



Self-healing elastomers

Comparison of methods

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<p>Abstract: Self-healing is used in biological systems found in nature. Man-made materials however do not usually have the capability of self-healing. Self-healing can be found in a variety of materials with polymers being one of the most researched ones. Elastic polymers, often referred to as elastomers, functions as elastic rubber in normal conditions and as a polymer near the glass transition temperature. This unique combination is beneficial and makes the material possible to use for a wide variety of products. This work consists of finding a self-healing elastomer that has good properties and can be fabricated in Arcada by a student. Four self-healing methods were chosen for review and are represented in this study. Four self-healing experiments representing the reviewed self-healing method were chosen and compared to one another in this study. The four self-healing methods selected were: heat stimulated self-healing, light stimulated self-healing, mechanochemical self-healing, and encapsulation. For the heat stimulated method an experiment using a Diels-Alder reaction was chosen. The light stimulated method was demonstrated by an experiment using dynamic covalent reshuffling of trithiocarbonates. As an experimental method for the mechanochemical self-healing a poly(urea-urethane) elastomer was chosen. The encapsulation's experimental method consisted of a microvascular network imbedded in the elastomer. All four methods are presented and reviewed in the following text. The methods were compared by cost, self-healing ability, user convenience and ease of fabrication. The mechanochemical method was evaluated to be the most favorable method to replicate in Arcada. The mechanochemical method had a relatively fast self-healing time, was moderately inexpensive and was able to heal itself in room temperature without an assisted stimulus.</p>	
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<p>Sammandrag:</p> <p>Självläkande material finns runt omkring oss i naturen. Vanliga material som människan skapat har dock inte naturligt självläkande egenskaper. Polymers är ett av de material som skulle ha stor nytta av självläkande egenskaper, på grund av materialets många användningsområden. Elastiska polymers, som mera vanligt benämns som elastomerer är polymers som beter sig som gummi i normala förhållanden och som plast vid temperaturer nära smältpunkten. Denna unika kombination gör elastomerer till material som kan användas till många olika saker. I detta slutarbete strävade jag efter att hitta den självläkande elastomer med bästa möjliga egenskaper, som senare kan tillverkas i Arcada. Eftersom området är brett, valdes fyra metoder med de bästa möjliga egenskaperna som presenteras i arbetet. De valda metoderna är värmeförorsakad självläkning, självläkning förorsakad av UV-strålning, mekanokemisk självläkning samt inkapsling. Fyra experiment valdes för att representera de fyra metoderna. Den värmeförorsakade självläkningen består av Diels Alder-bindningar. Självläkningen genom UV-strålning består av dynamisk kovalent omformning av tritioarbonater. Den mekanokemiska metoden baserar sig på ett material gjort av polyuretan och inkapslingen baserar sig på ett mikrovaskulärt nätverk som är inbyggt i materialet. Alla fyra experimentella metoder presenterades detaljerat i arbetet. Metoderna jämfördes sedan på basen av kostnad, självläkningsförmåga, användbarhet och på basen av hur lätt användaren kan läka materialet. Efter att samtliga metoder jämförts på basen av kriterierna som nämnts ovan, visade det sig att den mekanokemiska metoden hade de bästa egenskaperna. Med hjälp av den mekanokemiska metoden kan materialet utan stimulans och inom relativt kort tid läka sig själv i rumstemperatur.</p>	
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<p>Tiivistelmä:</p> <p>Itseparanevaa materiaalia löytyy kaikkialla ympärillämme luonnossa. Ihmisten luomat materiaalit eivät kuitenkaan itsessään sisällä itseparanevia ominaisuuksia. Itseparanevat ominaisuudet voisivat olla hyödyksi monessa eri materiaaleissa. Polymeeri on yksi materiaali, joka hyötyisi suuresti itseparanevasta ominaisuudesta. Elastiset polymeerit, joita yleisemmin kutsutaan elastomeereiksi, ovat polymeerejä, jotka normaaleissa olosuhteissa käyttäytyvät kuin kumi ja kuumassa lämpötilassa kuin muovi. Tämä erikoinen yhdistelmä tekee elastomeereistä ainutlaatuisen materiaalin, jolle löytyy monenlaisia käyttötarkoituksia. Työn tarkoituksena on löytää itseparaneva elastomeeri, jolla on parhaat mahdolliset ominaisuudet. Koska alue on laaja, olen valinnut neljä menetelmää, joilla on parhaat mahdolliset ominaisuudet. Valitut menetelmät ovat lämpöä stimuloiva itseparaneminen, itseparaneminen UV-säteilyn avulla, mekanokemikaallinen itseparaneminen sekä kapselointi. Neljä kokeellista menetelmää valittiin edustamaan itseparanevia menetelmiä. Itseparaneminen lämpöstimuloinnilla koostuu Diels-Alder sidoksista. Itseparannus UV-säteilyn avulla koostuu tritiokarbonaattien dynaamisesta kovalentista uudelleenjärjestämisestä. Mekanokemiallinen itseparaneminen muodostuu polyuretaanista ja kapselointimenetelmä koostuu mikrovaskulaarisesta verkostosta, joka on sisällytetty elastomeeriin. Kaikki neljä kokeellista menetelmää esiteltiin yksityiskohtaisesti työssä. Menetelmiä vertailtiin kustannusten, itseparanemiskyvyn, käytettävyyden ja sen perusteella kuinka helppo itseparanemisprosessi on käyttäjälle. Kun kaikki neljä menetelmää vertailtiin edellä mainittujen kriteerien perusteella, mekaaninen kemiallinen menetelmä oli selvä voittaja. Mekanokemiallisen menetelmän avulla materiaalin itseparaneminen tapahtuu nopeasti huoneenlämmössä ilman stimulointia. Lisäksi menetelmä on kohtuullisen edullinen.</p>	
Avainsanat:	Itseparantava, Elastomeeri, Diels-Alder, Polyuretaani, mekanokemiallinen.
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Table of Contents

1	Introduction.....	9
2	Overview of self-healing methods	11
3	Heat induced self-healing.....	14
3.1	Heat stimulated self-healing elastomer example	15
3.1.1	<i>Synthesis</i>	16
3.1.2	<i>Self-healing</i>	17
4	Light induced self-healing.....	19
4.1	Light stimulated self-healing elastomer	22
4.1.1	<i>Synthesis</i>	22
4.1.2	<i>Self-healing processes</i>	24
5	Mechanochemical self-healing	27
5.1	Mechanochemical autonomous self-healing elastomer	28
5.1.1	<i>Synthesis</i>	30
5.1.2	<i>Self-healing</i>	31
6	Encapsulation	33
6.1	Self-healing microvascular network.....	37
6.1.1	<i>Synthesis</i>	37
6.1.2	<i>Self-healing procedure</i>	40
7	Comparison of methods.....	43
7.1.1	<i>Cost</i>	43
7.1.2	<i>Self-healing ability</i>	44
7.1.3	<i>User convenience</i>	45
7.1.4	<i>Ease of fabrication</i>	46
7.1.5	<i>Summary of the comparison of methods</i>	47
7.2	<i>Discussion</i>	47
8	Conclusion	49
	Sammandrag	51
	References	58

Figures

Figure 1, Classification scheme of self-healing systems. (Soft Robotics toolkit, 2017).	12
Figure 2, The four self-healing systems represented in the thesis. 1. heat-induced self-healing (Liang, et al., 2017). 2. mechanochemical self-healing (Ying, et al., 2013). 3. light induced self-healing (Deretsky, 2011). 4. Encapsulation (Yang, 2016).	13
Figure 3, The four steps in the temperature profile of a heat stimulated self-healing process (Terry, et al., 2017).	14
Figure 4, the reaction of the material in the heat stimulated self-healing process (Terry, et al., 2017).	18
Figure 5, microscopic images of the material during the heat stimulated self-healing process (Terry, et al., 2017).	19
Figure 6, Reversible bonds formed by cycloaddition. The red area indicates where the new bonds are formed. (Habault, et al., 2013).	20
Figure 7, Self-healing bonds formed by reshuffling covalent bonds: a) disulfide. b) trithiocarbonate. c) allyl sulfide. (Habault, et al., 2013).	21
Figure 8, Reshuffling reaction between (1) TTC dicarboxylic acid and (2) TTC diester (Amamoto, et al., 2011).	24
Figure 9, The first self-healing method a) the material before and after the first self-healing cycle. b) the material before and after the second self-healing cycle. and c) the self healed material after the swelling test with anisole (Amamoto, et al., 2011).	25
Figure 10, a) the second self-healing method before and after the reaction, and b) the third self-healing method before and after the reaction (Amamoto, et al., 2011).	26
Figure 11, a) exchangeable reaction of aromatic disulfide bonds, b) diamine crosslinker used in reference material, c) process of how synthetic polymers 9a and reference material 9b were created (Rekondo, et al., 2014).	29
Figure 12, a) pristine sample of the self-healing polymer, b) and c) the cut sample of the self-healing polymer, d) after 2 h of contact, e) and f) the sample stretched after 2 h of contact (Rekondo, et al., 2014).	32

Figure 13, Self-healing illustration of common encapsulation methods, a) hollow fibers inside a polymer, b) Microspheres/microcapsules, c) microvascular network, and d) superparamagnetic nanoparticles (Yang, 2016).	33
Figure 14, Microvascular networks: a) blood vessels inside the human body, b) a 3D image of the microvascular network that drawn by Toohey et al, and c) the microvascular network developed by Toohey et al (Hansen, et al., 2009).	36
Figure 15, Scratch test panel cutting the coating with a close up in the upper left corner of how the specimen is placed in the test panel scratcher (Hansen, et al., 2009).	41
Figure 16, Set up of the four-point bending test with an acoustic emission sensor (Hansen, et al., 2009).	41
Figure 17, Average self-healing efficiency for 30 consecutive self-healing cycles. red pillars represent the material created by toohey et al and the blue pillar represents a microcapsule based network (Hansen, et al., 2009).	42

Tables

Table 1, Substances, equipment, amounts and costs of the substances (retrieved from Sigma-Aldrich) needed for the heat stimulated self-healing synthesis.	16
Table 2, Substances, equipment, costs and amounts of the substances (retrieved from Sigma-Aldrich) needed to make the photostimulated self-healing material.	22
Table 3 Substances, equipment, costs and amount of the substances (retrieved from Sigma-Aldrich) needed for the synthesis of a mechanochemical polymer.	30
Table 4, Substances and equipment, costs and amount of the substances to create the microvascular network.	39
Table 5, Comparison of substance costs for all four-experimental synthesis and the self/healing stimulus needed for all four methods.	43
Table 6, Self-healing ability and self-healing time of the four different experimental methods.	44
Table 7, User convenience, how easily the self-healing process can be performed with 1 being the easiest and 4 being most difficult.	45
Table 8, Time needed to create each synthesis and equipment needed for each synthesis that cannot be found in Arcada.	46

Table 9, Summary of comparison of methods, the methods are compared by a scale from 1 to 4. With 1 being most suitable and 4 being least suitable. 47

1 INTRODUCTION

Our bodies have the incredible capability of self-healing, e.g. a cut in our skin can heal after only a couple of minutes (van der Zwaag & Brinkman, 2015). This self-healing feature is something that is being replicated in many forms of synthetic industrial materials. Everything from self-healing concrete to self-healing elastic materials are under development. One of the areas that has received the most attention due to its wide variety of applications is self-healing polymers (van der Zwaag & Brinkman, 2015).

Self-healing although natural for the human body cannot normally be found in everyday materials. Metals, concrete, ceramics and polymers are prime examples of materials that can be more useful with a self-healing ability. Metals suffer from degradation under natural conditions even though they are not under stress. These conditions form micro cracks in metals and a self-healing ability could prevent or at least decrease the creation of micro cracks in metals. A problem in developing self-healing metals is that the metal atoms are so small. Damaged concrete starts to let water through cracks in the material structure. A self-healing ability in concrete would therefore be good in order to prevent water from flowing through the cracks in the damaged material. Ceramic composites with metal reinforced structures that can heal cracks have been developed for ceramics. Ceramics is a brittle material and cracks form easily, therefore a self-healing ability would lengthen the life-time of ceramics used today. (D. Hager, et al., 2010)

The main reasons why I have chosen self-healing as the subject of my thesis is that the biomimetic, solution often has the highest efficacy, efficiency and versatility. The human body is an incredibly well evolved machine and to replicate its self-healing ability in an easy and effective way could be groundbreaking when it comes to material science. The range of applications of self-healing materials are wide: from concrete and metals to elastic rubberlike plastics.

Elastic plastics called elastomers have been researched for different self-healing applications. Elastomers can be used for a variety of products from the automotive industries to medicine. Self-healing elastomers can for example be used as tires or wind shield wipers in the automotive industry. Elastomers can be used in medicine for example as artificial

limbs and muscles. As an alternative to people who have been in accidents where they have lost a limb or to help the lives of people with birth deficiencies (Terry, et al., 2017).

The reason why I chose elastomers is that it is a material that has interesting properties and can be used in such a wide variety of products.

Aims of the thesis

- Make a literature review of the basic self-healing methods
- Assess four experiments based on common self-healing methods
- Find out which experimental method is superior by the following qualities:
 - Cost
 - Self-healing ability
 - Self-healing time
 - User convenience
 - Ease of fabrication
- Create a platform for a future student who wants to make an experiment on self-healing elastomers.

Four self-healing methods were chosen for this thesis. Four experiments based on these methods were then chosen, analyzed and compared by the qualities represented in the aims of the thesis (cost, self-healing ability, self-healing time, user convenience and ease of fabrication). The results of the experiments compared were then presented and discussed.

The four self-healing methods chosen for this study are presented in four chapters along with the experimental methods chosen for the thesis. The experimental methods are then compared in a chapter and the conclusion is represented after the comparison of the four methods. A Swedish summary of the study is also presented in the very end of the thesis.

2 OVERVIEW OF SELF-HEALING METHODS

A set of self-healing polymers caught my eyes: self-healing elastomers. Elastomers are elastic polymers that are highly flexible. Polyisobutylene, polybutadiene and polyurethanes are some examples of elastic polymers. To make the internal structure stronger elastomers can be cross linked, which forms covalent links between the two different polymer chains. The cross-linked polymer is harder to pull out of position compared to a normal polymer which makes it bounce easier back to its original shape. Elastic polymers can be thermoplastics even though they are cross linked. Thermoplastic elastomers can be melted and shaped into a desired shape while heated. Rubbers are thermosets, which cannot be shaped while heated. The thermoplastic elastomer has rubber like features in normal conditions but act as a plastic when melted (Massey, 2003).

