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Review



Self-Healing Elastomers: A sustainable solution for automotive applications

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ABSTRACT

Among the most fruitful material-industry relationships is that of rubber and the automotive industry. Tires, seals, gaskets, hoses, tubes, soft, and damping parts are common applications in an industry that consumes more than 75 % of world rubber production. However, this relationship faces significant challenges. The difficulty of reprocessing rubbers due to their irreversible crosslinked network that ensures thermal stability, mechanical robustness and chemical resistance, makes them incompatible with the Circular Economy model. Numerous efforts are coordinated daily to overcome the Linear Economy model and achieve more environmentally friendly rubbers. Strategies like devulcanization, recycling, and self-healing are already being considered by several researchers and industries. Thanks to self-healing, a tire will be able to seal damage due to punctures or cracks. Thanks to self-healing, materials will be able to live longer and thus have an extended lifetime. This review delves into the key concepts of self-healing in the most commonly used elastomeric matrices in the automotive industry. While a more application-oriented approach is still necessary, the first steps have been taken towards future scalability in the sector. By analyzing the state-of-the-art taking into consideration the nature of the elastomeric matrix (natural or synthetic), as well as the different healing mechanisms (extrinsic, intrinsic and combinations), the chemistry behind them, and the mechanical performance, this review highlights the potential transformative impact of these concepts to revolutionize the industry and pave the way for a more sustainable future.

1. Introduction

Periods of human history have been classified according to the use that has been given to materials to satisfy humans basic needs. The discovery of new materials and the advance in the manipulation of those already known have implied reforms in social structures and have served to understand the evolution of humankind.

In the nineteenth century, cellulose was isolated, Charles Goodyear discovered vulcanization and patented it in the United States of America, while Thomas Hancock did the same in the United Kingdom, and Leo Baekeland invented bakelite, which would undoubtedly be the starting point of an industrial and commercial phenomenon. Despite these developments, the bases of polymers were still not understood, until in 1922 Hermann Staudinger published an article in which he presented the term *Macromolecule* (*Makromolekül*), thanks to the study of the Natural Rubber (NR) structure [1,2]. Later on, in 1950, the advances in the polymerization of polyethylene and polypropylene, allowed polymers to take over the scientific scene and industrial development [3,4].

Polymers brought with them huge advances to most industrial sectors. In fact, the world, as we know it today, is unimaginable without these materials; but certainly, the most prolific relationship that was consolidated in this period, between a material and a manufacturing sector, has been that between rubbers and the automotive industry.

While rubbers are also used in many other industries such as electronics (in cable sheathing, casings, buttons and keys), construction (in insulation, shock absorbers, flooring and roofing), aerospace (in seals and gaskets), medical (in gloves, syringes and catheters) and food (in conveyor belts), more than 75 % of the world's rubber consumption is dedicated to the automotive industry, and its rise has been essential for understanding the popularity of the automobile as a key transportation system in modern society. However, its use has not been limited only to automobiles, on the contrary, airplanes, short and long-distance trains and ships have also made rubber an essential material [5].

A modern automobile contains hundreds of parts, many of these made from rubber in their different forms (latex, soft rubber, hard

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rubber or foam rubber) [5,6]. The most impressive ones are tires, one of the greatest engineering achievements in the history of humankind. Tires can be made of at least three or four types of rubber (in its passenger version) that allow them to achieve the desired properties. Other classic applications worth mentioning are the seals, gaskets and hoses, essential for the correct operation of the engine, as well as internal and comfort parts.

Cooperation between the rubber and the automotive industry has been crucial in modern society, however, this cooperation faces some challenges. In the current environmental context, in which polymers have been presented as an environmental threat, the development of new advanced materials that fulfill different purposes such as the mimic of the strain-induced crystallization (SIC) of NR, the non-requirement of polluting additives to have a suitable performance, as well as the functionalization of the structure of the material that allows to obtain an adequate elastomeric behavior and an extended lifecycle, have required an additional scientific endeavor. Moreover, in the framework of the Circular Economy (CE) consumption model [7,8], elastomers and thermosets are incompatible because, despite great efforts, their reprocessing continues to be a demanding task. Thus, it has become essential to make them compatible with the CE model extending their lifetime, and one way to achieve it is by conferring them a self-healing capability. Thanks to self-healing properties, a tire would be able to repair itself after a puncture or, when cracked by ozone and/or oxygen degradation, a hose would be able to overcome a leak without the need for patches, and even railroad brackets support could be repaired *in situ*; the possibilities would be endless [9].

Even though the industrial scaling of self-healing materials (SHM) continues to be a challenge to overcome, the first steps have already been taken to study this property in the most common rubbers. This review presents the results of this preliminary research on elastomeric matrices that could be used in the automotive sector, such as NR and synthetic rubbers, like styrene-butadiene rubber (SBR), butadiene rubber (BR), butyl rubber (IIR), nitrile rubber (NBR), polyurethanes (PU), ethylene-propylene-diene rubber (EPDM), chloroprene rubber (CR), silicones (Q), among others. In order to explore the key concepts of self-healing, this review will examine all these matrices through the lens of one critical factor: the mechanism. Mechanisms can be (a) extrinsic, based on capsular and vascular networks systems; (b) intrinsic, relying on the chemistry of dynamic bonds and supramolecular interactions like hydrogen bonds, ionic interactions, coordination bonds, disulfide exchange, Diels-Alder chemistry, and many more, or (c) a combination between them. By considering these mechanisms, and the customization possibilities they offer, we can gain a deeper understanding of the transformative power of the self-healing technology. In the first section of this review, the key concepts of self-healing are briefly introduced and then, the different rubbers used in automotive applications (particularly in passenger cars) are detailed. Subsequently, the most relevant studies of recent years (2015–2022) that have had the objective of introducing healing functionalities in these types of rubbers are summarized and discussed. A brief section highlighting research on elastomer-based composite materials where the reinforcing filler plays a crucial role in repairability (providing some healing moieties) is also included. The review ends with a conclusion and outlook and future perspectives. Through this comprehensive approach, we can take a look through a new era of elastomers that are stronger and more sustainable than ever before.

2. Self-healing key concepts

Self-healing is defined as the ability to repair or restore damage [9–11]. This nature-inspired concept can be found in living organisms like plants and animals. In the last decades, this biomimetic solution has been successfully applied to human-made materials, considering four key concepts: 1) localization, 2) temporality, 3) mobility and 4) mechanism. These concepts and other self-healing basis have been extensively reviewed in the scientific literature [9,12]. This section will provide a brief discussion to put this phenomenon in context.

The concept of localization refers to the scale of the damage (i.e. damage size) to be repaired. Each type of injury (scratches, microcracks and/or catastrophic damage) will be susceptible to a different repair strategy. This means that self-healing approach depends on the localization of the damage. The second concept, temporality, is related to the time–dependent nature of the self–healing process. The localization also influences temporality, since depending on the scale of the damage, it will be more or less difficult to address. Temporality can be influenced by the third concept, mobility. Self-healing depends on the ability of the polymer chains or repair agent to move in or to the damaged area. If the system is restricted (for example, due to crosslinking points) repairability would take longer or might not even occur. That is why this property is a challenge in vulcanized elastomers, which behave as a thermosetting material. Achieving an optimal compromise between the mobility of the polymeric chains and the mechanical robustness provided by processes such as vulcanization is essential for the successful implementation of self-healing rubbers. The fourth and final key concept is the mechanism. Depending on the strategy used, self-healing can be achieved in two general ways: extrinsic or intrinsic self-healing. On one hand, extrinsic depends on an external healing agent that can be confined into the elastomeric matrix using capsules or vascular networks. On the other hand, intrinsic is characteristic of the elastomer and is based on the chemistry of dynamic bonds and supramolecular interactions, which are reversible by nature.

Recently, the authors [9] presented another universal classification of SHM based on their scientific evolution. They consolidate this evolution into four generations that comprehensively present the nature of the involved bonds and interactions (non-covalent, covalent or combinations between them). Fig. 1 summarizes these generations. The first generation involves all those materials with repair agents confined in capsules; the second involves those SHM based on a single dynamic bond; the third, refers to those that have healing agents confined in vascular nets and, finally, the most recent generation, combines any of the previous strategies, but mainly, the combination of different dynamic bonds that produces networks with properties *on demand*.

Most of the developments available in the literature fall within the second and fourth generation of SHM (intrinsic mechanisms). The redesign of elastomeric crosslinked networks based on dynamic bonds and supramolecular interactions is the most common approach [13]. The functionalization options in these polymeric chains (by means of epoxidation, carboxylation, halogenation, among others) provides healing moieties and/or facilitate their inclusion through subsequent reactions. Among the most followed intrinsic mechanisms are classified as a) non-covalent like hydrogen bonds, ionic interactions, and metal–ligand coordination, and b) covalent as Diels-Alder chemistry, disulfide bonds, transesterification reactions, among others. Fig. 2 summarizes most common strategies in elastomers for automotive applications. The polymer architecture (such as crosslink density, aggregation state or chain topology) is also a factor to be considered in the self-healing capacity [14]. Particularly in the elastomers group, the crosslink density plays a key role in the final healing performance of the material.

