J. Applied Membrane Science & Technology, Vol. 28, No. 3, December 2024, 1–8

Self-healing Materials: Unlocking New Potential in Membrane Technology

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Submitted: 10/6/2024. Revised edition: 27/10/2024. Accepted: 27/10/2024. Available online: 12/12/2024

ABSTRACT

Damage to the membrane is a significant challenge in membrane filtration process. Water pollution has emerged as a significant environmental issue due to the rising of untreated or partially treated wastewater being directly discharged into the rivers or oceans. Self-healing material that has the ability to localise response to damage in the meantime has come under the spotlight as the alternative means to cope with the issue of declined performance of membrane due to mechanical abrasion. It can be classified into two categories which are extrinsic and intrinsic, respectively. Extrinsic self-healing relies on the integrated healing agent in the membrane matrix that response to damage while intrinsic self-healing depends on the dynamic bonds between the polymeric materials that will trigger the autonomous repair through reversible chemical bonds. This short review provides an overview of the self-healing mechanisms of various materials and their potential for developing membrane with self-healing capability.

Keywords: Water pollution, self-healing, membrane, extrinsic, intrinsic

1.0 INTRODUCTION

Water covers up to 71 % of the surface of the globe making it one of the essential needs to sustain the ecological processes, human activities and the natural processes [1]. However, with the rapid development of technology and the escalating demands of modern life, water pollution has become a widespread and persistent global issue. Recent studies revealed that over two-thirds of the world's population is experiencing severe water scarcity that causes illness, desertification, environmental degradation and economic impact [2]. The major contributors to water pollution and scarcity are the expansion of population growth, climate changes and industrial activities. It was found that 50 % of human-generated wastewater is dumped untreated into rivers or oceans, endangering both the environment and human health [3].

The sixth sustainable development goal (SDG 6) aims to ensure the accessibility of clean water and adequate sanitary facilities through the improvement of infrastructure, protection and restoration of water-ecosystem and hygiene education among the public [4]. Water reclamation is a recovering process of useable water from municipal wastewater to ensure water security.

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DOI: https://doi.org/10.11113/jamst.v28n3.299

Treated wastewater reuse has emerged as an alternative to resolve water shortages and expand water resources to some potential uses such as agricultural and urban irrigations, industrial reuse, and ecological recreation [5].

Dyes are a non-biodegradable and toxic prevalent water pollutant that harms the environment and human health. The release of residual dye from industrial activities into the aquatic ecosystems constitutes a significant threat to the global environment [6]. Tartrazine is one of the dyes found in the effluent from many sectors such as the textile, food and cosmetic industries [7]. Numerous research has highlighted the possible deleterious impacts associated with the excessive intake of tartrazine including food allergies, induce of asthma and chronic urticaria [8]. Therefore, it is dominant to filter out the dye from the wastewater before discharging the effluent for further usage.

Throughout the pathway in combating water pollution, researchers have gained interest towards membrane technologies for removing particles and sediments. The membrane filtration market is dominated in the water and wastewater application segment for more than 50 % of the total industrial usage [9]. Membrane Technology is an effective way to supply safe and clean drinking water and household usage as it reduces the use of chemicals in water treatment and offers benefits in terms of effective purification and lower operating costs [10].

Several disadvantages of membrane filtration arise, including superficial damage where microcracks or cuts occur on the surface, serious damage such as fibre debonding and molecular scale damage. The macroscopic damage can be detected easily, however, it is a challenge in identifying the exact microscopic damage location [11-13]. Self-healing materials emerged as a solution to regain some or all of their function after experiencing external damage [14]. The self-healing ability is classified into extrinsic and intrinsic self-healing mechanisms, which will be discussed in the later section [11]. The efficiency of self-healing depends on the localization, temporality and mobility of the self-healing agent. Localization refers to the location and the extent of the damage. Moving on to temporality, it refers to the time taken for the healing event to occur. It is very crucial to make sure that the healing event takes place before the damage becomes irreversible. In the concept of mobility, the healing agents must diffuse towards the damaged region for the self-healing event to take place, and the polymer chain movements must encourage the bond reversibility [15]. This in-situ healing technique helps in minimising waste and increasing product longevity. So, it is very crucial to equip the membrane with the self-healing capability to lengthen the membrane lifespan.