The self-healing methods chosen for this study use both autonomous and non-autonomous self-healing materials. Autonomous self-healing materials are materials that do not need a stimulus to conduct the self-healing process, such as encapsulation and mechanochemical self-healing. Encapsulation is a method where a capsule with resin lies under the surface of the material and after the capsule has ruptured the resin fills up the hole and solidifies. Mechanochemical self-healing means that the self-healing mechanism is in the material structure and the material needs no stimulus to be triggered. The material is made of weak bonds that break under stress but reconnect independently when the material is no longer under stress without a stimulus. The mechanochemical self-healing materials are made up of weak hydrogen or weak metal-amine bonds. Non-autonomous self-healing methods consist of methods that need a stimulus to trigger the self-healing mechanisms in the material. The stimulus might be light, mechanical, chemical or heat. Non-autonomous systems that use heat as a stimulus, can be made up of covalent bonds, hydrogen bonds, ionomers and coordination bonds as depicted in Figure 1 below (Terry, et al., 2017).

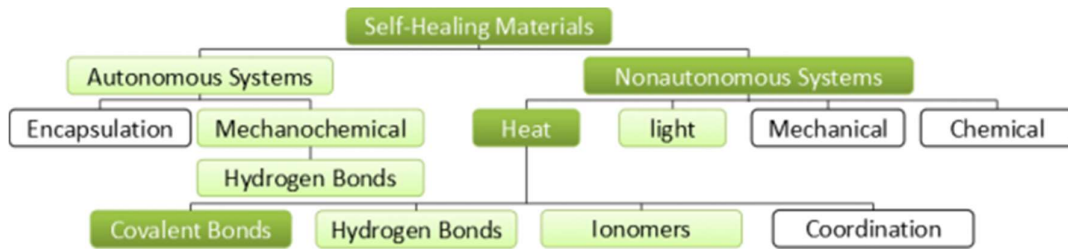


Figure 1, Classification scheme of self-healing systems. (Soft Robotics toolkit, 2017).

The thermo-reversible bonds that the non-autonomous heat stimulated self-healing materials are made up of are broken when the material is heated. The plastic like material will then heal itself by filling gaps created by the damage on the material (Terry, et al., 2017).

Four self-healing experiments typifying the four most pertinent, self-healing elastomer systems were reviewed in this work. The following self-healing systems were chosen for the study: heat induced self-healing, light induced self-healing, mechanochemical self-healing and encapsulation. Mechanochemical self-healing and encapsulation were chosen since they do not need a stimulus to be triggered and can therefore be healed in a variety of conditions. Whereas the non-autonomous heat- and light- triggered self-healing systems were chosen since they have more research done on them; good self-healing qualities could also be found in heat- and light induced self-healing experiments. The four methods chosen for this study can be viewed in Figure 2 below.

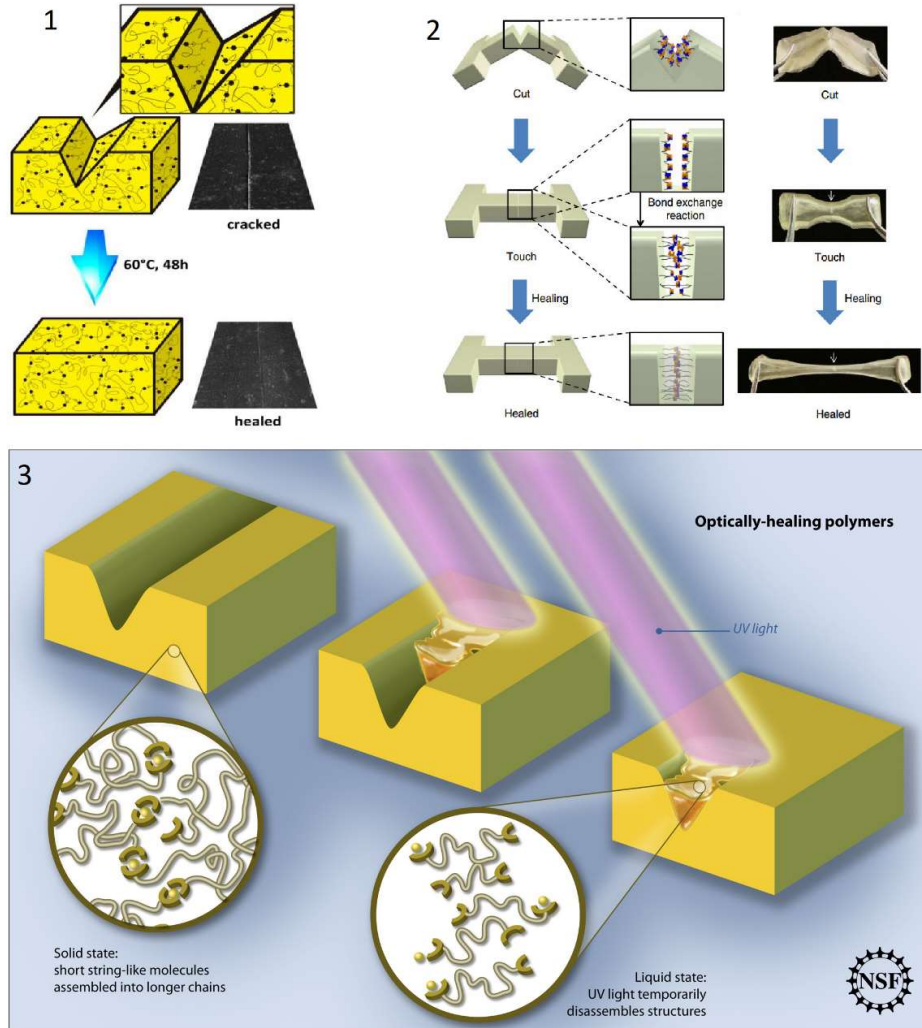


Figure 2. The four self-healing systems represented in the thesis. 1. heat-induced self-healing (Liang, et al., 2017). 2. mechanochemical self-healing (Ying, et al., 2013). 3. light induced self-healing (Deretsky, 2011). 4. Encapsulation (Yang, 2016).

3 HEAT INDUCED SELF-HEALING

Structures that are irreversible were first used in self-healing materials, these systems, however, had the problem of only being able to have one self-healing cycle. This is not an issue with reversible self-healing structures which are capable of many self-healing cycles. The downside, however, is that the heat induced self-healing is not an autonomous system (Syrett, et al., 2010). Heat induced self-healing is based on the idea of reversible bonds that break when introduced to heat. When these materials are heated the material becomes gel like and the cracks on the material vanishes by the mobility formed inside the bond broken structure of the material. The material is cooled back to room temperature after the healing is completed and the broken reversible bonds are formed again to give the material a solid structure in normal conditions. A typical self-healing cycle can be viewed closer in Figure 3 below. (Terryn, et al., 2017).

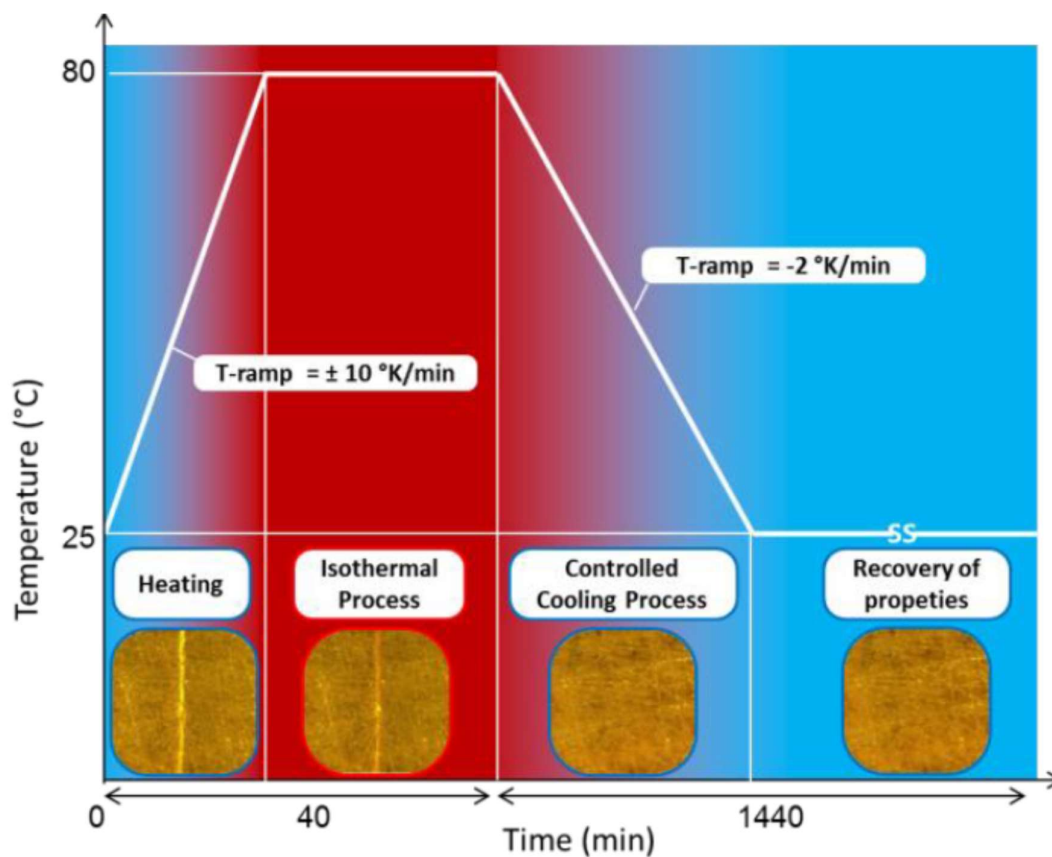


Figure 3, The four steps in the temperature profile of a heat stimulated self-healing process (Terryn, et al., 2017).

Heat induced self-healing can be achieved with reversible chemical cross-link bonds. Dynamic covalent bonds, radical based systems or super molecular interactions are some examples of what a self-healing thermo-reversible polymer can be made up of.

Dynamic covalent bonds can further contain a Diels-Alder reaction. Supramolecular interactions can be made by ionic interactions, halogen or hydrogen bonds, metal-ligand interactions, π - π interactions or host-guest interactions (Zechel, et al., 2017). Covalent bonds can be used for a larger variety of products than hydrogen bonds: hydrogen bonds break easily which means that their mechanical strength is weak compared to covalent bonds. The Diels-Alder method has a high glass transition temperature which indicates that a lot of energy is needed for the healing process, but at the same time a self-healing material containing a Diels-Alder reaction can be used in more extreme conditions (Yang, 2016). The Diels-Alder reaction is the most commonly used reaction when it comes to thermo-reversible self-healing based on covalent bonds (Terry, et al., 2017). The Diels-Alder reaction is one of the most common reactions that research regarding heat induced self-healing has been conducted on (Syrett, et al., 2010). For the three previous reasons a self-healing material based on the Diels-Alder reaction has been chosen as a representative example for the heat stimulated self-healing method in this study.

3.1 Heat stimulated self-healing elastomer example

A heat stimulated self-healing elastomer composed of a reversible Diels-Alder reaction was created in Vrije Universiteit in Brussels by Terry, S., Brancart, J., Lefeber, D., Van Assche, G., & Vanderborght, B. Soft robotic actuators and an artificial muscle were created from the material developed and the self-healing ability of the material was tested specifically for these two applications. The elastomeric material was made of thermo-reversible covalent networks based on the Diels-Alder reaction. The Diels-Alder reaction is based on a diene and a dienophile that are synthesized together forming the thermo-reversible chemical bond that the self-healing process is based on. In this case the diene is Furan and the dienophile is a Maleimide. The material created by Terry et al. was chosen as the heat stimulated method since the self-healing test results were better than expected, the material could potentially be made in Arcada and the Diels-Alder bonds

used have better mechanical properties than the non-covalent alternatives (Terry, et al., 2017).

3.1.1 Synthesis

The substances, equipment needed and the cost of the substances for this synthesis can be viewed in Table 1 below. Three different poly-(propylene glycol) bis-(2-aminopropyl ether), also referred to as Jeffamine, with different spacer lengths were used in the synthesis and are commercially called J400, J2000 and J4000. All costs in Table 1 below were retrieved from Sigma-Aldrich. The substance quantities were selected as the same amounts as the ones used in the experimental synthesis made by Terry et. al. The costs are presented as the amount found on Sigma-Aldrich closest to the amount needed for the synthesis.

Table 1, Substances, equipment, amounts and costs of the substances (retrieved from Sigma-Aldrich) needed for the heat stimulated self-healing synthesis.

Substances needed for synthesis	Amount used in synthesis	Cost	Equipment needed for synthesis
Furfuryl glycidyl ether (FGE 96%)	3.348 g	277 €	Heater
1, 1'-(methylenedi(1, 4-phenylene) bismaleimide (DPBM 95%)	2.833 g	46.9 €	Magnetic stirrer
J400	< 10 ml	126 €	Mold
J2000	5.890 g	72 €	Vacuum set up
J4000	8.762 g	72.5 €	Oven
Chloroform (min 99.9%)	49 ml	101 €	Oil bath

Jeffamine is referred to as J_x where x is M_n (number average molecular weight) of the three substances J400, J2000 and J4000. The synthesis consists of three steps. The first step is mixing FGE with a stoichiometric amount of J_x . In this step the mixture is heated and kept at 60 °C for at least 7 days while the mixture is stirred constantly. The first step is then finished by raising the temperature to 90 °C and keeping it at 90 °C for 2 days. The compound created is called (FGE- J_x). The second step is creating the Diels-Alder

polymers where (FGE- J_x) in a stoichiometric relationship is mixed with the DPBM. The mixed substance is then dissolved in chloroform at 25 °C for 24 hours while being constantly mixed. The third step is the formation of the shape of the material which is a sheet in this case and the dissolving of the chloroform by evaporation. The sheet is formed by pouring the solution into PTFE molds and heating the molds in vacuum up to 90 °C. After the chloroform is evaporated the molds are slowly cooled down to room temperature and the thermo-reversible networks are formed. The Diels-Alder sheets are then kept at room temperature in vacuum for 24 days to complete the synthesis (Terry, et al., 2017).

