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Perspective

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Bridging Polarity Gaps: Functionalized Elastomers for Sustainable Tyre Technologies

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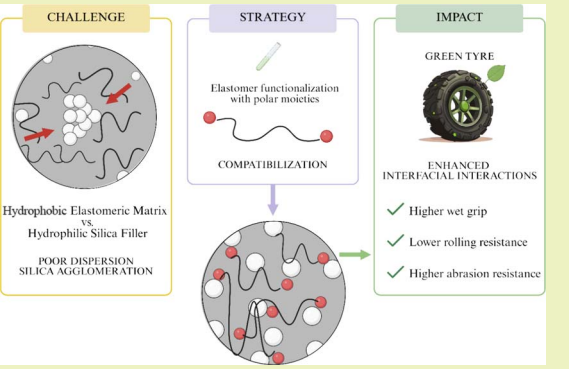
ABSTRACT: The transition towards sustainable, high-performance tyre technologies has accelerated the adoption of silica as a reinforcing filler, offering significant environmental and functional advantages over carbon black. This transition is of critical importance in light of the fact that tyre production and wear contribute substantially to global CO_2 emissions, microplastic pollution, and resource depletion throughout their life cycle. However, the inherent polarity discrepancy between hydrophilic silica and hydrophobic elastomers, such as styrene−butadiene rubber (SBR), persists as a significant impediment to the attainment of uniform dispersion and robust interfacial adhesion. This review critically examines chemical strategies for elastomer functionalization that enable improved silica compatibility, highlighting three major pathways: (i) functionalization during polymerization, particularly via living anionic polymerization, which affords precise control over architecture and chain-end chemistry; (ii) post-polymerization modification, with emphasis on thiol−ene "click" reactions for efficient grafting of polar moieties under mild conditions; and (iii) depolymerization-driven approaches, which valorize waste rubbers into telechelic oligomers, advancing circular economy principles. A mapping of functional groups, silanes, mercaptans, epoxides, and amino derivatives drawn from scientific and patent literature is provided, correlating chemical design with enhanced filler dispersion, reduced rolling resistance, and improved wet grip. Despite notable progress, challenges persist in industrial scalability, cost-effectiveness, and environmental impact. Future directions should prioritize green chemistry paradigms, multifunctional elastomers, and advanced characterization to unlock next-generation tyre materials aligned with sustainability goals and global efforts to mitigate environmental burdens.



KEYWORDS: *tyres applications, silica filler, functionalized elastomers, anionic polymerization, click chemistry, green tyre technology*

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1. INTRODUCTION

The functionalization of elastomers with polar moieties, to enhance their compatibility with a polar filler such as silica, has become a cogent area of research in the development of composites for demanding applications such as those in high-performance and sustainable tyres.[1]

Although early tyres were white due to the use of zinc oxide, the main industrial operators transitioned to carbon black for its structural reinforcement properties and UV protection. This technological shift offered such significant advantages that it overcame the market's initial resistance to the dark aesthetic of the product.[2]

It was not until the 1980s that silica-based composites were explored. Silica is generally considered an environmentally friendly filler because it can be derived from natural or waste sources.[3−6] In comparison to carbon black, it reduces hysteresis in elastomeric composites for dynamic mechanical applications, such as tyre compounds. This reduces rolling resistance and fuel consumption, as well as CO_2 emissions.[7−11] Furthermore, silica enhances wet traction of tyres.

Silica is made up of SiO_2 monomers, presenting on its surface hydroxyl groups (−OH), called silanol groups, as shown in Figure 1, which can be geminal, vicinal, or isolated.[12,13]

Because of this structure, its surface is highly polar. Instead, most diffused elastomers, which are generally composed of carbon and hydrogen, are hydrophobic.[14,15] Hence, the dispersion of silica into the polymer matrix is challenging, and not only because of the different solubility parameters.[16] Indeed, hydrogen bonds between the silanol groups lead to silica agglomeration, hence to the formation, in the elastomer matrix, of filler networks, which are disrupted by applying thermomechanical energy. Rubber composites exhibit strain softening phenomena known as Payne,[17−20] and Mullins,[21−23] effects. The Payne

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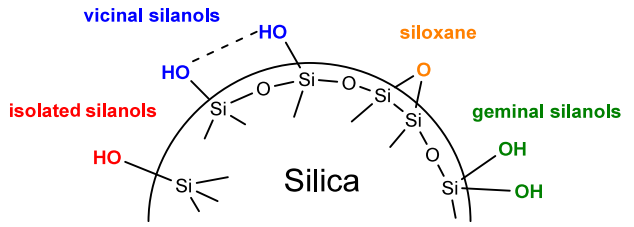

Figure 1. Silanol groups of silica.

effect represents non-linearity of the viscoelastic modulus which occurs under oscillation shear, while the Mullins effect occurs in large strain uniaxial cyclic stretching. They have been interpreted either with the agglomeration−deagglomeration process of the filler network above the filler percolation threshold,[24−27] or with the debonding of the filler from the polymer chains.[24,28−36]

To prevent silica agglomeration, shielding and coupling agents are traditionally used.

The surface energy of silica is reduced by modification with long-chain alcohols[37,38] or amines,[37,39] leading to a reduction in the extent of particle agglomeration. The enhancement of filler dispersion is counterbalanced by a diminution in adhesion between the two phases. The net result is a decrease in the reinforcing potential of the filler, attributable to excessive molecular slippage under an applied load. Fatty acids (mainly stearic acid)[40] and silanes without functional groups able to react with elastomer chains[41] are effective shielding agents but cannot reduce the ratio between the loss and the elastic modulus of the elastomer composite.

Sulphur based silanes are traditionally used, also at commercial level, as shielding and coupling agents.[41] The most diffused is (*bis*-(triethoxysilylpropyl)tetrasulfide) (TESPT),[42−50] which establishes covalent bonds with silica through the reaction of the ethoxy groups with the silanols, with the release of ethanol, as shown in Figure 2.