The self-healing concepts have been extensively reviewed in polymers, particularly in advanced applications such as soft robotics [15,16], soft electronics [17], biomedical [18] and structural applications [19]. However, shockingly, the most relevant application for elastomers (automotive sector) has not been thoroughly analyzed to date. This is a major oversight, as the automotive industry is the main consumer of elastomers, and the potential benefits of incorporating self-healing technology in this sector are massive. By filling this critical research gap, we get a glimpse of a new era of automotive materials that are not only stronger but also capable of self-repairing themselves, revolutionizing the industry and promoting a more sustainable future.

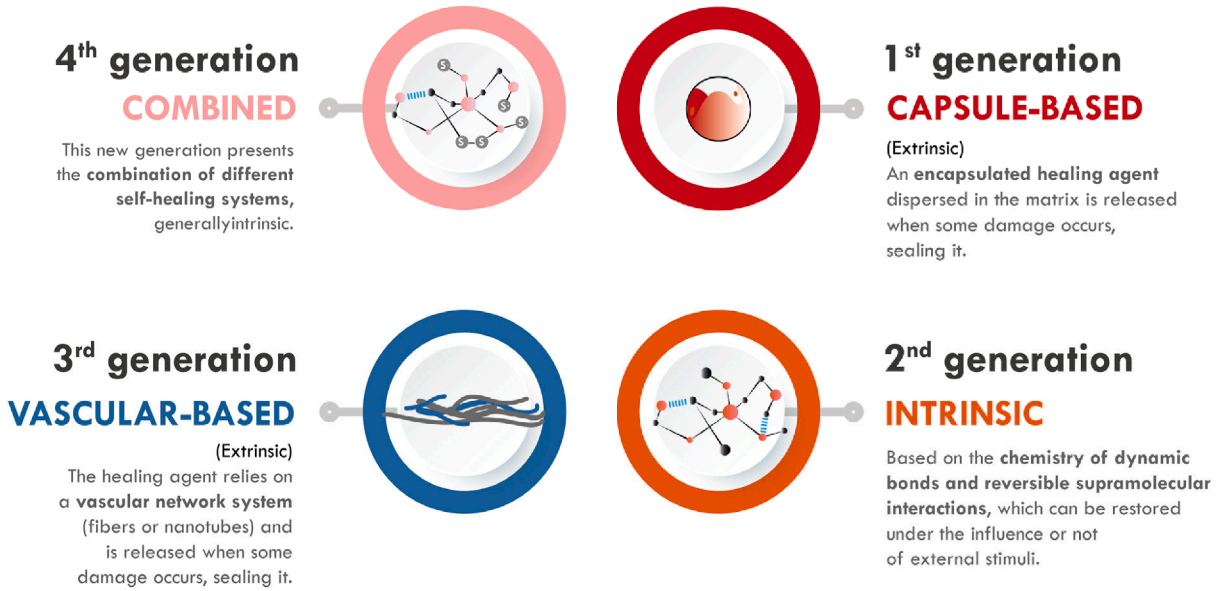


Fig. 1. Generations of self-healing rubbers.

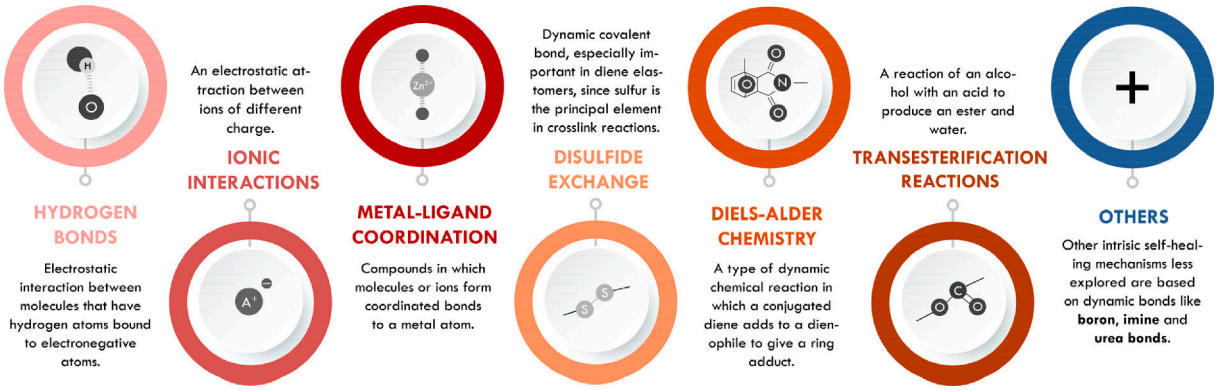


Fig. 2. Intrinsic self-healing strategies in elastomers for automotive applications. Adapted with permission of the Royal Society of Chemistry. [9].

3. Rubbers in automotive applications

As was stated before, among the most fruitful relationship between a material and an industry is that between the automotive industry and elastomers or rubbers [6,20]. At this point, it's important to clarify the use of the terms "elastomers" and "rubbers" as synonyms. While both terms refer to polymers, the American Society for Testing and Materials (ASTM) in ASTM D1566 standard [21] defines an "elastomer" as any elastic polymer. This definition includes thermoplastic elastomers that may not be in a vulcanized state, in addition to chemically crosslinked rubbers. In this context, "rubber" strictly refers to an elastomer in a modified state (crosslinked) that is essentially insoluble but can swell in boiling solvents. However, the word "rubber" is also used in other aspects of Polymer Science and Technology, such as in the "rubbery" state (above the glass transition of a polymeric material), raw rubber, or rubber glues. Although "rubber" is a broader term and more versatile, "elastomers" and "rubbers" have been used interchangeably in recent years to describe this group of materials characterized by their high deformability and elasticity, and are essential in the manufacture of a car. [5].

Today it is impossible to understand the advances in transport systems without looking at that relationship between the automotive industry and rubbers. According to the type of rubber used (natural or synthetic), it is possible to obtain multiple properties; excellent mechanical performance, good abrasion, tear and chemical resistance and thermal stability (at high and low temperatures), together with a unique elasticity among all available polymers [22].

A car has hundreds of parts of different sizes and shapes, manufactured with rubber and subjected to hazardous mechanical, thermal and chemical conditions. Brakes, seals (for engine, fuel, electrical and headlights systems), gaskets (for engine and fuel cell systems), hoses, electrical components, grommets, pieces for the ventilation and air conditioning system (HVAC), rubber-to-metal bonded parts, chassis, coatings, exhaust hangers, spark plug boots, interior and console panel, and of course, tires, to name a few [5,23]. Fig. 3 shows a scheme of common rubber parts in a passenger car.

Starting with the seals and gaskets, their main function is to prevent fluid from escaping and to hold two sections of one piece together. Depending on their location and the fluid with which they are in contact, they will require the use of one or another type of rubber. Generally, for the engine and fuel system, these seals and gaskets must be made of some type of NBR, fluoroelastomers and/or fluorosilicones that are characterized by their excellent chemical resistance to petroleum-derived fluids (oils, gasoline, etc.) and their good thermal stability [22,24]. Hoses for these systems must also meet the same requirements for resistance to organic solvents.

Brakes also require the use of rubbers. Its composition consists of a composite material made of multiple metals, ceramics and polymers,

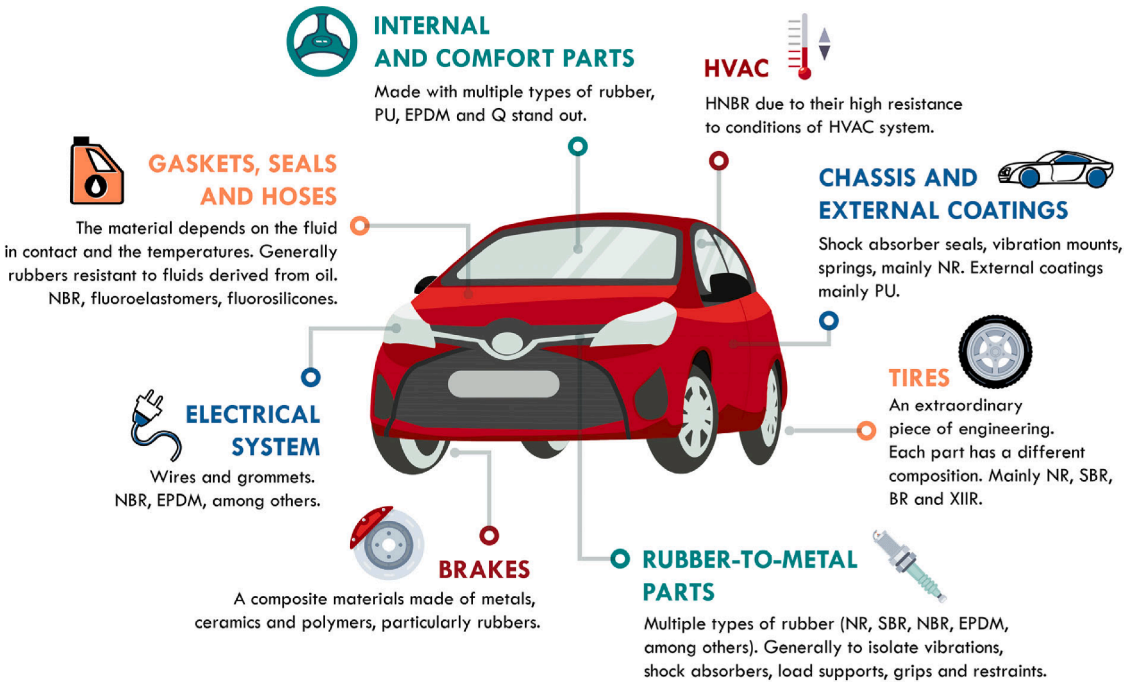


Fig. 3. Common rubber parts in a passenger car.

where rubbers stand out, thanks to their excellent abrasion resistance [22]. Brakes are one of the most important components of a car because they guarantee safety while driving and are often subjected to extreme temperatures generated by friction.