3.1.2 Self-healing

The self-healing process consists of four steps as can be seen in Figure 3 above. The first step is to heat up the material where the material is heated up in an oven at about 10 K min⁻¹ to 80 °C. The Diels-Alder bonds break during the heating. The second step is where mobility of the material increases, and the microscopic and macroscopic gaps begin to fill. The second step consists of keeping the material at the same temperature for about 35 min. The third step is cooling the material, this is where the Diels-Alder bonds form again after being broken. The cooling is performed at a slow rate, about -2 K min⁻¹ from 80 °C to 25 °C. The fourth step of the self-healing process is where the mechanical properties of the material are recovered. The recovery happens when the material is rested for 24 hours at 25 °C which completes the self-healing process. Figure 4 below shows what happens to the material in the different steps of the self-healing cycle (Terry, et al., 2017).

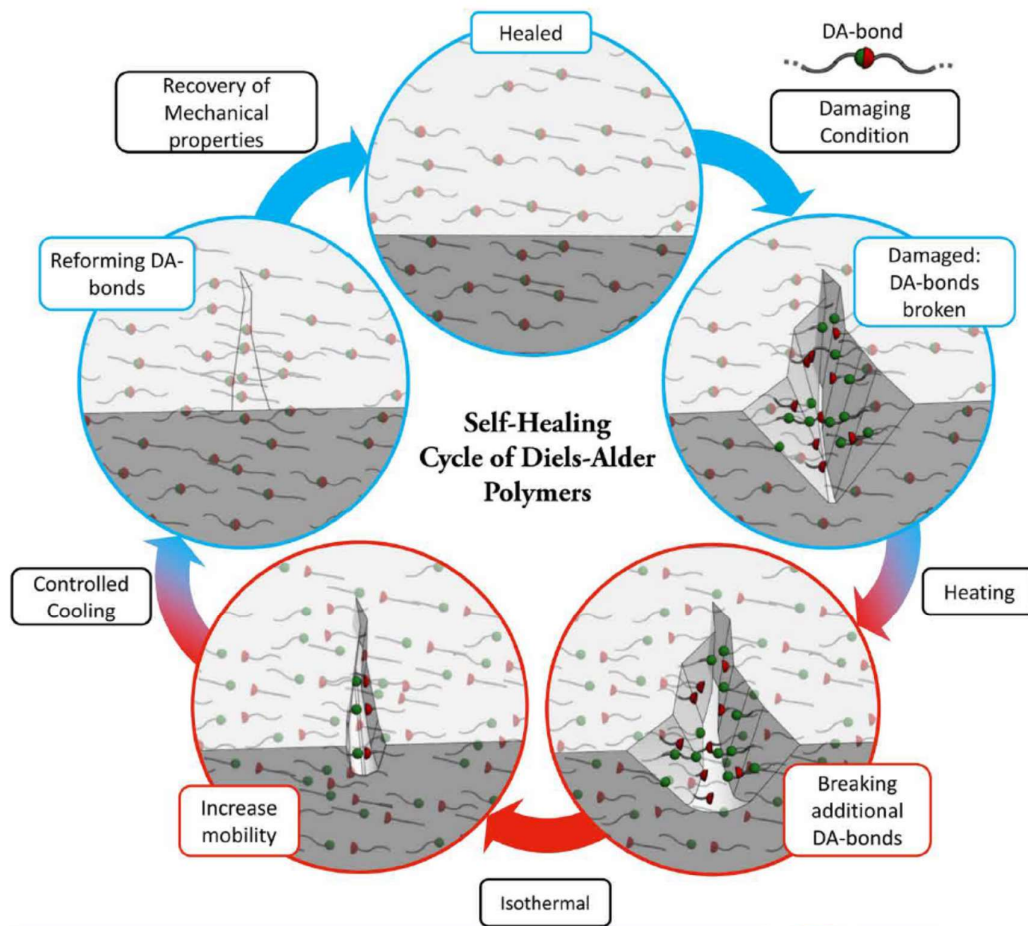


Figure 4, the reaction of the material in the heat stimulated self-healing process (Terry, et al., 2017).

Self-healing was performed by Terry, et al. by cutting the material with a scalpel or by pressurizing the material with air pressure until rupture. The broken material was then put through the self-healing process showed in detail in Figure 4. To demonstrate that the material can undergo multiple self-healing cycles the self-healed material was pressurized until rupture and mended twice. The point of rupture was not the same which means that the mechanical properties of the material almost completely recovered after self-healing (Terry, et al., 2017).

Figure 5 below shows what the self-healing steps look like on the manufactured material under microscope.

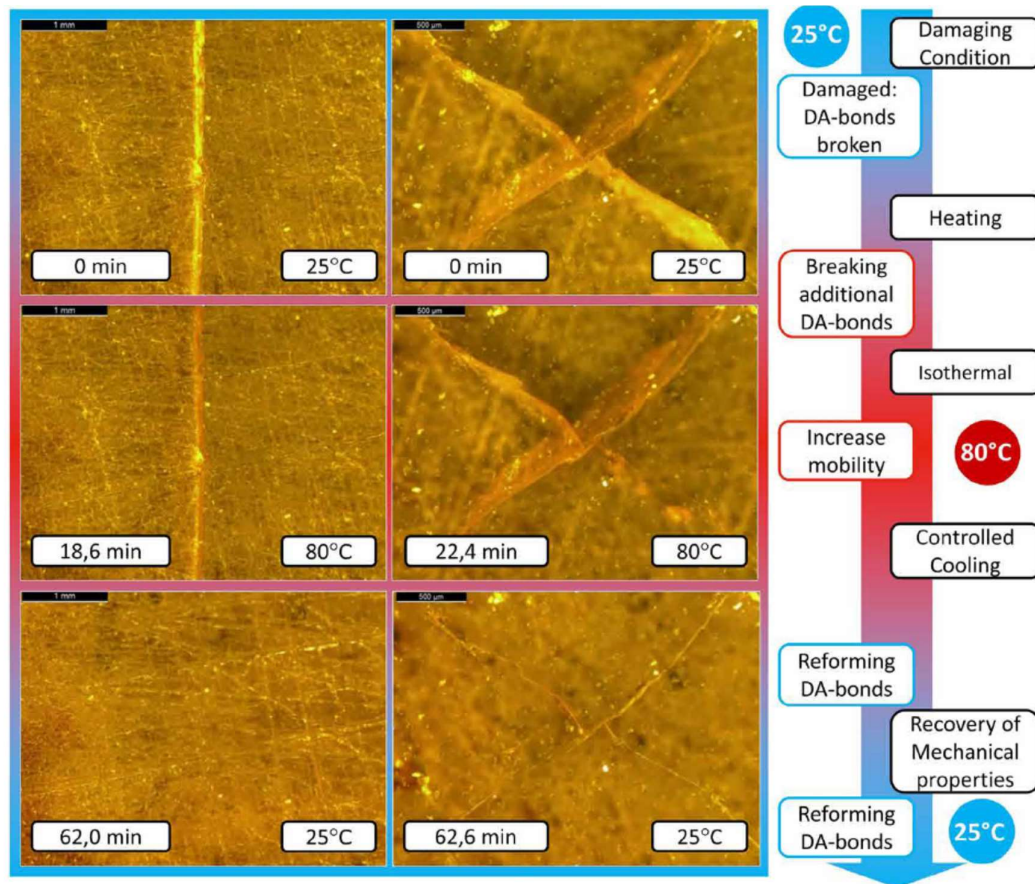


Figure 5, microscopic images of the material during the heat stimulated self-healing process (Terry, et al., 2017)

4 LIGHT INDUCED SELF-HEALING

Light induced self-healing, like heat induced self-healing, is based on controlled and reversible polymerization processes. The idea is based on the fact that reversible bonds break and reform when a reactive polymer is in contact with a stimulus. The depolymerization stage can increase mobility in the weak links so that the gel-like material partially fills cracks in the material. The stimulus can be heat, acidic or basic conditions or, as in this case, UV light. Self-healing with sunlight as a stimulus is appealing, however sunlight does not have the ability to penetrate deep into the materials and might therefore only be applicable to scratches on material surfaces (Mauldin & Kessler, 2013).

Light induced self-healing can be achieved using three different methods. The first method consists of using a photo crosslinking reaction between molecular parts that are photo reactive. The second method uses reshuffling that links up polymer chains on the opposite side of the cracks. The third method uses a photo thermal effect that breaks up non-covalent bonds that are on the same side of the crack to form new non-covalent bonds across the cracks surface.

The first method uses cycloaddition to form a dimer (two similar monomers). Figure 6 shows how the first method forms the reversible bonds during light treatment.

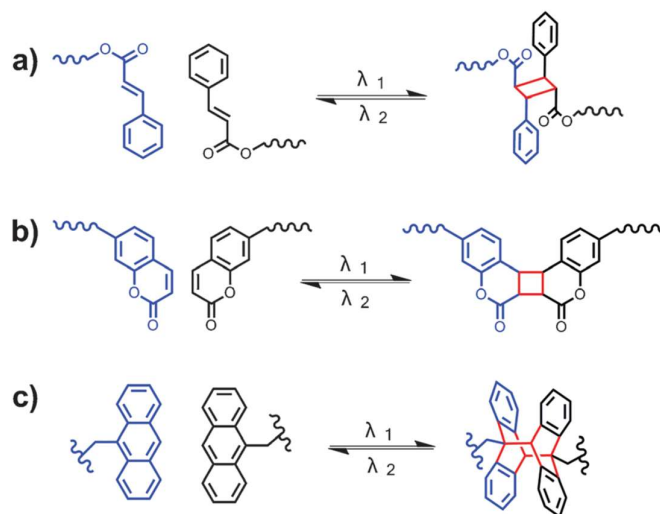


Figure 6, Reversible bonds formed by cycloaddition. The red area indicates where the new bonds are formed. (Habault, et al., 2013).

The second method can be used for reshuffling covalent bonds such as disulfides, allyl sulfides or trithiocarbonates. The UV-light breaks these covalent bonds and makes reactive radicals which combined form new bonds. Some of the new bonds are formed over the crack plane, which heals the crack on the material. Figure 7 shows how the three-different dynamic covalent bonds react under UV light.

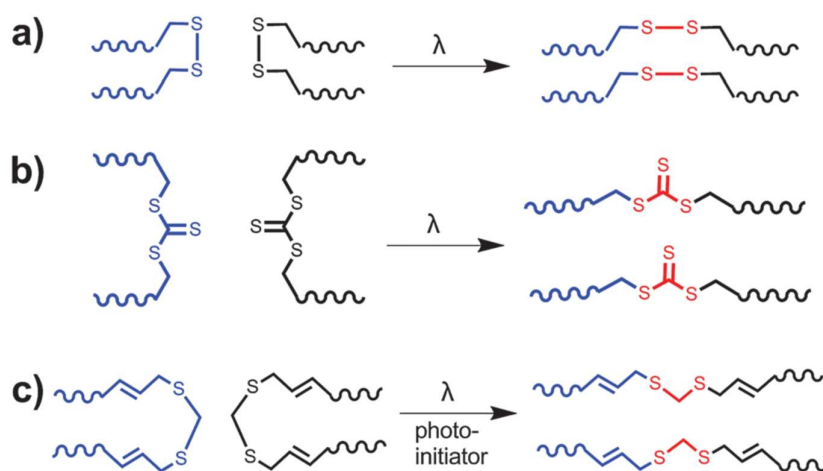


Figure 7, Self-healing bonds formed by reshuffling covalent bonds: a) disulfide. b) trithiocarbonate. c) allyl sulfide. (Habault, et al., 2013).

The photo thermal effect is the third method which uses a metallosupramolecular polymer that absorbs UV light. When treated the polymer heats up over its glass transition temperature from absorbing the UV light and the surface becomes a gel-like substance which fills the crack. The self-healing that occurs in the material is similar to the heat-induced self-healing (Habault, et al., 2013).

Moniruzzaman et al. used a photoresponsive azobenzene structure that could heal scratches up to 73% and fill a pinhole by 40% after the material was induced to UV light. The common problem in light induced self-healing is that the UV light heals scratches more effectively than holes. The deeper the scratch get the more difficult it gets for the UV-light to reach the broken structure. The issue makes it impossible for deep cracks or holes to be self-healed completely (Moniruzzaman, et al., 2016).

A see through photo induced self-healing method was developed by Amamoto et al. where this issue no longer occurred. In this case the UV light was able to reach deep into the sample which could be cut and completely healed multiple times due to the see through nature of the material. The light induced self-healing works by reshuffling trithiocarbonate (TTC) units with photostimulation. (The second method mentioned above, can be viewed in Figure 7 b). Although photo-stimulation can be conducted in room temperature an external stimulus is still needed (Amamoto, et al., 2011).

The method developed by Amamoto et al. was chosen as representative of the light induced self-healing method for this study since the material can be completely cut into two parts and mended into one part again. This is possible due to the optical clarity of the material.

4.1 Light stimulated self-healing elastomer

I chose photo-induced self-healing by reshuffling of TTC units as a light induced self-healing method. Using this method a completely cut material sample can be healed compared to partially healing cuts and scratches with other methods that use UV light as a self-healing stimulus.

Amamoto et al. made two samples of the self-healing material and proved the photoreversible reshuffling capabilities of the material by performing UV-irradiation on the material. The TTC units in the material structure can act as photo-initiators in reversible addition-fragmentation chain-transfer (RAFT) polymerizations. The photo responsive TTC can by dynamic covalent reshuffling be self-healed repeatedly (Amamoto, et al., 2011).

4.1.1 Synthesis

Substances, equipment, costs and amounts of the substances needed to make a photostimulated self-healing material can be viewed in Table 2 below. The cost is for a batch of the closest amount on Sigma-Aldrich compared to the amount used in the synthesis. (Amamoto, et al., 2011).

Table 2, Substances, equipment, costs and amounts of the substances (retrieved from Sigma-Aldrich) needed to make the photostimulated self-healing material.

