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Flame-Retardant Self-Healing Polymers: A Review

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Abstract: *Flame retardant self-healing polymers are materials that can withstand fire and repair themselves. They can be used in a variety of applications, such as fire protection materials, protective creams, and fire extinguishers. Developing multifunctional flame retardants (FRs) has become a strategy to reply on needs for advanced polymers. Self-healing polymers are an emerging class of advanced polymeric materials, which have been upgraded progressively, and recently have taken the advantage of fire safety. Correspondingly, diverse industries like aerospace, automotive, construction and consumer electronics are benefited from flame-retardant self-healing polymeric materials, which underlines their increasing contribution to modern technologies. The self-healing characteristics stem from intricate chemical and physical interactions, adopting self-directed repair mechanisms leading to eliminating the need for frequent replacements, subsequently lowering maintenance costs and environmental impact. This review summarizes advantages of self-healing polymers with emphasis on exploring highly innovative advancements among bio-based hydrogels, aerogels, coatings, thin films, lithium-ion batteries and advanced ionotronic skin (-i-skin) structures embedding sensing features for smoke detection and flame exposure warnings, further broadening their application in smart technologies and safety-critical infrastructure. The outcomes of reports outline challenges remaining in developing such multifaceted materials in view of lack of information due to limited or exclusive investigations. However, further research may facilitate exploring dehydration, thermal shielding, and free radical quenching mechanisms contributing to flame retardancy performance of flame-retardant self-healing polymers. Sustainability and circular economy requirements are briefly discussed, in addition to outlining remarks on future developments.*

Keywords: flame retardancy; polymer composites; fillers; magnesium hydroxide; fire; thermal properties; cladding

I. INTRODUCTION

Self-healing polymers are synthetic or artificially-created substances that have the built-in ability to automatically repair damages to themselves without any external diagnosis of the problem or human intervention.

Self-healing polymers are smart materials that can heal themselves after damage and restore their original sets of properties.

Self-healing polymers are smart materials that can heal themselves after damage and restore their original sets of properties . The spontaneous self-healing capabilities offer alternative solutions for damage repair of polymers, especially for crosslinked thermosets that are conventionally unrepairable and un-processable. Self-healing polymers are receiving growing interest in a wide variety of applications to promote the survivability and lifetime of polymeric products such as electronics, health care monitoring, and protective equipment.

To date, self-healing polymers can be broadly classified into two categories based on their self-healing mechanisms, namely the extrinsic self-healing and intrinsic self-healing . For extrinsic self-healing materials, the healing agent is usually embedded in the polymer matrix through microcapsules or vascular networks. During the polymer fracture, the capsules or vascular networks break, which releases the healing agents that can react with each other or interact with the matrix to heal the crack surfaces. Extrinsic self-healing is desirable for many applications that require automatic healing of damages without manual intervention. However, due to the consumption of a healing agent, it is less effective to repair the second damage at the same location of the material.

Self-healing polymers are materials that can repair themselves after damage, restoring their original properties. They are a growing area of research in materials science and engineering, and have many potential applications.

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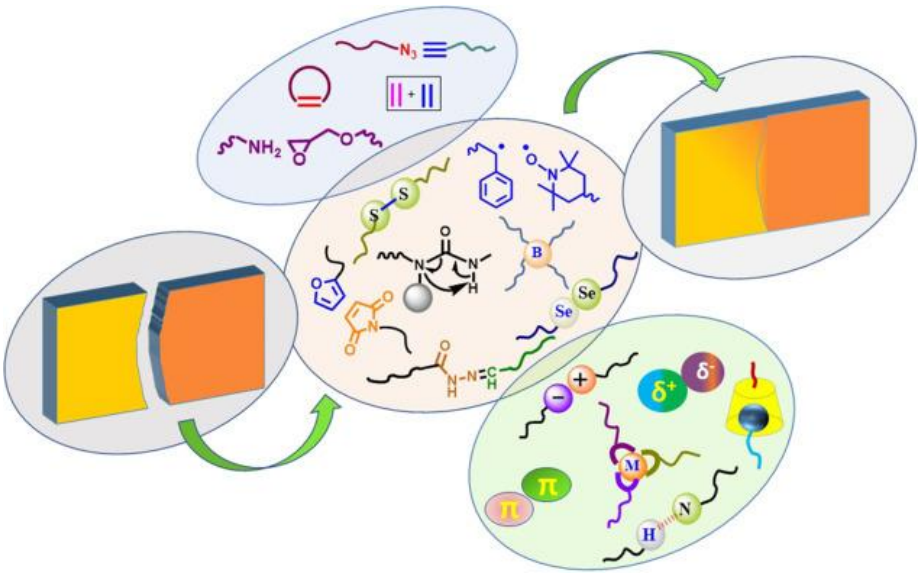
On the other hand, intrinsic self-healing materials based on dynamic bonding have been rapidly developed, which are repeatable without the concern of depleting the healing agent.

