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Self-Healing Polymers: Integrating Dynamic Bonds and Shape Memory Repair Mechanisms-a Review

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Abstract

Self-healing polymers (SHPs) are advanced materials designed to autonomously repair damage, inspired by biological systems. Initially, SHPs focused on embedding healing agents within polymers that would release upon damage. Over time, technological advancements have led to the integration of dynamic covalent and supramolecular bonds, enabling molecular-level self-repair without external intervention. SHPs now address not only mechanical integrity but also the recovery of electrical and optical functionalities. Mechanisms for self-healing include encapsulation of healing agents, dynamic bonds, nanomaterials responding to external stimuli, and shape memory effects (SMEs). Despite significant progress, challenges remain in balancing mechanical strength and self-healing efficiency. Research is ongoing to enhance the interplay between chemical and physical processes in self-repair, with a focus on sustainable materials. Synthesis methods for SHPs involve various chemical processes, such as microencapsulation, dynamic cross-linking, and reversible bonding techniques. Applications of SHPs span automotive, electronics, and energy storage industries, offering benefits like reduced maintenance costs, extended lifespan, and improved durability. Recent innovations include high-performance polymers capable of operating in harsh environments and more commercially viable, eco-friendly materials.

Keywords: “Self-healing Polymers” “Dynamic Bonds” “Shape Memory Repair”
“Supramolecular” “Interactions” “Mechanical Strength” “Sustainable Materials” “Chemical Processes”



1. Introduction

Self-healing polymers (SHPs) are designed to autonomously repair damage, inspired by biological systems, to enhance longevity and performance. Initially, they mimicked natural repair mechanisms, focusing on embedding healing agents within polymers that would release upon damage. Technological advancements have led to the integration of dynamic covalent and supramolecular bonds for molecular-level self-repair without external intervention [1-3]. The concept has evolved to address not only mechanical integrity but also the recovery of electrical and optical functionalities, highlighting the need for polymers that restore multiple properties after damage [8]. Technological advancements have integrated various mechanisms for self-healing. Encapsulation involves microcapsules filled with healing agents that are released when the material is damaged. Dynamic bonds and nanomaterials respond to external stimuli, facilitating the healing process. Shape memory effects (SME) have also been crucial, allowing materials to revert to their original shape, thereby closing cracks and restoring integrity [4]. Despite progress, challenges persist in balancing mechanical strength and self-healing efficiency. The need for sustainable materials due to environmental concerns has driven further research. Current studies focus on improving the interplay between chemical and physical processes in self-repair, exploring how molecular architecture affects shape memory-driven repair [5-7]. For a polymer to be capable of shape memory, two structural elements are required “Figure 1”: (A) permanent net points/junctions and (B) reversible molecular switching segments [63-65].

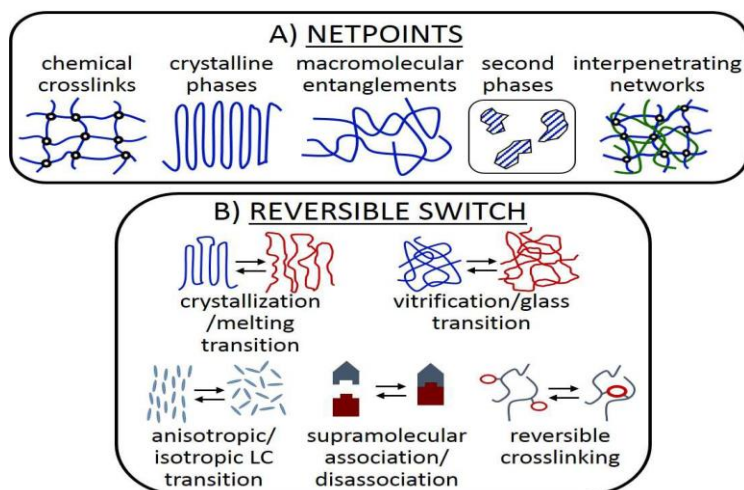


Figure 1. Structural requirements for shape memory polymers (SMPs): (A) The net-points/junctions can consist of chemical crosslinks, crystalline or glassy secondary phases, macromolecular entanglements, or interpenetrating networks. (B) The reversible molecular switch can be achieved using reversible crosslinking, supramolecular association/disassociation, or the glass, melting, or liquid crystalline (LC) transition. [66]