Substances needed for synthesis	Amount used in synthesis	Cost	Equipment needed for synthesis
Acetonitrile	5 ml	66 €	Nitrogen flow
TTC 4	1.01 g	216 €	250 mL three necked flask
n-butyl acrylate (BA)	5.6 ml	139,5 €	Ice bath

Anisole	5.8 ml	173 €	Vacuum
2,2'-azobis(iso-butyronitrile) AIBN	230 mg	45.25 €	two-neck glass tube
Dichloromethane	-	60 €	Degasser
			Syringe
			Small gas tubes
			Heater and oil bath

The synthesis consists of three phases where the first phase is preparing the TTC diester. The second phase is a reshuffling reaction between the TTC dicarboxylic acid and the TTC diester and the third phase is preparing the cross-linked polymer. To successfully make a self-healing elastomer only step three needs to be replicated.

The TTC diester was made in the following way: triphenylphosphine, Compound 1, THF and ethanol were put into a 250 mL three-necked flask. A nitrogen gas flow was then introduced to the solution and the solution was deoxygenated for 30 min. The flask was then submerged into an ice bath. Diethyl azodicarboxylate mixed with toluene was added into the mixture in the flask for over 20 min by dripping. The reaction was then stirred for 12 h at room temperature. After the solution had been heated at 40 °C for 4 h, a solution of aqueous sodium bicarbonate and chloroform were added. Chloroform was used to wash the aqueous layer twice. The layers were concentrated under vacuum after being dried with magnesium sulfate. Column chromatography was used to purify the leftovers on a silica gel that was 1 part ethyl acetate and 10 parts hexanes. A dark orange solid was created.

The reshuffling reaction between the TTC dicarboxylic acid and the TTC diester was made in the following way: a two-necked glass tube was filled with a mixture of TTC diester, TTC dicarboxylic acid and acetonitrile. Five freeze-pump-thaw cycles were used on the mixture for degassing. The UV irradiation was then performed by filling the tube with nitrogen gas and directing a 200 W UV lamp with the wavelength 220-390 nm towards the tube with a 25 cm gap between the lamp and the tube. The UV irradiation was performed at room temperature. A syringe was used to extract the ready samples from the tube. The reshuffling reaction can be viewed in Figure 8 below. (Amamoto, et al., 2011).

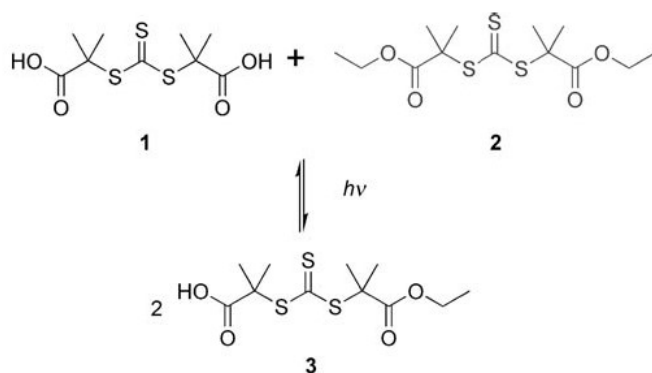


Figure 8, Reshuffling reaction between (1) TTC dicarboxylic acid and (2) TTC diester (Amamoto, et al., 2011).

Step three consists of making the cross-linked polymer and was done in the following way: small glass tubes, BA, anisole, AIBN and TTC cross-linker were put into a two-necked glass tube. The solution was degassed for three freeze-pump thaw cycles. The glass tube was put over an oil bath and filled with nitrogen gas. A heater was put under the oil bath and the mixture was heated at 60 °C for 24 h. The finished product was purified with a dichloromethane extraction for 15 h, and finally the cross-linked polymer was dried under vacuum to create a yellow solid (Amamoto, et al., 2011).

4.1.2 Self-healing processes

Three self-healing methods were conducted on the cross-linked polymer. The first one was conducted in a solvent (Figure 9 a) and the second one was conducted on the cross-linked-polymer in bulk state, in both cases the polymer was cut. In the third case the method used shredded cross-linked parts of a sample and this method was also conducted on the polymer in a solvent. To further demonstrate the self-healing capability of the material the first self-healing process was conducted twice. Once from the pristine material (Figure 9 a) and the second time using the healed material (Figure 9 b) from the first test. This two-step process was conducted five times to confirm the results from the first self-healing test.

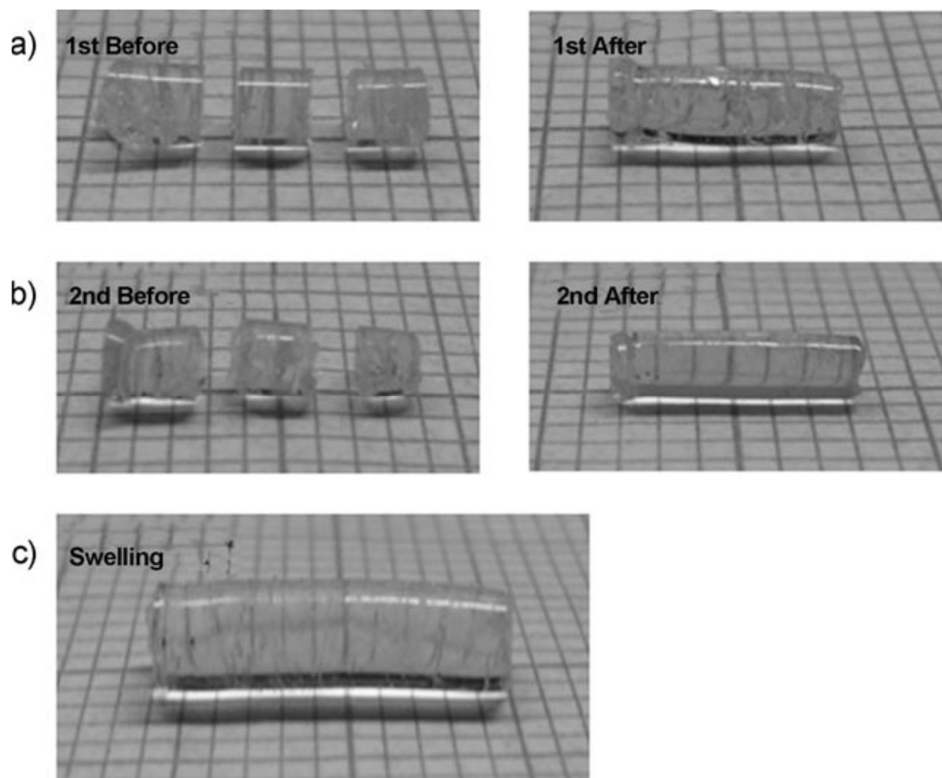


Figure 9. The first self-healing method a) the material before and after the first self-healing cycle. b) the material before and after the second self-healing cycle. and c) the self healed material after the swelling test with anisole (Amamoto, et al., 2011).

In the first self-healing process acetonitrile was used as a solvent since it does not absorb UV light. The material was cut from one solid piece into three separate pieces. The sample was put into a tube together with acetonitrile and placed under pressure from a 4g weight. The setup was held in nitrogen atmosphere for 30 min. The sample was then exposed to UV light. After 4 h of exposure to UV light the separated pieces formed a solid material again. The sample was held in the presence of UV light for 8h (Figure 9 a). The self-healed sample was cut into three pieces again and the same self-healing procedure was repeated one more time to ensure that multiple self-healing cycles can be performed by light induced self-healing (Figure 9 b). After the second cycle the material was dipped for 6 h in anisole to make sure that the material was fused chemically. If the material had been physically brought together then the material matrix would have broken when introduced to anisole. The swollen material after the procedure can be viewed in Figure 9 c) above. This two cycle self-healing process was conducted on 5 samples with similar results. The tensile modulus was measured after the first self-healing cycle as 65 ± 11 kPa.

The tensile modulus of the pristine sample was measured as 69 ± 6 kPa (Amamoto, et al., 2011).

The second self-healing test performed on the material was conducted without the presence of acetonitrile and rather on the polymer in bulk state. Since the chain mobility is lower in the bulk state compared to the solution the material is only partially cut and the reaction time was increased to 48 h. The sample was put in nitrogen atmosphere and under the pressure of a 10 g weight. After a reaction time of 48 h the cut was almost healed. The material before and after the self-healing process can be seen in Figure 10 a below. This test shows that in practice that the sample could be healed in bulk state by putting it into a mold and exposing it to UV light.

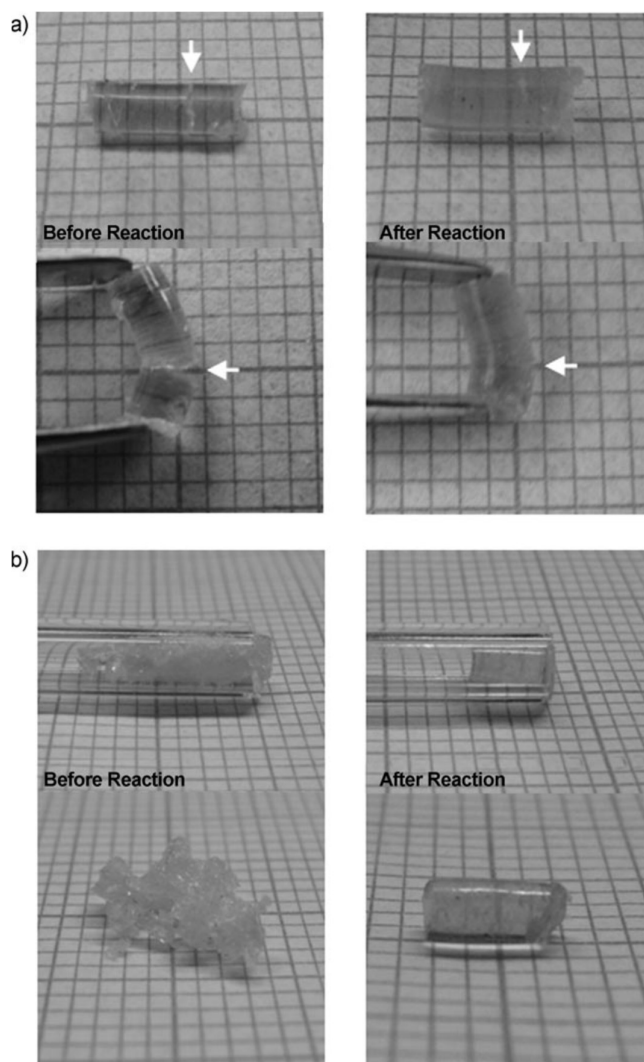


Figure 10, a) the second self-healing method before and after the reaction, and b) the third self-healing method before and after the reaction (Amamoto, et al., 2011).

The third self-healing method was conducted using a similar method to the first one. This time, however, the reaction was conducted on a shredded cross-linked polymer sample. After being submerged in acetonitrile in a quartz tube the sample was put under a 10 g weight and exposed to UV light for 24 h. After the self-healing reaction the sample was again chemically joined, and the separate particles became one piece. A successful swelling test with anisole was conducted once again on the sample. The third method can be viewed in Figure 10 b above.

5 MECHANOCHEMICAL SELF-HEALING

Mechanochemical self-healing, as in heat and light induced self-healing, is based on the chemical structure of the material. Yet again weak bonds that break and reform are essential. Polymers created by non-covalent reactions that are reversible can be used for self-healing. Usually the non-covalent reversible bonds are weak, this is a clear weakness when trying to make a durable material. There are some exceptions, however, such as host-guest interactions and quadruple hydrogen bonding. Covalent bonds that are dynamic such as the Diels-Alder reaction are stronger and are widely used to create self-healing polymers. Dynamic covalent bonds are not only used for stimulated self-healing but also for autonomous self-healing. Non-covalent interactions that use reversible exchange and dynamic covalent bonding have been used to create autonomous self-healing polymers that have reversible chemical bonds that can reform in room temperature. Amide bonds are of particular interest when it comes to this field. Amide bonds normally need extreme conditions to be reversed. Bulky substituents can be used to weaken the amine bond so that they can be broken in normal conditions. Reversing the amine bond can form ketene which is too reactive for the reversible interaction. A stable substance for isocyanate that reacts quickly with amines to form a urea bond can therefore be used as a reactant. Poly-urea and poly urethane-urea bonds have been used for autonomous self-healing purposes (Ying, et al., 2013). Weakened amino bonds were chosen as the mechanochemical self-healing reaction as they are mechanically stronger compared to normal hydrogen bonding which would be an alternative method. Rekondo et al. developed a self-healing poly (urea urethane) that contains both weakened amino bonds and quadruple hydrogen bonding. This combination forms a rapid self-healing material in

room temperature. The material can be completely separated and mended together by physical contact. The rapid self-healing ability and the fact that the material contains both hydrogen bonding and weakened amide bonding are the reasons why this method was chosen as the representative mechanochemical self-healing example for this study (Rekondo, et al., 2014).

5.1 Mechanochemical autonomous self-healing elastomer

The material division in a research center in Paseo Miram'ón in Spain developed an autonomous self-healing thermoset elastomer that can self-heal at room temperature (Rekondo, et al., 2014). The material is a poly (urea-urethane) elastomer which consists of covalent bonds that, do not break in normal conditions. These covalent bonds need to be weaker for the material to work as an autonomous self-healing material. The isocyanate (in this case isophorone diisocyanate IPDI) reacts with a diamine (in this case bis (4-methoxyphenyl) disulfide, DMSO) and forms the urea bond. The weak bonds that first breaks in the material are made up of sulfide end groups. The exchangeable sulfide bonds are more commonly referred to as aromatic disulfides and are known for exchanging at room temperature. The reversible disulfide reaction can be viewed closer in Figure 11 section a below. Figure 11a contains the actual self-healing substance, while Figure 11b only the reference material.

