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Review Article

Nano-reinforced self-healing rubbers: A comprehensive review

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ABSTRACT

In recent years, there has been a growing interest in self-healing rubbers due to their ability to repair mechanical damage autonomously. This capability is achieved by incorporating reversible dynamic cross-linked networks within the rubber matrix. Technological and scientific advancements have led to the development of nano-reinforced self-healing rubbers, focusing on enhancing mechanical strength while maintaining high self-healing efficiency and low dependence on external stimuli. This review discusses the latest progress in utilizing various nanofillers, including carbon-based, bio-based, hybrids, and other variants, to reinforce rubber matrices and improve self-healing properties. The review covers nanofiller characteristics, mechanical properties, and surface modification techniques. Favorable interactions between host matrices and fillers are highlighted, along with reinforcing theories and mechanisms. The sustainability aspects of these materials are also addressed, and their potential applications in cleaner production and sustainable manufacturing are explored, offering insights into the future prospects of nano-reinforced self-healing rubbers on a larger scale.

Introduction

The process of healing, a fascinating phenomenon in nature, has motivated scientists to create self-healing materials that can significantly improve durability, performance, and prolong their service life [1,2]. Self-healing, in essence, refers to a material's inherent ability to repair mechanical damage autonomously and restore its original physical state [3]. Over the last decade, researchers have focused on imparting self-healing properties to elastomers, given their wide range of potential applications. These applications include but are not limited

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Abbreviations: (MW)CNTs, (Multi-walled) carbon nanotubes; CB, Carbon black; EPDM, Ethylene propylene diene monomer; (E)NR, (Epoxidized) natural rubber; BIIR, Bromobutyl rubber; (r)GO, (Reduced) graphene oxide; CNC, Cellulose nanocrystals; ChNC, Chitin nanocrystals; CNF, Cellulose nanofibers; (X)NBR, (Carboxylated) nitrile butadiene rubber; (g)GTR, (Grafted) ground tire rubber; AA, Acrylic acid; SA, 3 methacryloxypropyltrimethoxysilane; SEM, Scanning electron microscopy; TESPT, bis[3-(triethoxysilyl)propyl]tetrasulfide; TESPD, bis[γ-triethoxysilylpropyl]disulfide; MEPTS, mercaptopropyltriethoxysilane; TEM, Transmission electron microscopy; (o)NR, (Oxidized) natural rubber; WNRP, Waste natural rubber powders; PSR, Polysulfide rubber; SBR, Styrene butadiene rubber; PDMS, Polydimethylsiloxane; RT, Room temperature; ZnO, Zinc oxide.

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to, coatings [4–6], sensors [7], personal protective equipment [8,9], as well as flexible electronics and electronic skin [10]. Devices equipped with self-healing capabilities can extend their service periods and enhance reliability and safety by minimizing the likelihood of failure, thereby providing inherent benefits to users. Furthermore, the literature pertaining to the field grows at a steady rate yearly, as shown in Fig. 1.

Elastomers, renowned for their exceptional mechanical properties, possess the ability to withstand significant forces without undergoing deformation [11]. Among elastomers, rubber stands out due to its innate elastic properties, which predispose it to self-healing abilities. This elasticity originates from the flexibility and mobility of rubber chains. Non-covalent interactions within rubber matrices play a critical role in repairing mechanical damage by facilitating chain reconstruction and redistribution [2,12]. Incorporating reversible cross-linked networks and dynamic bonds into rubber matrices not only endows them with self-healing capabilities but also facilitates reprocessing and recycling. Recent investigations have explored various methods to enhance self-healing, including the utilization of reversible non-covalent interactions like hydrogen bonds [13–15], metal–ligand coordination [16–18], ionic bonds, and cluster formation [19–21], as well as π-π interactions [22]. Hybrid systems combining multiple interaction types have also garnered attention [23]. Moreover, reversible covalent bonds, including Diels-Alder chemistry [24–26], imine bonds [27], and disulfide bonds [28,29], have emerged as fundamental intrinsic mechanisms for self-healing in rubber [30]. Fig. 2 illustrates common reversible covalent and non-covalent bonds introduced to rubber networks to promote self-healing properties. Besides bonding concepts, other key factors like localization, temporality, mobility, and selection of mechanisms are crucial for successful and robust self-healing processes. Another critical criterion for enhancing self-healing performance is the reliance on external stimuli, with the aim of being nullified [31–33]. External stimuli such as heat, light, UV irradiation, or environmental pH can induce polymer chain mobility, thereby efficiently restoring the material's mechanical integrity with minimal resources.

Formulating rubbers with both self-healing abilities and excellent mechanical performance poses a significant challenge, as optimizing one property often comes at the expense of the other. The self-healing performance of rubbers relies on a flexible and dynamically reversible cross-linked network. In contrast, mechanical strength is influenced by the rigidity and stability of this network, creating a delicate balance [24,34]. Hence, addressing these challenges is crucial. A commonly adopted strategy to tackle issues related to mechanical strength and robustness in rubber composites involves the incorporation of fillers. Besides enhancing mechanical properties, adding fillers at industrial manufacturing scales improves the cost-effectiveness of rubber products [35,36]. Introducing fillers allows for controlled restriction of rubber chains, leading to improved tensile strength, typically at the expense of elongation [37]. Nevertheless, novel strategies have emerged when faced with the trade-off between self-healing performance and tensile strength. These strategies center around functionalizing fillers with different reversible moieties to enhance interactions between the filler and the host material. This approach aims to improve filler dispersions, address differences in polarities, and overcome the incompatibility of functional groups. The goal is to establish strong yet dynamic chemical bonds that enable self-healing and restoration of specific material properties, including electrical conductivity and chemical resistance [9,38–41].

This article aims to address the existing knowledge gap by offering a comprehensive compendium regarding the advancements in filler surface functionalization and their applications to enhance self-healing and mechanical performance in rubbers. This review provides an overview of various nanoparticulate fillers that can be integrated into rubber matrices to enhance their self-healing capabilities. Additionally, it explores surface modification techniques applied to these fillers, focusing on enhancing their reinforcement potential. The review further highlights relevant reinforcing mechanisms of fillers in rubber materials, insights into the sustainability aspects of self-healing rubbers, and how it could potentially benefit the relevant stakeholders of this futuristic technology. It concludes by presenting perspectives on the outlook, prospects, and challenges associated with the technology of self-healing rubber, especially concerning larger-scale industrial applications. This comprehensive review aims to contribute valuable information to the field, facilitating a deeper understanding of the evolving landscape of self-healing rubber technology.

Integration of nanoparticulate fillers within rubber frameworks

Nanofillers, known for their diverse shapes and sizes, primarily comprise nanoparticles sized between 1 and 100 nm [37,42,43]. Their small dimensions and exceptionally high surface areas allow them to

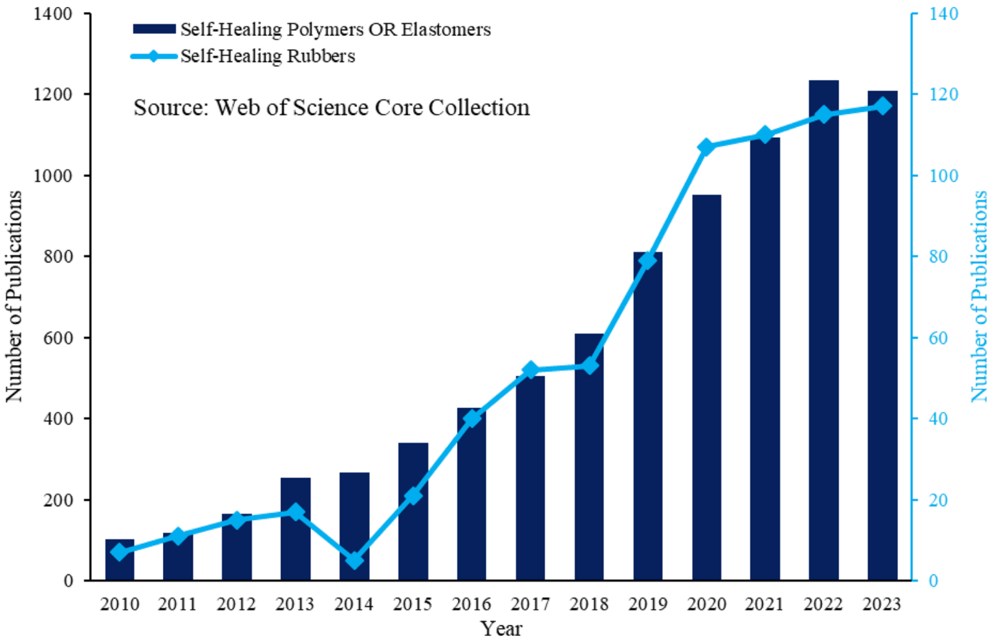

Fig. 1. Growth of scholarly literature on self-healing polymers and rubbers up to 2023.

