Self-Healing Elastomers

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It is impossible to describe the recent progress of our society without considering the role of polymers; however, for a broad audience, "*polymer*" is usually related to environmental pollution. The poor disposal and management of polymeric waste has led to an important environmental crisis, and, within polymers, plastics have attracted bad press despite being easily reprocessable. Nonetheless, there is a group of polymeric materials that is particularly more complex to reprocess, rubbers. These macromolecules are formed by irreversible crosslinked networks that give them their characteristic elastic behavior, but at the same time avoid their reprocessing. Conferring them a self-healing capacity stands out as a decisive approach for overcoming this limitation. By this mean, rubbers would be able to repair or restore their damage automatically, autonomously, or by applying an external stimulus, increasing their lifetime, and making them compatible with the circular economy model.

self-healing materials | self-healing rubbers | natural rubber | synthetic rubber | dynamic networks | supramolecular chemistry

1. Introduction

In the actual environmental context, polymers like rubbers are particularly critical due to their reprocessing difficulties. These macromolecular materials are composed of irreversible crosslinked networks that act as "*anchor points*", preventing the flow of polymeric chains. Consequently, the material cannot be reshaped [1], and a considerable amount of rubber waste could be generated. One of the strategies to solve this issue has been the recovery of end-of-life rubbers for their use as a diluent or reinforcing filler in new composite materials [2][3][4][5][6]. Also, the selective breaking of the crosslinking points, known as devulcanization [7][8][9][10][11], has been extensively studied; however, both strategies are considered insufficient. Thus, the redesign of crosslinked rubbers is mandatory. Most recent redesign strategies point toward building dynamic networks [1][12][13].

The creation of crosslinked polymers with dynamic networks has spawned a new generation of polymers known as DYNAMERS (*DYNAmic polyMERS*) [14][15]. The construction of these networks is based on multiple dynamic bonds and/or supramolecular interactions, like hydrogen bonds [16][17], ionic interactions [18], metal–ligand coordination [19], disulfide exchange [20], and Diels–Alder chemistry [21][22], among other covalent, non-covalent mechanisms and/or combinations between them [23][24][25][26][27][28][29][30]. The reversible nature of these networks can be controlled by an external stimulus, which can be temperature, pressure, electrical current, magnetic field, or further changes in the medium, such as pH [31][32][33][34][35]. In this way, the stimuli-responsive material would be able to release its

"*anchor points*", allowing the flow of its chains until it reforms and/or repairs. In fact, the use of dynamic networks is the most widespread self-healing strategy used in rubbers [1].

2. To Boldly Go Where No Material Has Gone before: Self-Healing Concepts

Self-healing is the ability to repair or restore damages [36][37][38][39]. To scientifically understand healing as a physical process, four key concepts must be considered in rubbers: (1) Mechanism, (2) Mobility, (3) Localization and (4) Temporality [40]. In elastomers, the success of the self-healing process goes hand in hand with the adequate selection of a mechanism that guarantees the necessary molecular mobility of the polymeric chains, as well as enough time for the restoration of the damage according to its location (on a macroscopic or microscopic scale) [41].

The first concept is the *mechanism*. Self-healing can occur extrinsically or intrinsically [42][43]. Extrinsic mechanisms are based on an external healing agent that is incorporated into the matrix in an encapsulated form, in vascular networks or freely dispersed. When damage occurs, these agents are released and/or flow through the damage area, sealing it. Despite being the first mechanisms used, according to the historical development, their use in rubbers is very limited due to the difficulties of preserving the stability of the agent during the conventional mixing process of rubber recipes (enormous shear forces) [40].

The intrinsic mechanisms are based on the creation of crosslinking points using dynamic covalent bonds or supramolecular interactions. On one hand, dynamic covalent bonds activate this character under different external stimuli and can occur through an associative or dissociative pathway. The associative pathway is characterized by a constant crosslink density during the exchange. Meanwhile, the dissociative one is characterized by a change in the crosslink density over time, due to an independent reformation and formation of the bonds [15][44]. On the other hand, supramolecular interactions are non-covalent in nature and have also been shown to be successful strategies to achieve repairability [15][45][46].

From a general point of view, intrinsic mechanisms can be classified as [42]:

1. Non-covalent intrinsic mechanisms, such as hydrogen bonds, ionic interactions, metal–ligand coordination, among others; and,
2. Covalent intrinsic mechanisms, such as disulfide bond exchange (associative), Diels–Alder chemistry (dissociative), transesterification reactions (associative), bonds based on boron and imines chemistry (dissociative), among others.

In recent years, the creation of hybrid networks by multiple combinations of covalent and non-covalent mechanisms has become remarkably widespread [1][40].