Recent innovations include developing high-performance polymers with enhanced self-healing properties, capable of operating in harsh environments. Efforts have also been directed at making these materials more commercially viable by refining polymerization techniques and integrating

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eco-friendly, sustainable materials [16]. Recent advances in materials capable of self-healing can be classified by a handful of approaches: (1) embedding reactive encapsulated fluids that burst open upon crack propagation to fill and repair damaged areas, [9,10] (2) incorporating reversible covalent and non-covalent bonds into existing structures capable of rebounding after damage, [11] (3) physically dispersing superparamagnetic or other nanomaterials that remotely respond to magnetic, electromagnetic, or other energy sources, [12,13] and (4) embedding living organisms capable of re-mending damaged structural features [14,15].

2. Mechanisms

These mechanisms illustrate the multifaceted approaches in developing self-healing polymers, which utilize a combination of physical, chemical, and potentially biological mechanisms to restore properties after damage. Understanding these mechanisms is crucial for advancing self-healing materials that mimic biological systems and provide practical applications. Each mechanism plays a critical role in how these materials recover from damage and maintain functionality, enhancing durability and longevity. The integration of these mechanisms into material design can lead to innovative solutions in various structural applications, ensuring the durability and longevity of materials.

2.1 Physical Mechanism

These mechanisms rely on the intrinsic properties of the polymer material itself, often involving physical interactions such as van der Waals forces or entropic recovery. For instance, the viscoelastic shape memory behavior allows the polymer to return to its original shape after deformation, utilizing its molecular mobility and entropic energy to facilitate healing without external intervention [17,18]. Solvent-assisted self-healing can enhance chain mobility across interfaces, allowing for healing through chain interdiffusion and entanglement, relying on physical properties rather than chemical reactions [19]. Interchain diffusion, crucial for self-healing in polymers, involves polymer chains moving across damaged areas to restore integrity by filling gaps [20]. Phase-separated morphologies enhance self-healing by improving phase interactions during damage [20]. Shape-memory effects in some polymers aid healing by realigning damaged areas [20]. Active nanoparticles can trigger self-healing by promoting chemical reactions or physical interactions [21,22]. Non-covalent interactions such as hydrogen bonding, van der Waals forces, and ionic interactions allow dynamic rearrangement of polymer chains, essential for self-healing, with systems combining dynamic bonds showing promising capabilities [23]. Microphase separation organizes polymer domains to inhibit chain slippage during deformation, maintaining integrity and allowing shape recovery [24,25]. Viscoelastic shape transformation releases stored energy to bring wound edges into contact for healing, similar to biological systems [fig s12,14]. Physical mechanisms enable materials to recover from damage without altering their chemical structure, through the reformation of physical bonds or movement of polymer chains, activated by stimuli like heat or pressure. In self-healing metals, mechanisms like liquid-based and solid-state healing (e.g., precipitation hardening) rely on atomic or molecular movement to close cracks and restore integrity [26] “Figure 2”.