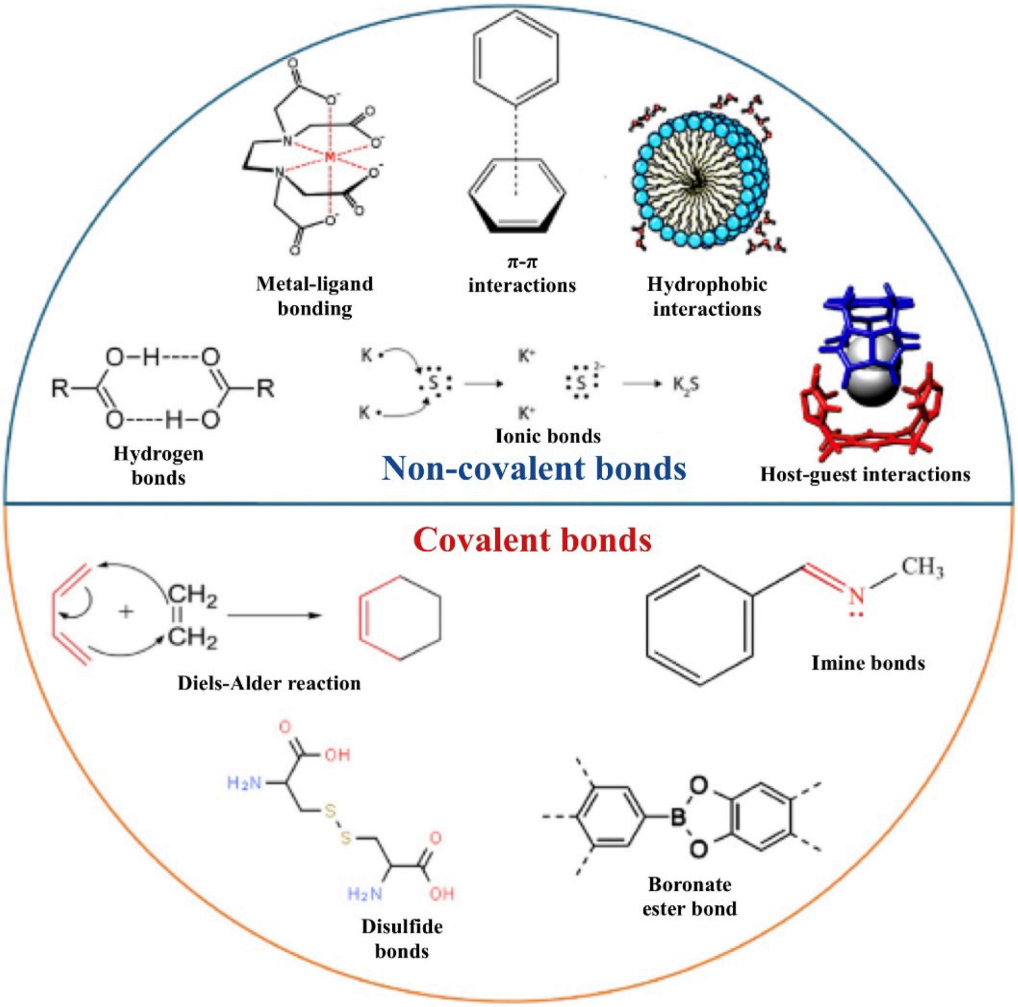

Fig. 2. Utilization of covalent and non-covalent bonds in self-healing rubbers.

substantially influence the properties of rubbers, even at relatively low concentrations [44–46]. In many instances, self-healing rubbers achieve high recovery percentages but exhibit low recovered tensile strengths of less than 1 MPa, limiting their practical applications [21,47]. Fillers are incorporated into the elastomeric matrix to address this limitation of enhancing mechanical properties. While this approach might affect self-healing capabilities, incorporating nanofillers such as functionalized MXenes [48,49], carbon nanotubes (CNTs) [50,51], graphene [52], sustainable biomaterials like nanocellulose [37,53–55], and unique supramolecular nanosheets [56,57] into the matrix shows potential for maintaining or even enhancing self-healing properties. This is attributed to dynamic exchange reactions and reversible stimuli-responsive bonds. Nevertheless, several critical factors should be considered when selecting these fillers, including size, concentration, surface chemistry, and dispersibility. Fig. 3 illustrates the classification of common nanofillers used in rubber reinforcement, highlighting their diverse characteristics.

Carbon-based nanoparticulate fillers

Carbon-based fillers play a significant role in traditional fillers utilized in the rubber industry to enhance material strength and resilience. A primary and widely used example is carbon black (CB), a reinforcement material integral to rubber formulations since World War I, constituting approximately 92 % of global production [58,59]. Other carbon-based derivatives, including CNTs, graphene, and MXenes, further expand the diverse range of fillers used [60–64]. Additionally, in certain cases, recycled or recovered rubber with high carbon content can serve as fillers in composite rubber systems, following physical processing methods such as cryogenic procedures and extrusion [65–68]. Since its initial application, carbon and its structural derivatives have demonstrated excellent compatibility with various elastomeric systems. They boast large surface areas and tunable functional groups, making them versatile choices [58]. Moreover, these carbon-based fillers are economically advantageous, as a higher percentage of these fillers allows for a reduction in the amount of rubber used in the formulation, serving as a cost-control strategy [58,69].

Carbon-based fillers, such as CB and CNTs, have been investigated for their potential to enhance the mechanical properties of self-healing polymers and rubbers [51,70]. For example, Zhang, et al. [71] incorporated CB as an active filler into an ethylene propylene diene monomer (EPDM) vitrimer system, creating a sustainable and robust material. A 10 phr increase in CB resulted in a 25 % rise in the tensile modulus of the material. The study demonstrated that EPDM composites with 70 phr CB positively impacted recovery ratios of modulus (∼100 %) and tensile strengths (>75 %) through three reprocessing cycles, attributed to the hydrodynamic effects of CB [71]. In another study, Le, et al. [62] studied the inclusion of CNTs as nanofillers in NR (natural rubber)/BIIR (bromobutyl rubber) composites modified with butyl imidazole to enhance the strength and conductivity of the resulting supramolecular self-healing elastomer. The investigation employed thermal and resistive heating (Joule heating) to facilitate the self-healing of the CNT/NR/BIIR composite. The addition of CNTs into NR/BIIR with imidazole affected

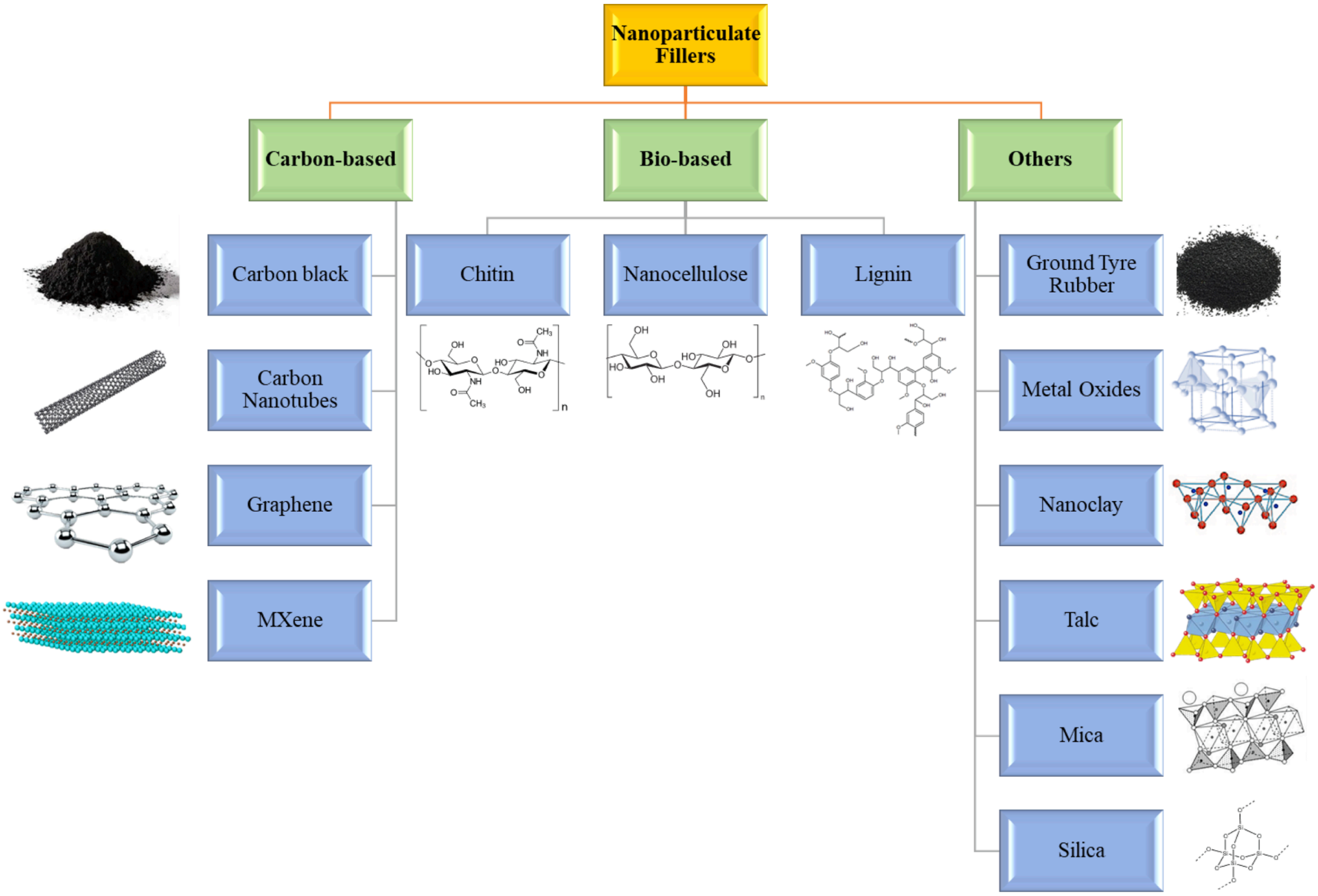

Fig. 3. Commonly applied nanoparticulate fillers in rubber composites.

its elongation at the break due to restrictions in rubber chain mobility. However, it did not compromise its tensile strength during thermal self-healing. The generation of a CNT network within the composite facilitated its reformation at the interphase during the healing process triggered by Joule heating, making it suitable for applications in the electrical and electronics industry [62]. Furthermore, the recovery of electrical and mechanical properties of NR with the incorporation of graphene in the latex formulation was investigated by Hernández, et al. [72]. The study concluded that graphene fillers played a crucial role in restoring electrical properties through forming percolation pathways and achieving a 70 % recovery in mechanical integrity. This was attributed to excellent interactions between the rubber and filler and effective load distribution at the interface [72]. In terms of mechanical strength, a similar observation was reported by Utrera-Barrios, et al. [73] when thermally reduced graphene oxide (rGO) was added to epoxidized natural rubber (ENR), enabling self-healing up to 85 % under room conditions. This improvement was attributed to enhanced H-bonding interactions. Meanwhile, Zhang, et al. [49] developed self-healing and flexible rubber-based composite materials intended for use as flexible electronic sensors by incorporating MXene, specifically titanium carbide (Ti_3C_2). The inclusion of MXene facilitated nearly complete strength recovery, attributed to the abundance of reversible H-bonds formed between the functionalized base rubber and fillers. Additionally, electrical conductivity was restored, laying the groundwork for the fabrication of smart sensors with an extended service life and enhanced reliability. This approach presents the versatility of incorporating advanced materials, such as MXene, to create multifunctional rubber-based composites suitable for applications in flexible electronic sensors.

