Self-healing of Epoxy Polymers

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Srushti Subhash Chavan : I wish to follow research in food technology, contributing a little to country's development. I have started working towards my ambition from the first day of the college. My curiosity and interest was aroused while reading the magazines in our library.

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Abstract

Polymer coatings, especially the commonly used epoxy resin coatings are subject to repeated formation of cracks and microcracks. The location of these cracks may be such that it is difficult to detect and treat them. This bio-inspired self-healing polymer has the ability to repeatedly heal itself, even at the same location. It involves the crack induced self -healing mechanism comprising of a microvascular network, carrying a healing agent. On crack formation healing agent reacts with catalyst embedded in the coating to form the required filler material.

Keywords: Polymer, Epoxy resins, DCPD, Grubb's catalyst, ROMP.

1. Introduction

Polymers are extremely large molecules which are formed by covalently binding a number of smaller molecules. The word 'polymer' is derived from the Greek word 'poly' meaning 'many' and 'meros' meaning 'part'[1].

The uses of polymers are diverse. In every sphere of our life, we see polymers playing a crucial role. Be it plastic, rubber, various fibers, surface coatings or adhesives, polymers are seen to dominate! Even the constituents of living beings such as proteins, cellulose are bio-polymers.

However structural polymers are susceptible to crack formations and so on. These cracks may be formed quite deep in the structure, thus making it difficult to detect them. Their repair is thus rendered almost impossible. Micro cracking induced by thermal and mechanical fatigue is also a long standing problem in polymer adhesives. Regardless of the application, once crack formation occurs, structural integrity is essentially compromised[2].

When polymers are used in micro-electronic components[2] or aerospace components[3], even the minutest disturbances in structure or design can create havoc. Quick and precise healing is essential in such cases.

So, here we elaborate upon the upcoming solution- 'Self-healing polymers'.

2. What is a Self-Healing Polymer?

In order to understand this, the best analogy will be that of the healing occurring in biological systems. It comprises of an intense vascular network that supplies the necessary biochemical components required for repeated healing.

Similarly, the epoxy substrate of the self-healing polymer is in the form of network of microtubules which carry the healing agent to areas of the polymer that get damaged. Thus healing is brought about, restoring the structural integrity[4].

3. Design

Self-healing mechanism of our polymer has drawn its inspiration from the healing in biological systems. We can better understand this through a direct comparison with the wound healing process that occurs in human beings.

Our skin is a protective layer. The outermost layer is called the epidermis, which is composed of sub layers. The layer below this is the 'dermal layer' which supplies blood to the epidermal layer, thus providing the necessary bio-chemicals for wound healing as also simultaneously helping to maintain the temperature.

A cut in the skin initiates the healing process. The blood with the necessary components reaches the wound site. Clot formation takes place, thus healing the wound. This cycle can occur repeatedly at the same spot due to an unlimited supply of the nutrient-laden blood and other cellular material[5].

Similarly, this design consists of a microvascular substrate wherein the healing agent i.e. Dicyclopentadiene (DCPD) circulates. This network consists of horizontal and vertical channels about 2×10^{-4}m in diameter. The vertical tubules serve to carry the healing agent to the uppermost coating, which is a solid epoxy resin in which the crack development has occurred. Whereas the horizontal tubules help to keep the network filled with the healing agent at all times.

The upper solid epoxy resin coating has the catalyst; benzylidenebis(tricyclohexylphosphine)dichlororuthenium also called Grubb's catalyst, embedded in it. (Figure 1).

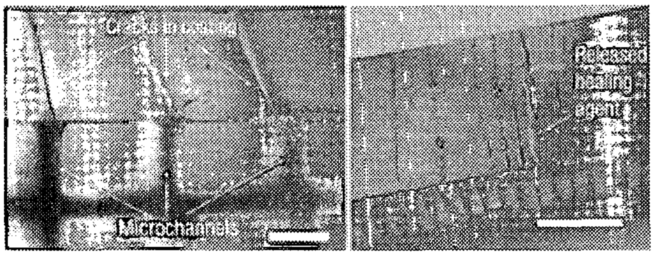


Figure 1 Microvascular Design

When a crack develops, healing agent rises due to capillary action. Embedded catalyst dissolves in crack-plane on coming in contact with the monomer, under ambient conditions. Thus the tough cross-linked polymer formed bridges the gap[2, 4, 5].