Rubber parts are also used in the chassis, specifically shock-absorbing seals, vibration mounts and air springs [23]. These parts ensure ride comfort and are characterized by requiring high resilience. Therefore, some of them can be made of NR and chloroprene (CR), but they can also be made of SBR, NBR, EPDM, among others [22,24].

A variant of nitrile rubber, known as hydrogenated nitrile rubber (HNBR), is commonly used for the HVAC system. CR and EPDM can also be used in cables for the electrical system, due to its excellent aging resistance and insulation, while NBR is preferred in grommets, which are usually placed to provide a cushioned area for the wire and protect them from sharp edges. Grommets can also be manufactured with EPDM, CR, Q and fluoroelastomers. Meanwhile, PU is mainly used in the interior of the car due to the versatility of its chemistry and the possibility of producing foams [22] with assured comfort, as well as paintings and coatings of the external structure.

Tires are among the most important parts of a car [5]. These are essential for mobility and for vehicle safety. They perform numerous functions: supporting the weight of the vehicle, providing grip between the vehicle and the road and acting as vibration-dampers, improving comfort, safety and the overall performance of the vehicle [8]. A passenger car tire is usually made up of at least three or four types of rubbers: NR, SBR, BR and IIR (especially their halogenated variants, XIIR). Meanwhile, tires for trucks and airplanes tend to incorporate higher amounts of NR than of synthetic rubbers to satisfy mechanical requirements [5,22]. Fig. 4a shows the composition of tires in weight percentages. However, all these materials are not in the same section of the tire, nor are they intended for the same function.

Three main characteristic areas can be distinguished in a tire with the naked eye: 1) the tread, which is the area in contact with the ground and, therefore, must have excellent abrasion resistance, which is essentially provided by BR in a mixture with SBR and/or NR; 2) the sidewall, which is the front area of the tire and the one that distributes the load and is made up mostly of NR with SBR or BR and, 3) the innerliner, which is the closest area to the rim and prevents the escape of air from inside the tire. This area must exhibit low gas permeability, which is why it is manufactured with XIIR [22]. Inside these three zones, there are other multiple parts, made from textile fibers (rayon, polyester, fiberglass and/or aramid), metallic cords, rubber belts and many chemical additives such as fillers (carbon black, CB, mainly), antioxidants, antiozonants, sulfur, accelerants, activators and process aids that complement the rubber recipe [8]. Fig. 4b summarizes all these parts in a cross-section view.

4. Self-healing rubbers for automotive applications

The research up to date in this self-healing field is characterized by being material-focused, primarily based on developing self-healing model systems. Once the conceptual framework is established, the mandatory next step would be the scaling up to the industrial level, but there are still some limitations to be solved. In the particular case of the automotive industry, this field of research is still new, and no application-focused materials have specifically been developed (with the required properties). As was stated in the previous section, the automotive industry requires specific and stringent performance requirements for the elastomeric materials used in each application. This is why NR is used for high-performance tire manufacturing due to its excellent resilience and mechanical properties. The gas impermeability of XIIR is leveraged to manufacture tire innerliner, and the abrasion resistance of BR is used to enhance the performance of passenger car treads. However, despite the importance of these aspects, the majority of self-healing elastomers studies are limited to analyzing tensile strength recovery. While a few exceptions do focus on surface crack recovery [57,63], this is not sufficient, and represents an important limitation in this review in order to analyze the full potential of the available research.

Functional tests that accurately mimic real-world service conditions are necessary to evaluate the full potential of self-healing materials. It is essential that studies on self-healing materials shift their focus to the recovery of specific functionalities such as fatigue resistance, aging resistance, puncture resistance, wear resistance, air tightness, among others. Only by considering the target application and associated functional requirements can we truly unlock the potential of self-healing

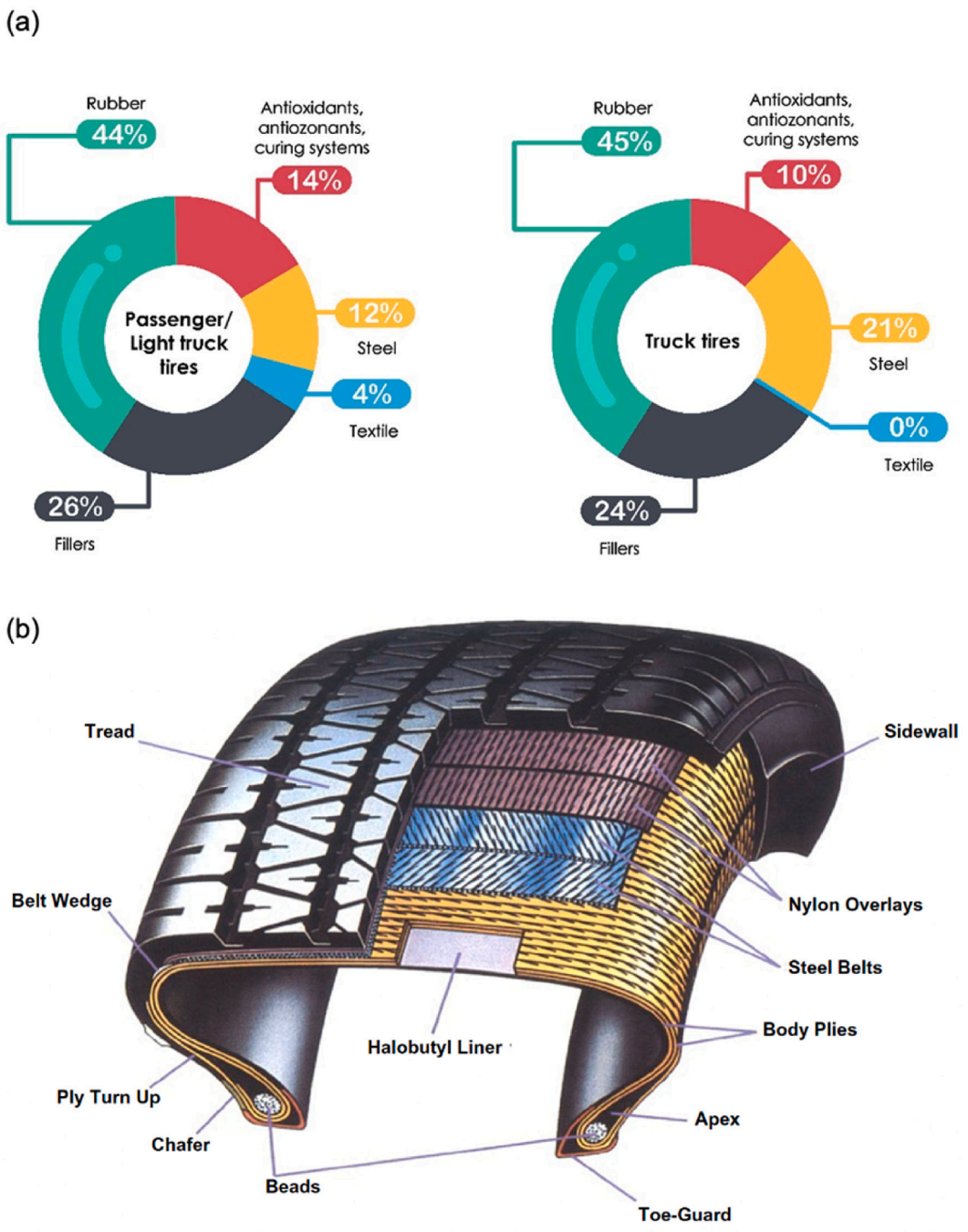


Fig. 4. A) composition of different tires in weight percentages, b) cross-section of a passenger tire. (a) reproduced with permission of elsevier [8] and (b) reproduced with permission of Academic Press – Elsevier. [5].

elastomers for use in the automotive industry.

Bearing that in mind, in this section, we detail the most recent studies (2015–2022) on self-healing NR and synthetic rubbers typically used in automotive applications, thoroughly discussing their underlying healing mechanisms. Different validated healing concepts are presented and the possibilities of applying them to the automotive industry are discussed.

4.1. Natural rubber

NR is the rubber with the highest production and consumption worldwide. Approximately 50 % of world production corresponds to NR, while the remaining 50 % is divided between all the synthetic variants. This predominance is essentially given both by its natural origin (it is extracted from the *Hevea Brasiliensis* tree) and by its excellent mechanical properties, thanks to its strain-induced crystallization ability. However, reaching a self-healing NR is not an easy task, because its chemical structure does not easily provide healing moieties. For that, some of its functionalized variants such as epoxidized natural rubber (ENR) and brominated natural rubber (BNR) are more frequently used, since they provide a greater reactivity that can improve the self-healing performance.