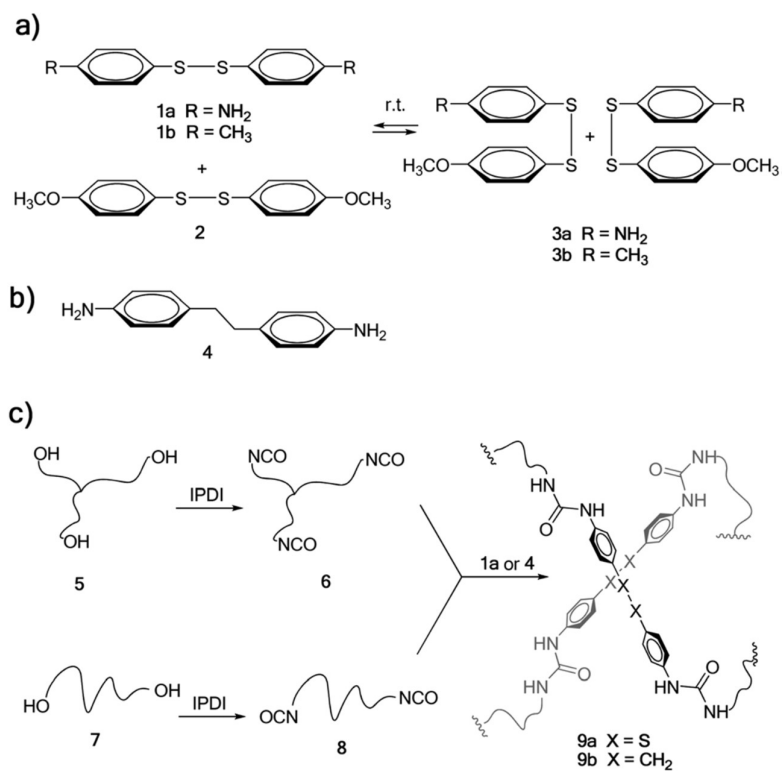


Figure 11, a) exchangeable reaction of aromatic disulfide bonds, b) diamine crosslinker used in reference material, c) process of how synthetic polymers 9a and reference material 9b were created (Rekondo, et al., 2014).

5.1.1 Synthesis

The substances, equipment, cost and amount of the substances that are needed to make a mechanochemical polymer can be viewed in Table 3 below. All costs were taken from Sigma-Aldrich.

Table 3 Substances, equipment, costs and amount of the substances (retrieved from Sigma-Aldrich) needed for the synthesis of a mechanochemical polymer.

Substances needed in the synthesis	Amount used in synthesis	Cost	Equipment needed for synthesis
Bis(4-aminophenyl) disulphide 98%	5.12 g	326 €	Heater
Poly (propylene glycol) (M_n 4000) (M_n 6000) is not available in Sigma-Aldrich.)	390 g	138 €	Vacuum setup
Poly (propylene glycol) (M_n 2000)	250 g	89 €	1 l glass reactor
Isophorone diisocyanate (IPDI 98%)	100.95 g	66 €	250 ml glass reactor
Dibutyltin dilaurate (DBTDL, 95%)	0.000742 g	26.10 €	Magnetic stirrer
Tetrahydrofuran (THF)	3 mL	64 €	Open mold

The synthesis of the self-healing polymer and its reference material is made up of four smaller syntheses. The first two syntheses are the synthesis of two pre-polymers later used in the synthesis of the self-healing elastomer and the reference material. The second two syntheses are the synthesis of the self-healing material- and reference material. The first pre-polymer is a tris-isocyanate-terminated pre-polymer and the second pre-polymer is a bis-isocyanate-terminated pre-polymer.

5.1.1.1 Tris-isocyanate-terminated pre-polymer synthesis

A 1 L glass reactor connected to a vacuum inlet and mechanical stirrer was filled with a mixture of PPG (M_n 6000) and IPDI. The mixture was heated to 70 °C and stirred under vacuum for 10 min. DBTDL was added to the mixture and it was stirred for another 45 min. under vacuum at 70 °C. The colorless liquid that was created was tightly sealed in a glass bottle.

5.1.1.2 Bis-isocyanate-terminated pre-polymer synthesis

A 1 L glass reactor connected to a vacuum inlet and mechanical stirrer was filled with a mixture of PPG (M_n 2000) and IPDI. This time the mixture was heated to 60 °C and stirred in vacuum for 10 min. The mixture was kept in vacuum and DTBL was yet again added to the mixture. The temperature was kept at 60 °C and stirred for another 70 min. The ready pre-polymer was kept in a well-sealed glass bottle.

5.1.1.3 Self-healing poly (urea-urethane) elastomer synthesis

Both tris- and bis-isocyanate pre-polymers were mixed along with bis (4-aminophenyl) disulphide 98% mixed in THF in a 250 mL glass reactor and kept in vacuum for 15 min. The mixture was then shaped over an open mold and cured at 60 °C for 16 h to form the ready self-healing polymer. The reference sample was made in the same way but instead of bis (4-aminophenyl) disulphide 98%, 4, 4'-ethylenedianiline (> 95%) was used and the amount of THF was different.

5.1.2 Self-healing

To perform self-healing tests on the self-healable polymer and the reference sample the tensile strength of the pristine self-healable polymer and the reference sample were tested before and after self-healing. The self-healable polymer was cut into two separate pieces as shown in Figure 12 b and c below. The polymer was then healed by the two sides being in contact with each other. The tensile strength was measured after 1, 2 and 24 h of self-healing. After 1 h of contact the polymer had retained 62% of its mechanical properties. After 2 h of self-healing the polymer had recovered 80% of its mechanical properties and after 24 h the polymer had recovered 97% of the mechanical properties of the pristine sample. After 2 h of self-healing it was no longer possible to break the self-healed bonds by pulling the mended material apart, as shown in Figure 12 e and f.

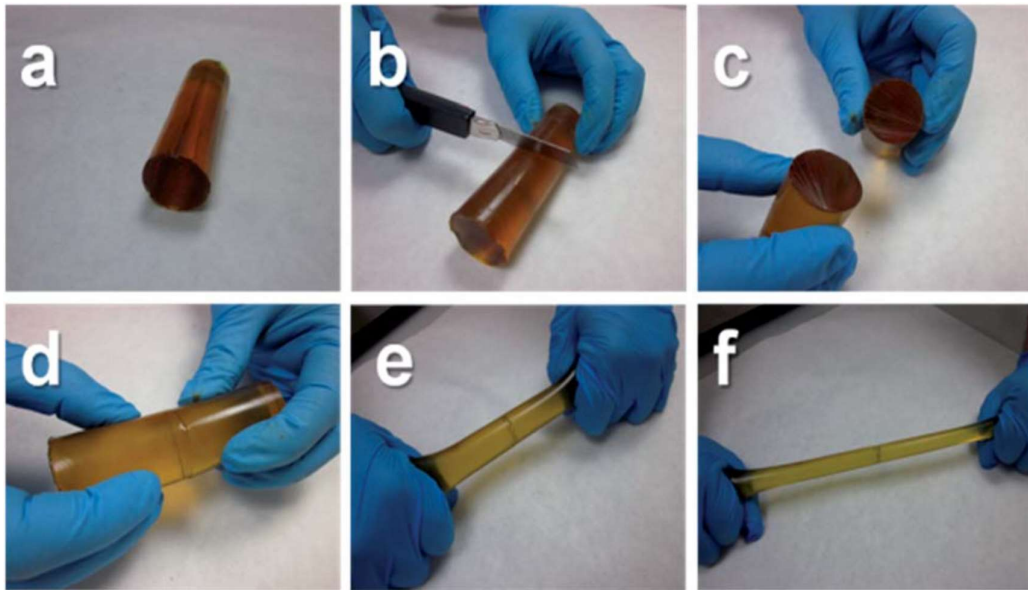


Figure 12, a) pristine sample of the self-healing polymer, b) and c) the cut sample of the self-healing polymer, d) after 2 h of contact, e) and f) the sample stretched after 2 h of contact (Rekondo, et al., 2014).

Tensile testing was also conducted on the reference sample before and after the same self-healing process as the original sample went through. The results of the reference sample was that after 1 h of self-healing, the material had recovered 50% of the original mechanical properties. Increasing the healing time over 1 h did not increase the recovery of the mechanical properties in the reference sample.

The self-healing ability works due to two reasons. The first reason is the quadruple H-bonds that are in the material structure. These bonds are also the reason why the reference sample partially recovered. The second reason is the disulfide bonds that were mentioned earlier. Disulfide bonds only exist in the original sample and not in the reference sample which is the reason why the original sample had a better self-healing capability than the reference sample. The quadruple H-bonds might help the quick self-healing ability in the original sample as the reference sample containing the H-bonds has a rapid healing time (Rekondo, et al., 2014).

6 ENCAPSULATION

Encapsulation is a self-healing method based on healing agents inside the polymer that heal the broken polymer from within the polymer structure. There are different structures of how the healing agents can be stored inside the material. Four common structures that have been used in self-healing materials are presented in Figure 13 below (Yang, 2016).

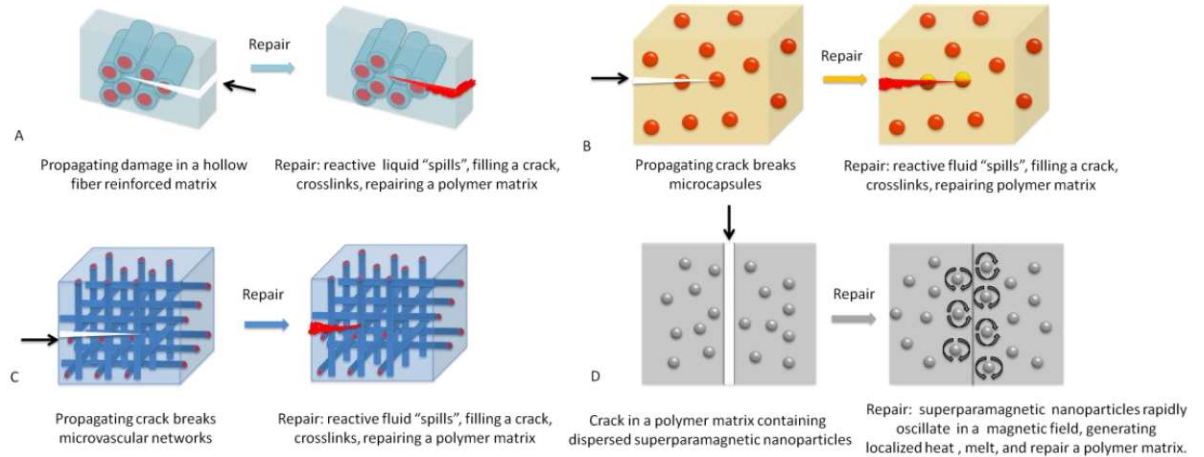


Figure 13, Self-healing illustration of common encapsulation methods, a) hollow fibers inside a polymer, b) Microspheres/microcapsules, c) microvascular network, and d) superparamagnetic nanoparticles (Yang, 2016).

Self-healing with hollow fiber reinforced matrixes (shown in Figure 13a) uses hollow fibers within the material that stores resin inside them. When a crack occurs in the material the liquid resin inside the fibers fill the crack and therefore the material self-heals. Epoxides are often used as healing agents in hollow fibers due to their beneficial adhesive properties (Yang, 2016). The hollow fibers inside the polymer give the polymer a higher tensile strength. Hollow fibers containing the modifying agent inside the polymer structure are filled so that the modifying agent stays in the fiber cavities until the polymer is completely cured. After curing the modifying agent is partially released from the cavities so that when a crack occurs in the material the healing agent fills up the crack with the use of one or more stimuli. Hollow-fiber reinforced matrixes with healing agent in polymer structures can be used as building material for bigger structures, even bridges could possibly be built using this method (IFI CLAIMS Patent Services).

Microcapsule self-healing (shown in Figure 13b) is as the name states microcapsules within the material structure. The capsules are filled with a healing-agent, when the material breaks the capsule cracks open and the resin fills the crack in the material and solidifies to form the self-healed material (Yang, 2016). Microcapsule self-healing is triggered by an external stimulus such as mechanical damage. Poly (urea-formaldehyde) is an example of a substance that can be used to create microcapsules. Microcapsule self-healing has the disadvantage of each capsule only being able to heal a fracture once (Blaiszik, et al., 2009).

Microvascular networks (shown in Figure 13c) consist of a network of tubes containing a healing agent within the material. The advantage of the microvascular system compared to normal microcapsule self-healing is that the microvascular system can heal a crack occurring on the same location multiple times. Where microcapsule self-healing can only heal a crack occurring on the same spot once. However, microvascular self-healing has a limited amount of healing cycles on each location depending on how much healing agent is stored in a tube (Sang-Ryoung, et al., 2017).

Superparamagnetic nanoparticles (shown in Figure 13d) inside the material start to oscillate when an oscillating magnetic field is applied. The oscillation speeds up the nanoparticles magnetic moment which creates magnetic energy that is converted to thermal heat and creates a material flow in the particular area where it is needed, and the broken material is healed. A partially separated film can be healed into a solid film again. The material similarly to microvascular networks can undergo multiple healing cycles in one area. The disadvantage of using oscillation as a healing trigger is that this encapsulation method is no longer autonomous. (Corten & Urban, 2009).

Microvascular networks can heal multiple cracks occurring in the same place which is a beneficial quality. Fiber enforced matrixes and micro capsule self-healing can on the other hand only heal a single crack for each fiber/capsule. Microvascular networks are autonomous self-healing networks which is a desired quality in all self-healing materials. Superparamagnetic nanoparticles imbedded in a polymer matrix can perform multiple self-healing cycles, but it is not an autonomous method as a magnetic oscillator is

needed for the self-healing to occur (Yang, 2016). The microvascular network was chosen as the encapsulation method further investigated due to the reasons mentioned above.

Microvascular systems can be found in nature, e.g. humans have a well-functioning blood vessel system imbedded in our bodies. Toohey et al. tried to replicate that system by creating a synthetic microvascular system that has both blue and red tubes as resin carriers (Hansen, et al., 2009). Figure 14 below shows both the microvascular system found inside the human body in and the microvascular network developed by Toohey et al. meant to imitate the human system.