Being the pioneer among conventional fillers, carbon and its derivatives continue to find extensive use, particularly in the automobile industry for reinforcing rubber in tires and treads, as well as in footwear, toys, and machinery conveyor belts. However, with the advancement in research on carbon-based nanomaterials, such as graphene and graphene oxide, their applications have expanded beyond mere reinforcement. These materials now play a key role in promoting self-healing properties and restoring electrical conductivity in smart materials. This evolution renders carbon-based fillers multifaceted, transcending their traditional role as reinforcers for rubber systems. Moreover, contemporary concerns regarding the environmental impact of carbon-based rubber composites upon reaching the end of their product lifespan have prompted a paradigm shift. Increasingly, there is an exploration of more sustainable alternatives for reinforcing rubber, with a focus on materials derived from natural resources or biomaterials [74]. This transition highlights a broader global commitment to the development and adoption of environmentally friendly materials and practices.

Biologically-derived nanoparticulate fillers

The growing awareness and concerns regarding the environmental impact of carbon-based fillers have led to a significant focus on seeking more sustainable alternatives for reinforcing rubber. Intensive research efforts have been directed towards exploring and functionalizing bio-resources and biomass as effective fillers in rubber composites [74,75]. Among the extensively investigated alternatives are natural fibers derived from agriculture, particularly nanocellulose and its various modified forms. These alternatives are favoured for their lower environmental footprint, cost-effectiveness, high strength, high aspect ratios, tunability, and excellent compatibility with various rubber systems [37,55]. Sustainable fillers can also originate from wood pulp and various crops such as jute, cotton, empty fruit bunches, and hemp. These materials offer sources of lignin, which is one of the most abundant natural materials on Earth and is readily accessible in the pulp and paper industry [37,76,77]. Recent reviews by Mohamad Aini, et al. [35] and Ridho, et al. [78] have shed light on the state-of-the-art methods for extracting, functionalizing, and utilizing lignin to reinforce rubber composites, contributing to sustainable material production. In addition to agricultural or plant sources, bio-fillers can be derived from crustaceans, such as shrimp and crab shells, insects, and fungal cell walls, in the form of chitin. Chitin is a naturally occurring polymer produced at a rate of up to 10^{11} tons annually, with a substantial portion being discarded as biomass [79]. Due to its relatively linear structure, certain chitin polymorphs exhibit nanofibrous structures, offering the potential for forming a reinforcement network within rubber matrices. The utilization of environmentally friendly bio-based fillers represents a significant step toward a circular economy and closed-loop manufacturing of products. The incorporation of these fillers has been proposed as a means to potentially improve the biodegradability of rubbers while simultaneously providing mechanical reinforcement to the composite [80–82]. The following studies explore the versatility of naturally occurring fillers, demonstrating their efficacy in reinforcement and their multifunctionality in imparting and augmenting self-healing properties to both natural and synthetic rubbers.

Polysaccharides like cellulose and chitin are environmentally friendly and robust nanofillers [2,83]. For instance, in a study by Cao, et al. [54], ENR was successfully reinforced with cellulose nanocrystals (CNCs) obtained from tunicates. The self-healing properties of the composite arise from dynamic H-bonds and chain diffusion between the oxygenous groups of ENR and the hydroxyl groups of CNCs. The resulting composite exhibited a high tensile of about 4 MPa with 20 phr CNC loading and achieved an outstanding 86 % healing efficiency, unlike neat ENR's 48 %. This study exemplifies the potential of polysaccharide-based nanofillers to enhance the mechanical and self-healing properties of rubber composites significantly.

In a parallel approach, Nie, et al. [84] utilized chain diffusion and H-bonding to develop a self-healing composite of ENR reinforced with chitin nanocrystals (ChNCs). The hemiacetal hydroxyl group in ChNCs disrupted the epoxy groups in ENR, forming a cross-linked network. The resulting ENR/ChNC composite exhibited increased tensile strength but reduced elongation at higher ChNC loadings due to enhanced hydrogen bonds that limited chain mobility. Notably, a 20 % ChNC loading in the ENR composite demonstrated exceptional self-healing capabilities, restoring 83 % of tensile strength and 95 % of strain at break, compared to 42 % and 12 % for neat ENR, respectively. While this approach showed promising results, the intricate nature of the ChNC modification process has limited its industrial-scale use. Meanehile, in a progressive example of industrial applications, Supramaniam, et al. [8] and Supramaniam, et al. [85] reported the use of bio-based cellulose nanofibers (CNFs) decorated with zinc oxide nanoparticles as reinforcing fillers and enhancers of self-healing in ENR composites, as illustrated in Fig. 4. 70 % and 92 % of strength and strain, respectively were recovered, after thermal healing. A prototype with these functionalities was also fabricated and successfully validated for reusable glove applications, presenting the potential of bio-based fillers in practical, real-world applications.

In a recent study by Utrera-Barrios, et al. [86], cellulosic fibers were utilized to reinforce blends of ENR and cellulose propionate self-healable composites. The study found that incorporating these fibers at a concentration of 5 phr resulted in optimal reinforcement and achieved greater than 100 % self-healing efficiency of the composite following a temperature-driven healing protocol (200 bar pressure, 150 °C for 12 h). The enhanced healing efficiency was attributed to the presence of hydroxyl groups contributed by the cellulose fibers, acting as sustainable fillers, which offered additional sites for dynamic and reversible H-bonding formation within the rubber matrix.

Metallic-based and silica nanoparticulate fillers

Beyond carbon and bio-based fillers, a limited number of studies explore the versatility of metallic components to enhance self-healing in rubber composites. The scarcity of such studies is justified by the common presence of a metal constituent, such as zinc in oxides or carbamates, in rubber compounding formulations for strength and curability. While certain investigations exploit existing metallic moieties to enhance self-healing through ionic interactions [8,21], several others focus on multi-metal-based constituents within independent rubber systems. Each metal component plays its designated role in providing strength and contributing to forming a dynamic filler-matrix network [87,88].

In a novel approach, Liu, et al. [87] proposed the design of a hierarchical dynamic cross-linked network to minimize the trade-offs between strength and self-healing properties. In their system, two iron-

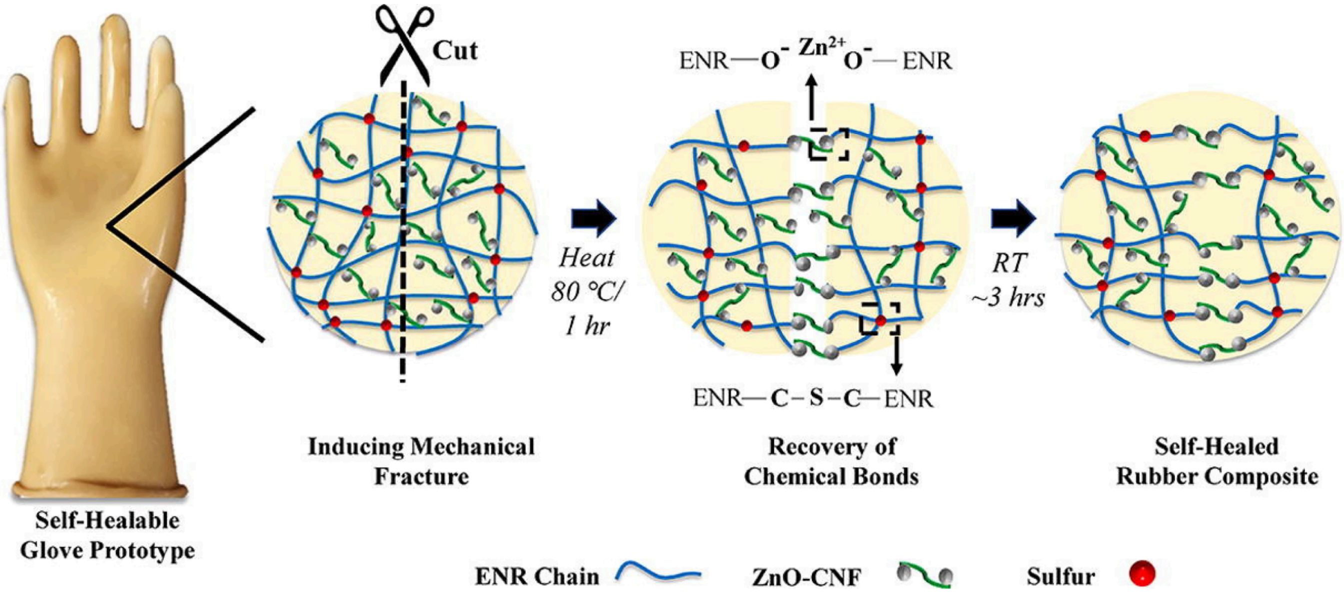

Fig. 4. Prototype of a self-healing glove using ENR filled with functionalized CNF decorated with zinc oxide. Copyright 2022, Elsevier. Reproduced with permission from Supramaniam, et al. [8]

based chemicals, namely iron chloride hexahydrate and iron (III) oxide, were used to establish the dynamic cross-linked network alongside existing zinc species present in compounded carboxylated nitrile butadiene rubber (XNBR). The concept of a hierarchical cross-linked network, excelling in stiffness and toughness through spatial hierarchy, was introduced to address the challenges of self-healing rubbers, as depicted in Fig. 5. The XNBR composite self-healed up to 66 % after 1 h under near-infrared irradiation heating, facilitated by metal coordination bonds. Moreover, the superior network formation endowed the XNBR with magnetic responsiveness and shape memory capabilities triggered by light and heat.

Silica or silicon dioxide (SiO_2) is another widely used reinforcing filler in rubber processing, particularly in automotive tires [89]. The presence of multiple oxygenous functional groups surrounding the silicon atom makes it easily compatible as a bridging cross-linker between metal ions within rubber matrices. While incorporating SiO_2 in rubber systems was initially aimed at improving mechanical strength, it was expected to negatively impact self-healing performances due to increased restrictions in rubber chain mobility [90]. Recent studies have indicated that, through careful tuning and functionalization, the incorporation of SiO_2 can gradually become independent of self-healing properties [91–94]. Sattar, et al. [95] highlighted in their study that functionalized NR with proteins and phospholipids bonded well with SiO_2 through metal-ion-mediated heteroaggregation and H-bonds. The cluster was further bridged with a silane coupling agent for enhanced strength. The synthesized NR-SiO_2 composite recovered up to 87 % of its mechanical strength after exposure to 50 °C for 24 h. This significant healing capability was attributed to dynamic H-bonding sacrificial networks and ionic interactions, demonstrating the potential of carefully tailored SiO_2 incorporation for enhancing self-healing performance in rubber composites.