The second concept is *mobility*. It is a priority concept for self-healing, regardless of the mechanism. In the case of the intrinsic ones, the mobility of the chains will be mandatory to guarantee the success of the exchange reactions. If the rubber network is very impeded, more severe conditions are required (e.g., high temperatures) that could seriously compromise the stability of the material [40].

The third concept is *localization*. It is related to the scale of the damage. According to the literature, repair on a microscopic scale is easier than on a macroscopic one. This is completely expected from the physical point of view. In addition, this localization will also have a considerable influence on the repair conditions. At larger scales, the required repair conditions will be more severe [40][41].

The last concept is *temporality*. Ideally, self-healing would be an automatic process, but in practice, it is time-dependent. This dependence is also strongly related to the external stimulus used. One of the greatest complexities of self-healing as a scientific strategy stems from the consideration of all these variables and conditions that must be exhaustively optimized to guarantee a compromise between self-healing capacity, mechanical performance, and material integrity [40].

3. Current Developments in Self-Healing Elastomers

3.1. Self-Healing Natural Rubber

Natural rubber (NR) consists of *cis*-1,4-polyisoprene chains [47]. It is the only natural macromolecule completely constituted by carbon (C) and hydrogen (H) atoms, obtained from multiple varieties of plants and fungi, where the most commercially representative is the *Hevea Brasiliensis* tree [48]. NR is characterized by having high elasticity, even in the unvulcanized state, due to a naturally occurring network of the non-rubber components, which is responsible for its green strength and facilitates the strain-induced crystallization behavior characteristic of this material [49][50][51][52][53][54].

NR has its origin in South America, but currently, the largest production is concentrated in Southeast Asia, with Thailand and Indonesia concentrating more than 50% of the world's production. Among its most common applications is the manufacture of large tires, especially for aircraft, vehicles, and heavy machinery, as well as bridge mounts, anti-vibration devices, conveyor belts, and other high-performance elastomeric parts [47].

Due to the demands of its processing, NR is not among the most studied rubbers for self-healing; however, Spanish scientists were pioneers in the study of this material, taking advantage of the existence of sulfur crosslinked points that can serve as healing moieties. **Table 1** shows the studies available in the literature.

Table 1. Self-healing natural rubber research conducted in Spain (2012–2022).

Matrix	Mechanism	Healing Moieties	Filler	Reference
NR	Covalent intrinsic	Diels–Alder chemistry	Unfilled	[55]
ENR	Non-covalent intrinsic	Hydrogen bonds	Unfilled	[56]
NR	Covalent intrinsic	Disulfide exchange	Graphene oxide	[57]
ENR	Combined intrinsic	Hydrogen bonds + Transesterification reactions	Graphene oxide	[56]

3.2. Self-Healing Synthetic Elastomers

Most commercially relevant elastomers are of synthetic origin, representing over 55% of world production [58]. From a basic point of view, synthetic rubbers and elastomers have been created to replace NR in those scenarios where it does not perform well: at high and low temperatures, outdoors, in contact with petroleum-derived solvents, as well as to avoid gas permeability. Styrene-butadiene rubber (SBR), carboxylated nitrile rubber (XNBR), silicone elastomers and poly(urea-urethanes) (PUU), are some examples. **Table 2** shows the studies available in the literature on self-healing materials (identified as elastomers or rubbers by their authors).

Table 2. Self-healing synthetic elastomers research conducted in Spain (2012–2022).

Matrix	Mechanism	Healing Moieties	Filler	Reference
SBR	Covalent intrinsic	Disulfide exchange	Unfilled	[41][59]
XNBR	Non-covalent intrinsic	Ionic interactions	Unfilled	[60]
PUU	Covalent intrinsic	Disulfide exchange	Unfilled	[61][62]
Polyamide ionene	Combined intrinsic	Ionic interactions + Hydrogen bonds + π-π stacking	Unfilled	[63]

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Matrix	Mechanism	Healing Moieties	Filler	Reference
Ionic elastomer	Non-covalent intrinsic	Ionic interactions	Unfilled	[64]
SBR	Covalent intrinsic	Disulfide exchange	GTR [1]	[59][65]
SBR	Covalent intrinsic	Disulfide exchange	dGTR [2]	[66]
XNBR	Non-covalent intrinsic	Ionic interactions	GTR	[60]
Silicone elastomer	Covalent intrinsic	Thiol exchange	Ag nanoparticles	[67]

[1] Ground tire rubber (GTR) from end-of-life tires. [2] Devulcanized ground tire rubber (dGTR) from end-of-life tires.