The sulphur atoms in TESPT enable the formation of chemical bonds with the elastomer chains, during vulcanization. The occurring of this reaction during compounding leads to premature scorch, with increase in viscosity and poor processability of the rubber compounds.[47] During vulcanization, TESPT can also act as a sulphur donor or as an accelerator.[48]

Some of the authors proposed a new class of coupling agents, *Janus* pyrrole molecules, which react with silica and elastomers, avoiding ethanol release and premature crosslinking during compounding.[49]

Another strategy consists in the *ex-ante* modification of silica with elastomers, of high or low molecular mass, containing polar groups: either a polar elastomer,[50] or a traditional hydrocarbon elastomer with a polar group as chain end.[51] Li *et al.* grafted silica with epoxy functionalized elastomers like poly(ethylene-co-vinyl acetate-co-glycidyl methacrylate),[50] enhancing the dispersion and interfacial bonding of silica in the rubber matrix, leading to improved mechanical properties and performance.

Sek *et al.* chemically coupled functionalized S-SBR onto silica,[51] generating a hybrid organic−inorganic filler that was then formulated into model tyre tread compounds. Anchoring S-SBR onto silica accelerates vulcanisation, resulting in a shorter scorch time and faster cure. This is attributed to the hydrophobisation of the silica surface and reduced adsorption of accelerators. The improved reinforcement was rationalised through the physical entanglement and co-curing of silica-grafted chains with the matrix rubber.

Anyszka *et al.* grafted long oligomeric polymer brushes onto the silica surface acting as molecular "hooks", while the cross-linked rubber matrix acts as the "loops". Unlike rigid chemical cross-links, these interactions function through a hook-and-loop mechanism. The highly mobile oligomer brushes act as 'hooks' that physically interlock with the rubber 'loops'. Once the stress is released, these brushes quickly re-engage and 're-hook' into the elastomer matrix, ensuring a remarkable recovery rate.[52]

One of the authors added a minor amount of low-molecular-weight, chain-end functionalized isoprene oligomers to a standard isoprene rubber matrix, improving silica dispersion and significantly reducing filler networking without needing to alter the chemical nature of the primary bulk elastomer.[53]

Functionalized elastomers, which represent the core of this review, are effectively employed to bridge the polarity gap between hydrophilic silica and the hydrophobic hydrocarbon elastomer matrix.[4] Elastomers with polar groups are indeed increasing in importance. They also enhance the properties of elastomer composites based on sp^2 carbon allotropes, such as carbon black[54] and graphene nanoplatelets.[55] Various studies have demonstrated that these modifications enhance the interaction of the elastomer chains with silica, resulting in superior material properties.[46,51]

Far from the objective of being exhaustive, this review reports on the main functionalization methods of elastomers and on the effects on the properties of the elastomer composites, as it arises from the analysis of both scientific and patent literature.

The review is organized in three sections. The first one sheds light on the functionalization methods, from the chronological evolution to their chemical aspects and mechanisms. The second part discusses the effects on the elastomer composites. The last section focuses on the future directions, pointing up the main challenges, specifically scalability, cost-effectiveness, and environmental issues. A SWOT analysis provides a holistic view that considers not only the chemical and physical rigor of

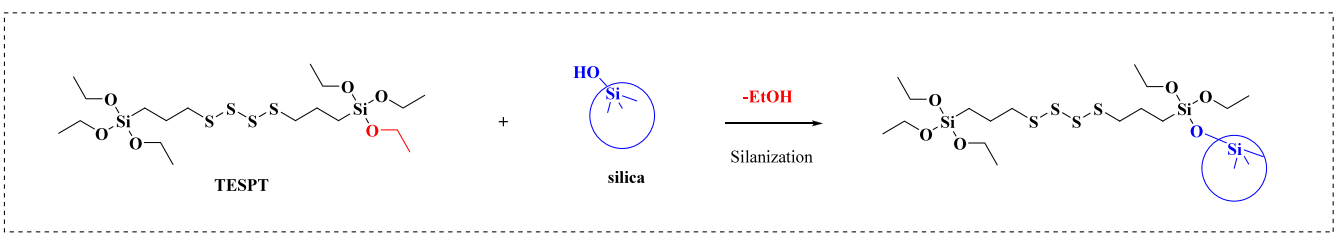

Figure 2. Condensation reaction among TESPT and silica, also known as silanization. This process results in ethanol releasing from TESPT.

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the processes, but also their technological readiness and potential for integration into current tyre production lines.

2. FUNCTIONALIZATION OF ELASTOMERS

The functionalization methods discussed in this review are summarized in Figure 3.

They can be categorized into three main approaches: functionalization during polymerization, post-polymerization modifications, and controlled polymer chain cleavage or depolymerization.

Functionalization through living anionic polymerization is one of the cornerstone techniques in this field and enables functionalization in both α and ω positions. Living anionic is used for the preparation of S-SBR, the main polymer in a tyre tread compound. To overcome the stereochemical limitations of anionic polymerization, which fails to yield high 1,4-cis content, the synthesis of functionalized diene homopolymers is performed via the pseudoliving insertion polymerization of 1,3-butadiene using catalysts for insertion polymerization.

Among the post-polymerization strategies, the thiol-ene 'click' reaction stands out for its efficiency in preparing various functional polymers through simple chemical modifications.

Depolymerization and oxidative cleavage are increasing their importance as functionalization techniques, also for their contribution to polymers recycling and circular economy.