Progress in nano-reinforced self-healing rubber composites

Table 1 provides a comprehensive summary of recent advancements in nano-reinforced self-healing rubbers. The selection criteria for studies included in this table focused specifically on fillers that serve dual roles, namely mechanical reinforcement and simultaneous enhancement of self-healing properties within the base rubber composite. The categorization is based on different types of fillers utilized in rubber matrices, along with their measurable impact on the composite's mechanical properties and self-healing capabilities.

Methods for nanofiller surface modification

Achieving molecular compatibility between nanofiller surfaces and the base polymer matrix poses a significant challenge in rubber reinforcement. This challenge arises from the tendency of nanofillers to agglomerate within the polymer network. Agglomeration leads to an uneven distribution of the filler, creating stress sites that facilitate crack propagation, as discussed in a study by Saman, et al. [113]. To address this issue, surface modification or functionalization of nanofillers has emerged as a promising and straightforward approach, as demonstrated by numerous recent investigations.

Among the various modification methods, surface chemical modification emerges as the most widely employed technique for rubber reinforcement. This category includes surface grafting, coupling, and esterification reactions [114]. These methods involve altering the chemical properties of nanofillers, providing precise control over their surface characteristics and allowing for the customization of intended functional groups. Chemical functionalization enhances compatibility between hydrophobic rubber molecules and hydrophilic nanofillers, improving dispersion uniformity [115,116]. It also enables the incorporation of specific functional groups on the nanofiller's surface, promoting molecular-level interactions and enhancing mechanical properties such as tensile strength and abrasion resistance while

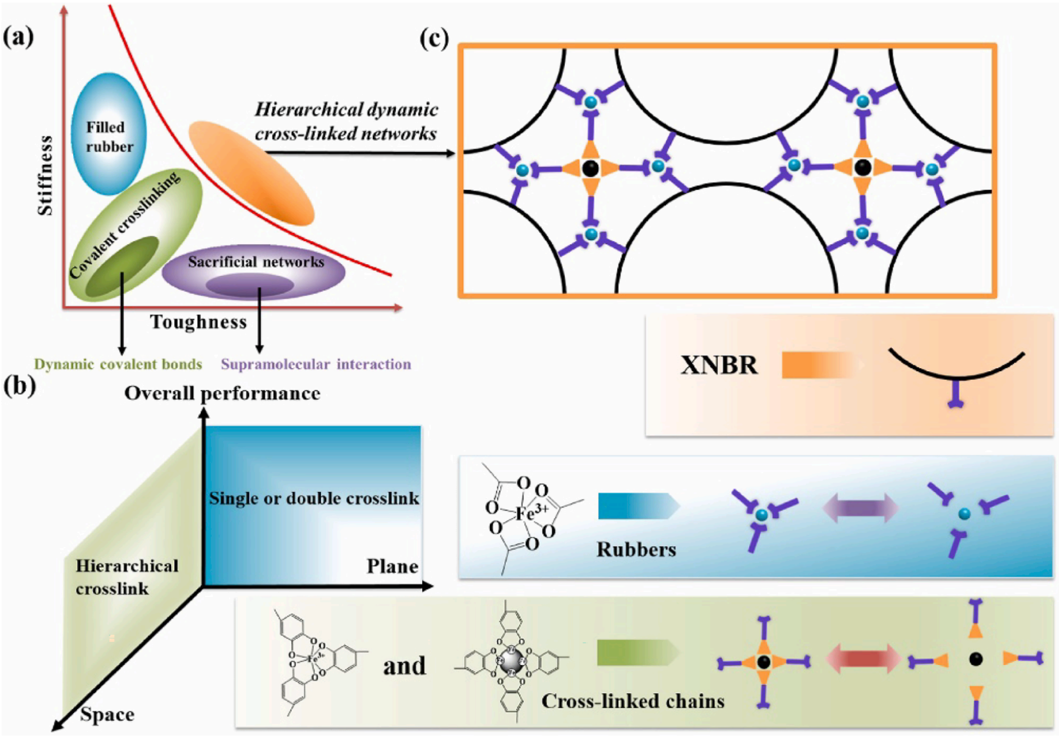

Fig. 5. (a) Evaluating stiffness and toughness: A comparative analysis of the hierarchical dynamic cross-linked network and other dynamic interactions; (b) Design strategy with orthogonally tunable mechanical, spatial hierarchy; (c) Proposed interactions of the hierarchical dynamic cross-linked network. Copyright 2023, Elsevier.
Reproduced with permission from Liu, et al. [87]

Table 1
Current developments in nano-reinforced self-healing rubbers.[1] *.

Filler				Base Rubber	Self-Healing Parameter				Tensile Strength (MPa)		Strain (%)		Ref.
Category	**Material**	**Size**	**Loading**[2]		**Mechanism**	**Condition**	**Duration**	**Performance (%)**[3]	**Before**	**After**	**Before**	**After**	
Carbon-based	Furfuryl-terminated MWCNT	*n/a*	5 wt%	Furfuryl-grafted SBR	Diels-Alder chemistry	100 °C	5 h	~ 71	3.5	2.5	~ 485	~ 405	[26]
Carbon-based	CNT	9.5 nm diameter; 1.5 μm length	3 phr	Epoxidized NBR	Metal-ligand coordination bonds	80 °C	9 h	~ 145	1.15	1.65	300	375	[46]
Carbon-based	Asparagine-modified MXene	500 mesh (unmodified)	10 wt%	3,4-dihydroxy-benzaldehyde-modified PDMS	Imine and H-bonding	RT	24 h	98.4	1.81	1.78	81	90	[49]
Carbon-based	CNT and CB	CNT: 9.5 nm diameter; 1.5 μm length; CB: 30 nm diameter	5:7.5 = CNT:CB as 20 phr	Butyl-imidazole modified BIIR/NR blend	Ionic interactions	120 °C	30 min	38	1.79	0.68	2746	502	[50]
Carbon-based	Cryo-grounded GTR	*n/a*	20 phr	SBR	Chain interdiffusion and reversible disulfide bonds	70 °C	12 h	33	2.90	0.97	546	180	[66]
Carbon-based	MWCNT	9.5 nm diameter; 1.5 μm length	5 phr	Butyl-imidazole modified BIIR/NR blend	Ionic imidazolium cluster formation	15 V Joule heating (100 °C)	1 h	35.3	4.25	1.50	980	400	[62]
Carbon-based	Graphene	1–2 nm thickness; 70 μm lateral size	0.25 phr	NR	Disulfide exchange reactions	70 °C	7 h	60	0.45	0.27	462	370	[72]
Carbon-based	Reduced GO	n/a	0.50 phr	ENR 50	H-bonding	25 °C	24 h	~ 83	1.85	1.55	431	~ 390	[73]
Carbon-based	CB	Grade N330	30 phr	NR	Ionic cluster interactions	RT	10 min	80	~ 0.75	~ 0.60	~ 580	~ 560	[96]
Carbon-based	CB	*n/a*	10 phr	Pyridine modified BIIR	Ionic cluster interactions	80 °C	12 h	106	~ 7.50	~ 8.00	~ 1700	~ 1500	[97]
Carbon-based	Graphene nanoplatelets	8–15 nm thickness, 1.5 μm length	1 wt%	Silicone rubber	Hydrogenous functional groups	250 °C	2 h	~ 87	1.4	1.2	~ 210	~ 240	[98]
Carbon-based	Serine-modified Ti_3C_2-MXene	400 mesh	6 wt%	Serine-modified ENR 50	Supramolecular H-bonding	RT	1.5 h	99.3	4.55	4.52	388	404	[64]
Carbon-based	Poly(acrylic acid)-grafted GTR	800–1000 μm	6 phr	XNBR	Ionic cluster interactions	100 °C	10 min	~ 70	10.7	7.5	850	510	[99]
Carbon-based	GTR	0.8–2.0 mm	10 phr	SBR	Disulphide bonds	70 °C	7 h	40	2.51	1.00	617	*n/a*	[100]
Carbon-based	Acid-modified GTR and CB	GTR: 0.8–2.0 mm; CB: Grade N330	20 phr GTR, 20 phr CB	SBR	Ionic cluster interactions	130 °C	5 h	~ 85	~ 6.4	~ 5.5	*n/a*	*n/a*	[101]
Carbon-based	Ionic liquid-modified GO	0.86 nm (interlayer spacing)	3 phr	XNBR	Supramolecular ionic network	40 °C	24 h	85.2	6.1	5.2	1730	*n/a*	[102]
Carbon-based	Graphene nanosheets	5–10 μm diameter, 3–10 nm thickness	10 wt%	Carboxylated PDMS	H-bonding	25 °C	24 h	84.6	0.65	0.55	380	115	[103]
Carbon-based	CB	*n/a*	6 phr	Bis(3-aminopropyl)-terminated PDMS	Diels-Alder chemistry, covalent networks	130 °C, then 80 °C	5 min (130 °C), 48 h (80 °C)	84	0.375	0.315	42	36	[104]
Bio-based	ZnO-functionalized CNF	~ 25 nm (unfunctionalized)	5 phr	ENR 50	Ionic interactions	80 °C	1 h	70	4.05	2.83	989	910	[9,85]
Bio-based	Tunicate CNC	10–20 nm diameter, 500 nm-2 μm length	20 wt%	ENR 40	Supramolecular H-bonding	RT	24 h	87	4.04	3.52	200	185	[54]
Bio-based	Chitin nanocrystals	100 nm	20 wt%	ENR 40	Supramolecular H-bonding	50 °C	12 h	95	1.19	1.13	530	519	[84]
Bio-based	Cellulose fibers	12–15 μm diameter, 50–350 μm length	5 phr	ENR25:Cellulose propionate blend [70:30 phr]	H-bonding	150 °C	12 h	~ 105	1.3	1.4	557	557	[86]

(*continued on next page*)

Table 1 (*continued*)