3.1. Design Previously Used

The design used prior to this bio-mimetic self-healing system comprised of microcapsules embedded in the epoxy substrate. The concept of a microvascular network was not used. The rest of the design was almost identical. The surface coating of a solid epoxy resin had catalyst particles embedded in it. The microcapsules were filled with the healing agent. When a crack was formed in the coating, and if it was deep enough, the microcapsule below it would also get ruptured. Thus the healing agent would enter the crack. It would react with the embedded catalyst to seal the crack in the coating. The material of which the microcapsule was made had to be selected with great care. It was necessary to consider properties such as thickness of the wall of the microcapsule, its toughness, relative stiffness and strength of interface between the microcapsule and the epoxy matrix[2]. (Figure 2).

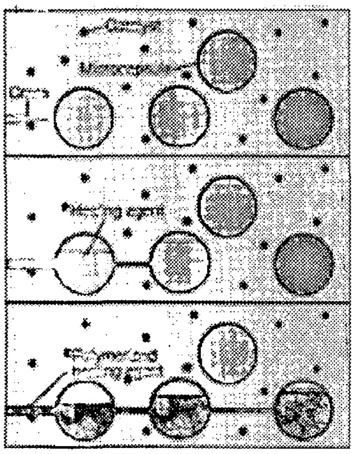


Figure 2: Microcapsule Design

Although this design also enables site-specific self-healing, it can allow healing only once. As soon as the healing agent from the ruptured microcapsule gets exhausted, healing is no longer possible.

4. Epoxy Resin

It is a class of polymeric materials consisting of one or more epoxide groups.

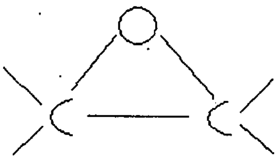


Fig.3. Epoxide Group

The word 'Epoxy' is derived from the Greek prefix 'ep' which means 'over and between' and 'oxy' the combining form of oxygen.

Epoxy resins were first offered commercially in late 1940s and now have significant industrial importance. This is primarily due to their diverse, useful properties like mechanical strength and toughness, resistance to chemicals, moisture and corrosion, low shrinkage upon cure and dimensional stability[1].

4.1 Applications[6]

They are used in

4.1.1 Protective coatings (use > 50%)

Epoxy resins are widely used in paint industry as they have a special property to get formulated into paints that have different physical forms and require different techniques of applications and excellent adhesion to many substrates. These resins are used for internal lining of pipes that carry natural and wet gas as it increases the throughput of gas and also gives corrosion protection.

4.1.2 Structural applications

Epoxy resins are used in filament winding, low and high-pressure moldings. It can also be used as the matrix in preparation of laminants, in which glass fiber is used as reinforcement.

4.1.3 Semiconductors encapsulants

Electronic components like capacitors, resistors, chokes, relays, printed circuits, transistors; diodes, thyristers, etc. are protected by resins as resin encapsulation provides better heat dissipation.

4.1.4 Adhesives

Epoxy adhesives are used for bonding smooth, non-porous surfaces of small area in relation to the size and weight of the object under repair. Epoxy resin provides good strength to the object. They are also used to bond and seal header tanks to tubes in equipments like tubular heat exchangers and oil operators. Epoxy adhesives also reduce fluttering and rattling of engine bonnets and boot lids of vehicles at high speeds. Underground railway tracks have been secured directly to the smooth floor of the tunnel by epoxy adhesive bonding, so that the tracks did not require ties or setting in gravel bed.

4.1.5 Aerospace components

Epoxy bonded honeycomb panels possessing high strength to weight ratios together with good thermal and vibration resistance are widely used in aircrafts, helicopters, space vehicles and satellites for fuselage doors, side panels, floors, elevators, rudders, trim tabs, pod assemblies, loading ramps, etc.

4.2 Recent uses

1. Lithographic inks
2. Photo resists for electronic industry

Due to all these remarkable properties, it is being used as surface coating and substrate in the self-healing of polymers[1].