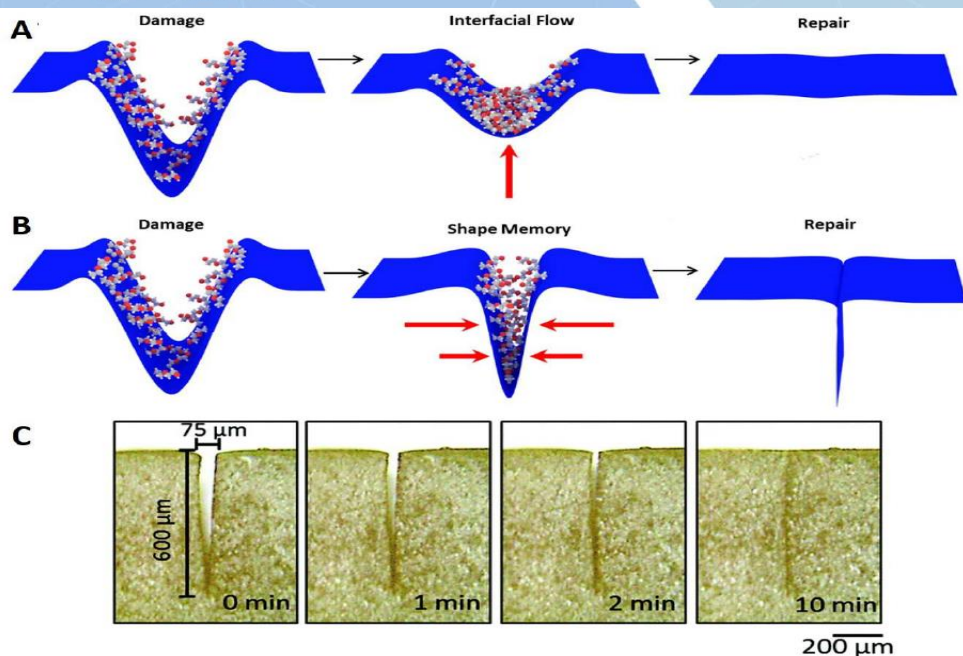


Figure 2. Graphic depiction of physical repair mechanisms driven by (A) interfacial flow and (B) shape memory. [67]. (C) Optical microscope images of shape memory driven wound closure of a polyurethane film [68].

2.2 Chemical Mechanism

Chemical mechanisms involve the formation and reformation of chemical bonds to repair damage, including dynamic covalent bonds that can break and reform under specific conditions, restoring the material's strength and integrity [27]. These mechanisms may involve chemical reactions at the damage site, re-bonding fractured surfaces, either intrinsically through macromolecular interactions or extrinsically with pre-embedded healing agents [19]. Covalent bond formation techniques, such as dynamic covalent bonding, create new bonds to repair damage [4]. Supramolecular chemistry uses non-covalent interactions, like hydrogen bonding or ionic interactions, enabling reversible, repeated healing [21,22]. The reactive chain ends with reactive groups at polymer ends facilitate healing by forming new bonds upon damage [21,22]. Dynamic covalent bonds that reform after breaking allow materials to recover integrity, essential for designing effective self-healing materials [23]. Dynamic bonds capable of reversible breaking and reforming, such as urethane-urethane hydrogen bonding in microphase-separated polymers, enhance self-healing [24]. Reversible interactions between polymer segments, like urethane-ester interactions in nanophase-separated polymers, influence the healing process [24]. Chemical mechanisms refer to chemical reactions that repair damage, including the formation of new bonds or rearrangement of existing ones, with examples like supramolecular chemistry facilitating healing through interactions like hydrogen bonding [28-32]. These mechanisms may also involve the release of healing agents that chemically bond to damaged surfaces, sealing cracks [26].

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2.3 Biological Mechanism

Biological mechanisms refer to self-healing processes inspired by biological systems, such as organisms' ability to heal wounds, mimicking these processes in materials [20]. Metabolic processes in mammals, like the inflammatory response and collagen production, are key to healing wounds [20]. In plants, damage triggers chemical signals initiating repair, similar to synthetic materials designed to respond to damage [20]. The article parallels synthetic systems with biological self-healing processes, noting that understanding these processes can inspire synthetic material development [33-36]. Biomimicry of natural systems, like *Delosperma cooperi* leaves healing wounds through tissue bending or contraction driven by stored elastic stress, is highlighted [24]. Biological mechanisms mimic natural healing processes found in living organisms, such as skin healing after a scrape, inspiring biomimetic self-healing materials [37]. Biological mechanisms involve bio-inspired strategies to enhance self-healing in synthetic materials [37].