Polymers' modification leads to the introduction of functional groups in different positions of the polymer chains, either at the end or along the backbone chain, as illustrated in Figure 4. Synthetic procedures are summarized as follows:

1. Functionalized initiator. A functionalized initiator, typically an alkyl lithium, triggers the polymerization (e.g., of butadiene and styrene), resulting in polymers with functional groups at the α-position of the chain.
2. Chain-end functionalization. This technique involves adding a functional group to the end (ω position), of a polymer chain grown through a living polymerization, typically anionic.
3. In-chain functionalization: on the backbone. This technique involves copolymerizing hydrocarbon monomers (e.g., styrene and butadiene) with a functionalized monomer, thus incorporating functional groups directly into the polymer backbone. This approach enables functional groups to be distributed uniformly along the main chain.
4. In-chain polymerization: on the lateral substituent. Functional groups are added to side groups of the polymer chain.

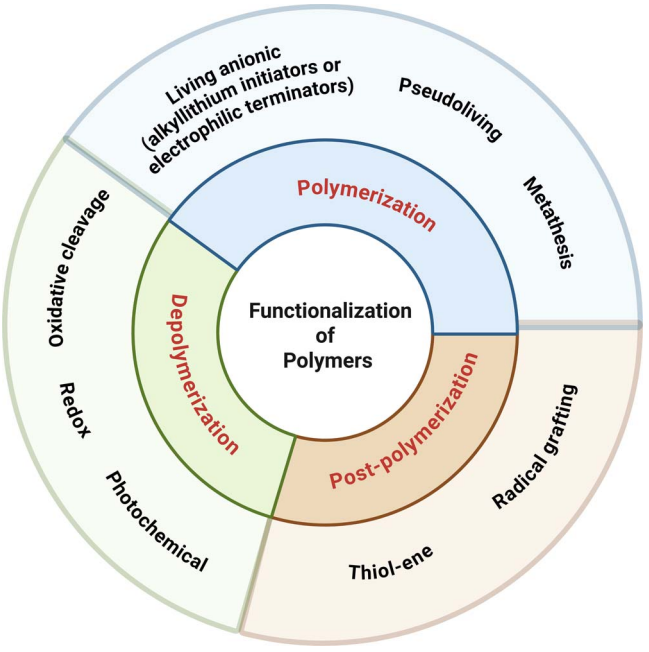

Figure 3. The functionalization strategies explored in this work. Created in https://BioRender.com.

Each of these methods offers unique advantages, enabling the synthesis of functionalised polymers with tailored properties to enhance performance in a variety of applications.[56]

These functionalization processes lead to the introduction of families of functional groups. Most explored are shown in Figure 5. They are carboxylic acid, epoxy, alcohols/urethanes/amides, silanes, mercaptans, and amines/imidazoles.

The interactions range from weak, reversible hydrogen bonds, typical of carboxylic acids, alcohols, and amides, to strong, irreversible covalent linkages provided by epoxy and silane groups. Furthermore, the inclusion of nitrogen-based groups (amines/imidazoles) introduces acid-base synergies particularly effective with acidic silica surfaces, whereas sulfur-based mercaptans remain vital for direct rubber crosslinking.

Hence, the strength of interfacial interaction depends on the types of functional group as well as on their amount.[57]

The extent of functional groups plays indeed a key role. According to Bohm *et al.*, an excessive degree of functionalization can lead to over-saturation of the silica surface, preventing the adsorption of other rubber chains, hence reducing the bound rubber content and promoting chain slippage at the interface. This, in turn, could compromise the overall mechanical reinforcement and modulus of the vulcanizate.[26]

In recent decades, the functionalization of elastomers has been the subject of extensive research efforts, both in academia and in industry, documented by the increasing number of publications and patents, as it is shown in Figure 6.

The bar charts reveal the exponential growth of scientific publications, while the patents number went through a substantial growth from 2013 to 2016, with a decline in recent years. The industrial sector could be in a phase of technological consolidation and/or refinement, while basic research is still flourishing.

2.1. Silica as Reinforcing Filler in Elastomer Composites: Timeline and Milestones

The integration of silica into elastomer composites was pursued through multifold approaches, from silica modification to elastomer functionalization. Figure 7 illustrates the timeline, with main milestones.

The oil crisis of 1973 represented a pivotal moment for the rise of "green tyres", with manufacturers prioritizing the reduction of fuel consumption.[58] In the 1970s, silica was the subject of study with regard to its properties. However, the technology required to make silica an effective reinforcing filler was not yet sufficiently advanced. The use of TESPT in silica based composites was patented in 1972.[59] Studies on silica properties were indeed available,[60] but silica was used only in special tyres, such as off-road tyres, as it did not effectively promote the

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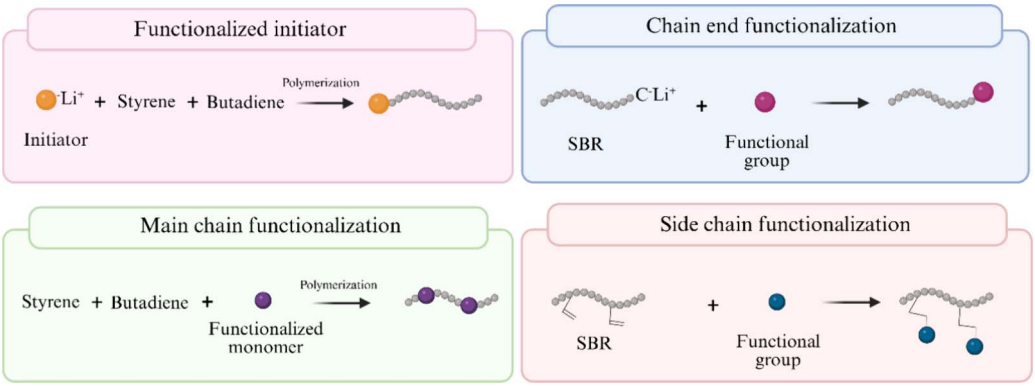

Figure 4. Functionalization approaches: initiator, chain end, main chain and side chain functionalizations. Created in https://BioRender.com.