Filler				Base Rubber	Self-Healing Parameter				Tensile Strength (MPa)		Strain (%)		Ref.
Category	**Material**	**Size**	**Loading**[2]		**Mechanism**	**Condition**	**Duration**	**Performance (%)**[3]	**Before**	**After**	**Before**	**After**	
Bio-based	Nanochitosan	200 nm	20 wt%	XSBR	Hybrid supramolecular network, ionic interactions	RT	24 h	92	1.3	1.2	1030	*n/a*	[105]
Bio-based	Chitosan and amino-triethoxysilane-modified CNC	Chitosan: n/a; CNC: 353 nm length, 6–8 nm diameter	3 phr chitosan; 2 phr CNC	ENR	Supramolecular H-bonding	80 °C	4 h	~ 88	2.30	2.02	576	*n/a*	[106]
Bio-based	Carboxylated CNF	4–10 nm diameter; ~ 200 nm length	5 phr	NR	Ionic bonding, H-bonding	RT	6 h	94	~ 1.75	~ 1.65	~ 390	~ 380	[107]
Bio-based	Carboxymethyl chitosan	800 nm	10 wt%	ENR 40	Supramolecular H-bonding	RT	12 h	~ 90	1.92	1.72	~ 275	~ 275	[108]
Bio-based	Sodium alginate	*n/a*	15 phr	ENR 25	Extrinsic flow of polycaprolactone, H-bonding, and ionic bonding	110 °C	12 h	~ 105	9.2	~ 9.7	1156	~ 1272	[109]
	Calcium alginate		20 phr					~ 110	11.5	~ 12.7	1150	~ 1323	
Bio-based	Lignin alkali	*n/a*	6 phr	ENR 50	Diels-Alder chemistry	180 °C	15 min	83	7.5	6.2	525	*n/a*	[110]
Metallic	Methacrylic acid (MAA) + ZnO (in excess)	50 nm (ZnO)	MAA:ZnO = 2:1.4; theoretical equivalent 40 phr	NR	Supramolecular ionic network	RT	20 min	100	1.89	1.89	435	415	[21]
Metallic	Fe_3O_4	20 nm	10 phr	XNBR	Metal coordination bonds	Near-infrared irradiation (120 °C)	1 h	66	9.24	6.10	888	700	[87]
Metallic	Ag nanoparticles	20 nm	10 wt%	Amino-modified PDMS	Disulphide bonds, metal–ligand interactions	RT	24 h	91.2	2.4	2.2	1762	1600	[88]
Hybrid	Silica and MWCNT	Silica: 10 nm; MWCNT: 10 nm tube diameter	5 phr silica; 5 phr MWCNT	BIIR/NR blend	Ionic cluster formation	24 V Joule heating (130 °C)	30 min	50	~ 10	~ 5	700	350	[111]
Others	Halloysite nanotubes	*n/a*	2 phr	NR	Supramolecular ionic network	RT	10 min	85.7	0.789	0.676	*n/a*	*n/a*	[112]
Others	Silanized silica	10 nm (unmodified)	30 phr	1-butylimidazole-modified BIIR	Ionic interactions	70 °C	16 h	43	18.9	8.10	880	625	[92]
Others	Silica	*n/a*	10 phr	NR	Ionic interactions	RT	10 min	68.9	4.22	2.91	800	~ 575	[90]
Others	Silica	*n/a*	50 phr	NR	Supramolecular ionic network	50 °C	24 h	~ 87.5	~ 20.0	~ 17.5	~ 340	~ 270	[95]

[1] Values listed in Table 1 are as reported in individual studies. The stress–strain curves provided would be approximated in cases where mechanical property values were not explicitly reported.

[2] Loading refers to the optimal filler concentration added to the base rubber latex based on individual studies that provided the highest self-healing performance. Units are as reported in individual studies.

[3] Self-healing performance is calculated from the ratio of the recovered tensile strength against the original tensile strength of the same composite.

[*] Abbreviations: (MW)CNT – (multi-walled) carbon nanotubes; CB – carbon black; GTR – ground tire rubber; GO – graphene oxide; CNC – cellulose nanocrystals; CNF – cellulose nanofibers; SBR – styrene-butadiene rubber; (X)NBR – (Carboxylated) nitrile butadiene rubber; PDMS – polydimethylsiloxane; (E)NR – (epoxidized) natural rubber; BIIR – bromobutyl rubber; RT – room temperature.

improving self-healing capabilities.

Grafting, considered one of the most appealing methods, involves attaching polymer chains or specific chemical bonds to the surface of a nanofiller. This process includes surface activation, functionalization, and forming strong covalent bonds such as carbon–carbon, carbon–sulfur, and carbon–oxygen bonds. Improved nanofiller dispersion within the rubber leads to enhanced self-healing properties, tensile strength, and modulus.

In a study by Utrera-Barrios, et al. [99], zinc oxide and XNBR were combined to create dynamic ionic clusters with abilities to heal under the thermal stimulus. Polyacrylic acid-modified ground tire rubber (gGTR) was introduced as a sustainable reinforcing nanofiller to enhance this self-healing capability. The functionalization process is schematically represented in Fig. 6**(a)** [99,117]. Incorporating gGTR significantly increased the healing efficiency of the XNBR composite from 15 % to 70 %. This addition improved its mechanical strength, as shown in Fig. 6**(b)** and Fig. 6**(c)**, and enhanced chemical resistance. The study concluded that self-healing efficiency correlated with cross-link density and molecular mobility, highlighting a reciprocal relationship between cross-linked networks and the need for mobility in the healing process. The ionic XNBR composite exhibited limited healing capability due to restricted molecular mobility, hindering cluster reformation. Similar characteristics and trends have been observed in other self-healing NR systems [12,21].

In a separate study by Jia, et al. [38], silane-modified silica was employed as a cross-linker to synthesize a self-healing EPDM rubber composite. A reversible Diels-Alder reaction cross-linked furan-modified EPDM rubber with silica that had been modified using 3-methacryloxypropyltrimethoxysilane (SA), as depicted in Fig. 7**(a)**. After heating the mixture at 80 °C for 12 h and washing, SA-modified silica (m-silica) was obtained. M−silica served dual roles as a reinforcing filler and a cross-linking agent, promoting uniform dispersion, as observed in Fig. 7**(b)** to Fig. 7**(e)** across varying filler contents. Silica surface grafting with SA was responsible for this uniform dispersion, limiting agglomeration and improving compatibility with rubber, thereby improving reinforcement and providing additional cross-linking points for rubber chains. Wu, et al. [118] also observed that SA surface grafting of fillers reduces agglomeration and enhances compatibility with rubber composites and elastomeric systems.

An extensively employed technique involves using silane coupling agents as common choices for surface modification of nanofillers. These compounds are selected to enhance the bond between organic polymers and inorganic substrates by addressing differences in compatibility and surface properties [119]. Operating at the interface, these agents create a strong, cohesive bond. Silica, ranking second only to CB in terms of consumption in the rubber reinforcement sector [38], is commonly used in “green tires” for its advantageous qualities. However, it tends to aggregate due to the presence of hydroxyl groups [120–122]. Silane coupling agents such as bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT), bis[γ-triethoxysilylpropyl]disulfide (TESPD), and mercaptopropyltriethoxysilane (MEPTS) are then employed to modify silica, enhancing its compatibility with rubber. This modification promotes better dispersion by establishing a ‘coupling bridge’ for interparticle interactions [123–125]. Moreover, Sallat, et al. [92] devised a self-

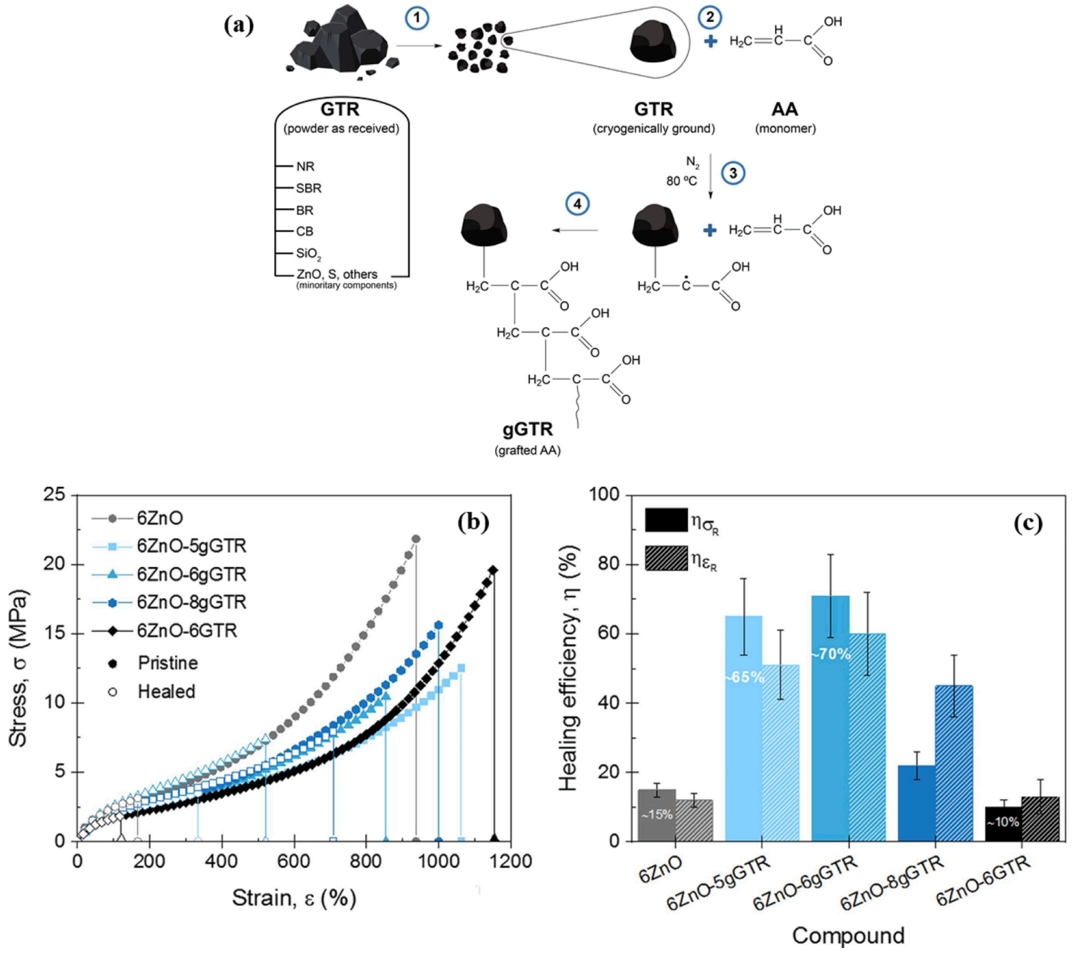

Fig. 6. (a) Grafting reaction between GTR and acrylic acid (AA); (b) Stress–strain curve of gGTR-XNBR composites; (c) Healing efficiencies of gGTR-XNBR composites. Copyright 2020, Elsevier.
Reproduced with permission from Utrera-Barrios, et al. [99]