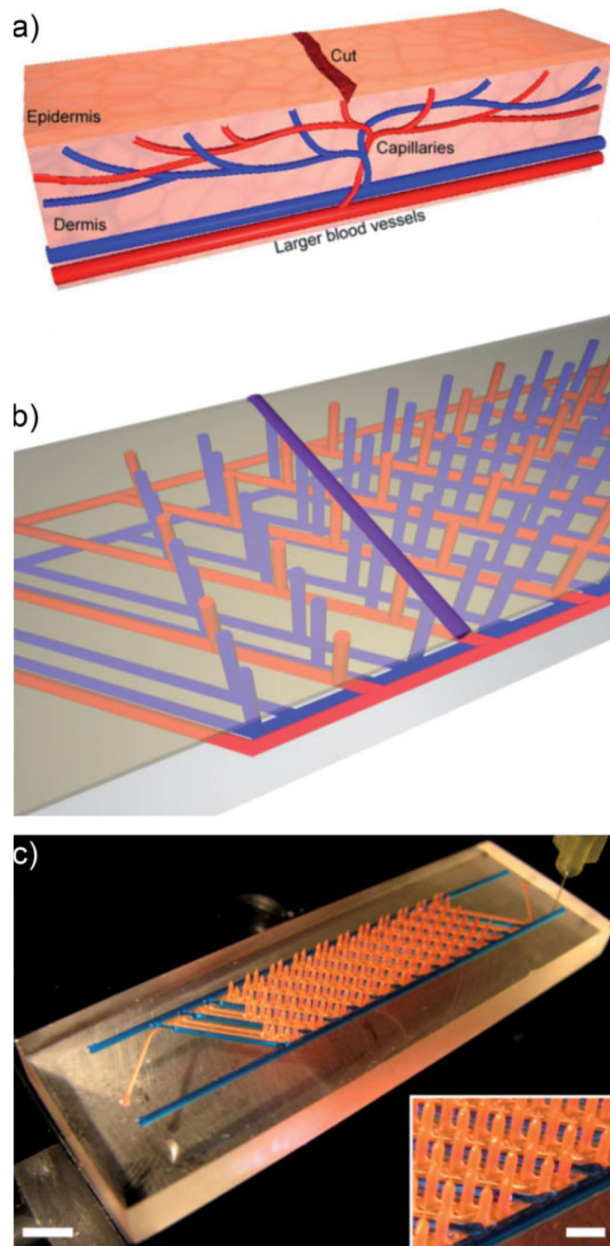


Figure 14, Microvascular networks: a) blood vessels inside the human body, b) a 3D image of the microvascular network that drawn by Toohey et al, and c) the microvascular network developed by Toohey et al (Hansen, et al., 2009).

Williams et al. developed a sandwich material with a microvascular tube system imbedded inside the material. A two-fluid network system was developed where an epoxy resin and a hardener were used in the network. The system is made up of a 3D microvascular network that can autonomously heal itself multiple times (Hansen, et al., 2009).

6.1 Self-healing microvascular network

The microvascular networks developed by Williams et al. similar to the one shown in Figure 14 above can self-heal up to 30 cycles whereas the one developed by Toohey et al. only has the ability of self-healing up to 7 cycles. Therefore, the method with a dual network that Williams et al. developed is the one which I chose for this study. The dual system consists of an epoxy resin and hardener that is carried by two separate networks. When a point in the network is broken the resin and hardener flows out from the tubes and solidifies when in contact with one another.

6.1.1 Synthesis

The substances, equipment, cost and amount of the substances needed to make the microvascular network are shown in

Table 4 below. The costs for the substances were retrieved from Sigma-Aldrich, Fischer Scientific, Ecorr Systems, Polysciences Inc and E.V.Roberts. The combined cost for microcrystalline wax, Purester 24 and Epikure 3046 hardener was assumed to be 100 €.

Table 4, Substances and equipment, costs and amount of the substances to create the microvascular network

Substances needed for synthesis	Amount used for synthesis	Cost	Equipment needed for synthesis
Microcrystalline wax		Undefined, but assumed to be relatively minor/trivial/negligible	Magnetic stirrer
Heavy mineral oil	< 1 L	83.50 €	Heater
Pluronic F127 (triblock copolymer)	< 250 g	92.50 €	3 mL syringes
VCPI-414 (aqueous degreaser solution)	< 1 container	11.9 €	Oven
Purester 24 (Fugitive wax)		Undefined, but assumed to be relatively minor/trivial/negligible	Refrigerator
Diethylenetriamine	0.576 ml	23.10 €	330 and 100 μm nozzles
EPON 828 resin	4.8 ml	117 €	Three-axis robot
EPON 8132 resin	19.2 ml	113.57 €	Customized software for three-axis robot
Epikure 3046 hardener	9,6 ml	Undefined, but assumed to be relatively minor/trivial/negligible	Vacuum
Microcrystalline wax, Purester 24 and Epicure 3046 hardener		100 €	Degasser

At first microcrystalline wax is prepared by mixing heavy mineral oil with microcrystalline wax. The substances are heated to 100 °C where the substance melt and the mixture is mixed for 10 min. The formed solution is put into 3 ml syringes and placed into an oven at 70 °C until the ink solidifies. The syringes are then cooled to room temperature and a triblock-copolymer is created by mixing Pluronic F128 and BASF in deionized water. The deionized water is cooled down and kept at 5°C and the copolymer is slowly

stirred into the deionized water to form the fully solved solution. The mixture is then put into a refrigerator for 12 h to remove trapped air left in the mixture. After the mixture has been cooled it is loaded into 3 *ml* syringes and warmed up to room temperature.

To form the microvascular network pre-cured epoxy substrates are used as carriers. The wax ink was first dispersed onto the epoxy substrates and then the pluronic ink was dispersed onto the epoxy substrates. The pluronic ink formed a support layer for the basis of new ink deposition layers. The two-step procedure was done until the preferred microvascular network was created. The structure was then penetrated with the same epoxy material as the underlying layer and cured at 20 °C for 24 h. The pieces were then cut and the pluronic ink was removed by dissolving it in water. After that the pieces were dried, penetrated with the same epoxy material and cured. The material was then polished and heated to 80 °C to make it possible to remove the wax. The wax was removed by applying a light vacuum and excess ink was removed by ultra-sonication. A mixture of diethylentriamine in EPON 828 resin was put onto the surface after being degassed for 30 min. The coating was then cured at 25 °C for 6 h and another 9 h at 30 °C. The coated specimen was polished and the wax that was disappearing was removed by a 35 °C heating procedure and by applying light vacuum (Hansen, et al., 2009).

6.1.2 Self-healing procedure

To test the self-healing ability of the material one microvascular network was charged with EPON 8132 (epoxy resin) and the other network was charged with Epikure 3046 (epoxy hardener). The coating was cut 5 – 10 μm by a test panel scratcher under a constant load between 6 – 10 *N*. A four-point bending test was then conducted on the specimen with an acoustic emission sensor measuring the load-time data from the bending test. Figure 15 shows where the coating was scratched with the test panel scratcher and Figure 16 shows where the specimen was set in the four-point bending test (Hansen, et al., 2009).

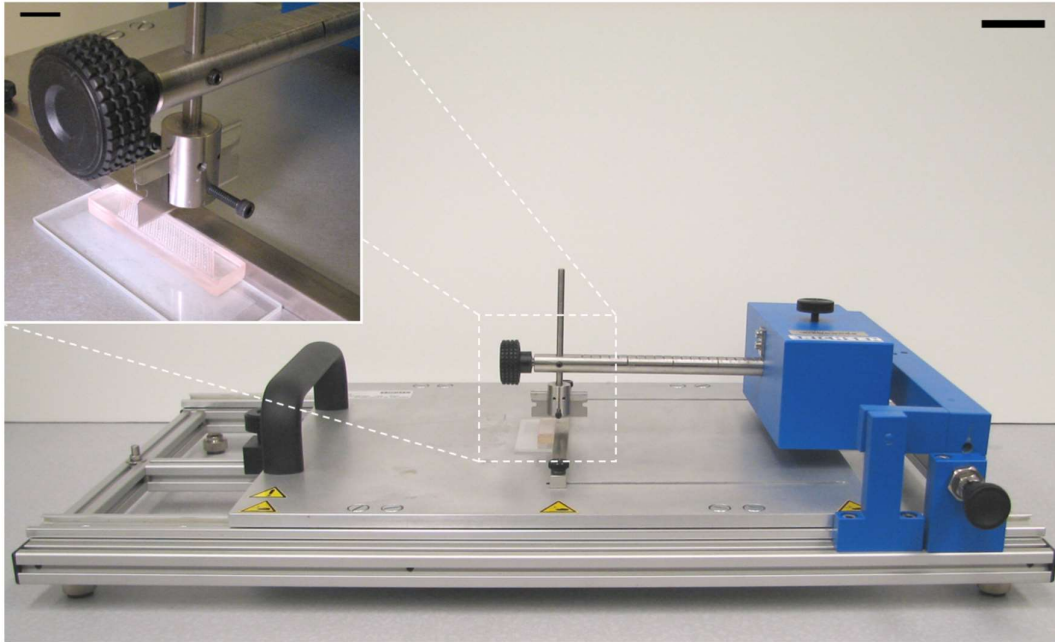


Figure 15, Scratch test panel cutting the coating with a close up in the upper left corner of how the specimen is placed in the test panel scratcher (Hansen, et al., 2009).

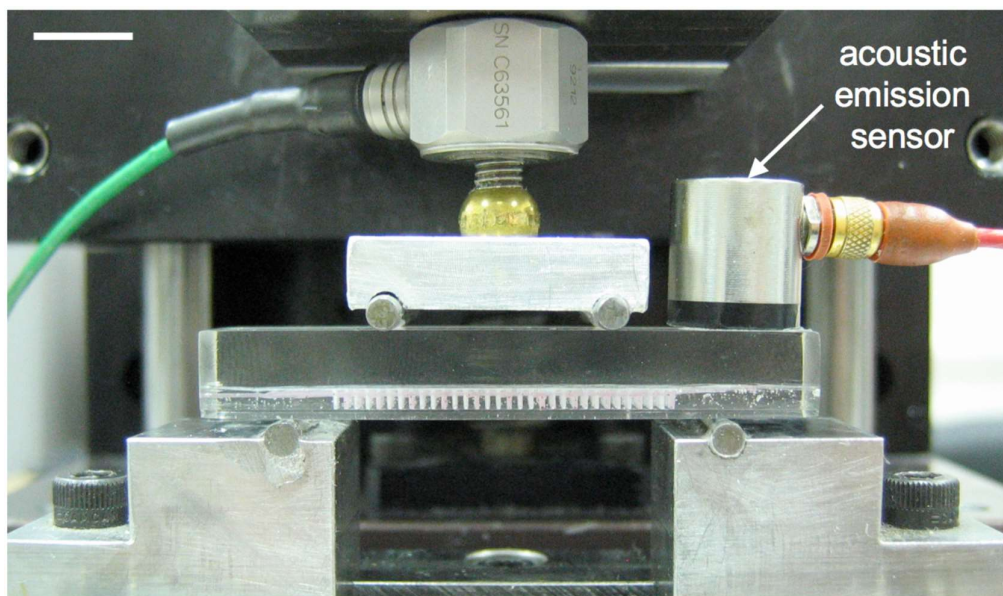


Figure 16, Set up of the four-point bending test with an acoustic emission sensor (Hansen, et al., 2009).

A digital oscilloscope is used to collect the data from the acoustic emission sensor. The data is analyzed by computer and the load under which the crack in the sample reopened is determined. Hansen et al. uses “healing efficiency”, η , to determine how well a sample heals after a self-healing procedure. η is measured by taking the fracture load of the healed

sample divided by the fracture load of the original sample as shown in Equation 1 below (Hansen, et al., 2009).

$$\eta = \frac{P_{healed}}{P_{original}} \quad (1)$$

The specimen were tested for 50 self-healing cycles and held at 30 °C for 48 h between each self-healing cycle to cure the crack that occurred in the specimen. Average healing efficiency for 30 self-healing cycles were measured from the bending data of 8 samples. The average healing efficiency was then plotted into a figure and compared to the average self-healing efficiency of the microvascular network created by Toohey et al shown in Figure 14 b and c. The plotted average healing efficiency can be seen in Figure 17 below were the black pillars represent the average healing efficiency of the eight-specimen developed by Hansen et al. The red pillars represent the healing efficiency of the microvascular network developed by Toohey et al. and the blue pillar represent a microcapsule based self-healing system (Hansen, et al., 2009).

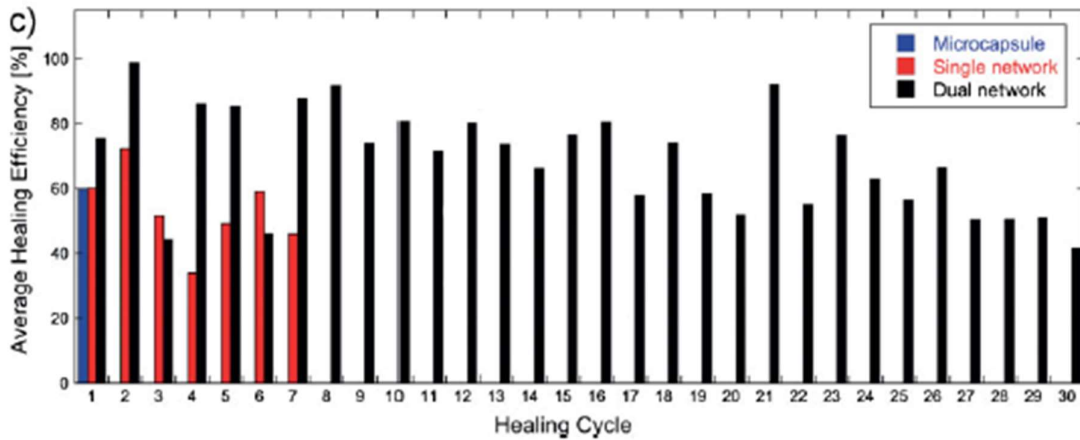


Figure 17, Average self-healing efficiency for 30 consecutive self-healing cycles. red pillars represent the material created by toohey et al and the blue pillar represents a microcapsule based network (Hansen, et al., 2009).

Figure 17 shows that even after quite a few cycles the material is almost able to withstand as much load as the original sample. After 30 cycles the material can still take on half of the original load before breaking. The dual network created by Hansen et al. has superior self-healing qualities compared to the single network developed by Toohey et al.

7 COMPARISON OF METHODS

The self-healing experiments described above are now compared here by cost, self-healing ability, user convenience and ease of fabrication below. The self-healing experiments where given numbers 1-4 in, were number 1 represents the most successful and number 4 represents the least successful method in each category To emphasize the results a summary of comparisons is made where all earlier areas of comparisons are evaluated.