Most of the self-healing studies in this family of rubbers can be classified as part of the second and fourth generation of SHM, with a widespread use of dynamic bonds and supramolecular interactions. This is due to the difficulties of incorporating capsules and vascular networks capable of withstanding the shear forces that rubber is subjected to

during mixing and the possibility that the spread of damage may not be enough to promote the break of the healing agent reservoirs. Table 1 summarizes the research on self-healing NR, some of its variants such as ENR and BNR, and blends with thermoplastics such as polylactic acid (PLA). Table 1 also provides a summary of the following information: tensile strength (TS), the higher healing efficiency (η, only if it was reported as a function of the TS values in both virgin and healed states), and the optimal healing conditions in terms of temperature and time.

The most desired application of self-healing NR in the automotive industry should be tires. Various healing concepts have already been proven in this rubber, although not specifically oriented to tires. As an example, Xu et al. [25] introduced ionic interactions in the NR. This type of interactions is among the most effective approaches to achieve self-healing in rubbers. Their strategy was based on peroxide-induced controlled vulcanization to generate massive ionic crosslinks through the polymerization of zinc dimethacrylate (ZDMA). They controlled the vulcanization process to retard the formation of the peroxide-induced (-C—C-) network and successfully generated a reversible supramolecular arrangement built primarily by ionic bonds. Without the restriction of non-dynamic covalent crosslinks, the NR chains in the ionic supramolecular network have sufficient mobility (key concept) to repair themselves. After 5 min at room temperature, they were able to achieve efficiencies of up to 95 % (for tensile strengths), although the stress values where very low (less than 1 MPa).

Hernandez Santana et al. [35] tried to take a further step towards the applicability of self-healing materials using common ingredients in a traditional NR formulation (sulfur-based vulcanization). The objective was to study the metathesis of the di- and poly-sulfide bonds present in the rubber network. It was found that the dynamic character of these bonds was responsible for promoting self-healing and full recovery of mechanical properties at moderate temperatures (less than 70 °C), bearing in mind that the initial material was not fully cured.

The DA reaction has also been considered for the development of self-healing NR. Tanasi et al. [34] followed a three-step procedure: 1) NR was reacted with maleic anhydride; 2) furan groups were grafted onto the maleated rubber; 3) the pendant furans were crosslinked with a bismaleimide, resulting in a thermoreversible adduct that led to the formation of the crosslinked network. The modules at low deformations recovered 80 % of their initial value after a healing protocol of 4 h at 130 °C (for the *retro*-DA reaction) and then, up to 7 days at 40 °C (for the re-formation of DA adducts).

The main results arising from these three different repair strategies reflect high healing efficiencies. However, the mechanical performance of the rubber is still low. Further investigations must focus on improving the strength of NR, if it is going to be considered as departing point for the design and development of self-healing tire treads. This challenge is intended to be overcome with the fourth generation of self-healing materials, which seeks to combine different types of mechanisms that contribute to both properties (healing and mechanical strength). Cheng et al. [42] prepared an ENR with a dual crosslinked network based on disulfide bonds (covalent intrinsic) and hydrogen bonds (supramolecular interactions, non-covalent intrinsic). As a result, the ENR showed high mechanical strength (greater than 9 MPa), high self-healing efficiency (up to 98 % at 120 °C for 24 h) and full recyclability (100 % recovery of mechanical performance). These results are undeniably promising for tires in which NR can be partially substituted by ENR.

Shock absorber seals, vibration mounts, springs, and rubber-to-metal parts can also be potential applications for self-healing NR. Recently, Najwa et al. [28] prepared a self-healing NR through a mechanism with reversible metal thiolate ion networks. The developed materials were able to repair themselves at room temperature without any external stimulus. It was also found that self-healing increased by 60 % the lifespan in fatigue, so it could be considered for systems associated with the chassis, where the resistance of the NR is widely valued.

Table 1
Research on self-healing NR and derivatives between 2015 and 2022, classified by generations. [(a).]

Matrix	Type of mechanisms	Healing moieties	TS (MPa)	η(%)	Healing temperature (°C)	Healing time	Reference
Second generation							
NR	Non-covalent intrinsic	Ionic interactions	0.65	100	RT	20 min	[25–28]
			1.89	76	RT	5 min	
			0.70	100	RT	10 min	
			2.75	100	RT	10 min	
ENR	Non-covalent intrinsic	Ionic interactions	9.57	79.8	80	60 min	[29]
BNR	Non-covalent intrinsic	Ionic interactions	0.35	94	RT	less than 1 min	[30]
NR	Non-covalent intrinsic	Ionic interactions	7.47	87	80	120 min	[31]
ENR/PU	Non-covalent intrinsic	Hydrogen bonds	12.33	87	60	50 min	[32]
ENR	Non-covalent intrinsic	Metal-ligand coordination	2.55	55	60	96 min	[33]
NR	Covalent intrinsic	Diels-Alder chemistry	1.47	38	130 / 40	4 h / 72 h	[34]
NR	Covalent intrinsic	Disulfide bonds	0.50	80	70	7 h	[35,36]
			0.35	N/R	70	7 h	
NR	Covalent intrinsic	Disulfide bonds	6.00	70	140	30 min	[37]
ENR	Covalent intrinsic	Transesterification reactions	5.00	80	160	3 h	[38,39]
			1.60	80	200	30	
ENR/PLA	Covalent intrinsic	Shape memory-assisted	1.75	83	70	3 h	[40]
Fourth generation							
ENR	Non-covalent + covalent combined	Hydrogen bonds Boron-based bonds	1.86	N/R	RT	N/R	[41]
ENR	Non-covalent + covalent combined	Hydrogen bonds Disulfide bonds	9.30	98	120	24 h	[42]
ENR	Non-covalent + covalent combined	Metal-ligand coordination Boron-based bonds	9.55	98	80	24 h	[43]
ENR	Non-covalent + covalent combined	Hydrogen bonds Disulfide bonds	1.02	143	120	60 min	[44]
ENR/PLA	Non-covalent + covalent combined	Shape memory-assisted Disulfide bonds	2.58	90	80	12 h	[45]
ENR	Non-covalent combined	Hydrogen bonds Ionic interactions	4.50	75	70	6 h	[46]
ENR	Non-covalent combined	Ionic interaction Metal-ligand coordination	1.33	92	RT	3 h	[47]

[(a)] If the healing efficiency is reported in terms other than TS recovery, such as fracture energy, crack recovery, etc., it is denoted as "N/R". If any other parameter is not specified, it is denoted as "N/S". Some TS values that are not explicitly reported by the authors are estimated from stress-strain curves.

Recently, Mandal et al. [46] presented an effective methodology to introduce ionic domains into ENR. In an initial stage, the influence of different azole derivatives and ethylenediamine as a vulcanization system was analyzed by rheometric studies (Fig. 5a). The selection of the best molecule was made based on the increment of torque of the curing curve, with 1*H*-imidazole exhibiting the best results (Fig. 5b and Fig. 5c). This was explained from a chemical reaction between the oxirane ring and the 1*H*-imidazole molecule, that gave way to the formation of a covalent bond and an ionic pair. The end result is the development of a crosslinked network through the combination of ionic interactions and hydrogen bonds, supported by covalent bonds, without requiring any additional additives for vulcanization (Fig. 5d). The presence of the dynamic bonds was responsible for the recyclability of the composites and the self-healing capacity of up to 90 % on the tensile strength (4.5 MPa), without affecting its elongation at break (about ~ 700 % strain).

4.2. Synthetic rubbers

As previously mentioned, synthetic rubber variants represent close to 50 % of world production, being the automotive industry the main user. These rubbers can be classified into any of the four generations of SHM. Unlike NR that requires conventional mixing in a two-roll mill or an internal mixer, some synthetic rubbers (e.g., silicones and PU) allow other processing and vulcanization methods that facilitate the incorporation of capsules and vascular networks (first and third generation of SHM); however, the vast majority of studies has also been based on the chemistry of dynamic bonds and supramolecular interactions (second and fourth generation).

Table 2 summarizes the recent research on self-healing synthetic rubbers commonly used in automotive applications such as SBR, BR, NBR (and its variants, like carboxylated nitrile rubber, XNBR and HNBR), IIR (and its halogenated variants, like brominated butyl rubber, BIIR), PU, Q (such as polydimethylsiloxane, PDMS), CR and blends with thermoplastic such as polyvinyl chloride (PVC).