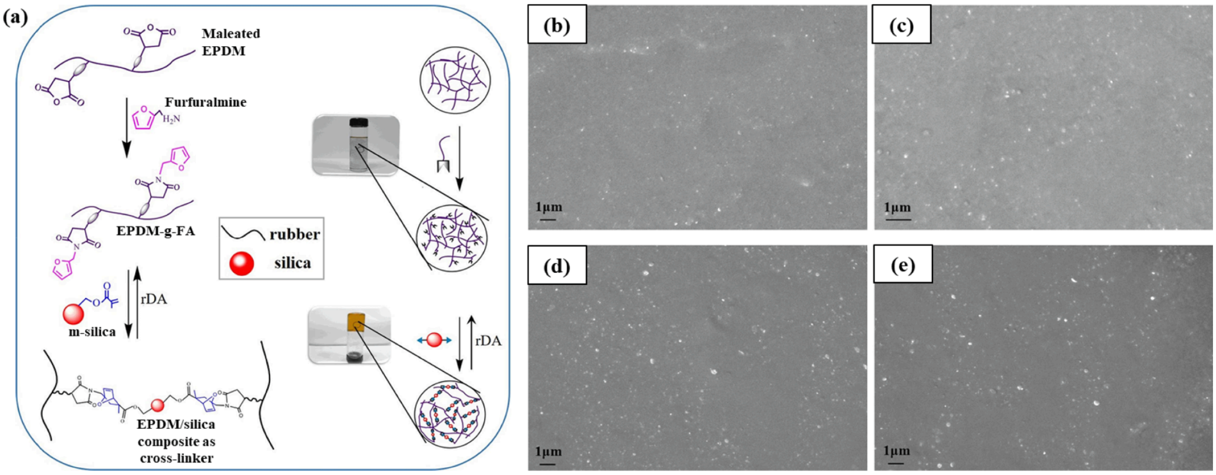

Fig. 7. (a) Pathway for synthesizing EPDM/silica composite for rubber cross-linking; SEM images of EPDM composites loaded with m-silica at concentrations of (b) 15 phr; (c) 25 phr; (d) 35 phr, and (e) 45 phr. Copyright 2020, Elsevier.
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healing rubber composite by ionizing BIIR with 1-butylimidazole. Silanized particles featuring imidazolium or aliphatic functional groups were incorporated to facilitate rubber-filler interactions. The even distribution of fillers within the rubber matrix led to elongation-at-break values reaching approximately 1000 % and tensile strength of 19 MPa. While both initial and recovered tensile strengths showed improvements, the increase in initial tensile strength was more significant than that of recovered strength, resulting in a lower self-healing performance.

The esterification of nanofillers represents another method of surface chemical modification to enhance rubber reinforcement. In this approach, ester functional groups are introduced onto the nanofiller's surface through chemical reactions, typically involving the reaction of a hydroxyl group on the nanofiller with a carboxyl group from the modifying agent. Esterified nanofillers demonstrate improved dispersion within the rubber matrix, leading to enhanced compatibility and superior interfacial adhesion. In a study by Guo, et al. [64], the team developed a self-healing material known as the Ti_3C_2 MXenes/rubber-based supramolecular elastomer (NMSE) for intelligent sensing applications. Fig. 8**(a)** illustrates the esterification process visually, where MXene nanosheets were etched using lithium fluoride/hydrochloric acid (LiF/HCl) and subsequently esterified with serine at 100 °C, employing a water-soluble catalyst. This resulted in S-MXene, where hydroxyl groups on the MXene surface were chemically linked with carboxyl groups from serine, establishing supramolecular H-bonding. Serine-grafted epoxidized natural rubber (S-ENR) latex was introduced as an isolation phase. TEM analysis in Fig. 8**(b)** revealed the segregated and organized MXene nanostructure resulting from this addition, and the resulting NMSE

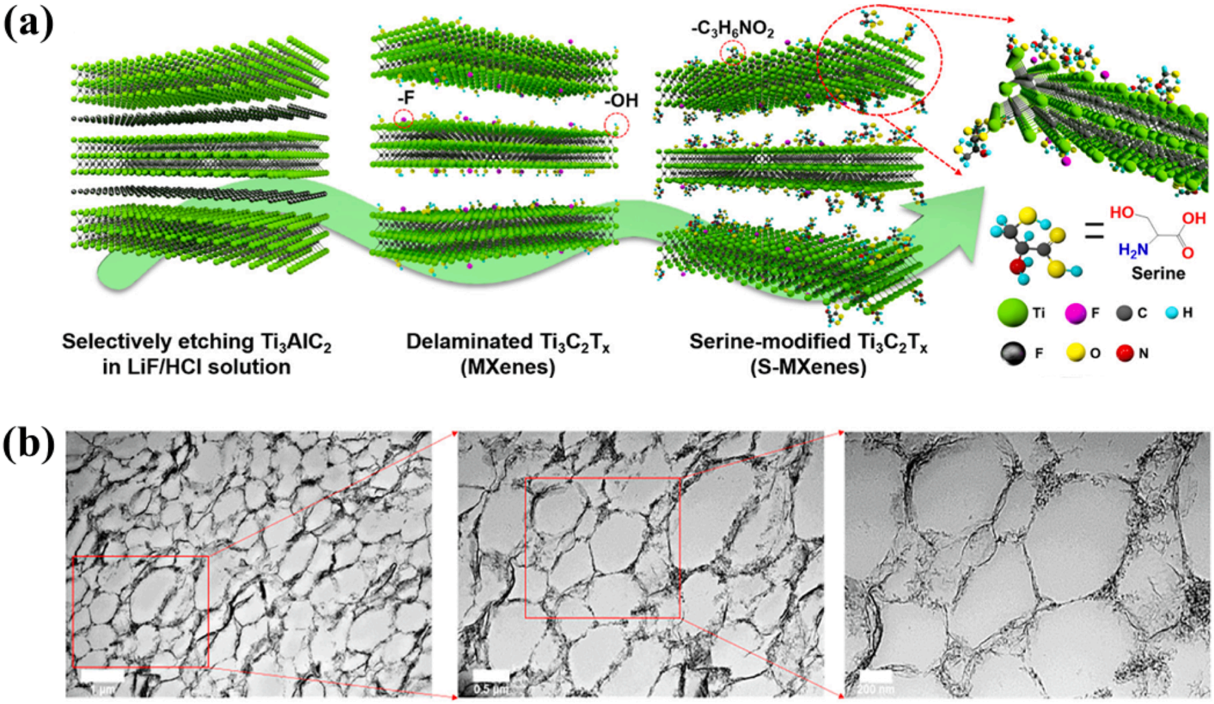

Fig. 8. (a) Surface modification of MXene nanosheets by serine through esterification reactions; (b) TEM images of well-organized MXene nanostructures in NMSE. Copyright 2020, American Chemical Society.
Reproduced with permission from Guo, et al. [64]

exhibited remarkable self-healing properties at room temperature, featuring a unique structure that enhanced its mechanical strength and sensitivity.

Various factors must be taken into account when choosing a method to modify the surface functional groups of nanofillers. These include the type of nanofiller, the desired functional group attachment, operating conditions, yield, and solvent usage. However, it is important to note that each method has its own set of advantages and disadvantages (Table 2), highlighting the need for a thorough review of modification techniques before making a selection.

Theoretical frameworks and mechanisms for rubber reinforcement

Strengthening rubber is essential for improving its mechanical properties and overall durability. Incorporating nanofillers is a common strategy to enhance the material's strength. The reinforcing effects of nanofillers on rubber are influenced by their size, structure, and surface activity. The formation of hard-percolating fillers within soft rubber matrices typically leads to improved mechanical properties [42]. In the context of self-healing rubber nanocomposites, the reinforcement mechanisms are versatile and complex, owing to the heterogeneous nature of the system and the cross-linking structures inherent in rubbers that contribute to their elasticity.

However, there is a growing interest in exploring novel fillers and various combinations of filler-rubber matrices to achieve high reinforcement performances with low filler loadings. The theory of rubber reinforcement, as depicted in Fig. 9, encompasses four main components [42]. According to a pioneering study by Payne [137] on particulate fillers, it was highlighted that the filler-filler network could potentially rupture even at minor strains. Four major contributors influence the storage modulus level in filled rubbers. Polymer network formation, hydrodynamic effects, and filler–rubber interaction are strain-independent, whereas filler–filler interaction is strain-dependent and influenced by filler nature and interactions with the rubber matrix. These interactions serve as crucial elements in understanding and elucidating the mechanisms behind rubber reinforcement.

The incorporation of nanofillers into rubber composites contributes to an increase in modulus. Due to their high surface area, nanofillers foster improved interactions with the rubber matrix, enhancing mechanical properties. The nanoscale dimensions create numerous contact points, facilitating effective load transfer between the filler and polymer and further enhancing strain values. **Eq. (1)**, known as the Einstein-Guth-Gold relation, approximates the relationship between the modulus of rubber filled with nanofillers and their corresponding volume fractions [139]. However, this hydrodynamic effect equation applies primarily to rubbers filled with materials exhibiting poor reinforcing potential or fillers with a volume fraction of spherical particles (Ø) below 0.3. Recognising its limitations, **Eq. (2),** known as the Guth-Smallwood relation, was introduced to accommodate correction factors for considerations such as particle aggregation, non-spherical filler shapes, and non-uniform morphologies [139].

$$E_c = E_0(1 + 2.5\varnothing + 14.1\varnothing^2) \quad (1)$$

$$\frac{E_c}{E_0} = 1 + 0.67f\varnothing + 1.62f^2\varnothing^2 \quad (2)$$

where E_c and E_0 are the Young's moduli of the filled composite and the unfilled rubber matrix, respectively. The ratio $\frac{E_c}{E_0}$ represents the reinforcement factor, *f* represents the aspect ratio of the fillers, defined as the ratio of the length to breadth of the filler, and Ø represents the volume fraction of spherical particles.