4. Challenges, Perspectives, and Outlook

Until now, different matrices (natural and synthetic) with potential industrial applications have been studied. However, there is still much work to be done. Although it is true that efforts point towards the scalability of self-healing concepts in commercial applications, a comprehensive understanding of the underlying self-healing mechanisms, as well as the optimization of its conditions, is still pending. The redesign of elastomeric compounds to exhibit this capability requires the consideration of three main conditions (**Figure 1**):

1. The construction of a dynamic but stable and robust network serving temperatures to guarantee excellent mechanical performance,
2. The minimization of components that can hinder the mobility necessary to achieve healing (e.g., secondary irreversible networks) and,
3. The optimization of the appropriate conditions (temporality and external stimulus) for each repair mechanism. In turn, these conditions must be compatible with the material stability, to avoid its deterioration during the healing protocols.

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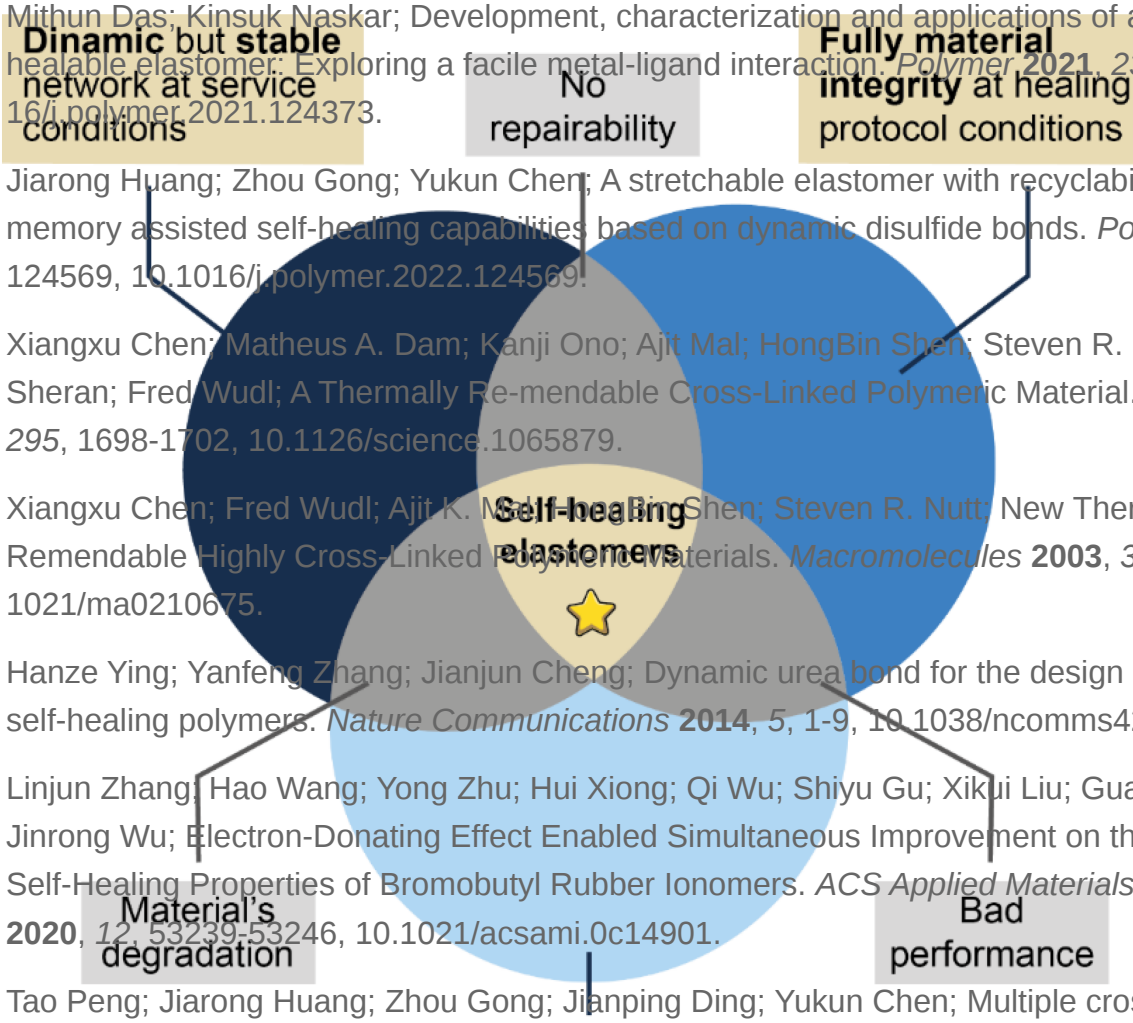

Figure 1. Venn diagram illustrating optimal healing conditions.

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On the other hand, the commercial prospect, and the corresponding life cycle assessment (LCA) that corroborates its environmental impact. When all these conditions are matched, the massive scalability of self-healing materials will be an irreversible fact, and we will have taken one of the definitive steps towards the consolidation of a truly sustainable society.

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