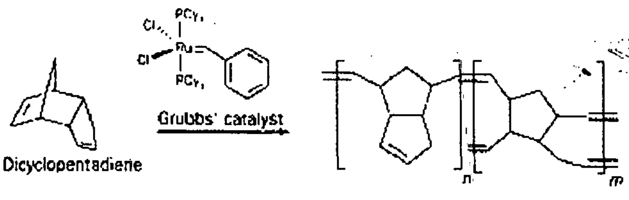
4.3 Preparation of microvascular substrate

Direct-write assembly method is used to make microchannels in the epoxy resin substrate. They are made using a fugitive organic ink together with a robotic deposition apparatus. Fugitive ink is composed of 60 wt% petroleum gel (Vaseline) and 40 wt% microcrystalline wax. This is placed in a syringe 2×10^{-4}m in diameter. At this stage, the epoxy resin is still in its uncured form. The syringe is held on a device that increases the pressure of air to approximately 2.9×10^{6} Pa. Microtubules thus fabricated are composed of an array of cylindrical rods of 2×10^{-4}m in diameter such that the distance between each of them is 2×10^{-3}m (i.e. ten times that of their diameter) in a given single layer. Layers are rotated by 90° and also shifted by 1×10^{-3}m in plane, thereby leading to the formation of a tetragonal geometry. The epoxy resin is then allowed to cure at room temperature for 48 hours. Finally the substrate is cut in the desired fashion and polished to obtain the required microtubules. Thereafter the fugitive ink is removed by heating the substrate to a temperature of 75°C, while simultaneously applying a light vacuum[7].

5. Healing mMechanism

5.1. Reaction

The polymerization reaction responsible for the self-healing is as follows[2]:



PCy$_3$ = Tricyclohexylphosphine

Fig.4 Cross linked polymer network

5.1.1 Metathesis

It is a reaction, which involves combination, decomposition and displacement.

A bimolecular process, involving the exchange of bonds between two chemical species which are reacting.

There are three types-

1. Sigma bond metathesis
2. Anion cation exchange metathesis
3. Olefin metathesis

5.1.2. Olefin metathesis

An organic reaction which involves redistribution of olefinic bonds. It can be represented as follows:

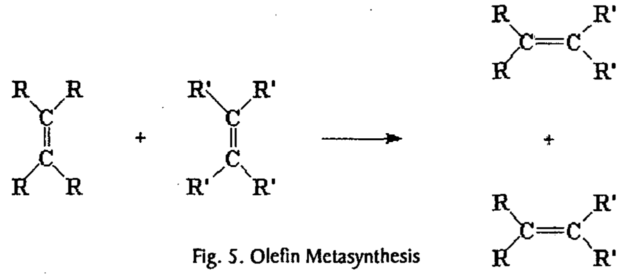


Fig. 5. Olefin Metasynthesis

This reaction was discovered in 1920s. Fifty years later scientists found out that this could be used to make tough polymers [16]. They are of two types-

1. Acyclic Diene Metathesis
2. Ring Opening Metathesis Polymerization

5.1.3. Ring Opening Metathesis Polymerization (ROMP)

Reaction used in the self-healing polymer is ROMP. Ring of an olefinic cyclic compound opens up to form a polymer.

Our healing agent endo-DCPD gives this reaction to yield poly DCPD, which is a polymer with a cyclic olefin in a pendant group. This pendant olefin can react to give a cross linked polymer.

This is the ring opening metathesis polymerization reaction (ROMP) of DCPD monomer in presence of Grubb's catalyst i.e.benzylidenebis(tricyclohexylphosphine)dichlororuthenium. This yields a solid, tough cross linked polymer which is used as filler material.

5.1.3.1. Mechanism of ROMP

Study of mechanism of this reaction shows that it is a dissociation reacting involving a 14 electron intermediate. It is seen that phosphine group of catalyst [(PCy $_3$) 2 (Cl$_2$) Ru CHPh] (Cy = cyclohexyl) is substituted by olefin substrate [17]. The impact of using different ligands on initiation rate of catalyst is being studied and a suitable combination for improved efficiency is being sought[18]..

