Highly Stretchable, Room Temperature Self-Healing Polymer via Crosslinking and Intermolecular Network

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Introduction

In the United States, the cost of damage due to degradation of various infrastructure within all industries combined is approximately $276 billion annually, with $17.6 billion being attributed to production and manufacturing.\(^1\)

With that being said, the presence of a self-healing material can save millions of dollars in repair costs of various materials. Unlike other polymers found in daily life, self-healing materials obtain the ability to intrinsically or extrinsically heal their structures caused by external damage. Microscopic damage is detrimental to material functionality, and the use of self-healing materials can quickly diminish the issues found with repairing heavy materials. Self-healing materials are categorized into two groups: (1) intrinsic healing materials (2) extrinsic healing materials. Extrinsic materials work by forming catalyst containing nano-capsules filled with healing agents, that when ruptured, release a mechanism of repair to fill microscopic damage; while intrinsic materials work in various ways including, but not limited to, reforming covalent bonds, supramolecular networks, and metallic coordination complexes.\(^2\) Intrinsic healing materials can induce a mechanism of repair from external energy (heat/light) or through reversible “sticky” bonds. Self-healing materials have gained significant attention for their various applications in:

- Electronics and Robotics
- Manufacturing
- Aerospace
- Medicine

Limitations of Current Materials

Several limitations are present with each synthesis method that limit the material use and applications. Many of these methods only allow the self-healing material to work under very specific conditions.

### Method

<table>
<thead>
<tr>
<th>Catalyst Containing Microcapsules</th>
<th>Limited/Temporary healing ability</th>
<th>Cannot repair repeated damage</th>
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<tbody>
<tr>
<td>Healing from Energy</td>
<td>External energy source is needed to initiate healing (Light/Heat)</td>
<td>Nonreversible</td>
</tr>
<tr>
<td>Supramolecular Interactions</td>
<td>Poor healing ability at room temperature</td>
<td>Microphase separation of monomer subunits</td>
</tr>
</tbody>
</table>

![Fig 1. Cost of damage in production and manufacturing annually in the United States.](image)

Supramolecular Network and Material

![Fig 2. (a) TDI-PTMEG-IP Polymer Visualization of Supramolecular network formed by added substituents (TDI x IP). (b) Representation of reversible damage and healing mechanism](image)

A hydrogen bond is strong intermolecular dipole-dipole force formed between a hydrogen and an electronegative atom.\(^3\) High hydrogen bonding creates rigidity and viscosity, while low hydrogen bonding forms a highly stretchable material. By adding specific hydrogen-bonding subunits, the polymer is able to have both high tensile strength and self-healing ability with the right ratio. The self-healing polymer utilizes various hydrogen bonding substituents and a poly (oxy-1,4-butenedi) (PTMEG) backbone to form a high tensile strength material with fast self-healing ability at room temperature. Unlike many other materials, the given polymer has healing under various conditions, allowing for a variety in applications. Figure 2 represents the hydrogen bonding network formed by Toxylene-2, 4-diisocyanate (TDI) and isophorone diisocyanate (IP) and their reversible b-bonds.

### Synthesis

A one-pot method was used to synthesize the polymer to decrease contamination.

1. Addition of chemicals
2. Constant stirring
3. Viscous liquid formed

![Fig 3. FTIR result of self-healing material (TDI-PTMEG-IP)](image)

![Fig 4. Development of thin polymer coupon for tensile strength testing starting from wet polymer](image)

Experimental Results

Conclusions

Based on literature, a high tensile strength and efficient self-healing materials is rare to find. Thus, the proposed intrinsically healing material aims to maintain high tensile strength and efficient self-healing ability in various environments. The addition of various b-bonding substituents and the use of a Schlenk line setup allows for effective synthesis of the polymer under various gas environments, increasing quality and quantity of the material.

Future Outlook

The future outlook of this project includes the utilization of varying ratios of b-bonding substituents in conjunction with a PTMEG backbone. The project also seeks to compare a PDMS backbone with a PTMEG backbone to test the varying tensile strength and self-healing ability. The polymers will be characterized by various techniques such as DSC, tensile testing, and healing in various environments (high salt, under water, extreme hot or cold)

References


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