In the process of reinforcing rubber with nanofillers, changes in the properties of the matrix upon contact with filler surfaces play a significant role in determining the reinforcement potential. The strength of

Table 2
General advantages and disadvantages of common nanofiller surface chemical modification methods.

Surface Chemical Modification	Advantages	Disadvantages	Ref.
Surface Grafting	• Improved control over surface chemistry • Enhanced interfacial adhesion • Minimized leaching of modifier molecules into base matrix due to reduced detachment of grafts during processing • Reduced agglomeration through better dispersion of nanofillers • Compatibility with a wide range of matrices and filler materials • Highly customizable to meet specific application needs • Controllable functionalization of surface properties, such as hydrophobicity and hydrophilicity	• Harsh reaction conditions or toxic reagents may be necessary depending on the graft, posing environmental and safety concerns • Achieving complete coverage and uniform grafting can be challenging, resulting in heterogeneous properties • The multistep synthesis process is complex and may incur high costs in certain systems • Expertise is needed to select optimal grafting agents, determine reaction conditions, and execute solvent removal and purification methods • Structural characteristics of the material may be affected by the modification process	[126–129]
Coupling Reactions	• Strong covalent bonds form between the nanofiller and base matrix • Compatible with a wide range of matrix systems • Capable of functionalizing various types of nanofiller materials • Effective in reducing nanofiller agglomeration, leading to improved dispersion throughout the matrix	• Limited control over the density and distribution of coupling sites on the surface of the nanofiller • Formation of by-products from residual unreacted coupling agents • Intricate chemistry and sensitive to processing parameters, which require meticulous optimizations • Some coupling agents can release volatile organic compounds during reactions • Unclear coupling reaction mechanisms between rubbers and silica as a common non-carbon filler	[128,130–133]

(continued on next page)

Table 2 (*continued*)

Surface Chemical Modification	Advantages	Disadvantages	Ref.
Esterification Reactions	• Facilitates the formation of stable ester bonds, thereby improving overall composite stability • Straightforward approach in reducing hydroxyl density in nanofillers • Provides the capability to control the extent of modification and surface functionalization • Improves the thermal stability and chemical resistance of nanofillers	• Acid catalysts may involve significant costs • Demands careful optimization of reaction parameters • Susceptible to side or reverse reactions, potentially yielding undesired by-products • Exhibits slow reaction kinetics • Achieving high conversion and yield is challenging due to non-uniform surfaces and complex reaction conditions	[64,134–136]

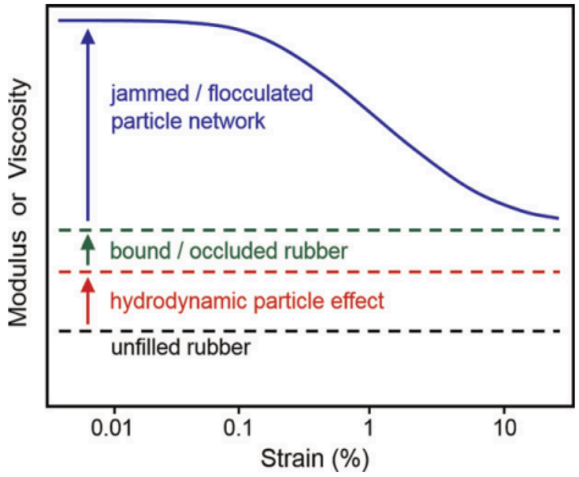

Fig. 9. Schematic illustrating various contributions to the modulus and viscosity of rubber. Copyright 2016, Elsevier.
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the interaction between the matrix and filler directly impacts rubber composites' stiffness. A more enhanced interaction at the interface between the filler and rubber can increase the material's modulus. This mechanism exhibits non-linear behaviour in materials, attributed to the dynamic processes of bonding and debonding between the matrix and filler [42,44,59,140].

Moreover, the possibility of forming filler networks exists beyond the percolation threshold or critical concentrations. Percolation, characterized by a notable increase in modulus, redistributes stress or loads within such a network, leading to a sudden increase in material stiffness. The effectiveness of this phenomenon relies heavily on the interparticle distance among reinforcing fillers within the rubber matrix. Filler-matrix interactions exert a more pronounced influence on reinforcing nanocomposites compared to filler agglomeration or percolation. The strength of the interactions between filler and rubber plays a crucial role in determining the mobility of rubber chains directly attached to the filler particles or located near the filler-rubber interface, as opposed to those connected to the filler matrix. A comprehensive examination of these interactions can offer valuable insights into the self-healing properties of rubber.

Several factors play a role in determining the efficiency of fillers in reinforcement. Tubular fillers, for instance, should possess a high aspect ratio, a low percolation threshold, good dispersion, suitable alignment, and effective transfer of stress at the interface to be considered effective. Similarly, for layered fillers, achieving complete exfoliation of the layers is crucial for facilitating efficient load transfer between rubber and filler, ultimately enhancing reinforcement performance [141]. Furthermore, the adsorption of rubber chain entanglements across extensive nanofiller interfacial areas leads to increased cross-link junctions, resulting in a higher composite modulus and, consequently, higher rubber stiffness [42]. Theories related to interfacial adhesion reinforcement and filler-induced crystallization reinforcement effects have also been explored [142–144]. The theory of interfacial adhesion reinforcement asserts that stronger adhesion contributes to better composite reinforcement as stress is effectively transmitted through the matrix-filler interface. Moreover, larger filler interfacial areas under consistent adhesion strength also enhance composite reinforcement. On the other hand, the theory of filler-induced crystallization reinforcement suggests that incorporating inorganic particles into crystalline polymers serves as heterogeneous nucleation sites, increasing crystallinity and, consequently, strengthening and rigidifying the material's compositional structure [142].

For example, Shen, et al. [145] developed a self-healing oxidized NR (oNR) composite film by incorporating sodium alginate as a reinforcing filler and utilising a reversible supramolecular cross-linker. Within 10 min under ambient conditions, samples containing 20 phr SA exhibited a tensile strength of 6.5 MPa and 80 % self-healing efficiency. The hydroxyl and carboxyl functional groups in the sodium alginate and the oNR formed H-bonds, promoting self-healing, as depicted in Fig. 10**(a)**. Due to the chain diffusion of oNR molecules and reversible hydrogen network, the samples could heal swiftly at ambient conditions. The morphological structure of the composite was examined via TEM, as shown in Fig. 10**(b) to 10(d)**, and tt was observed that the formation of hydrogen bonds between the rubber matrix and regenerated sodium alginate aggregated, indicating superior reinforcement upon healing and rapid responsiveness.

Sustainability aspects of fillers in self-healing rubber systems

Material sustainability is increasingly recognized as a crucial aspect for maintaining balance in the planet's triple bottom line across various sectors, particularly manufacturing [31]. This emphasis on sustainability has spurred research, design, and development efforts towards creating sustainable self-healing composites. According to Khan, et al. [146], covalent adaptable networks feature dynamic covalent bonds within polymer network materials, offering a promising avenue for developing sustainable, functional, and recyclable self-healing materials. Beyond extending the service life of rubbers, covalent adaptable networks have the potential to reduce maintenance costs through their self-healing attributes. Furthermore, they play a pivotal role in decreasing waste sent to landfills by facilitating material reprocessing, aligning with a closed-loop processing pathway [146]. Key considerations on how the design and material selection contribute to the successful development of a sustainably filled, self-healable rubber composite are outlined in Fig. 11.

In addition to gloves and tires, which are recognized as major contributors to rubber waste, the disposal of rubber condoms, styrene-butadiene rubber (SBR) sourced from discarded automotive materials, and industrial rubber waste are exacerbating the global rubber waste issue [147,148]. Notably, the incorporation of waste rubber as fillers has garnered attention for its potential to improve the physical and mechanical properties of composites. Research findings have highlighted that adding rubber waste can enhance the mechanical properties of virgin rubber, including modulus, tensile strength, and elongation while

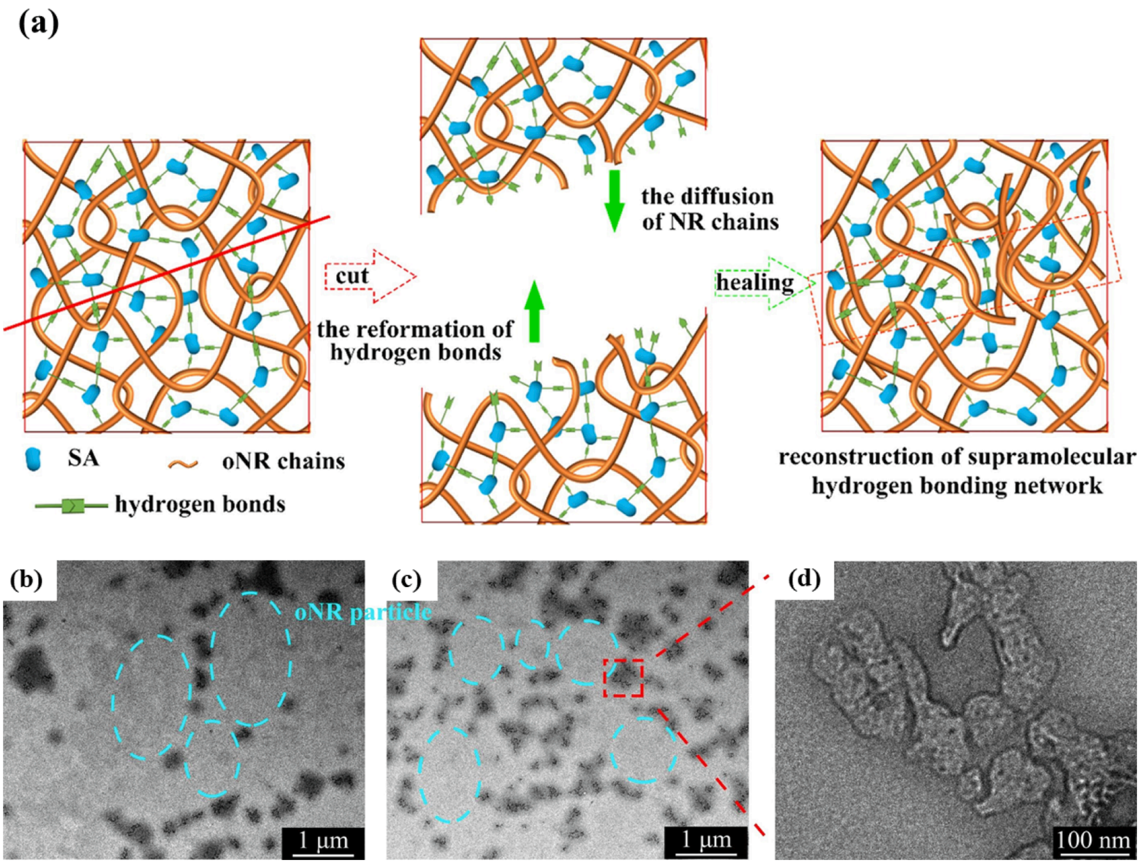

Fig. 10. (a) Schematic depicting the self-healing mechanism of oNR/SA composite film; TEM micrographs of (b) oNR/SA-5; (c) oNR/SA-15; and (d) an increased magnification of oNR/SA-15 revealing the aggregation of sodium alginate filler with NR chains. Copyright 2021, Elsevier.
Reproduced with permission from Shen, et al. [145]