Rapid polymerization can be obtained at even ambient conditions in several minutes.

5.2. Healing Agent

Dicyclopentadiene (DCPD)

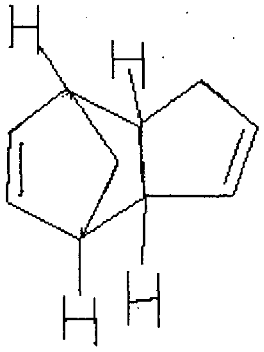


Figure 6. Structure of Dicyclo Pentadiene

IUPAC name: 4,7-methano-1, 4-indene-3a, 4,7,7a-tetrahydro.[8]

5.2.1. Preparation

DCPD is prepared by dimerization of CPD by the Diels-Alder Reaction [1].

[Diels-Alder reaction involves the 1,4 addition of an alkene to a conjugated diene to form an adduct of a six membered ring]

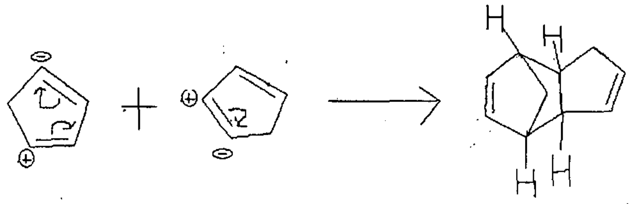


Fig. 7. Diel's Alder Reaction

DCPD

Cyclopentadiene (CPD) contains conjugated double bonds. Hence it can undergo Diels-Alder reaction with almost any unsaturated compound. This reaction is spontaneous and exothermic.

Steam cracking operation also yields DCPD and CPD as side products.

Healing agent should posses low viscosity in order to easily flow in the crack plane and also makes possible the complete coverage of exposed surface [5].

5.3. Benzylidenebis (tricyclohexylphosphine) dichlororuthenium (Grubb's Catalyst)

5.3.1 Structure

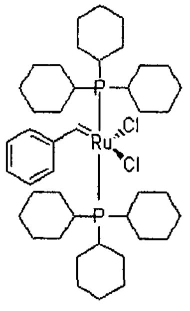


Fig. 8 Grubb's Catalyst

5.3.2 Properties

Ruthenium is a transition element and is capable of forming complexes.

In the early 1990s, Bob Grubbs developed a series of Ru catalyst [10]. In this Ru complex, the material is not in its highest oxidation state and is supported by PR_3 ligands. Catalyst shows great tolerance to functional groups like Bronstead acids and secondary amines. Some can even operate in H_2O[2]. Thus it is widely used as a catalyst in numerous reactions such as Ring Opening Metathesis Polymerization, Ring Closing Metathesis polymerization, Acyclic Diene Metathesis and Cross Metathesis reactions. It is a purple solid [12].

This catalyst is recyclable and may be more reactive than its homogenous counter parts. Besides its easy reactivity with dienes, makes it suitable for the title reaction.

5.3.3. Synthesis of Grubb's Catalyst

$RuCl_3$ and 1,5-cyclooctadiene are the primary ingredients, which are reacting to give a polymer complex.

This complex is then treated with Tricyclohexylphosphine and NaOH. The treatment is done under pressure with a supply of H_2 gas, at a temperature of 90°C. This yields $RuH_2(H_2)_2L_2$ (L=trihexylphosphine). This is then suspended in pentane. Further it is first treated with $PhCHCl_2$ to give the desired Grubb's catalyst[12]. For achieving better solubility in DCPD, Grubb's catalyst needs to be recrystallised using methylene chloride and acetone by a method described by Jones et al[13]. Resulting crystals of catalyst have rod like shape and average length of 10^{-5}m, diameter of 7.5×10^{-5}m which forms large groupings which have diameter 1.5×10^{-4}m [5].

Nowadays, a modified version of Grubb's initiator $[Ru(CHPh)Cl_2(Cy_2PCH_2SiMe_3)_2]$ (Cy = cyclohexyl) is also being studied for use in ROMP. This modification can give better control over molecular weight distribution of resultant product [15].