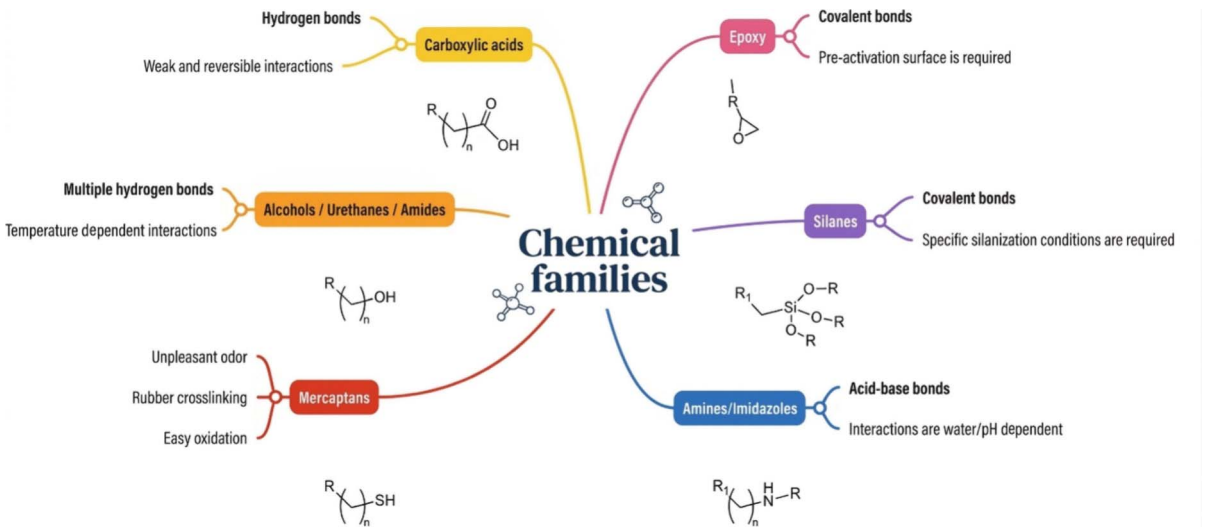

Figure 5. Visual map of the chemical families of reactive moieties to enhance interactions with silica.

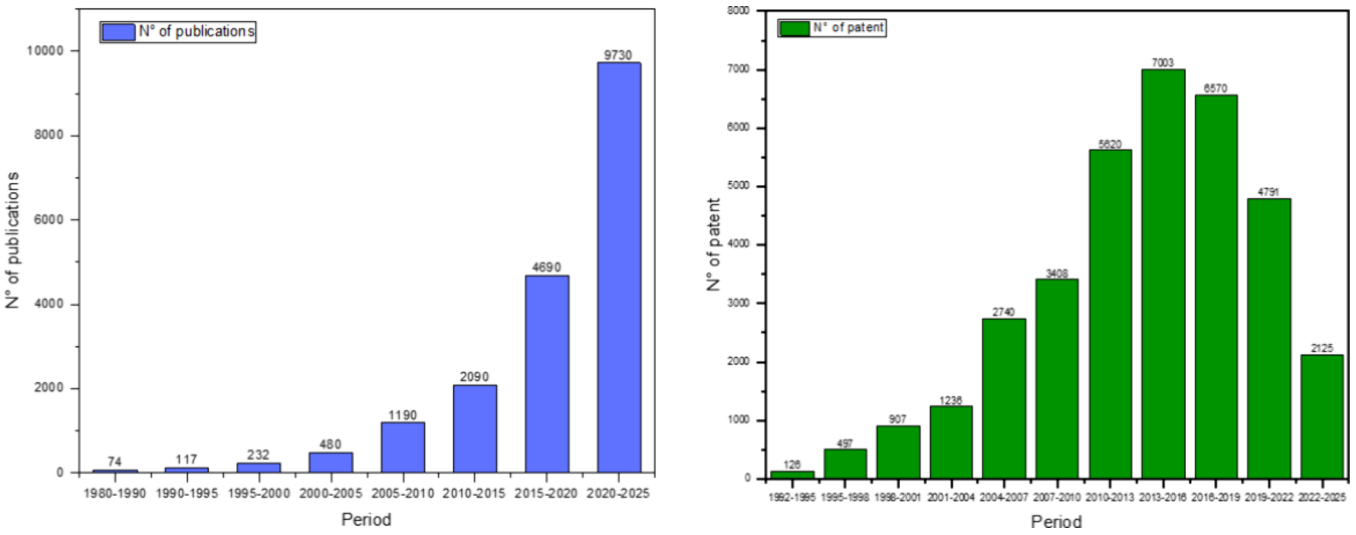

Figure 6. Mapping the functionalized elastomer landscape. Number of pubblications (on the left) and number of patents (on the right) during the 1980−2026 period.

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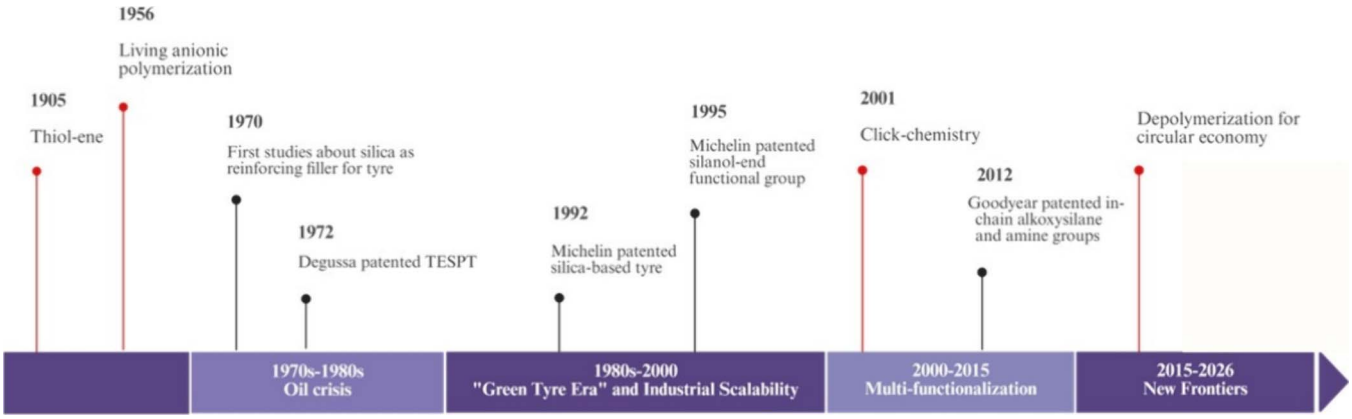