2.0 EXTRINSIC SELF-HEALING

In extrinsic self-healing techniques, the healing agent is encapsulated in the "container" such as the microcapsules, hollow fibres and microvascular network. The healing agent can be made of cross-linkable monomers and catalysts, liquid metal alloys or any compound that can aid in healing the damaged region [14]. As depicted in Figure 1, the healing agent is embedded in the polymer network [16]. When damage occurs, the encapsulated healing agent cracks, causing the chemical to leak out and subsequently healing event will occur. It is known as an autonomous process [14].

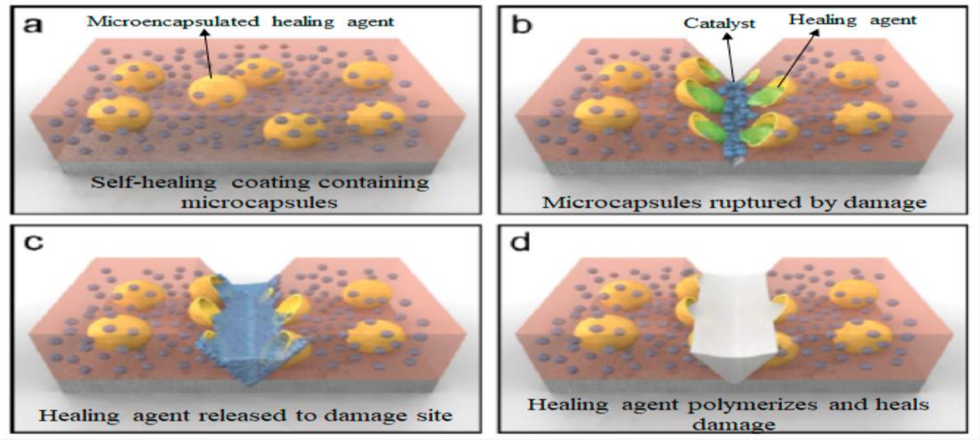

Figure 1 Mechanism of Extrinsic Self-healing [16]

Extrinsic self-healing mechanism is useful as the healing agent performs instantaneous localised response to damage without any external triggers [15]. Besides, it does not have to modify the chemical properties of the polymer to attain self-healing characteristics. However, the healing agent incorporated in the polymer during fabrication will be used up as the agent can only provide the reparation once. Therefore, once the healing agent is depleted, the polymer will lose its healing ability and the damage is irreversible [14].

The concept of microencapsulation self-healing mechanism was first introduced by White, *et al*. (2001) [17]. It was reported that the fabrication of microcapsules was done through the polymerization of urea-formaldehyde (UF) as the shell material. The study was done on an epoxy matrix which also contained Grubbs' catalyst that were mixed with microcapsules containing liquids dicyclopentadiene (DCPD) as the healing agent. When a microcrack developed in the matrix, it tends to expand and penetrate through the microcapsules results in the discharge of liquid DCPD to fill up the cracked damage area. Ring-opening metathesis polymerization (ROMP) process was triggered whenever the DCPD reacted with the Grubbs' catalyst forming a cross-linked network. The result showed a 75% fracture recovery in toughness which is applicable for other brittle materials.

In the work of Lee (2018) [18], microencapsulated technology had been demonstrated in membrane application. Since aromatic diisocyanates are more reactive than aliphatic ones due to their ability to give the N of the N=C=O group a negative charge, which facilitates the production of urethane bonds, aromatic toluene diisocyanate prepolymer (TDI) was used to produce the shell component. Furthermore, the methyl diphenyl diisocyanate (MDI) molecule was chosen as a core material due to its distinct relative reactivity despite sharing a similar molecular structure with the TDI molecule. Formation of the core-shell microcapsules was through the emulsification of both solutions. With the addition of 1,4 butanediol (BD) as the chain extender, BD and TDI had a dominating reaction that produced a polyurethane (PU) layer encircling the MDI core. The PU layer could prevent the diffusion of the water molecule into the capsules. With the addition of microcapsules, it showed that the water flux could be recovered after damage at different degrees. The healing efficiency was affected by the amount of microcapsules included. For instance, full recovery of water flux was achieved at 10 wt % of 0.1 g surfactant. In contrast, flux recovery decreased with the increasing concentration of surfactant due to the decrement effectiveness of the microcapsule breakage.