3. Self-healing Polymers

Self-healing polymers (SHPs) can be categorized based on their mechanisms and material compositions. [Acrylate/Methacrylate-Based Polymers] utilize reversible plasticity-type shape recovery to facilitate self-healing. Upon exposure to heat, they recover from indentations created at ambient conditions and can be engineered to exhibit specific healing properties depending on the formulation used [27]. [Polyurethanes] undergo shape memory effects due to their hard and soft segments. When heated, they recover their original shape, effectively healing scratches or cuts. Their ability to store and release energy during the damage-repair cycle is crucial for their self-healing capabilities [27]. [Epoxy] exhibit shape memory effects, enabling recovery from damage under thermal conditions. The combination of their chemical structure and thermal responsiveness makes them suitable for various applications requiring durability and repairability [27]. [Polycaprolactone (PCL)-Based Thermoplastic Polyurethanes] feature a semi-interpenetrating network structure. PCL chains diffuse across damaged areas upon heating, facilitating wound closure and restoring mechanical strength [38-40]. [Nanomaterial-Enhanced Polymers] incorporate nanomaterials that respond to external stimuli, such as magnetic fields or heat, improving the overall efficiency of the healing process [41].

Self-healing polymers can also be categorized into intrinsic and extrinsic types. [Intrinsic Self-Healing Polymers] heal through physical, chemical, or supramolecular interactions without external agents. Examples include [Polyurethane], which uses hydrogen bonding and other non-covalent interactions to facilitate healing, and [Polyethylene], which reforms physical bonds upon heating [19]. [Extrinsic Self-Healing Polymers] require external healing agents, such as microencapsulated materials, which are released upon damage. Examples include [Microencapsulated Healing Agents] within the polymer matrix, which break and release healing agents to restore the polymer's integrity, and [Thermosetting Polymers] that incorporate microcapsules filled with reactive monomers that polymerize upon release, effectively sealing cracks and restoring mechanical properties [19]. [Hybrid Self-Healing Polymers] combine intrinsic and extrinsic mechanisms, using polymer blends to benefit from both healing processes, enhancing their overall performance and durability [19,42,43].

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Other notable types include [Capsule-Based Self-Healing Polymers], which use microcapsules filled with healing agents embedded within the polymer matrix. When damaged, the capsules break, releasing the healing agent that fills the cracks and restores the material's integrity [44,45]. [Vascular-Based Self-Healing Polymers] incorporate a vascular network within the material, allowing for a continuous supply of healing agents to the damaged area, enhancing the healing process [44,45]. [Polymers with Combined Self-Healing Mechanisms] integrate intrinsic healing with capsule or vascular systems, leveraging the advantages of multiple mechanisms to improve healing efficiency and performance [46-48]. [Covalent Dynamic Bond-Based Polymers] use dynamic covalent bonds that reform after being broken, while [Noncovalent Dynamic Bond-Based Polymers] rely on non-covalent interactions like hydrogen bonding to achieve self-healing [44,49].

[Dynamically Cross-Linked Polymers] utilize reversible covalent or non-covalent interactions, allowing the material to flow and re-establish connections when damaged. [Shape Memory Polymers (SMPs)] can return to a predetermined shape when exposed to a specific stimulus, such as heat, facilitating self-healing by reverting to their original form after deformation. [Bioinspired Self-Healing Polymers] mimic biological healing processes, incorporating mechanisms similar to those found in human skin or other biological tissues [16].