Figure 7. Timeline of the evolution of functionalization strategies for silica-based tyre.

reinforcement of the composite. Studies presented then the potential of silica to reduce hysteresis without compromising abrasion resistance.[61] A milestone was represented by Rauline's patent for the silica-based compounds: SBR obtained in solution, with high vinyl content, was combined with a grade of silica with high surface area and high oil absorption, finally combining the mechanical reinforcement with reduced hysteresis at high temperature.[62] Nevertheless, the control of the filler networking of silica in elastomer composites remained a critical issue. Living anionic polymerization, first revealed from Szwarc *et al.*,[63] was then applied and developed by Quirk[64] in his inspiring works, which established paths for the introduction of reactive moieties at the polymers chain-ends. In 2001, Sharpless' pioneering work in click-chemistry marked a significant advancement in the research for the introduction of functional groups along the polymer chain,[65] particularly with regard to thiol-ene reaction, firstly introduced in 1905 by Posner.[66]

Nowadays, scientific literature reports a plethora of synthetic techniques, which are designed to ensure safety, sustainability and cost-effectiveness for industrial scalability. An emergent research area focuses on the depolymerization of polymer chains to produce functionalized telechelic oligomers. These intermediates can be used as building blocks to engineer new elastomer architectures, specifically designed to enhance filler-polymer interactions in silica-based tyres.[67] From the next paragraphs, main functionalization techniques are discussed, beginning with chain end functionalization through living and pseudo living polymerization, then presenting the functionalization of the backbone chain.

2.2. Functionalization During Polymerization

Functionalization during polymerization led to the synthesis of chain-end-functionalized polymers. It includes chain end functionalization via i) living polymerization (by introducing functional groups during the initiation or propagation stages), ii) pseudo living polymerization and iii) metathesis polymerization.

2.2.1. Chain End Functionalization Through Living Polymerization. The methodology of living anionic polymerization, especially using alkyl lithium initiators for styrene, diene, and (meth)acrylate monomers, is ideal for creating chain-end-functionalized polymers with precise structures. This process avoids spontaneous chain termination and chain transfer reactions, maintaining stable anionic polymer chain ends after all the monomer is consumed. As a result, this technique enables the synthesis of well-defined, chain-end-functionalized polymers with very low compositional heterogeneity.[64,68,69] Figure 8 summarizes the main anionic polymerization mechanism and the initiators/terminators presented in the section.

2.2.1.1. Functionalization by Termination With Electrophilic Reagents. In general, ω-functionalized polymers can be synthetized through electrophilic reagents post anionic polymerization reaction. In fact, the products of living anionic polymerization are polymers chains with carbanionic chain ends which can react with electrophilic species.[68]

2.2.1.1.1. Carbonation. The synthesis of carboxy-terminated polymers is possible by simple reaction between polymeric organolithium compound and gaseous carbon dioxide, obtaining side products. Indeed, aldehydes and alcohols are formed, next to

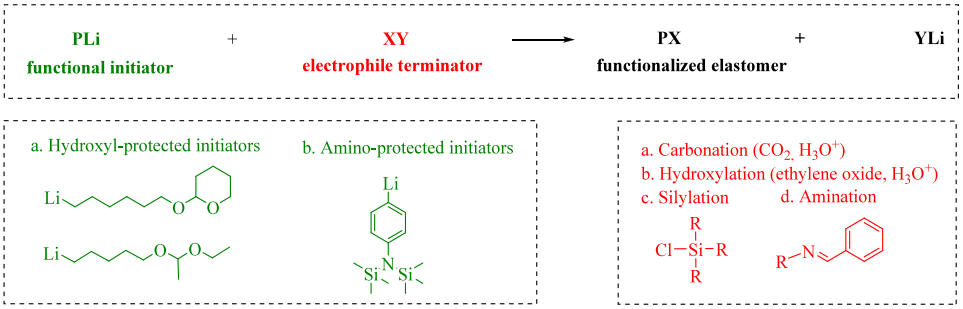

Figure 8. Terminal functionalization of elastomers using protected initiators or electrophilic terminators.

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ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

the desired carboxylated product by aggregation of the chain ends in hydrocarbon solution.[68−71]

2.2.1.1.2. Hydroxylation. The preparation of hydroxyl-terminated polymers from polymeric organolithium compounds by reaction with ethylene oxide is one of the few simple and efficient functionalization reactions. The reaction of poly(styryl)-lithium with excess ethylene oxide in benzene solution produces the corresponding hydroxyethylated polymer in quantitative yield without formation of detectable amounts of oligomeric ethylene oxide blocks.[72]

Specific functionalization methods using a variety of different epoxides have been reviewed by *Quirk et al.*[72] Based on reactivity, application, conditions, substituents and chain length, hydroxy-group can be added also by reaction with propylene oxide, butene oxide, styrene oxide, 3,4-epoxy-1-butene, 3-glycidoxypropyltrimethoxysilane, oxetane and formaldehyde.