Among all the synthetic variants, SBR is the synthetic rubber with the highest consumption and production. The authors [89,90] have pioneered its use as a SHM. They have shown that this vulcanized material with a conventional, sulfur-based crosslinking system (typical for applications in tires) can recover up to 50 % of its tensile strength (between

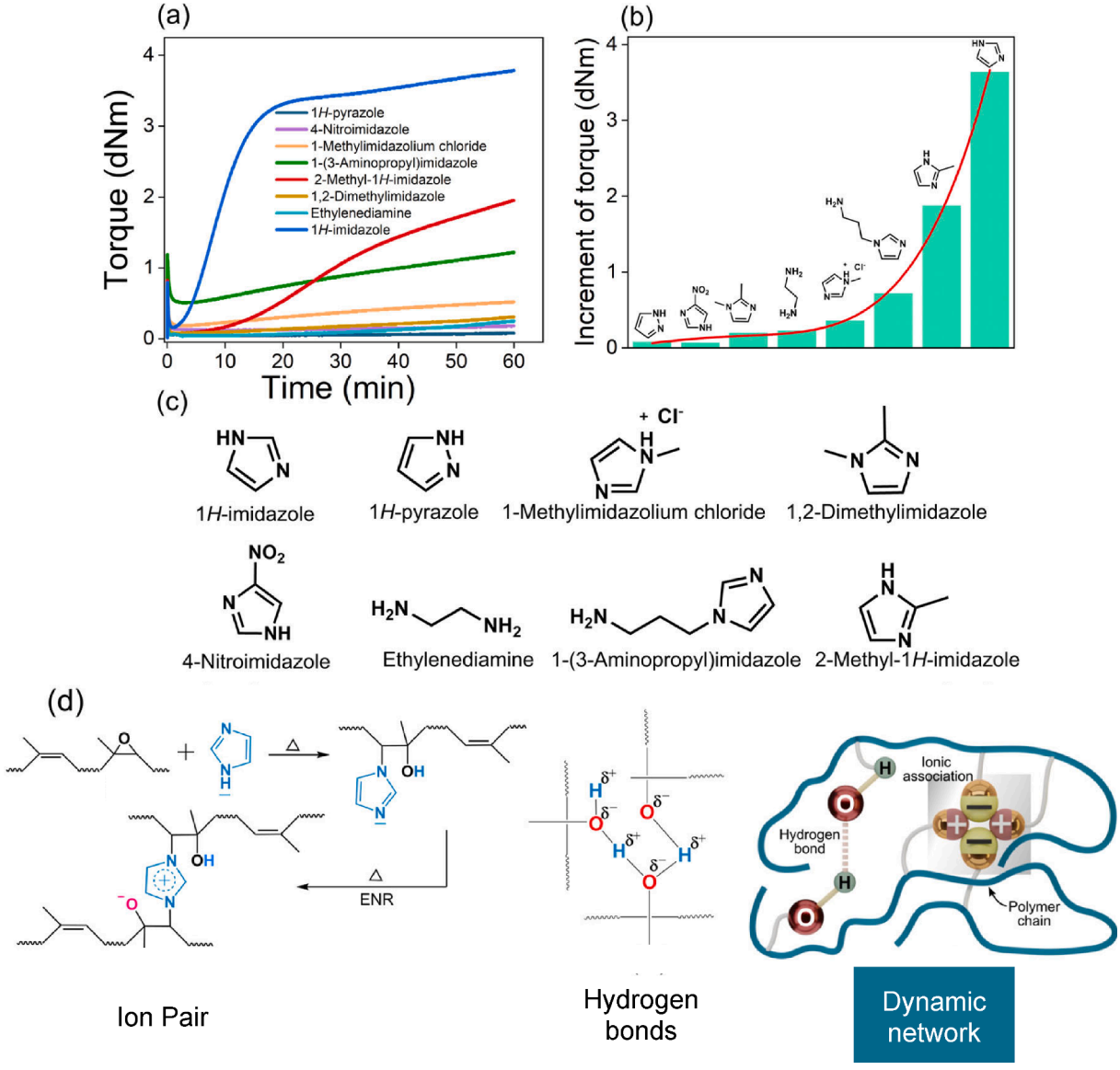


Fig. 5. (a) Curing curves of ENR with different azole derivatives and ethylenediamine, (b) increment of torque and (c) chemical structure of azole derivatives and ethylenediamine, and (d) scheme of the ion pair, hydrogen bonds and dynamic network formation. Adapted with permission of American Chemical Society. [46].

Table 2
Research on self-healing synthetic rubbers between 2015 and 2022, classified by generations. [(b).]

Matrix	Type of mechanisms	Healing moieties	TS (MPa)	η (%)	Healing temperature (°C)	Healing time	Reference
First generation							
PDMS	Extrinsic	Capsule-based	1.39	72	RT	24 h	[48]
PU	Extrinsic	Capsule-based	N/S	N/R	RT	24 h	[49,50]
			N/S	N/R	RT	7 days	
Second generation							
BR	Non-covalent intrinsic	Hydrogen bonds	3.15	90	RT	12 h	[51]
PDMS	Non-covalent intrinsic	Hydrogen bonds	0.23	100	RT	120 min	[52–56]
			0.17	75	80	12 h	
			0.52	88.5	80	24 h	
			0.013	100	70	60 min	
			1.75	120	120	120 min	
BR	Non-covalent intrinsic	Hydrogen bonds	14.00	N/R	80	N/S	[57]
BIIR	Non-covalent intrinsic	Ionic interactions	9.00	N/R	RT	192 h	[58–61]
			6.00	N/R	120	10 min	
			9.00	N/R	100	24 h	
			8.10	90	60	24 h	
EPDM	Non-covalent intrinsic	Ionic interactions	0.95	95	100	60 min	[62]
EPDM	Non-covalent intrinsic	Ionic interactions	12.00	N/R	89	24 h	[63]
PDMS	Non-covalent intrinsic	Ionic interactions	3.08	45	120	12 h	[64,65]
			0.25	98	100	12 h	
NR/IIR	Non-covalent intrinsic	Ionic interactions	0.71	99	RT	5 h	[66]
XNBR	Non-covalent intrinsic	Ionic interactions	8.25	98	150	10 min	[67]
NBR	Non-covalent intrinsic	Metal-ligand coordination	4.20	greater than90	190	60 min	[68]
PDMS	Non-covalent intrinsic	Metal-ligand coordination	1.12	N/R	120	24 h	[69–75]
			0.35	90	60	20 h	
			0.23	N/R	RT	48 h	
			0.65	N/R	RT	48 h	
			0.75	94.7	−20	60 min	
			0.61	98	RT	31 h	
			0.20	95	RT	24 h	
PU	Non-covalent intrinsic	Metal-ligand coordination	12.7	100	60	24 h	[76]
XNBR	Non-covalent intrinsic	Metal-ligand coordination	3.80	89.5	RT	24 h	[77]
SBR	Covalent intrinsic	Diels-Alder chemistry	3.60	N/R	100	5 h	[78]
EPDM	Covalent intrinsic	Diels-Alder chemistry	6.40	N/R	160 / 80	10 min / N/S	[79]
PDMS	Covalent intrinsic	Diels-Alder chemistry	0.58	95	140 / 80	3 h / 24 h	[80–84]
			N/S	N/R	110 / 50	2 h / 5 h	
			0.80	93	130 / 80	45 min / 48 h	
			0.35	N/R	130 / 80	10 min / 48 h	
			0.421	97.16	135	15 min	
PU	Covalent intrinsic	Diels-Alder chemistry	6.50	N/R	120	15 min	[85–88]
			13.49	78.7	130 / 65	30 min / 24 h	
			6.83	62.1	120 / 60	30 min / 24 h	
			21.00	greater than90	130 / 65	2 h / 12 h	
SBR	Covalent intrinsic	Disulfide bonds	1.58	50	70	7 h	[89,90]
			1.33	56	70	12 h	
BR	Covalent intrinsic	Disulfide bonds	3.25	75	110	12 h	[91,92]
			1.50	N/R	N/S	N/S	
CR	Covalent intrinsic	Disulfide bonds	9.00	N/R	120	5 h	[93]
PDMS	Covalent intrinsic	Disulfide bonds	1.00	80	N/S	48 h	[94]
PU	Covalent intrinsic	Disulfide bonds	11.00	N/R	80	4 h	[95]
SBR	Covalent intrinsic	Boron-based bonds	2.00	90	80	24 h	[96]
PDMS	Covalent intrinsic	Imine bonds	0.12	94	RT	12 h	[97,98]
			0.40	97	RT	1 h	
PU	Covalent intrinsic	Urea bonds	8.50	N/R	RT	24 h	[99]
Third generation							
PDMS	Extrinsic	Vascular based	1.35	N/R	RT	24 h	[100–103]
			N/S	N/R	RT	24 h	
			1.30	N/R	RT	N/R	
			N/S	N/R	RT	N/R	
Fourth generation							
BIIR	Non-covalent combined	Hydrogen bonds Ionic interactions	6.00	39	70	60 min	[104]
PDMS	Non-covalent combined	Hydrogen bonds Ionic interactions	0.95	N/R	RT	24 h	[105]
PDMS	Non-covalent combined	Hydrogen bonds Ionic interactions	0.21	115	80	5 h	[106]
PU	Non-covalent combined	Hydrogen bonds Van der Waals forces	0.35	100	50	N/S	[107]
PU	Non-covalent combined	Hydrogen bonds Host-guest interactions	11.07	92.29	100	36 h	[108]
PU	Non-covalent combined	Hydrogen bonds Metal-ligand coordination	14.80	92	RT	130 h	[109]
PDMS	Non-covalent combined	Metal-ligand coordination $\pi-\pi$ stacking	2.60	90	RT	36 h	[110]

(*continued on next page*)

Table 2 (*continued*)