Polymer substrates capable of self-healing are beneficial for electronic devices as a means to extend the service time and reduce maintenance costs. Strategies for developing self-healing polymers have moved toward avoiding the complex integration and compatibility concerns over extrinsic healing agents. The efficient self-healing is generally realized through the formation of reversible interactions between the dynamic polymer chains of two fractured surfaces. However, on the macroscopic level, the voids in the highly porous polymer mesh prevent it from providing adequate close interfaces for the dynamic reorganization to occur. Thus most published researches on self-healing nanofibers are still based on the concept that the self-healing agents are encapsulated in the core parts of core-shell fibers . The phenomena that surface area decreases with temperature and time on the same timescale constitutes a unique property for self-healing materials. Based on that, the completely pure electrospun self-healing nanofibers mesh without any matrix polymers or additives are firstly reported using the aromatic disulfide-based. The interfibrillar fusion resulted from self-healing is observed because the fibrous structure tends to aggregate for reduced thermodynamic free energy over time, finally resulting in a transparent nonporous film. This report serves an inspirable strategy for the fabrication of self-healing fibers by synthetic novel polymers with appropriately controlled glass transition temperature (Tg) through special molecular engineering, so that the interfibrillar fusion at the temperature above the Tg can be realized. However, further exploration on polymer nanofibrous mesh with reversible self-healing feature and scalable fabrication approaches are still desired and may be accessible on the progress of polymer chemistry.

Self-healing polymer materials have received great attention in the past two decades due to the minimization of system breakdown, decrease in the cost of maintenance, and increased working life with increased safety index. Designing self-healing polymeric material requires the interplay of chemical reactions and physical network remodeling. This chapter deals with various chemistries involved in the development of self-healing polymeric materials. Three main chemistries of self-healing systems are irreversible covalent bond formation via extrinsic microcapsules self-healing process, reversible dynamic covalent chemistry, and reversible supramolecular interactions to improve the multiple healing times through intrinsic self-healing process. The development of self-healing polymer is just advancement of the conventional polymers by introducing self-healing properties which are utilized in various fields such as biomaterials, bioelectronics, sensors, actuators and coating, paints technologies, electronics or energy devices such as membranes, 3D/4D printing, tissue engineering, soft robotics skin, and analyze their potential for real-world high-performance applications.



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Applications of Self-Healing Polymers

The class of polymers that are capable of repairing/healing in response to damage or cracks and have the ability to restore their original functionality with/without any external stimuli via a combination of chemical and/or physical processes are known as self-healing polymers . According to Wool and O'Connor, the principle stages of healing of thermoplastic polymers are: (a) surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion, and (e) randomization. Self-healing can be achieved through extrinsic or intrinsic healing mechanisms [18]. The extrinsic healing mechanism is achieved by incorporating an external healing agent in the form of microcapsules or micro-vascular networks and a catalyst. A damage event rips the microcapsules or micro-vascular networks and releases the monomer into the crack plane, where it comes into contact with a catalyst and triggers polymerization to heal the crack. For instance, Dietrich et al. [19] dispersed microcapsules containing liquid dicyclopentadiene (DCPD) in an epoxy matrix containing a Grubbs catalyst. Upon damage, microcracks form and propagate, and when they penetrate through the microcapsules, the liquid DCPD is released. The liquid comes in contact with the catalyst and undergoes ring-opening metathesis polymerization to form a cross-linked network that eventually heals the cracks. On the other hand, intrinsic self-healing materials are based on dynamic supramolecular, noncovalent interactions or dynamic covalent bonds [20]. Self-healing can also be achieved using metal-ligand coordination bonds.

II. CONCLUSIONS

Self-healing polymeric materials or smart materials are inspired by the self-healing property of biological membranes in humans as well as in plants. The microencapsulated healing material displays better healing efficiency than the vascular and shape-memory healing strategies. The process of self-healing for regaining the deformities is activated by various physical and chemical reactions like Diels-Alder conjugation, π-π bonding, randomization, diffusion, etc. resulting in greater stiffness and higher healing efficiency in the nanocomposites. Polymeric materials are widely used in the medical field as they are easily available and cost-effective. The further use of self-healing composites provides improvement in fatigue resistance and greater tensile strength extending the applications in material science as well as in biomedical field for tissue engineering, wound healing and implantation by healing the biological membrane and tissues without any replacement. Such nanocomposites are also used in drug delivery system for loading the drug and targeting it to site-specific and sustained release actions, wherein the self-healing of the material is triggered by pH, heat or light. Although research studies reported the self-healing properties of polymers, very limited evidence is available on self-healing polymeric materials. Several ambiguous principles and mechanisms need to be focused on before analyzing the composites in biological systems and extend the applications in polymer sciences, engineering and biomedical field. The progressive approaches and studies for developing ideal self-healing polymers are required for the enhancement of applications with superior physical and chemical properties. Moreover, incorporation healing agents in next-generation polymeric material would impart certain properties like self-diagnosis, self-control and self-healing into the formulation and serve as a crucial material for various applications. These vast-arrays based concepts might be useful for further development of ultimate materials and offers an opportunity for the treatment of several conditions like bone and dental injury, cancer therapy, etc

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