[Microphase-Separated Polymers] exhibit distinct microdomains, allowing for enhanced mechanical properties and self-healing capabilities. The microphase separation creates regions that can store elastic energy during deformation, crucial for shape recovery after damage [9-11]. [Nanophase-Separated Polymers] have smaller domain sizes, contributing to their self-healing efficiency due to their unique domain sizes and degrees of heterogeneity [24]. [Living Organism-Embedded Polymers] incorporate biological components for healing, mimicking biological systems that autonomously repair themselves [50]. [Self-Healing Composites with Dispersed Agents] act like a clotting mechanism, where healing agents are released to fill cracks and initiate the healing process, while those with [Vascular Networks] mimic biological blood vessels, allowing for a continuous supply of healing agents [37]. [Hydroxyl End-Functionalized Polymers] participate in chemical reactions to facilitate healing [26]. Self-healing polymers are crucial for applications in electronics and energy devices, enhancing their reliability and durability [51].

4. synthesis

Self-healing polymers can be synthesized using various methods that leverage different chemical mechanisms.

Reversible Bonding Techniques: Dynamic cross-linking involves dynamic cross-linkers with reversible bonds like Diels–Alder bonds, facilitating self-healing at elevated temperatures. Molecular networks are designed with both reversible and permanent cross-linking sites to maintain structural stability while allowing chain mobility during healing [52].

Microcapsule-Based Strategies: Healing agents are encapsulated in microcapsules that break upon damage, releasing the healing agent to repair the polymer. This approach can trigger healing at specific temperatures, matching operational conditions of polymer dielectrics (50–80 °C). Anionic

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polymerization uses anionic polymerization where the initiator is integrated into the epoxy's molecular chain, minimizing the catalyst's negative impact on dielectric properties [53].

Coordination Chemistry: Utilizes metal ions and ligands to form coordination complexes that link polymer chains, allowing for disassociation under mechanical stress and reformation upon stress removal, enabling self-healing [54-56].

Reversible Chemistry: Intrinsic self-healing polymers are synthesized using reversible chemistry, including supramolecular interactions or dynamic covalent bonds, allowing polymers to re-bond after damage [57].

Supramolecular Interactions: Uses interactions like hydrogen or ionic bonds to create networks with both strength and healing capabilities. For example, a double-network elastomer can be created by altering the supramolecular network [58].

Tailoring Molecular Structures: Adjusting the polymer backbone or incorporating specific functional groups to enhance healing properties improves mechanical strength and self-healing efficiency [57].

Environmental Stability Enhancements: Strategies like creating micelle-like structures or grafting protective groups onto polymer chains shield dynamic bonds from moisture and other environmental factors, improving stability [8].

Composite Approaches: Incorporating fillers or other materials into the polymer matrix enhances mechanical properties and self-healing capabilities, improving toughness and durability [57].

Reaction Synthesis: Promising for fabricating nanocomposites, particularly those difficult to obtain through traditional sintering. Nanometer-sized SiC particles synthesized through this method enhance self-crack healing rates [26].

Catalytic Processes: Catalysts like CuBr_2 combined with 2-methylimidazole form complexes used in self-healing applications, resulting in a high production rate [59,60,61].

Diels-Alder Reactions: Modified monomers dissolved in a solvent undergo cross-linking upon heating to form a solid film. This reaction can be reversed (retro-DA) by applying heat, allowing the material to re-establish the cross-links and heal itself [26,62].

Hydrolysis and Chemical Reactions: Hydrolysis can initiate the healing process by cutting the carbonate bond in a polymer, increasing the concentration of reactive end groups that can recombine and heal the material. Specific catalysts are often required to accelerate the reaction [26].

the synthesis and production methods of self-healing polymers are diverse and involve various chemical processes, including microencapsulation, reaction synthesis, catalytic reactions, Diels-Alder reactions, and hydrolysis. Each method contributes to the unique properties and

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effectiveness of self-healing materials. These synthesis methods are crucial for developing self-healing polymers that can be effectively integrated into electronic and energy devices, enhancing their durability and functionality [51].