Matrix	Type of mechanisms	Healing moieties	TS (MPa)	η (%)	Healing temperature (°C)	Healing time	Reference
PDMS	Covalent combined	Disulfide bonds Imine bonds	0.30	N/R	RT	4 h	[111]
PU	Covalent combined	Disulfide bonds Imine bonds	34.60	N/R	65	60 min	[112]
PU	Covalent combined	Disulfide bonds Diels-Alder chemistry	11.25	N/R	60	5 min	[113]
PU	Non-covalent + covalent combined	Hydrogen bonds	0.43	N/R	RT	24 h	[114–120]
		Disulfide bonds	7.70	97.4	RT	24 h	
			9.50	96	N/S	6 h	
			5.01	100	60	6 h	
			3.0.39	95	80	12 h	
			20.00	98	90	24 h	
			25.20	greater than90	100	120 min	
PDMS	Non-covalent + covalent combined	Hydrogen bonds Imine bonds	0.17	95	60	60 min	[121]
BR	Non-covalent + covalent combined	Hydrogen bonds Imine bonds	1.50	100	80	10 min	[122]
PDMS	Non-covalent + covalent combined	Metal-ligand coordination Imine bonds	0.05	88	RT	48 h	[123]
PU	Non-covalent + covalent combined	Metal-ligand coordination Diels-Alder chemistry	3.25	100	65	3 h	[124]
PDMS/PU	Non-covalent + covalent combined	Hydrogen bonds Diels-Alder chemistry	1.05	99	140 / 80	30 min / 24 h	[125]
PU	Non-covalent + covalent combined	Hydrogen bonds Diels-Alder chemistry	37.11	91.8	120	10 min	[126]
PU	Non-covalent + covalent combined	Shape memory effects	22.50	N/R	80	5 min	[127,128]
		Disulfide bonds	5.33	93.43	80	24 h	
SBR	Non-covalent + covalent combined	Hydrogen bonds Disulfide bonds	3.85	76	85	24 h	[129]

[(b)] If the healing efficiency is reported in terms other than TS recovery, such as fracture energy, crack recovery, etc., it is denoted as "N/R". If any other parameter is not specified, it is denoted as "N/S". Some TS values that are not explicitly reported by the authors are estimated from stress-strain curves.

1.4 and 2.3 MPa) thanks to the disulfide exchange mechanism, activated at 70 °C for 7 h and 10 bar pressure.

BR is one of the most consumed synthetic elastomers that finds almost exclusive use in tires. Wang et al. [51] carried out a self-healing strategy in BR combining covalent and non-covalent networks. The sacrificial part consisted of hydrogen bonds, while the covalent (irreversible) part, responsible for mechanical robustness, was based on thiol-ene reactions. The result was a material with self-healing capability (up to 95 % efficiency) and shape memory thanks to the reformation of hydrogen bonds at room temperature, without external stimuli and with tensile strength greater than 1 MPa. These studies, together with those of NR, could definitely lay the foundations for the formulation of new self-healing tire treads, but much research lies ahead.

Recently, Saha et al. [57] presented a solid-state methodology for producing self-healing commercial BR. It is also one of the few studies in the area of synthetic rubbers conceived directly towards automotive industry applications, such as tire sidewalls, tire tread, etc. In this work, a malic anhydride (MAH) grafting reaction was employed, using previously optimized doses. The MAH grafting slightly improved the mechanical properties of the starting rubber, but considerably limited its elongation at break (~4.4 times lower than BR without grafting). This reaction endowed the rubber with sites capable of react during reactive mixing with ring opening amine-based adducts. In this way it was possible to create a supramolecular network formed by hydrogen bonds. Thanks to this network, the materials exhibited thermally assisted self-healing capacity, being able to seal a microcrack after a healing protocol at 70 °C, in an unspecified time, unlike BR without grafting (Fig. 6).

The tirés innerliner can also be made out of self-healing rubbers. In a first approach, Das et al. [58] incorporated ionic interactions into BIIR. In their initial studies, they were able to build a network of halobutyl rubber using an excess of butylimidazole as precursor of ionic interactions, with an excellent tensile strength value (greater than 5 MPa). After 192 h at room temperature, the material recovered almost all its elongation (about 950 %). This proven strategy certainly opens the doors to assess its suitability for tire innerliner.

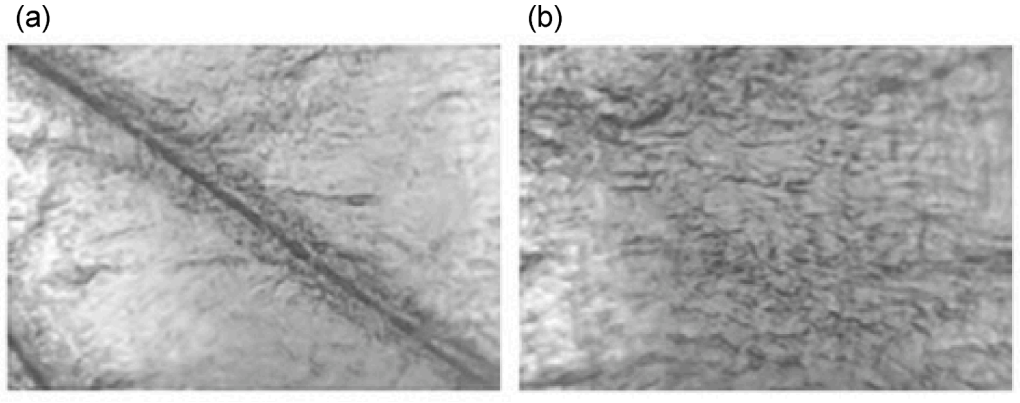


Fig. 6. Scratch in (a) non-modified BR and (b) BR-g-MAH after a healing protocol at 70 °C. Adapted with permission of Wiley Periodicals LLC. [57].

Ionic interactions have also been incorporated into EPDM. This diene rubber stands out in the industry thanks to the ease of processing and a set of properties that makes it especially useful as insulation of electrical system wires, window, and door profiles, as well as other internal and comfort parts of the vehicle. Zhang et al. [62] used peroxide-induced polymerization and grafting of ZDMA to formulate an ionically crosslinked EPDM. Repair efficiencies of up to 95 % were achieved after 1 h at 100 °C. As can be seen comparatively between the last two studies presented, despite both dealing with ionic interactions, the time and temperature requirements are opposite. This fact shows that self-healing strategies and protocols are not exclusive and must be adapted to the elastomeric matrix, taking into consideration the self-healing key concepts and the final application.

Among all the synthetic rubbers available, PDMS and PU stands out for the versatility of its chemistry and for the multiple behaviors that can be achieved by varying the monomers involved in its synthesis. For this reason, it is not surprising that both are the most studied synthetic elastomers in the field of unfilled self-healing materials. In automotive applications these two elastomers are especially important for internal and comfort parts.

Li et al. [71] prepared PDMS capable of self-repairing at temperatures as low as −20 °C. For this purpose, a crosslinking network based on 2,6-pyridinicarboxamide ligands coordinated with Fe(III) centers through different interactions was created. First, a strong pyridyl-iron one, able to stay fixed during healing, and two weaker carboxamide-iron ones through the nitrogen and oxygen atoms of carboxamide groups, able to break and reform easily. This strategy would be responsible for the high stretching and self-healing capacity of the developed material.

Wang et al. [76] have prepared PU using metal–ligand motifs. The metals have been obtained from ferric chloride ($FeCl_3{\cdot}6H_2O$), terbium trifluoromethanesulfonate ($Tb(OTf)_3$) and zinc trifluoromethanesulfonate ($Zn(OTf)_2$), while the ligand has been diamidepyridine (DAP). With a healing protocol of 60 °C for 24 h, efficiencies of up to 100 % have been achieved with the use of Fe- and Tb-, with tensile strengths of up to 13 MPa and elongations at break close to 1000 %. Undoubtedly, these results demonstrate the possibility of the use of PU in automotive interior applications, such as seats, dashboards and other soft parts, as well as external coatings.

Other chemicals have also been used in PU. Feng et al. [85] were able to crosslink a PU with DA moieties, but requiring higher temperatures (up to 120 °C) and shorter times (15 min). Efficiencies of up to 70 % (tensile strength 6.5 MPa) were achieved in those PU with soft segments of higher molecular weight and lower contents of hard segments (which hinder mobility). Meanwhile, in those with predominance of hard segments, they were not able to overcome the barrier of a 15 % healing efficiency.

Moreover, combined networks have been explored in PU. Yeh et al. [113] prepared PUs that integrate two types of dynamic covalent bonds: those derived from DA and disulfide bonds. The result was an elastomeric matrix with fast healing capability, recyclability and high transparency. Fig. 7 shows a schematic representation of the single and dual strategy and a self-healing concept scheme.

4.3. Rubber composites

The incorporation of reinforcing fillers selectively functionalized with healing moieties has recently been considered as a twofold strategy to improve the mechanical performance as well as the healing capability of SHM. Although this review does not seek to make an exhaustive analysis of this area, some selected studies with potential application in the automotive field are presented in Table 3.