7.1.1 Cost

The four methods presented above, heat induced self-healing, light induced self-healing, mechanochemical self-healing and encapsulation were compared below in the following way. The substances needed for each synthesis were calculated and compared and the stimulus needed for self-healing pointed out in Table 5 below.

Table 5, Comparison of substance costs for all four-experimental synthesis and the self/healing stimulus needed for all four methods.

Method	Cost	Stimulus
Heat stimulated self-healing	775.5 €	Heat
Light stimulated self-healing	699.75 €	UV light
Mechanochemical self-healing	709.10 €	None
Encapsulation	541.57 €	None

The costs were calculated by taking the costs of the substances needed for synthesis from Tables 1-4 and adding the cost of each substance to get the material cost for the synthesis for each method. The prices shown in Table 5 are the substances costs for all four self-healing experiments, tax and shipping are not included. Creating one of the materials may lead to additional costs depending on the location of the experiment and equipment available. All prices for the three first self-healing methods were taken from Sigma-Aldrich. Prices for the fourth method were taken from Sigma-Aldrich, Fischer Scientific, Ecorr Systems, Polysciences Inc and E.V.Roberts.

The encapsulations experimental method was the cheapest and therefore given number 1. Light stimulated self-healing and mechanochemical self-healing were both given number 2 as their costs were so close to each other. The heat stimulated self-healing was the most expensive method and was therefore given number 4.

7.1.2 Self-healing ability

Self-healing ability represents how well the mechanical properties of the material recover after the material has undergone self-healing compared to the pristine material. Self-healing ability also indicates the number of self-healing cycles a material can undergo and the time it takes for the material to go through one self-healing cycle. Self-healing ability, self-healing time and recovery of the mechanical properties after one self-healing cycle are presented in Table 6 below.

Table 6, Self-healing ability and self-healing time of the four different experimental methods.

Method	Recovery of mechanical properties after one self-healing cycle	Self-healing cycles	Self-healing time
Heat stimulated self-healing	≈ 100 %	2+	25 h
Light stimulated self-healing	≈ 94 %	2+	8.5 h / 48 h
Mechanochemical self-healing	≈ 97 %	2+	24 h
Encapsulation	≈ 80 %	≈ 30	48 h

Recovery of properties are at the highest in the heat-stimulated self-healing, this experiment was, however, not tested in the same way as the other methods. Encapsulation has by far the best proven self-healing cycles, but the other experiments did not measure the maximum self-healing cycles rather just recovery of mechanical properties. Light stimulated self-healing has the shortest self-healing time. The light stimulated method was, however, healed in a solvent and if you take away the solvent the time increases to 48 h.

The self-healing time and recovery of mechanical properties were taken more into account than self-healing cycles. Heat stimulated self-healing and mechanochemical self-healing have similar self-healing times and a similar recovery of mechanical properties.

Therefore, both methods are given number 1. Light stimulated self-healing and encapsulation have a similar self-healing time, the light stimulated self-healing has a better recovery of mechanical properties while encapsulation can perform more self-healing cycles. Both methods are therefore given number 3.

7.1.3 User convenience

User convenience is defined as to how convenient the self-healing procedure is. Does the average user have the possibility to self-heal the material assessed? What equipment is used in the self-healing procedure? And does the average user have that equipment? Table 7 shows how the materials are ranked with user convenience: number 1 being the easiest to use and number 4 being the most difficult one to use.

Table 7, User convenience, how easily the self-healing process can be performed with 1 being the easiest and 4 being most difficult.

Method	User convenience
Heat stimulated self-healing	3
Light stimulated self-healing	4
Mechanochemical self-healing	2
Encapsulation	1

User convenience was evaluated in the following way. Both mechanochemical self-healing and encapsulation are autonomous methods which means that self-healing can be conducted where the material is used without an external stimulus and are therefore both given number 1. Heat stimulated self-healing needs heat to self-heal the material, for example an oven. An oven is something that is accessible for the average person moreover the method is given number 3. Light stimulated self-healing is given number 4 since the method needs a UV light source for self-healing which is not an accessible item for the average user.

7.1.4 Ease of fabrication

Ease of fabrication is defined as the time and special equipment needed for synthesis. Special equipment could be defined as equipment that is not present in Arcadas lab. Both the special equipment- and time needed for synthesis can be viewed in Table 8 below.

Table 8, Time needed to create each synthesis and equipment needed for each synthesis that cannot be found in Arcada.

Method	Time needed for synthesis	Equipment not found in Arcada.
Heat stimulated self-healing	34 days	-
Light stimulated self-healing	≈ 44 h	-
Mechanochemical self-healing	≈ 20 h	-
Encapsulation	≈ 85 h	Air pressure multiplier dispensing system, three axis robotic deposition stage.

Each step where time is not mentioned was given the time stamp of 1 h. For example, “The formed solution is put into 3 ml syringes and placed into an oven at 70 °C until the ink solidifies” (Hansen, et al., 2009). As there is no timeframe mentioned the timeframe is assumed to be 1 h. Ultra-sonication, an air pressure multiplier dispensing system and a three-axis robotic deposition stage are needed for the encapsulation synthesis and cannot be found in Arcada. All other synthesis can be performed in Arcada without further equipment needed.

Ease of fabrication which is based on time of synthesis and equipment needed for synthesis that is not available in Arcada was evaluated in the following way. Mechanochemical self-healing has the shortest synthesis time with no equipment needed that is not available in Arcada and is therefore given number 1. Light stimulated self-healing has a bit longer synthesis time than mechanochemical self-healing but no equipment that cannot be found in Arcada is needed in light stimulated self-healing. Light stimulated is therefore given number 2 in the ease of fabrication category. Heat stimulated self-healing has the by far the longest synthesis time at 34 days, but no equipment is needed for the synthesis that cannot be found in Arcada. Heat stimulated self-healing is therefore given number 3 in ease of fabrication. Encapsulation has the second longest synthesis time and is the only

method that requires equipment for the synthesis that cannot be found in Arcada and is therefore given number 4.

7.1.5 Summary of the comparison of methods

A summary of the comparisons is presented by ranking the self-healing methods from 1 best suitable to 4 least suitable. The method with the least total points will be the most accessible and beneficial to be adopted in Arcada.

Table 9, Summary of comparison of methods, the methods are compared by a scale from 1 to 4. With 1 being most suitable and 4 being least suitable.

	Heat stimulated self-healing	Light stimulated self-healing	Mechanochemical self-healing	Encapsulation
Cost	4	2	2	1
Self-healing ability	1	3	1	3
User convenience	3	4	1	1
Ease of fabrication	3	2	1	4
Total points	11	10	5	9

7.2 Discussion

Encapsulation is the cheapest method at 542 € with light stimulated- and mechanochemical self-healing being relatively cheap at close to 700 €. The heat stimulated method is a bit more expensive to replicate at 778 €.

Heat stimulated self-healing ($\approx 100\%$) and mechanochemical self-healing (97%) have the best recovery of mechanical properties. However, the heat stimulated self-healing was measured over pressure rather than tensile testing and can therefore not be compared in the same way as the other methods. Encapsulation seems to have an incredible ability to heal up to 30 cycles compared to the three other methods. This is not true, however, as the other methods were only tested for one or two cycles and they might be able to self-

heal for more cycles than tested in the experiments. The encapsulation has the worst self-healing ability at 80% and by 30 cycles it is down to 50%. More research should be done on the self-healing cycles of the different methods to get a clearer result. Light stimulated self-healing in a solvent had the shortest self-healing time, however, as all the other methods were self-healed in bulk state the light stimulated self-healing time in bulk state (48 h) were the one used in the analysis. This makes the mechanochemical self-healing and heat stimulated self-healing the two faster self-healing methods and encapsulation and light stimulated self-healing the two slower methods.

The encapsulation-, mechanochemical- and heat stimulated self-healing methods are all relatively easy for any user to perform self-healing on. Nothing is needed for encapsulation, only physical contact where the cut or crack is needed to trigger the mechanochemical self-healing and an oven is needed to trigger the heat stimulated self-healing. The light stimulated method however needs a UV light source, which most people do not have at home. This makes the light stimulated method less attractive if one method is chosen.

All the other methods except the encapsulation method can be adopted in Arcada without any additional equipment which makes the encapsulation method less attractive to replicate in Arcada.

The summary of the comparison of methods shows that the heat-induced self-healing experimental method is least attractive to replicate followed by the light-stimulated self-healing method and encapsulation. I, however, think that the heat-stimulated method is worth more investigation since the drawbacks are only time and money. The self-healing capability of the methods needs more research and the method is therefore underestimated in Table 9. The drawbacks in light-stimulated self-healing (user convenience) and encapsulation (additional equipment needed) are bigger drawbacks than the ones presented for the heat stimulated self-healing method. The mechanochemical self-healing method is therefore the best alternative to replicate in Arcada both from the research done so far and also in my opinion.

8 CONCLUSION

All the aims set out in the beginning of my work were achieved. A literature review of the basic self-healing methods was performed, and four experiments based on the methods were assessed. A superior method (mechanochemical self-healing) was found by comparing all four experimental methods by the defining qualities (cost, self-healing ability, user convenience and ease of fabrication).

Heat stimulated self-healing works with reversible bonds that break up when they are heated. The chosen experimental method uses Diels Alder bonds that are made up of a diene and a dienophile. The bonds break up when the material is heated up over the glass transition temperature and the material becomes gel like which leads to a smooth surface and removal of cracks within the structure. Heat induced self-healing has a long synthesis time but a short self-healing time and accessible self-healing method, equipment that is needed to create the synthesis can be found in Arcada and the synthesis is the most expensive of the four methods.

Light stimulated self-healing like heat stimulated self-healing works by reversible bonds that reform. This time, however, the bonds break by directing UV light towards the material. The experimental method is based on reshuffling of covalent bonds. When the specimen is radiated with UV light reactive radicals form, which then combine and form new bonds over the crack plane surface that makes the material whole again. Light induced self-healing has a relatively short synthesis time but a long self-healing time in bulk state and a non-accessible self-healing method. All the equipment that is needed to produce the light induced self-healing elastomer can, however, be found in Arcada. The light induced self-healing is a relatively cheap experiment to conduct at close to 700 €.

Mechanochemical self-healing is also based on a reversible mechanical bond. In this case the bond is made up of an isocyanate and a diamine that form a urea bond. This urea bond has sulfide end groups known as aromatic disulfides which exchange in room temperature. The mechanochemical synthesis has the shortest synthesis time, the shortest self-healing time and the self-healing process can be conducted by the average user without difficulty. The mechanochemical synthesis can also be replicated in Arcada without any

unavailable equipment. The price to manufacture the material is relatively cheap at 700 €.

Encapsulation uses an imbedded material in liquid form inside the material that fills up cracks when an impact or scratch reaches deep enough inside the material. The experimental method is based on a microvascular network that has both an epoxy resin and a hardener imbedded inside the material. When a crack occurs the network releases both the resin and the hardener which makes the network effective. The encapsulation experiment has a relatively short synthesis time and has the most accessible self-healing method. However, the encapsulation method has a long self-healing time and Arcada does not have all the equipment needed for the synthesis. Encapsulation is the cheapest experiment to replicate at under 550 €.

The mechanochemical self-healing method is therefore the superior method in this study. Table 9 also clearly shows that the mechanochemical experimental method would be the superior method to recreate if one method out of these four is chosen for recreation.

A future student who wants to make a self-healing elastomer has here a platform which makes it easier for them to commence an experimental project on producing a self-healing elastomer with good properties.

I recommend that if a student follows up on this by making a self-healing elastomer that they go with the mechanochemical or heat stimulated method. I also recommend that a proper self-healing cycle test should be done on the material created. Where the test will show how many self-healing cycles a mechanochemical or heat induced self-healing material can withstand, and how much of the mechanical strength is preserved in each self-healed sample after each cycle.

SAMMANDRAG

Syftet med slutarbetet var att hitta en självläkande elastomer med de bästa möjliga egenskaperna enligt de följande kriterierna: förmånlig att konstruera, bra självläkningsförmåga, användarvänlig och att den är lätt att producera.

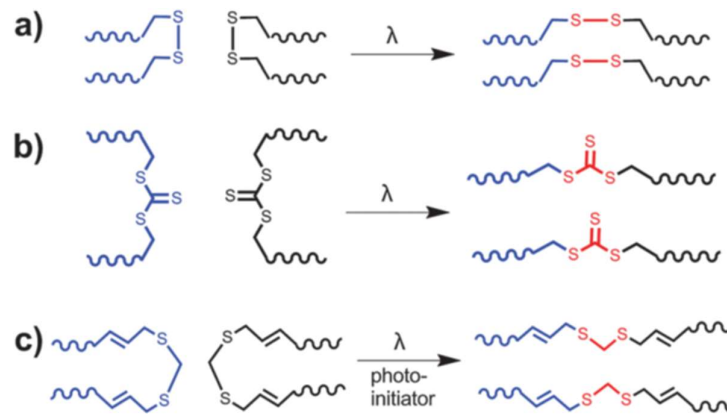
Fyra metoder valdes för att representera självläkning på grund av att ämnet är så pass brett. De följande metoderna valdes: värmeförorsakad självläkning, självläkning förorsakad av UV strålning, mekanokemisk självläkning samt inkapsling. Fyra experiment på basen av de fyra valda självläkningsmetoderna gjordes och jämfördes enligt kriterierna som nämns ovan.

Det finns både autonoma och icke autonoma självläkningsmetoder. De icke autonoma metoderna behöver något som utlöser självläkningen, som värme eller UV strålning medan de autonoma metoderna läker sig själva utan hjälp. De autonoma metoderna är mekanokemisk självläkning och inkapsling medan de icke autonoma metoderna är värmeförorsakad självläkning och självläkning genom UV strålning.

Värmeförorsakad självläkning baserar sig på kemiska bindningar som är reversibla. Dessa bindningar bryts upp när de värms upp till en tillräckligt hög temperatur och mobiliteten i den kemiska reaktionen ökar, till följd av detta läks repor som finns på ytan av materialet. Värmeförorsakad självläkning kan basera sig på många olika bindningar, jag valde att jämföra ett experiment som baserar sig på Diels-Alder bindningar på grund av att bindningarna har bättre egenskaper än alternativa metoder. Diels-Alder bindningar baserar sig på att en dien och en dienofil sammanförs. I det valda experimentet sammanförs en furan och en maleimid som utgör den termoreversibla bindningen.