3.0 INTRINSIC SELF-HEALING

Another concept was intrinsic self-healing which depends on the chemistry of the dynamic bonds. Dynamic bonds can be categorised into two groups which are covalent and non-covalent bonds that are reversible under equilibrium conditions [15]. Due to its reversible properties, the material can be repaired after damage. The material is designed by functionalizing the interacting group between the polymer to perform the reversible healing process [14]. In contrast with the extrinsic method, the intrinsic self-healing mechanism is more stable as it does not have to encapsulate the healing agent into the matrix. As a result, intrinsic self-healing does not have the issue of depletion of the healing agent and it is capable of multiple recoveries [19]. healing mechanism has its drawbacks too. The healing process is relatively slower than the extrinsic method due to its slow kinetic bond reorganization. Besides, material recovery efficiency is highly dependent on the mobility of the reversible iterative reformation of the bond [14]. Therefore, it is very important to determine the functional group of the polymer matrix to ensure that the reformation of bonds between the functional group is applicable.

The mechanism of intrinsic self-healing is better explained in Figure 2 [20]. As the healing agent is in the form of a function group within the polymer matrix, the healing event will not be activated spontaneously when the damage happens to the polymer matrix. Unlike the extrinsic method, the intrinsic method normally needs an external stimulus such as heat, light, water or pH. These stimuli will trigger the reversible healing event to happen [19-20].

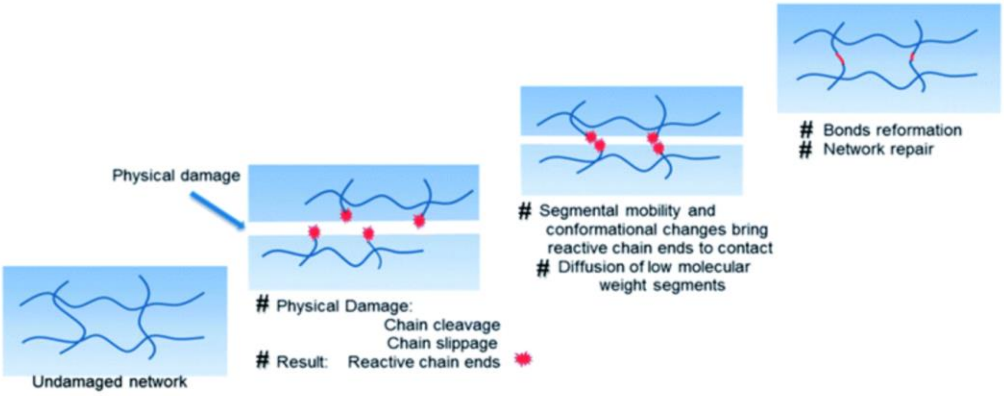

Figure 2 Mechanism of Extrinsic Self-healing [20]

3.1 Non-covalent Bond

The non-covalent bond refers to the intermolecular forces between molecules without the sharing of electron pairs. For example, the metal-ligand coordination, π-π stacking interactions and the most widely applied mechanism is the hydrogen bond. Less energy is required for the formation and breaking of non-covalent bonds, therefore this bonding is weaker. In addition, due to its low energy requirement, the application of these non-covalent reversible bonds is highly susceptible to the environment where diffusion of the healing agent can be effective even at room temperature. This contributes to the reversibility of the process as the damaged bond can easily and spontaneously be reformed without any external intervention [14].

A study done by Lan (2019) [21] demonstrated the first hydrogen-bonded self-healing photo-like membrane. The graphite carbon nitride (g-C_3N_4) acts as the nanosheet for water filtration and is catalysed with the Fe-containing polyoxometalates (Fe-POMs). It has been discovered that the re-polymerization of hydrolyzed molecules into dense membranes depends critically on the intermolecular hydrogen-bond interactions between carbon nitride nanofibers. It can be seen that the g-C_3N_4 membranes incorporated with the Fe-POMs could retain a constant COD rejection rate of about 40 % as compared to the pristine g-C_3N_4 after five batches of filtration experiment.

3.2 Covalent Bond

It was mentioned in the last Section 3.1 that non-covalent bonds are weak and unstable. Conversely, covalent bonds often have a higher bond energy, allowing the material to have satisfactory mechanical properties and the capacity to heal itself. Due to this fact, the covalent-based self-healing material requires an external stimulus as the energy needed to form bonds is greater than the thermal energy present at ambient temperature [14]. The self-healing efficiency of the associated polymer can be optimized by altering the types of reversible dynamic bonds and the mobility of the chain. It must also take into consideration the degree of damage. For instance, the interfaces of damaged positions need to be sufficiently close to one another at the macroscopic level to support the dynamic reorganisation process; at a molecular level, the resulting polymers must offer a large number of dynamic interactions to provide sufficient dynamics of the polymer chain [19].