5. Applications

Self-healing coatings and materials are used in automotive paint and interior components [27]. These materials recover from minor scratches and dents, maintaining aesthetic appeal and reducing the need for repairs, leading to lower maintenance costs and improved vehicle longevity [27]. In the automotive industry, self-healing polymers (SHPs) are used for coatings and interior materials to autonomously repair scratches and dents, enhancing vehicle longevity and aesthetic appeal, and reducing the need for repairs and maintenance. They are integrated into components like bumpers and panels to recover from minor impacts [19]. Self-healing polymers in tires can automatically seal punctures, enhancing safety and extending tire lifespan, reducing the need for frequent replacements and maintenance, and contributing to sustainability [8]. Self-healing coatings protect automotive surfaces against scratches and minor damages, maintaining the aesthetic and functional integrity of vehicles over time [8]. These polymers in coatings and components enhance durability by automatically repairing scratches and minor damages, maintaining the aesthetic and structural integrity of vehicles. Applied in vehicle interiors (dashboards, seats), these polymers recover from wear and tear, extending component lifespan. The automotive sector features self-healing clear coats like Nissan's "Scratch Guard Coat," which repairs scratches from car washes, off-road driving, or fingernails, restoring aesthetics for up to three years [26]. Self-healing materials enhance the durability of automotive components, reducing maintenance costs and extending vehicle lifespan, especially in high-wear areas like bumpers and body panels. Self-healing polymers are utilized in flexible electronics, circuit boards, and protective coatings [27]. They can repair micro-cracks and damage in electronic components, ensuring reliability and extending the lifespan of devices, which is particularly important in wearable technology and smartphones. SHPs are increasingly applied in the electronics sector for flexible and durable components, such as protective coatings for screens and casings, allowing self-repair from scratches and cracks. This property is valuable in consumer electronics where device longevity and appearance are critical. Furthermore, self-healing polymers can be used in circuit boards, enhancing reliability by recovering from mechanical stress or damage [19]. In flexible electronic devices, SHPs repair themselves after mechanical damage, maintaining functionality in wearable technology and other flexible devices [8]. They are also employed in the encapsulation of electronic components, providing protection against environmental factors and recovering from minor damages, ensuring longevity and reliability [8]. In the electronics sector, SHPs are crucial for flexible devices like wearable electronics and electronic skins, recovering from mechanical damage to ensure continuous functionality and reliability [51]. They are integrated into energy storage devices such as batteries and supercapacitors, restoring electrical conductivity after damage and enhancing longevity and performance [51]. In flexible circuits and displays, self-healing materials recover from scratches and damage, maintaining functionality and appearance, crucial for consumer electronics subjected to wear and tear. Self-healing coatings can protect electronic devices against environmental damage like moisture and dust, enhancing longevity and reliability of electronic components.

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Self-healing materials are applied in aircraft components and structural materials [27]. These polymers can autonomously seal cracks and damages that may occur during flight, enhancing safety and reducing the risk of catastrophic failures. This is vital for maintaining the integrity of lightweight materials used in modern aircraft. In aerospace applications, SHPs are crucial for enhancing the durability and safety of aircraft components. They are used in structural components that experience fatigue and stress during flight, reducing maintenance costs and improving the lifespan of critical parts like wings and fuselage. Self-healing coatings also protect against environmental damage such as corrosion and abrasion, common in aerospace environments [19]. In structural components, SHPs autonomously repair cracks and damages, enhancing safety and reducing maintenance costs [8]. In composite materials for aircraft, self-healing polymers improve durability and performance, significantly extending the lifespan of aerospace components [8]. These polymers can autonomously repair micro-cracks and damages during flight, maintaining safety and performance at high altitudes and under varying pressure conditions. Incorporating SHPs into composite materials provides an additional layer of safety by ensuring damage can be repaired without extensive maintenance [51]. The aerospace industry increasingly utilizes self-healing polymers in composite materials to recover from micro-cracks and damages, ensuring structural integrity and safety [26]. Additionally, self-healing polymers are being explored for space applications, where their ability to autonomously repair damage is critical for maintaining the functionality of spacecraft and satellites.