2.2.1.1.3. Silylation. Polymers can be functionalized with silicon-based groups, and they are widely used. The reaction of polymeric organolithium compounds with a variety of silyl halides is a very efficient reaction that is not complicated by competing side reactions.[72,73]

2.2.1.1.4. Amination. The introduction of an amino group at the polymer chain-end in anionic conditions is a significant occurrence, due to the acidity of the nitrogen-hydrogen bond. Using protected amine is the solution. The primary amination of organolithium polymers can be obtained using N-trimethylsilyl-protected imines with no acid α-hydrogen, to avoid side reactions. While secondary chain-end amine can be obtained using *N*-benzylidenemethylamine.[69]

2.2.1.2. Functionalization by Functionalized Alkyllithium Initiators

An alternative procedure for the preparation of end-functionalized polymers is to use alkyl lithium initiators which contain functional groups. Because most functional groups of interest (e.g., hydroxyl, carboxyl, amino) are not stable in the presence of either simple or polymeric organolithium reagents, it is generally necessary to use suitable protecting groups in the initiator. A suitable protecting group is one that is not only stable to the anionic chain ends but is also readily removed upon completion of the polymerization. There are several distinct advantages in the use of a functionalized initiator, such as the possibility to synthetize α- or α, ω-functionalized polymers.[68]

2.2.1.2.1. Hydroxyl-Protected Initiators. Acetal protecting groups like 2-(6-lithio-n-hexoxy)-tetrahydropyran and ethyl 6-lithiohexyl acetaldehyde acetal can be used as initiators for polymers synthesis, to introduce hydroxy group, after mild acid hydrolysis.

2.2.1.2.2. Protected Amine-Functionalized Initiators. Schulz and Halasa[74] used *N,N*-bis(trimethylsilyl) amine to protect the primary amine group during polymerization. This protection prevents unwanted proton transfer that would otherwise disrupt the polymerization process. The bis(trimethylsilyl)amine groups could be readily hydrolysed under acidic conditions, restoring the primary amine functionality in the polymer.

Tertiary amine-functionalized polymers are easier to prepare than their primary amine counterparts. Stewart, Shepherd, and Service[75] developed a method to produce 3-dimethylaminopropyllithium in benzene with over 90% yield, which was then used to polymerize butadiene in hexane at room temperature, resulting in polybutadienes with high 1,4-microstructure. Pitsikalis and Hadjichristidis[76] used the same initiator to create three-armed star-branched polybutadienes, which were then linked with methyltrichlorosilane. Lawson, Antkowiak, and colleagues[77] developed tertiary amine-functionalized phenyllithium initiators for low-hysteresis elastomers. These initiators produced polymers with tertiary amine and reactive benzaldehyde end-groups, depending on the specific conditions used.[68]

2.2.2. Chain End Functionalization Through Pseudo Living Polymerization

A pseudo living polymerization mimics the behaviour of a living propagation. Lanthanides based catalysts are known to promote pseudoliving polymerizations and the neodymium-based ones emerged as prominent choices for both industrial scale-up and academic research due to their high activity, exceptional regiospecificity, and unique ability to mediate reversible chain transfer.[78,79]

In neodymium-mediated systems, this process is commonly known as Coordinative Chain Transfer Polymerization (CCTP),[80−82] which operates through a dynamic equilibrium between a catalytically active species and a passive species. The active species consists of a polymer chain attached to a transition metal or lanthanide center (the pre-catalyst), while the dormant species involves a polymer chain linked to a main-group metal-based chain transfer agent (CTA), typically an organoaluminium or organomagnesium compound. In this equilibrium, the polymer chain is rapidly transferred between the neodymium center and the CTA via a bimetallic bridge. Because the concentration of the CTA is usually much higher than that of the neodymium pre-catalyst, most polymer chains at any given moment are present in a dormant state on the aluminium or magnesium atoms. This mechanism ensures that all chains have an equal probability of growth, resulting in a narrow molar mass distribution and a linear increase in with respect to monomer conversion.[82,83]

This finding is pivotal for the industrial production of polymers with controlled architectures, such as high cis 1,4-content polybutadiene (up to 99%),[84] and for the efficient functionalization of polymers employed in the manufacture of high-performance tyres. A variety of functionalizing agents have been demonstrated to react with pseudo living polybutadiene.[85−95]

2.2.3. Metathesis Polymerization

The ring opening metathesis polymerization (ROMP), to polyalkenamers, was first perfomed by Giulio Natta and coworkers with the aid of anionic coordination Ziegler catalysts.[96] Over the past fifty years, olefin metathesis has assumed fundamental importance in organic and polymer synthesis. The process is based on the trans-alkylidenation of two double bonds, which is facilitated by metal complexes.[97−102] Indeed, the mechanism has been refined thanks to the development of highly active and functional group-tolerant catalysts, such as those developed by Schrock[103] and Grubbs.[104,105]

In the elastomers' field, the development of ROMP,[106−108] together with acyclic diene metathesis polycondensation (ADMET),[109,−112] enable the synthesis of defined and controlled polymer architectures, such as cis-1,4-polybutadiene hydroxy and iodo terminated,[113] polynorbornene derivatives,[114] poly[carbo(dimethyl)silane].[115]

2.3. POST-POLYMERIZATION FUNCTIONALIZATION

Post-polymerization functionalization is defined as the chemical modification of a pre-formed polymer scaffold, with the

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ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

objective of introducing functional groups along the chain. The techniques employed are click-chemistry reactions, thiol-ene or 1,3-dipolar cycloaddition, and radical grafting.