The primary challenge of incorporating reinforcing fillers into a self-healing elastomeric material lies in the inherent trade-off between self-healing and mechanical performance [9,89]. Typically, the incorporation of fillers leads to a reduction in the mobility of polymeric chains, which hinders the self-healing capability. Consequently, the successful integration of high filler content, such as those used in the automotive industry, that delivers both high repair efficiencies and optimal mechanical performance remains as an ongoing issue. To address this dichotomy, current research is centered on involving the filler in the repair process [79,144,146,147]. By incorporating healing moieties into the

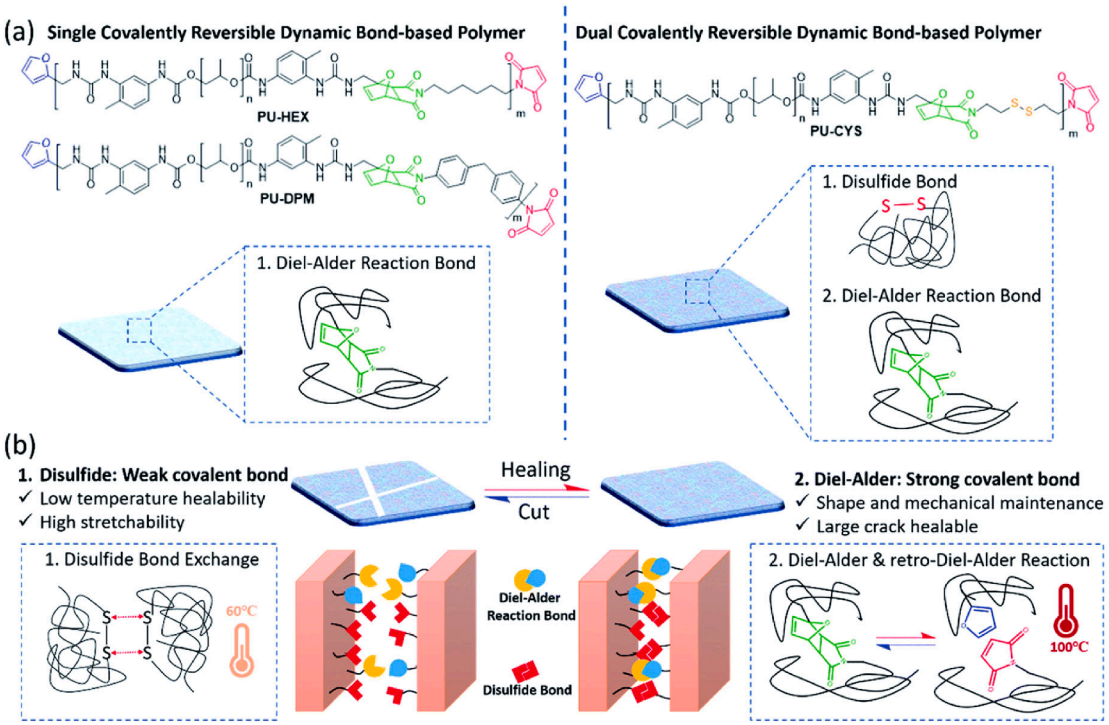


Fig. 7. (a) Single and dual crosslinked network strategy and (b) self-healing concept scheme in PU. Reproduced with permission of Royal Society of Chemistry. [113].

Table 3
Selected research on self-healing natural and synthetic rubber composites. [(c).]

Matrix	Filler	Type of mechanism	Healing moieties	TS (MPa)	η (%)	Healing temperature (°C)	Healing time	Reference
ENR	Chitin	Non-covalent intrinsic	Hydrogen bonds	1.19	83	RT	24 h	[130]
ENR	Cellulose	Non-covalent intrinsic	Hydrogen bonds	4.04	N/R	RT	24 h	[131]
ENR	GO	Non-covalent intrinsic	Hydrogen bonds	1.85	82	RT	24 h	[132]
ENR	Chitosan	Non-covalent intrinsic	Hydrogen bonds	1.92	90	RT	12 h	[133]
ENR	Chitosan + Cellulose	Non-covalent intrinsic	Hydrogen bonds	2.30	88	80	4 h	[134]
NR	CB	Non-covalent intrinsic	Ionic interactions	less than 1	70	N/S	10 min	[135]
XNBR	GTR	Non-covalent intrinsic	Ionic interactions	20.00	70	100	10 min	[136]
BIIR	CB	Non-covalent intrinsic	Ionic interactions	13.00	100	100	12 h	[137]
BIIR/NR	CNT + CB	Non-covalent intrinsic	Ionic interactions	4.00	N/R	130	30 min	[138]
NBR	CNT	Non-covalent intrinsic	Metal-ligand coordination	1.10	90	80	9 h	[139]
ENR	Bentonite	Covalent intrinsic	Transesterification reactions	4.50	100	150	3 h	[140]
NR	GO	Covalent intrinsic	Disulfide bonds	0.35	70	70	7 h	[141]
SBR	GTR	Covalent intrinsic	Disulfide bonds	2.51 2.90	50 33	70 70	7 h 12 h	[89,90]
NR	Silica	Non-covalent combined	Hydrogen bonds Ionic interactions	18.50	79.01	50	24 h	[142]
ENR	Chitosan + CNT	Non-covalent and covalent combined	Hydrogen bonds Borate ester bonds	3.61	59	60	24 h	[143]
SBR	GTR + CB	Non-covalent and covalent combined	Ionic interactions Disulfide bonds	6.20	90	130	5 h	[144]
ENR + Polycaprolactone	Alginates	Extrinsic and intrinsic combined	Ionic interactions Hydrogen bonds	11.50	100	110	12 h	[145]

[(c)] If the healing efficiency is reported in terms other than TS recovery, such as fracture energy, crack recovery, etc., it is denoted as "N/R". If any other parameter is not specified, it is denoted as "N/S". Some TS values that are not explicitly reported by the authors are estimated from stress-strain curves.

reinforcing particles, a boosted effect can be achieved that enhances healing efficiencies while simultaneously increasing mechanical behavior.

The first filler to be considered is carbon black (CB). It is the most widely used filler in the rubber industry, so its usage in different elastomeric matrices is not surprising [148]. Zhang et al. [137] have reported the development of BIIR compounds filled with CB and crosslinked through ionic interactions (ionomers). The strong interfacial interaction between the filler and the rubber (bound rubber) gives the ionomer high mechanical properties. Despite this fact, the healing efficiency can be regulated up to 100 %, depending on the filler content and the temperature. This study demonstrates that CB reinforcement is feasible to improve the mechanical properties of self-healing elastomers, which opens a window for its exploration in all rubbers used by the automotive industry.

The second most widely used synthetic filler in rubbers is silica. However, its usage does not quite reach the extension of the CB due to the difficulty of achieving a good dispersion in the rubber matrix, requiring expensive coupling agents. Despite the above, in suitable proportions and with particle size reduction strategies, it can exhibit outstanding reinforcing power. Sattar et al. [142] studied the self-healing of silica-reinforced NR. They reported the development of a supramolecular network, thanks to the hydrogen bonds and electrostatic interactions between the filler particles and the NR lipids and proteins, in addition to that of mono-, di- and polysulfides bonds. Such network enabled the recovery of up to 79 % of the tensile strength in the virgin state (18.5 MPa), with the application of 50 °C for 24 h. This study stands out for the good mechanical performance, which brings the SHM concept closer to specific applications that demand mechanical robustness.

The research into CB and silica fillers is particularly relevant, given their fundamental role in tire development [5,24]. CB is highly effective in providing exceptional abrasion resistance, while silica offers outstanding dynamic performance, specifically in wet and dry grip, and rolling resistance, which are the critical aspects of the tire tread magic triangle [149]. For other parts that do not require a light color, such as hoses, seals, and gaskets, CB is commonly used due to its excellent rubber-filler interactions with most general-purpose matrices, which translates into an efficient reinforcement capacity [150]. However, the environmental impact of its production process is a major concern.

In recent years, the development of new recipes using natural, renewable, and more sustainable fillers has increased steadily, motivated by the need to reduce the environmental footprint of rubbers [151]. The focus on sustainable fillers aligns with the growing trend of promoting eco-friendly materials in tire manufacturing and other industries.

Some natural fillers, such as cellulose, chitin and chitosan, alginates, and clays have also been investigated [151]. Nie et al. [130] successfully prepared ENR/Chitin nanocrystals (CNC) compounds without conventional crosslinking agents. With this strategy, it was possible to form a supramolecular network based on hydrogen bonds between the hydroxyl groups of the CNC and the epoxy group of the ENR. With 20 wt% of CNC, the tensile strength was doubled (up to 1.19 MPa) compared to that of pure ENR. With this filler content, the compound exhibited an impressive healing efficiency of 83 % of its maximum stress and 95 % of the original elongation at break without any external stimulus and at room temperature.

Another approach in the development of self-healing composites has been the incorporation of waste material as a sustainable strategy. A pioneering research line of the authors has considered the use of ground tire rubber (GTR) as reinforcing filler and healing precursor. In early studies, they reported its use in XNBR (ideal for seals, gaskets and hoses) [136] and in SBR (ideal for tires) [89]. In XNBR, the incorporation of selectively functionalized GTR can increase the repair efficiency from 15 % to 70 %, approximately, without detriment to the mechanical properties and chemical resistance of XNBR.