Self-healing polymers are explored for use in medical devices, implants, and drug delivery systems [27]. They can provide enhanced biocompatibility and the ability to recover from mechanical stress, which is essential for devices that experience movement within the body. Additionally, self-healing properties can improve the longevity and functionality of implants. The medical field benefits from SHPs through their application in wound dressings and implants, where they can mimic biological tissues and provide a conducive environment for healing. In wound care, these materials can autonomously close and protect injuries, reducing infection risk and promoting faster recovery. In implants, SHPs enhance biocompatibility and longevity, allowing better integration with the body and reducing the need for replacement surgeries [19]. Self-healing polymers are being explored for use in biomedical devices, such as implants and prosthetics, where they can adapt to the body's environment and repair themselves, maintaining functionality and biocompatibility [8]. In wound dressings, these materials can mimic the natural healing process, providing a protective barrier while promoting tissue regeneration [8]. SHPs are beneficial in applications like stents and prosthetics due to their ability to heal after mechanical stress, enhancing biocompatibility [51]. Self-healing materials are being developed for artificial bones and teeth, extending the service life of implants and improving patient outcomes [26]. Additionally, self-healing materials in wound dressings respond to damage by sealing wounds and promoting healing, beneficial in medical settings.

6. Challenges

The development of self-healing polymers presents significant challenges related to sustainability, durability, and environmental impact. One primary goal is to minimize energy consumption and waste production, aiming for efficient designs that support recycling or upcycling, contributing to a circular economy [4]. Ensuring durability is crucial, especially for long-lasting applications like

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construction or transportation, which require polymers with tunable properties to meet various needs [4]. The environmental impact of materials used in these polymers must be carefully managed, considering their entire lifecycle from production to disposal to prevent ecological damage [4]. Designing polymers to mimic biological systems involves complexity, as it requires a deep understanding of molecular features and interactions, potentially increasing resource consumption [4]. Integration into existing manufacturing and recycling systems is challenging, necessitating compatibility with current technologies and collaborative efforts across industries [4]. The balance between self-healing efficiency and mechanical strength remains a key issue; faster healing can lead to softer, less durable materials [48]. Standardizing methods for evaluating self-healing efficiency is lacking, making it difficult to compare different materials [48]. Additionally, the energy-intensive production processes for these polymers raise concerns about their environmental footprint [24]. Ensuring that self-healing materials are environmentally friendly involves addressing trade-offs between performance and sustainability, such as improving physical properties while managing recycling efforts [16,24]. Overall, while self-healing polymers offer promising solutions, overcoming these challenges is crucial for their successful development and environmental compatibility.

7. Conclusion

The development of self-healing polymers represents a significant advancement in materials science, offering solutions to enhance the longevity and functionality of various applications. The integration of dynamic covalent and supramolecular bonds has allowed SHPs to repair at the molecular level autonomously, without external intervention. This evolution has extended the capabilities of SHPs from merely restoring mechanical integrity to recovering electrical and optical properties, making them versatile for a wide range of industries including automotive, electronics, and energy storage.

Despite these advancements, challenges remain in optimizing the balance between mechanical strength and healing efficiency. Ongoing research aims to improve this balance, focusing on sustainable materials that address environmental concerns. Future directions include enhancing the interplay between chemical and physical processes in self-repair mechanisms and exploring new molecular architectures that improve shape memory-driven repair processes.

The promising applications and continual innovations in SHPs suggest a future where materials can self-repair efficiently, leading to reduced maintenance costs, extended product lifespans, and improved overall performance in various high-demand environments. Continued interdisciplinary research and development are essential to overcoming existing challenges and fully realizing the potential of self-healing polymers in practical applications.



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