2.3.1. In Chain Functionalization Through Click-Chemistry

The concept of "click"-chemistry reaction, introduced by K. Barry Sharpless,[65] describes a series of chemical reactions that should ideally occur fast, selective, atom-economic, under mild conditions, with high yield and easy to purify.[65,113−116]

By using monomers with different functionalities it is possible to tune some polymers properties such as degree of cross-linking, degradability, shrinkage stress and other physical features.[117]

2.3.1.1. Radical Thiol-Ene. The thiol-ene reaction is the addition of a thiol to an "ene" bond, usually a carbon−carbon double bond, to form an alkyl sulfide, better known as hydrothiolation reaction.[118] The radical thiol-ene proceeds via a chain process involving initiation, propagation and chain transfer, and termination steps, as described in Figure 9.[117,119]

Thiol-ene reaction has its applicability for the functionalization of polymers, even if it's limited to low-molecular-weight thiols/olefins. Lately, this technique is widely used to enhance the mechanical properties, chemical resistance, and biocompatibility of elastomers.[120]

Generation of radicals is possible via the thermal decomposition of initiators or photo-cleavable initiators.

2.3.1.1.1. Initiated by UV-light. The thiol-ene reaction typically proceeds via a radical chain mechanism, which is commonly initiated by UV irradiation. This starts with the photocleavage of a suitable photoinitiator to generate a thiyl radical. UV-light initiation offers precise spatiotemporal control, enabling rapid curing, solvent-free processing and minimal heat generation.[121] This is particularly advantageous for encapsulating heat-sensitive materials or fabricating complex microstructures.[122] The inherent atom economy, rapid kinetics and robustness against oxygen inhibition (compared to traditional radical polymerization) further highlight the usefulness of UV-initiated radical thiol−ene reactions in various fields.[120,123]

Photoinitiators play a crucial role in determining the efficiency and characteristics of UV-light initiated polymerizations, including the thiol-ene "click" reaction, by generating reactive species when light is absorbed.[124] Broadly, photoinitiators are categorized into two main types based on their radical generation mechanism: Type I (cleavage) photoinitiators and Type II (abstraction) photoinitiators.[125,126]

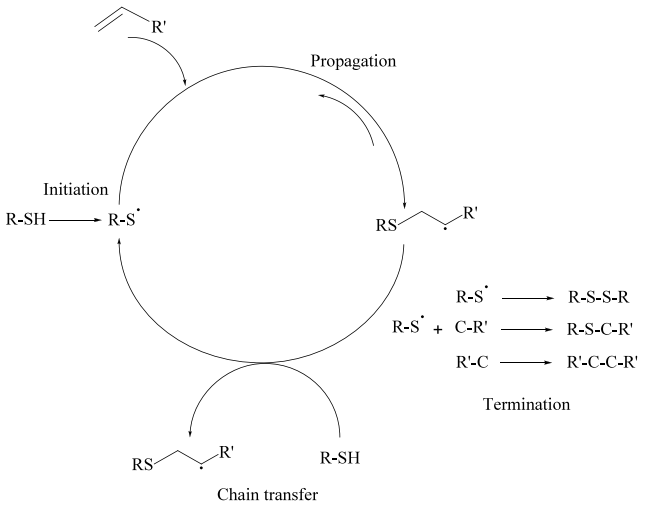

Figure 9. General mechanism of a radical thiol-ene reaction.

Type I photoinitiators, also known as unimolecular photoinitiators, undergo direct homolytic cleavage upon UV irradiation, generating two active radicals that can immediately initiate polymerization. Prominent examples include acetophenones such as DMPA (2,2-dimethoxy-2-phenylacetophenone), often referred to by its trade name Irgacure 651, and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184). Due to its high efficiency and non-yellowing properties, Irgacure 184 is the industry standard for clear topcoats in wood and furniture finishing, where surface hardness and aesthetic clarity are paramount. Another important class comprises acylphosphine oxides, e.g., 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO).[127] These initiators are highly efficient, providing rapid polymerization kinetics and are particularly effective in formulations requiring fast curing speeds, such as 3D printing (SLA/DLP) and optical fiber coatings, even in highly viscous media. Phosphine oxides exhibit reduced oxygen inhibition and good through-cure properties in thicker sections due to their stronger absorption in the long-wavelength UV region.[128]

In contrast, Type II photoinitiators operate via a bimolecular mechanism, requiring a co-initiator (typically a tertiary amine or thiol) to generate radicals through hydrogen abstraction from the co-initiator upon excitation by UV light. Common Type II initiators include benzophenones, thioxanthones (e.g., Irgacure ITX) and camphorquinone (CQ). The use of ITX is particularly prevalent in pigmented printing inks (offset and screen printing), as its spectral sensitivity helps overcome the "inner-filter effect" where pigments absorb the UV light needed for curing. Similarly, Camphorquinone represent the cornerstone of dental restorative composites, as its ability to be activated by safe, visible blue light (approx. 470 nm) allowing for chair-side polymerization.[129] Upon excitation, the Type II photoinitiator abstracts a hydrogen atom from the co-initiator, yielding a ketyl radical from the photoinitiator and a highly reactive radical from the co-initiator (e.g., an aminoalkyl radical or a thiyl radical).[130] Their dependence on a co-initiator means that its choice can significantly influence the overall reaction kinetics and final polymer properties. The selection between Type I and Type II initiators is therefore critical, depending on factors such as desired curing speed, thickness of the material, spectral overlap with the UV source, and the specific application requirements.[131,132]

2.3.1.1.2. Initiated by Thermal Energy. Heat initiation normally makes use of thermal radical initiators (TRIs) such as azobis(isobutyronitrile) (AIBN) or peroxides (e.g., benzoyl peroxide, BPO).[133−136]

Advantages of thermally initiated thiol-ene reactions include the potential for processing thick or opaque material where UV light cannot penetrate effectively, as well as the potential for minimized processing equipment due to elimination of the need for UV lamps.[137] The process also allows for more generous reaction conditions, such as easy control of the reaction temperature, which in turn regulates the rate of reaction and end-polymer properties. However, the process of thermal initiation presents technical challenges. In contrast to UV-light activation, which exhibit spatiotemporal control, this reaction lacks such specificity, consequently precluding its restriction to a particular moment or area. This has been shown to increase the

