quantitative evaluation of healing.

Keywords: polymer, heal, fracture, crack, DSC, DMA, DCDC

1. INTRODUCTION

A traditional highly cross-linked polymer is irreparably damaged when covalent bonds are broken. This damage, whether due to mechanical or thermal processes, can accumulate to the point of failure. If the material is easily accessible, a technician can manually repair the material and extend its service life. There are cases where the material is not easily accessible, however, including many aerospace and biological applications. Here, a material with a built-in mechanism for repairing damage is valuable. Even for more common applications, where manual repair is possible, a healable material could save significant time, effort and cost.

There are several approaches to constructing a healable material. One approach is to embed microcapsules filled with a liquid healing agent.1 When a microcapsule is broken by a propagating crack, the agent flows into the crack and hardens. This is a type of irreversible healing, where the repair results from a process that cannot be reactivated. Another approach is to design a material with a reversible healing mechanism that can be activated multiple times. One such material is a polymer with thermally reversible cross-linking bonds resulting from a Diels-Alder (DA) cycloaddition.2,3 After fracture, these bonds can be reestablished, restoring material toughness.

In the present work, we study two Diels-Alder-based polymers, 2MEP4FS and 2MEP3FT. Thermal and mechanical properties are studied using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Fracture and healing behaviors are studied using the double cleavage drilled compression (DCDC) geometry.

1.1 2MEP4FS

Polymer 2MEP4FS is a slight modification of the polymer 2MEP4F presented in [3]. Both versions were developed by Wudl et al. The polymer is highly cross-linked, formed from a Diels-Alder cycloaddition (Scheme 1) between a multi-dienophile (tetrafuran, 4FS) and a multi-diene (bismaleimide, 2MEP). The synthesis procedure of 4FS was refined by Dr. Haim Weizman (UCSD Chemistry Department), yielding a higher purity material than used by Plaisted and Nemat-Nasser in [4].
Dynamic mechanical analysis shows the polymer has a storage modulus in excess of 3 GPa at 40°C and a glass transition temperature of ~108°C as measured by the peak of tan δ. Fracture tests indicate that cracks can be completely repaired under ideal conditions. Over the course of multiple healings, the stresses required for re-fracturing the material were nearly the same or even slightly higher than for the virgin material (Figure 1).

Figure 1. Comparing the stresses required for crack growth over multiple healings (stresses normalized by the virgin fracture stress). The plot is a representation of a data set presented in [4]

1.2 2MEP3FT

An alternate furan monomer, 3FT (Scheme 2), was developed by Dr. Weizman as a replacement for 4FS. The new monomer consists of three furan groups bonded to a central triazine ring. This approach is easier to synthesize than 4FS and predicted to have a longer shelf-life and higher stiffness. It’s polymerized with 2MEP to create 2MEP3FT polymer.
2. METHODOLOGY

The polymers were created from stoichiometric ratios of monomers 2MEP and 4FS or 3FT. The DSC samples were prepared by hand mixing the monomers at room temperature. The DMA sample was prepared by melting the 2MEP, mixing in the 4FS and pouring the polymerizing solution into a mold. The process is elaborated in [4]. Due to laboratory mixing conditions, later calculation indicates a ~10% error in the DMA sample’s stoichiometric ratio. After DMA testing, the sample was repurposed for DCDC testing. Polymer 2MEP3FT was not DMA or DCDC tested.

2.1 Differential scanning calorimetry (DSC)

Thermal experiments were conducted using a TA Instruments 2920 Differential Scanning Calorimeter with the liquid nitrogen cooling accessory. Polymer samples were tested in hermetically sealed aluminum pans over a temperature range of 25°C to 140°C. The temperature was ramped at 3°C/min, with an additional ±1°C/min modulation, allowing the reversible and non-reversible parts of the heat flow to be separated.

After testing, the samples were generally allowed to air cool slowly. But if the next test was intended to identify the presence of DA bonding, the sample would be removed from the DSC chamber while at 140°C and quickly dropped into a bath of liquid nitrogen. Quenching the sample in this manner prevented DA bonds from reestablishing, allowing them to be observed during the subsequent DSC scan.

2.2 Dynamic mechanical analysis (DMA)

Thermal and mechanical properties were measured using a TA Instruments 2980 Dynamic Mechanical Analyzer. Tests were conducted using single cantilever bending at 1 Hz over a temperature range of 25°C to 135°C ramped up at 3°C/min.

2.3 Double cleavage drilled compression (DCDC) testing

Crack healing was quantified using the double cleavage drilled compression fracture test. The test subjects a column of material with rectangular cross section and central, through-thickness hole to unidirectional compression (Figure 2). Cracks are driven axially outward from the hole until they are arrested by the frictionally-fixed end conditions. After testing, the sample is quickly healed to avoid contamination or degradation of the crack surfaces.

Figure 2. The double cleavage drilled compression (DCDC) fracture test.
It has been determined that DCDC crack healing is the most effective when conducted using a two step process. The sample is first placed in a vise under light pressure normal to the crack plane. This ensures the crack faces come together and physically touch. The vise has been preheated to 85°C and is returned with the sample to an 85°C oven. After 30 minutes, the pressure on the sample is released, and the temperature is raised to 95°C for the second healing step. After another 30 minutes, the oven is turned off and allowed to slowly cool to room temperature over several hours.

3. RESULTS

3.1 Thermal
Initial DSC tests of 2MEP3FT were promising, showing a significant increase in glass transition temperature over 2MEP4FS. But subsequent DSC testing showed no thermal reversibility of the DA bonds, indicating the material will not heal cracks. No further study of 2MEP3FT was conducted.

DSC tests of polymer 2MEP4FS yielded results similar to those previously observed in [4]. DMA testing also gave similar results to [4], although the glass transition temperature (the peak of tan δ) was a few degrees higher.

3.2 Mechanical
The storage modulus of 2MEP4FS obtained by DMA was slightly higher than [4]. Crack healing was not complete, however. The healing times, temperatures and pressure were varied, but healed fracture stresses never returned to virgin levels.

4. CONCLUSIONS AND FUTURE DIRECTION
The reason for the failure of 2MEP3FT to exhibit the DA reaction associated with healing is unclear. One possibility is the 3FT molecule is too stiff; flexibility may be required for healing to occur. Polymer 2MEP4FS exhibited the DA reaction as expected, but only demonstrated partial healing during fracture testing. The cracks visually disappeared, but the stresses required to propagate new cracks never returned to the levels observed in the virgin sample. It is suspected that sample geometry may be limiting healing. Using the DMA sample for fracture testing meant it was significantly smaller and thinner than the samples in [4]. This leads to more crack surface area near the sample’s free surfaces where crack healing is more challenging and likely incomplete. The 2MEP4FS should be tested using the original geometry in [4] for appropriate comparison.

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