Other sustainable strategies such as cryogenic (-cryo) or waterjet (-WJ) grinding to decrease particle size (which increases the reinforcing power) and devulcanization (d-) have been employed on GTR for subsequent reuse as a filler in self-healing SBR blends. Núñez–Carrero et al. [152] demonstrated through a design of experiment (DOE) that partial devulcanization (breaking of some points of the irreversible crosslinks)

of GTR at medium (71 °C) and high temperatures (200 °C) facilitates its incorporation in large quantities (up to 30 phr and 40 phr, respectively) in new elastomeric recipes increasing the tensile strength of the virgin material up to four times. Besides, grinding also allows the incorporation of up to 30 phr of waste material. In terms of healing efficiency, all prepared compounds exhibit full modulus recovery at low deformations (50 %), regardless of the processing technique employed in GTR (Fig. 8a). Furthermore, the properties at the breaking point (Fig. 8b and Fig. 8c) show higher efficiencies with 30 phr of grinded material, but may be influenced by a drastic reduction of the ultimate stress. With this study, the trade-off between repair efficiency and mechanical performance was evidenced through a systematic analysis. As was stated before, it is quite common in self-healing elastomers, that the higher the mechanical performance, the lower the healing efficiency, essentially due to restrictions on chain mobility imposed by typical reinforcing fillers or crosslinking points.

Very recently, Araujo-Morera et al. [144] presented a study that breaks that dichotomy between mechanical performance and self-healing. In this research, SBR composites were developed by combining modified GTR (mGTR) with CB. The modification of GTR was performed with the aim of providing its surface with active functional groups that can contribute to self-healing. The compound reinforced with 20 phr of mGTR and 20 phr of CB maintains the healing efficiency of unfilled SBR (~80 %) and improves its tensile strength by ~ 300 %, achieving a trade-off between both properties, thanks to a combination of disulfide exchange and ionic interactions capable of organizing themselves into multiplets and clusters, dynamic higher-order structures that act as reinforcing sites.

All these examples can serve as a reliable proof of the possibility of reaching self-healing capability in rubbers with potential use in automotive applications. The challenge is not easy, but the goal is worth it in the current environmental context, in which more sustainable materials are required, compatible with the CE model. The ball is in the hands of the scientific community, the automotive and rubber industries, waiting for more and better collaboration strategies that will enable us to achieve this goal in less time.

5. Conclusions

Many developments have been accomplished so far, studying a wide range of different rubber matrices (natural and synthetic) and their underlying healing mechanisms. Fig. 9 summarizes all the research presented on unfilled rubbers taking into consideration the Top 8 most consumed elastomeric matrices in the automotive industry. The Sankey Diagram was employed in this section to visually illustrate the dispersion of research on diverse types of self-healing mechanisms (left node) across various elastomeric matrices with potential applications in the automotive industry (right node). The thickness of each distribution path (links) is directly proportional to the number of literature-based articles available. As can be seen, the group of tire rubbers dominates the area representing ~ 38.2 % of all the literature reviewed, followed by PDMS (~34.83 %) and PU (~17.98 %). Nonetheless, this field of research is still new and the published work to date has primarily focused on characterizing self-healing model systems with more conceptual than realistic applications. Thus, the future seems to be towards an application-specific full optimization. The development of research highly focused on the recovery of specific functionalities according to the target application (wear resistance, puncture resistance, air tightness, to mention a few) instead of the exclusive recovery of tensile strength must be the next step.

Another primary obstacle encountered during this research pertained to the challenge of comparing the available studies. It is evident that there is a pressing need to establish measurement standards in the field of self-healing, which would enable comparisons of the outcomes obtained in diverse investigations. The absence of universally recognized methodologies has resulted in each study presenting specific conditions, impeding fair comparisons between mechanisms, matrices, and applications. Addressing this issue is crucial in enhancing the reliability and validity of future research endeavors in this area.

6. Outlook and perspectives

Among the very wide array of applications for rubber, the automotive sector accounts for more than 75 % of production. This strong link between transport and rubber does not only come from tires, but from a wide number of parts and components including hoses, dynamic seals, pipes, shock absorbers, engine mountings, fan belts, coatings, among others. Manufactures believe that they have a responsibility to their customers to support the longevity of vehicles by ensuring that they can be serviced, repaired and maintained. In this sense, the development of self-healing rubbers should be considered as a key technology in the upcoming years.

A report from *N*-tech [153] estimated that the largest market for SHM was going to be found in the automotive industry with an income of $1.6 billion by 2020. According to *N*-tech, suppliers of SHM can build on the existing demand for anti-scratch coatings, as well as the fact that the automobile industry is currently very interested in making both the interiors and exteriors of cars more sustainable as part of their competitive strategy. As an example, Ford and Nissan have developed self-healing films for protecting the car from damage and scratches, which are expected to be implemented on a commercial scale [154]. Also, brands such as Lamborghini and Goodyear have been working on developing self-healing cars and tires, respectively.

Automotive-oriented self-healing elastomers promise an exciting prospect for design engineers, although three key issues must be solved to ensure their scaling-up to a commercial stage. A complete understanding of the healing mechanism is mandatory; future research should be devoted to transmitting reversible interactions into commercial polymers. The processability of self-healing systems also requires more research, to improve the manufacturing stage. And finally, the cost of these systems needs to be decreased so they can be industrially attractive.

However, that does not stop us from conceiving how self-healing elastomers will fit into future designs. In the upcoming years, cars

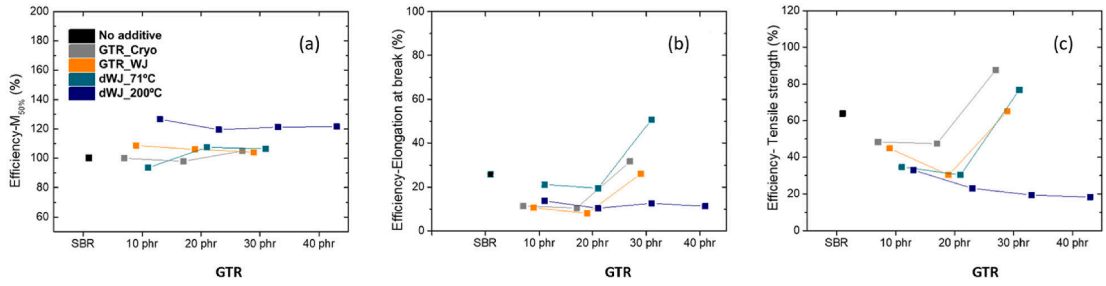


Fig. 8. Healing efficiency of SBR/GTR blends of (a) modulus at 50 % strain (M50), (b) tensile strength, and (c) elongation at break. Adapted with permission of Elsevier [152].

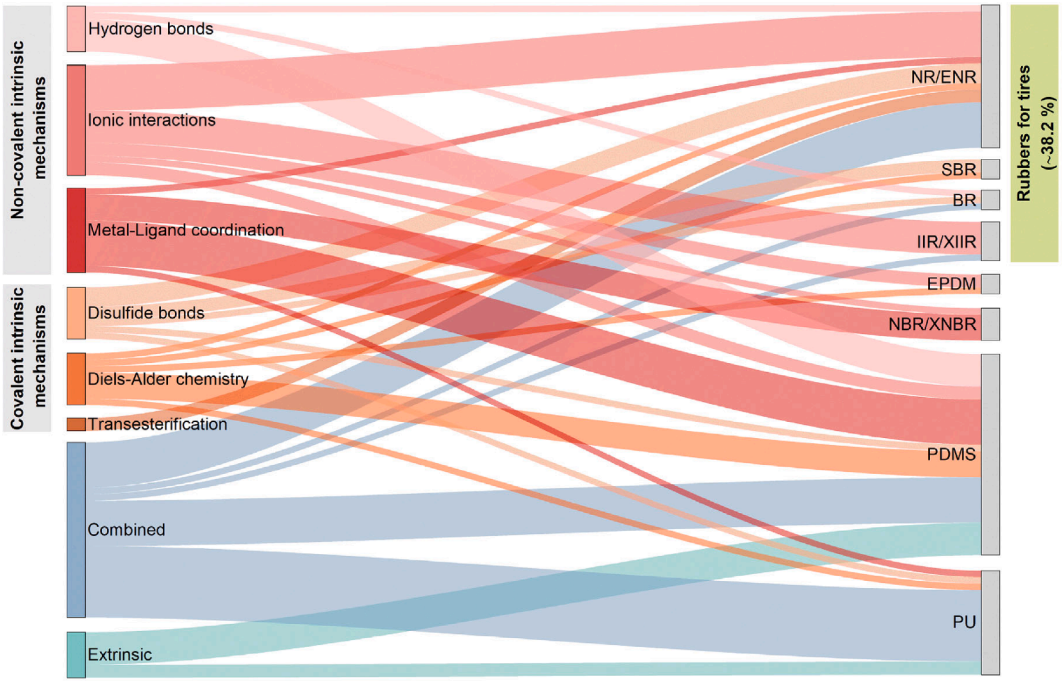


Fig. 9. Summary of the works available in the Top 8 most consumed elastomers for the automotive industry in a Sankey diagram.

constructed of lightweight and self-healing CFRP chassis will travel on concrete roads that autonomically repair, and punctures or cracks in the tires will be repaired while rolling. The development of such areas of self-healing technology will truly revolutionize the automotive industry.

CRediT authorship contribution statement

Saul Utrera-Barrios: Conceptualization, Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Raquel Verdejo:** Conceptualization, Writing – review & editing, Visualization, Project administration, Funding acquisition. **Miguel Ángel López-Manchado:** Conceptualization, Writing – review & editing. **Marianella Hernández Santana:** Conceptualization, Validation, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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