5.4. Effect of concentration of Grubb's Catalyst[5]

Concentration of Grubb's catalyst embedded on coating affects the number of healing cycles that can occur. The use of different concentrations of Grubb's catalyst i.e. 2wt%, 5wt% and 10wt% was studied by the following method:

5.4.1. Procedure

Initially a single crack is made to get induced in each of surface coatings containing different amounts of the catalyst. Acoustic Emission Sensor is kept on the beam to detect crack opening events during testing. The load on polymer at the time when the critical acoustic event occurs is noted using digital oscilloscope. The crack is then allowed to heal. Once again the crack is intentionally formed at same spot, avoiding use of testing material which develops multiple cracks. This cycle of loading, crack formation and healing is repeated number of times till healing can no longer take place. From the data thus obtained, one can analyze the toughness of polymers after one or more healing events. Healing efficiency can therefore be calculated using the formula:

$$\eta = \frac{P\ (\text{healed})}{P\ (\text{virgin})}$$

Where P is the applied load when crack occurs ? is the efficiency.

5.4.2. Observations

The observed results with regard to healing efficiency and toughness of newly formed polymer showed that a small scatter in the data occurs in different healing cycles and the peak recovery of 70% is achieved after the second healing cycle. Maximum number of times that healing can occur is seven. Beyond this the polymer is no longer is no longer healed.

It was found that when the concentration of the catalyst is 2 wt% healing could take place maximum three times. When it contained 5 wt% catalyst healing occurred maximum four times, while a concentration of 10 wt% allowed maximum seven healing events to occur. It was found that on an average two, three, four healing cycles occurred for concentrations of 2 wt%, 5 wt% and 10 wt% respectively. 0 wt% catalyst did not allow the process of healing. Grubb's catalyst gets deactivated to some extent due to amines in the uncured epoxy resin coating material. Hence the actual catalyst concentration is less than that mentioned.

Besides, the coverage of the fracture plane is also affected by the changes in catalyst concentration.2 wt5 and 5 wt% gave only scattered, localized good coverage of the fracture plane. On the other hand, 10 wt% gave nearly complete coverage.

6. Applications

6.1 Aerospace components

Space travel, research to find life on bodies other than earth, exploring asteroids, Kuiper-belt objects and so on, is on a forefront today. During these space voyages the smallest defect in design, in the form of fracture or crack etc. can lead to unsuccessful termination of mission with mere losses. This can well be avoided using this self healing polymer technique.

6.2 Microelectronic Components

Today, telecommunication and electronics are making our world smaller. The use of micro electronics is thus on the increase. Efforts are being made to decrease the size of electronic equipment and to improve communication. Defects in microelectronic components used therein, hinder their application. These defects are usually difficult to detect. Our self-healing polymer technique can help to solve this problem.

Pumps. These are heart of the plant and hence if they are shut down for repair can lead to great losses in terms of money, time and production efficiency.

This self healing polymer technique can also be extended further to brittle materials like ceramics and glass.

7. Advantages Over Earlier Self-Healing Techniques

Healing of polymers was a technique used previously as well. But those techniques used microcapsules filled with healing agent embedded in the epoxy resin substrate. A crack would induce rupture of these microcapsules; thus initiating the process of healing. However once a localized region was depleted of healing agent further repair at the same spot was not possible[2, 4, 5].

In our bio-mimetic self-repairing system recurring damage can be taken care of. The previous technique of self-healing polymers may be able to heal more than one times. However, that is possible only in the presence of external intervention in the form of heat treatment and application of pressure. On the other hand, our self-healing can take place under ambient conditions.

8. Limitations

The ability for repeated self-healing is limited by the amount of catalyst available. With each healing cycle, the active catalyst gets used up and its concentration decreases in the coating. Healing efficiency therefore decreases and finally healing stops when no more catalyst is accessible at the location although there is a continuous supply of the monomer.

8.1 Ongoing research to overcome limitations[5]

Research still continues to achieve unlimited healing cycles similar to that in biological beings. It involves the use of new microvascular designs based on integrated dual networks. For instance, two part epoxies may be used. Thus, this approach can further be extended to integrate pumps, valves and internal reservoirs, as also to introduce new functionalities like self-diagnosis or self-cooling through circulation of molecular signals, coolants or other species.

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