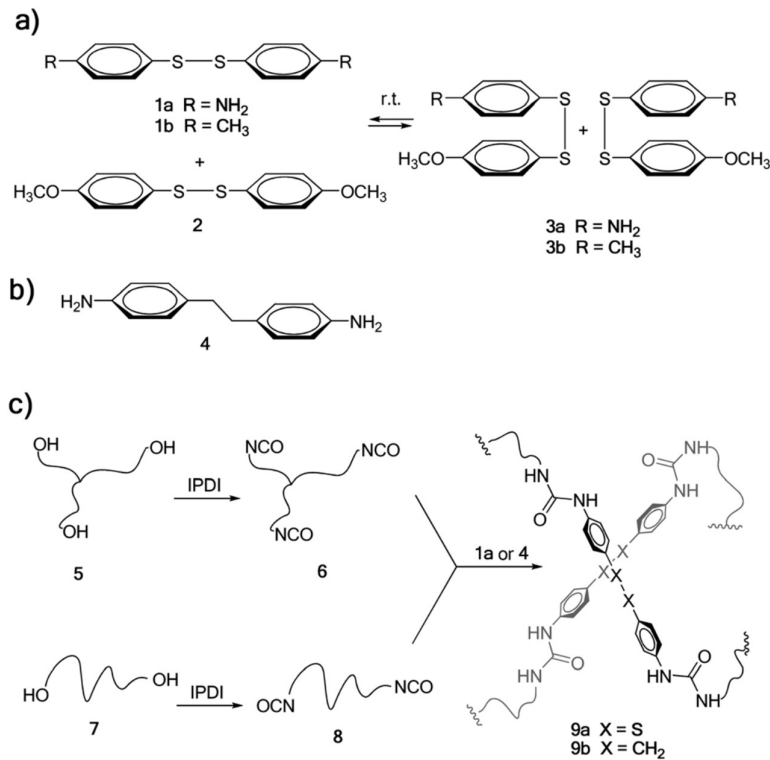
Självläkning förorsakad av UV strålning är liknande som den värmeförorsakade självläkningen. Också här används reversibla bindningar för att utlösa självläkningen. Skillnaden är att i detta fall bryts bindningarna upp när materialet utsätts för UV strålning. Den experimentella metoden som jag valde baserar sig på att blanda om trithiokarbonater. När trithiokarbonaterna blandas om så bryts bindningar som ligger på samma sida sprickan, upp och nya bindningar uppstår. En del av de nya bindningarna som uppstår

formas nu över sprickans yta och på så sätt läks sprickan i materialet. Figur 1 b visar hur den experimentella metodens kemiska bindning ser ut.



Figur 1, b) visar hur reaktionen som baserar sig på omblandning av trithiokarbonater ser ut (Habault, et al., 2013).

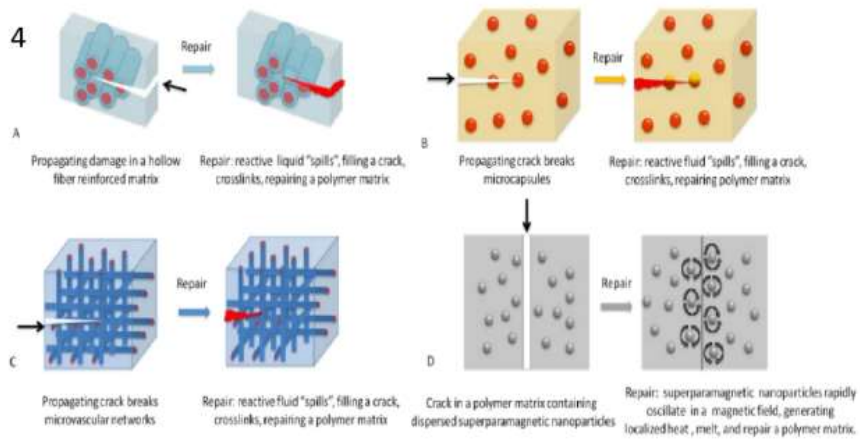
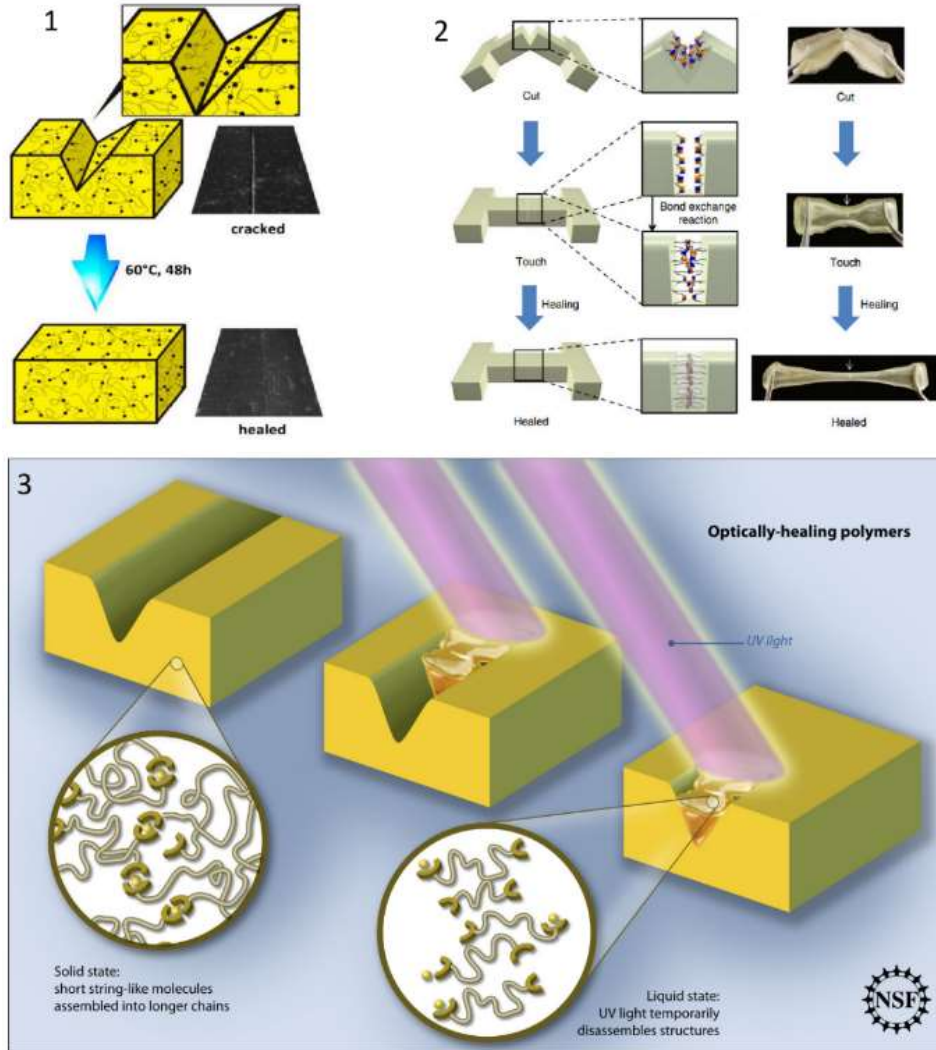
Mekanokemisk självläkning baserar sig på ett material som läker sig själv utan yttre krafter i rumstemperatur. Också denna metod baserar sig på svaga bindningar som bryts upp och återförenas. Problemet med mekanokemisk självläkning har varit att bindningarna är svaga eftersom dessa ska ha möjlighet att brytas upp och återförenas i rumstemperatur. Ett exempel är mekanokemisk självläkning med vätebindningar där de svaga vätebindningarna gör att materialet inte kan ha en hög mekanisk styrka. Dynamiska kovalenta bindningar som omformas i rumstemperatur kan vara en lösning på detta problem. Bindningarna är starkare och behöver i vanliga fall också yttre krafter för att rubbas. Eftersom denna metod är autonom så måste de dynamiskt kovalenta bindningarna försvagas. Som experimentell metod för den mekanokemiska självläkningen valde jag polyurea-uretan bindningar. Bindningarnas end grupper är sulfider, mer kända som aromatiska disulfider som bryts upp och återförenas i rumstemperatur. Figur 2a visar hur disulfidbindningarna ser ut och Figur 2c visar hur det självläkande materialet (9a) skapades.



Figur 2, a) vändbara bindningar som skapats av aromatiska disulfider, och c) bindingarna i det mekanokemiskt självläkande materialet (9a) (Rekondo, et al., 2014).

Inkapsling är en självläkningsmetod som använder kapslar som ligger inuti materialet. Kapslarna innehåller harts som läcker ut när kapseln går sönder, hartsen fyller sprickan i materialet och stelnar. Den stelnade hartsen har nu täckt sprickan som uppkommit i materialet och materialet har på så sätt läkt sig själv. Inkapsling kan delas in i fyra grupper: fiberförstärkt matris, mikrokapslar, mikrovaskulärt nätverk, och superparamagnetiska nanopartiklar. Jag valde mikrovaskulärt nätverk som experimentell metod för att representera inkapsling, på grund av att den är autonom och dess självläkande förmåga. De tre andra metoderna som representerar inkapsling har inte de båda ovannämnda egenskaperna.

De fyra valda metoderna kan ses på Figur 3 nedanför. 1. Representerar värmeförsakad självläkning 2. Representerar mekanokemisk självläkning. 3. Representerar självläkning genom UV-strålning och 4. Representerar inkapsling.



Figur 3, De fyra självläkningsmetoderna. 1. värmeförsakad självläkning. 2. mekanokemisk självläkning. 3. självläkning genom UV-strålning. 4. Inkapsling (Yang, 2016).

De fyra experimentella metoderna analyserades och jämfördes på basen av kriterierna som framkom i syftet: förmånlig att konstruera, bra självläkningsförmåga, användarvänlighet och lätt att producera.

Kostnaden för materialen räknades genom att räkna ihop utgifterna för de enskilda ämnen som behövs för att producera materialet. Kostnaderna jämförs i Tabell 1 nedanför.

Tabell 1, Kostnaderna för ämnen som behövs för att producera de fyra materialen, stimuli som behövs för att utlösa självläkningen nämns också.

Metod	Kostnad	Stimuli
Värmeförorsakad självläkning	775,5 €	Värme
Självläkning förorsakad av UV-strålning	699,75 €	UV-strålning
Mekanokemisk självläkning	709,10 €	-
Inkapsling	541,57 €	-

Självläkningsförmågan jämfördes med hjälp av tre faktorer: materialets återhämtningsförmåga, självläkningsantal, och självläkningstid. Syns i Tabell 2 nedanför.

Tabell 2, materialets återhämtningsförmåga, självläkningsantal och självläkningstid.

Metod	Materialets återhämtningsförmåga	Självläkningsantal	självläkningstid
Värmeförorsakad självläkning	≈ 100 %	2+	25 h
Självläkning förorsakad av UV-strålning	≈ 94 %	2+	8h 30 min/48 h
Mekanokemisk självläkning	≈ 97 %	2+	24 h
Inkapsling	≈ 80 %	≈ 30	48 h

Användarvänlighet, alltså hur lätt det är för användaren att självläka materialet. Skalan 1-4 bedömer i vilken mån kriterierna uppfylls, där nummer 1 är det bästa möjliga och nummer 4 är det sämsta (syns i Tabell 3 nedanför).

Tabell 3, Användarvänlighet bedöms med skalan 1-4. Nummer 1 representerar materialet som är lättast att använda medan nummer 4 representerar materialet som är svårast att använda.

Metod	Hur enkelt en konsument kan självläka materialet
Värmeförorsakad självläkning	3
Självläkning förorsakad av UV-strålning	4
Mekanokemisk självläkning	2
Inkapsling	1

Värmeförorsakad självläkning fick nummer 3 eftersom en värmekälla behövs för att utföra självläkningen t.ex. en ugn. Självläkning förorsakad av UV-strålning fick nummer 4 eftersom en UV-lampa behövs, som de flesta inte har tillgång till. Mekanokemisk självläkning fick nummer 2 eftersom att materialet måste vara i kontakt med sig själv för att få självläkningen att fungera. Inkapsling fick nummer 1 eftersom metoden inte behöver någonting för att utlösa självläkningen.

Sista kriteriet var att materialet måste vara lätt att producera, detta tydliggörs i Tabell 4 genom att jämföra både tiden det tog och utrustningen som behövs för att producera materialet som inte är tillgängligt i Arcada.

Tabell 4, hur enkelt materialet är att producera, tiden det tar för att göra materialet och utrustning som inte är tillgänglig i Arcada som behövs för att producera materialet.

Metod	Tid för att utföra syntesen	Utrustning som behövs för syntesen som inte hittas i Arcada.
Värmeförorsakad självläkning	34 dagar	-
Självläkning förorsakad av UV-strålning	≈ 44 h	-
Mekanokemisk självläkning	≈ 20 h	-
Inkapsling	≈ 85 h	Booster (Air pressure multiplier dispensing system), treaxlad depositionsplattform.

Resultatet av de fyra kriterierna sammanfattas och presenteras i Tabell 5 nedanför.

Tabell 5, sammanfattning av resultaten av de fyra kriterierna. Skalan 1-4 med 1 som bästa resultat (markerad med grön färg) och 4 som sämsta resultat (markerad med röd färg).

	Värmeförorsakad självläkning	Självläkning förorsakad av UV-strålning	Mekanokemisk självläkning	Inkapsling
förmånligast att konstruera	4	2	2	1
bästa självläkningsförmåga	1	3	1	3
bekvämt för användaren	3	4	1	1
lätt att producera	3	2	1	4
Totalt	11	10	5	9

Skalan i tabellen går från 1-4, nummer 1 representerar bästa möjliga resultat, medan nummer 4 representerar det sämsta möjliga resultat. Eftersom lägre nummer betyder ett bättre resultat i varje kategori, så är den självläkningsmetod med lägst antal totalpoäng den bästa metoden. Materialet som baserar sig på den mekanokemiska metoden är alltså det material som lönar sig att producera i Arcada.

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