There are few fabrication approaches for intrinsic covalent self-healing polymer while the best-known approach will be the Diels-Alder. Diels-Alder (DA) reaction is a thermally reversible reaction which is desirable to design for a heat-responsive self-healing polymer. The reversed action of the DA reaction is known as the retro-DA reaction where during high temperature, the respective functional groups were prone to regenerate and reforming bond upon cooling. The DA reaction is a cycloaddition between a diene and a dienophile with an electron-withdrawing group where the bond formed is thermally unstable. Taking furan-maleimide groups into the discussion, the maleimide group has two C=O bonds which are electron-withdrawing group that made the maleimide group electron insufficient and more reactive to the diene group which is furan in this case as shown in Figure 3 [22]. However, a simple DA reaction between one furan and one maleimide exhibited comparatively poor chain mobility which limits the polymer from the self-healing application [22].

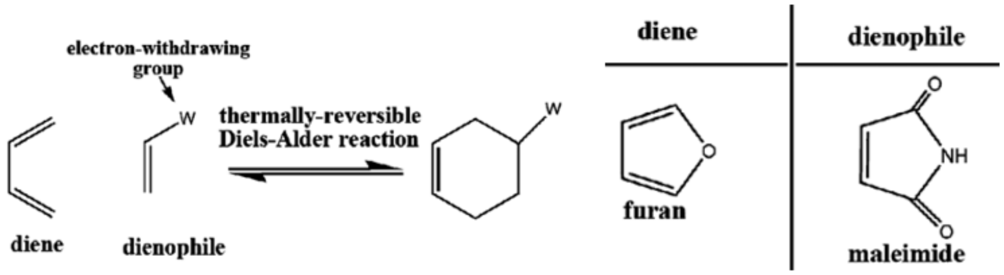

Figure 3 Diels-Alder Reaction Between Diene and Dienophile [22]

Further modification has been made on the furan-maleimide group to have better self-healing efficiency through DA reaction. As reported by [23], multi-furan (F) and multi-maleimide (M) were used to form a highly cross-linked polymer known as 3M4F. The research showed that in the polymer network of 3M4F, the retro-DA reaction was more preferable than a bond-breaking degradation event when the heat was induced to it. With the healing temperature between 120 to 150 °C, it was observed that the self-healing efficiency could reach about 41% and 50%, respectively. This showed that the thermal-sensitive polymer projected a better self-healing effect during high temperature. Also, several healing cycles were tested during the experiment, proving that the DA reaction between furan-maleimide group were applicable for multiple healing cycle with a recovery of 80% [23].

3.3 Others

Apart from that, the disulfide bonds is an alternative to perform self-healing. The mechanism was classified into a [2+2] metathesis and a [2+1] radical-mediated. The disulfide bonds break and form concurrently in the [2+2] metathesis reaction mechanism. A 97 % of the healing efficiency was achieved in the reaction between poly(urea-urethane) based on aromatic disulfide metathesis, suggesting the possible complete recovery in the performance [24].

4.0 CONCLUSION

The exploration of self-healing mechanisms in membrane technology presents a promising avenue for enhancing the durability and efficiency of membranes used in various applications, particularly in water treatment. Self-healing membranes are designed to autonomously repair damage, thereby extending their operational lifespan and maintaining performance without the need for frequent replacements or manual repairs. Both extrinsic and intrinsic self-healing approaches offer unique advantages and contribute to the overall efficacy of self-repairing membranes. The main difference between both mechanisms is the repeating healing ability in the intrinsic approach compared to the single-healing in the extrinsic mode. The distinct properties of both mechanisms make a great impact on the self-healing performance in the membrane technology. Some recommendations arise in the choosing of suitable mechanism such as the bonding interaction between the polymeric materials in order to achieve the maximum self-healing capability. Besides, future studies on the fabrication method such as the formation of polyelectrolyte multilayer (PEM) and factors affecting the self-healing performances, for instance, the stability of the bonding between the polymeric materials need to be considered as well.

ACKNOWLEDGEMENT

The authors would like to thank UTAR for providing facilities and guides to finish this project.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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