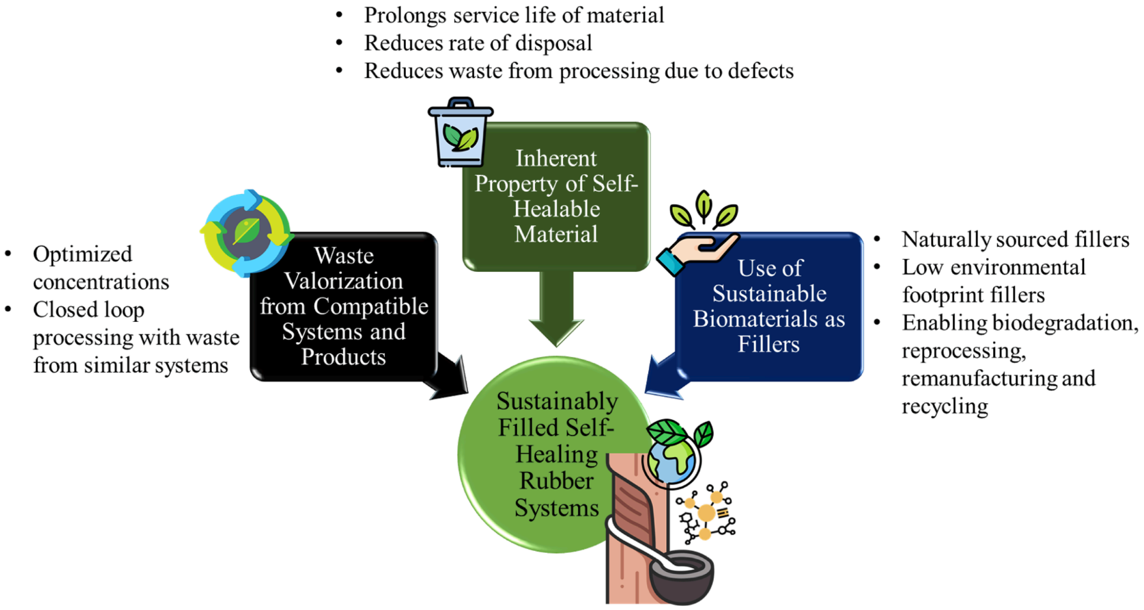

Fig. 11. Enhancing sustainability in self-healing rubber systems through innovative design and material selection.

reducing dependence on conventional fillers [149–153].

Several studies, including those by Araujo-Morera, et al. [66] and Araujo-Morera, et al. [101], have explored the potential for sustainable rubber products in the automotive industry. They developed an innovative self-healing tire compound using SBR as the base matrix and repurposed GTR as the reinforcing filler. Systematic investigations demonstrated that the SBR/GTR compounds fully recovered their stiffness and relaxation times following cyclic deformation. The research findings suggested that incorporating GTR as a sustainable filler could reduce fuel consumption and increase rolling resistance while preserving healing and wet grip characteristics, representing essential factors for safe tire applications. Furthermore, the use of constituents from waste tire rubber to maintain the chemical resistance and mechanical strength of other rubber systems establishes a closed loop of effective rubber processing and application.

Ye, et al. [154] have generated a self-healing rubber using a substantial quantity of waste natural rubber powders (WNRPs), providing an economical and sustainable solution for damping materials application. This study re-crosslinked WNRPs through a thiol–ene reaction with polysulfide rubber (PSR), resulting in reclaimed rubber that is both reprocessable and self-healable. While an increased PSR content proved beneficial for cross-linking density and conversion, it had a detrimental effect on the mechanical properties. Notably, the developed rubber exhibited impressive self-healing abilities, recovering over 90 % of its mechanical properties from physical damage after 24 h at 100 °C. In a separate study, Utrera-Barrios, et al. [155] presented an innovative approach by utilizing waste from toner cartridges to produce self-healing elastomeric composite materials. They formulated a thermoplastic elastomer by optimizing the interaction between high-impact polystyrene and XNBR derived from the waste, resulting in a material with robust mechanical and self-healing properties. It exhibited a tensile strength of 6.6 ± 0.2 MPa and a notable recovered strength magnitude when subjected to heat and pressure within 1 h. Additionally, the study verified that waste toner powder, characterized by a high CB and silica composition, substantially enhanced the mechanical strength of rubber composites, exhibiting an improvement of up to 50 %. This shows the promising potential of waste valorization in enhancing rubber systems.

Beyond relying on used tires or wastes with high carbon content, an alternative strategy for advancing the sustainability of self-healing rubbers involves the utilization of renewable biomaterials as functional fillers to replace their conventional counterparts. The gradual elimination of conventional fillers such as CB, silica, mica, and talc is becoming more prevalent due to increased awareness of environmental concerns associated with large volumes of product disposal at the end of their life cycle. Noteworthy investigations by Supramaniam, et al. [8] and Supramaniam, et al. [85] explored the use of sustainable cellulose nanofibers decorated with zinc oxide. These nanofibers served dual purposes, acting as reinforcements for the ENR polymer matrix and enhancing self-healing efficiencies through intrinsic ionic interactions. A concentration of 5 phr of the functionalized filler led to a six-fold improvement in tensile strength and a 70 % enhancement in the self-healing performance of the composite. Furthermore, rubber composites incorporating sustainable filler components have been recognized for their potential to enhance reprocessing capabilities and biodegradability upon disposal [154,156,157]. However, the design of rubber composites that seamlessly integrate both self-healing properties and high biodegradability remains scarce and has yet to be comprehensively documented. Consequently, there is ample room for further research on self-healing rubber systems, with further studies exploring the aspects of sustainability and biodegradability.

From a broader perspective, there are no projected or reported quantifiable statistics on how reinforced self-healing rubber composites can benefit industrial manufacturers or the environment due to the infancy and novelty of the technology. Conceptually, the incorporation of sustainable fillers with self-healing technology in rubbers could be a gamechanger in the multibillion-dollar industry with global coverage. Self-healable reinforced rubbers, as aforementioned, benefit numerous stakeholders throughout its lifecycle in various ways, such as:

- Improved material and end-user product durability from the presence of reinforcing fillers and inherently embedded self-healing technology;
- Reduced waste generation throughout the product lifecycle from reduced product defects during manufacturing, potentially improved biodegradability and lower frequency of product replacement;
- Better energy and resource efficiency as there would be lower demand for natural and synthetic raw materials as a result of better product durability;
- Improved economic turnover due to optimized resource consumption;
- Provides a foundation of technical and commercial knowledge for further technological advancements and market analyses in the field.

Challenges, future prospects and concluding remarks

In the recent decade, much progress has been achieved in the filed of reinforcing self-healable rubbers as research rapidly transitions towards more sustainable engineering and greener chemistry in manufacturing. Nevertheless, numerous challenges still exist that require smart solutions to successfully embed self-healing technology and its associated reinforcing mechanisms in existing systems of everyday products. The process of mimicking biological self-healing phenomena with chemistry alone is not up to par. It matches natural healing, which consists of a blend of numerous healing mechanisms happening concurrently. Furthermore, with ongoing research, development and innovation in this advancing field, there still exist inconsistencies in findings, such as in terms of tensile strength, healing efficiency and stimuli dependence. Other factors include the scale of healable damage and technological feasibility (in terms of healing duration and temperature). In retrospect, the functionality of rubber has progressed by leaps and bounds with reinforced self-healing technology. It would be indeed remarkable and interesting to see how this technology further advances in the near future.

To conclude, smart rubbers endowed with self-healing technology are at the forefront of environmental preservation and sustainability efforts, aiming to minimize waste during manufacturing and enhance end-user product reliability. The exploration and advancement of functional nanofillers for self-healing rubber composites have become a prominent trend in materials sciences, polymers, and rubber technology. The crucial role of nanofillers lies in maintaining or improving the mechanical properties of fractured rubber after recovery without disrupting the dynamic reversible chemical bonds, which remain crucial for self-healing. External stimuli, such as heat or irradiation, are additional factors that can be applied to enhance self-healing performances further. Therefore, finding the optimum point where all these factors mutually benefit rubber composites is essential for designing a polymeric system that is strong, robust, durable, and easily adaptable for industrial-scale production. However, further research is necessary to achieve improved healing rates, higher strength recovery magnitudes, and independence from external stimuli. The continuous development of nanofillers, particularly those derived from biomaterials, holds promise for innovative solutions and enhanced product sustainability with reduced environmental impacts. With strategic and effective research approaches, the widespread adoption of self-healable rubbers could surpass expectations in the near future.

CRediT authorship contribution statement

Darren Yi Sern Low: Data curation, Visualization, Writing – original draft, Writing – review & editing. **Sharon Mintarno:** Validation, Writing – original draft. **Nirvedita Rani Karia:** Visualization, Writing – original draft. **Sivakumar Manickam:** Resources, Writing – review & editing. **Khang Wei Tan:** Resources, Writing – review & editing. **Mohammad Khalid:** Resources, Writing – review & editing. **Bey Hing Goh:** Supervision, Writing – review & editing. **Siah Ying Tang:** Conceptualization, Project administration, Supervision, Writing – review & editing.

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.

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