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ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

risk of premature polymerization during high-temperature processing steps. This is particularly relevant in cases where the decomposition temperature of the initiator is too close to the required temperatures for mixing or extrusion.[138] Moreover, heat generation resulting from the exothermic reaction itself needs to be well controlled, especially in bulk systems, to prevent thermal runaway.[139] These characteristics results in a reduced scalability when compared with UV-light reactions. Despite these considerations, thermally initiated thiol-ene chemistry remains a viable approach for bulk polymerization processes, crosslinking of materials without the need for light exposure, or integration into established thermal production processes.[122]

2.3.1.1.3. Catalysed by a Base or a Nucleophile. Thiol-click reactions that depend upon the nucleophilicity of the thiol component proceed with a wide range of rates according to the substrate and its propensity for nucleophilic attack by either thiols or thiolate anions. Reactions are initiated by strong bases, which can be added separately as a catalyst to increase the reaction rate. The rate increases with the nucleophilicity of the catalyst.[140] Additionally, increasing electron deficiency of the double bond increases the thiol addition rate.[141] A significant difficulty with thiol coupling reactions is the susceptibility of free thiol functionalities to oxidation to disulfides, which can be avoided by removing oxygen from the reaction environment.

Even if the process leads to the same product (thioeter) there are two main mechanistic differences:

(1) Base-catalysed pathway, where the base directly deprotonates the thiol to generate the thiolate anion, which is the nucleophile that attacks the alkene. The bases used for this application are primary or secondary amines, such as hexylamine ($C_6H_{13}NH_2$), di-n-propylamine ($NH(C_3H_7)_2$), and triethylamine at room temperature under bulk conditions.[120]

(2) Nucleophile-initiated pathway in which the nucleophilic catalyst such as dimethylphenylphosphine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) first attacks the electron-deficient alkene to form a carbanion/enolate intermediate, which then deprotonates the thiol to generate the reactive thiolate anion and regenerate the catalyst. This mechanism is often faster.[142]

2.3.1.2. 1,3-Dipolar Cycloaddition

The 1,3-dipolar cycloaddition is a chemical reaction between a 1,3-dipole and a dipolarophile to form a five-membered ring. First studies were conducted by Smith[143] and then developed by Huisgen in the '50s.[144−146]

This technique is also reported in literature, and it is employed for the functionalization of elastomers as discussed below in the text in Section 3.[147,148]

2.3.2. Other Functionalization Techniques

In the patent literature, radical grafting was also used as post-polymerization method to functionalize elastomer along the chain.[149,150] The radical grafting process is typically initiated by a free radical initiator, such as an organic peroxide, which creates reactive sites along the polymer backbone. The reaction is efficiently carried out through thermomechanical processing within a co-rotating twin-screw extruder. Inside the extruder, the elastomeric base and the functionalized monomers are subjected to high temperatures, and intense shear forces for a short duration. The selection of monomers can tune the properties of the modified polymers.

2.4. FUNCTIONALIZATION THROUGH DEPOLYMERIZATION

The term depolymerization is used to include all situations in which reduction of macromolecular size occurs without change of chemical composition or alteration of the monomer unit structure.[151]

Functionalization of polymers via depolymerization is a sophisticated approach that combines the breakdown of polymers into smaller units with the strategic introduction of functional groups. This process allows for the transformation of existing polymers into new materials with enhanced properties or novel functionalities. By carefully controlling the depolymerization conditions, such as temperature, catalysts, and the choice of reagents, it is possible to achieve precise modification of the polymer's chemical structure. This technique is particularly valuable for recycling and upcycling polymer waste, converting it into high-value materials with specific applications in different fields. Additionally, functionalized depolymerization can lead to the production of tailor-made monomers and oligomers, offering a pathway to more sustainable and innovative material design.[152]

Figure 10 summarizes NR depolymerization strategies.

2.4.1. Photochemical Depolymerization

Sunlight and ultraviolet light can cause covalent bond cleavages in certain substances, with consequent formation of free radicals. In the presence of UV light, this via can produce telechelic liquid natural rubber with hydroxyl termination. Under ultraviolet irradiation, hydrogen peroxide undergoes cleavage yielding hydroxyl radicals. These radicals then interact with the C−H labile bond in alpha to give hydroxyl end groups leaving behind the macroradicals.[153]

2.4.1.1. Oxidation at Elevated Conditions. Masticated NR dispersed in toluene, containing 30−40% of hydrogen peroxide, when heated at 150 °C in a reactor at 14−20 atm of pressure, leads to the formation of hydroxyl telechelic natural rubber with Mn between 2500 and 3000 g/mol. The efficiency obtained through this method is low because of side reactions.[154]

2.4.1.2. Redox Depolymerization. This depolymerization method exploits an appropriate mixture of oxidizing and reducing agents (a redox couple). The redox couple can cleave polymer chains with the introduction of reactive terminal groups on the resulting oligomers. This method is employed to depolymerize NR to yield telechelic liquid natural rubber.

The oxidizing agent can be organic peroxide, hydrogen peroxide, atmospheric oxygen or ferric chloride-oxygen, coupled with a reducing agent, such as an aromatic hydrazine or sulphanilic acid. The average molecular weight obtained using this technique is between 3000 and 35000 g/mol. Depolymerization can be carried out either in an organic solvent or directly in the latex phase. One example of this process is the depolymerization reaction of NR in the latex phase, using phenylhydrazine as reducing agent and atmospheric oxygen as an oxidizing agent, owing to it being economically viable on an industrial scale.

Another interesting example is provided by Tangpakdee *et al.*,[155] who were able to demonstrate that a redox couple

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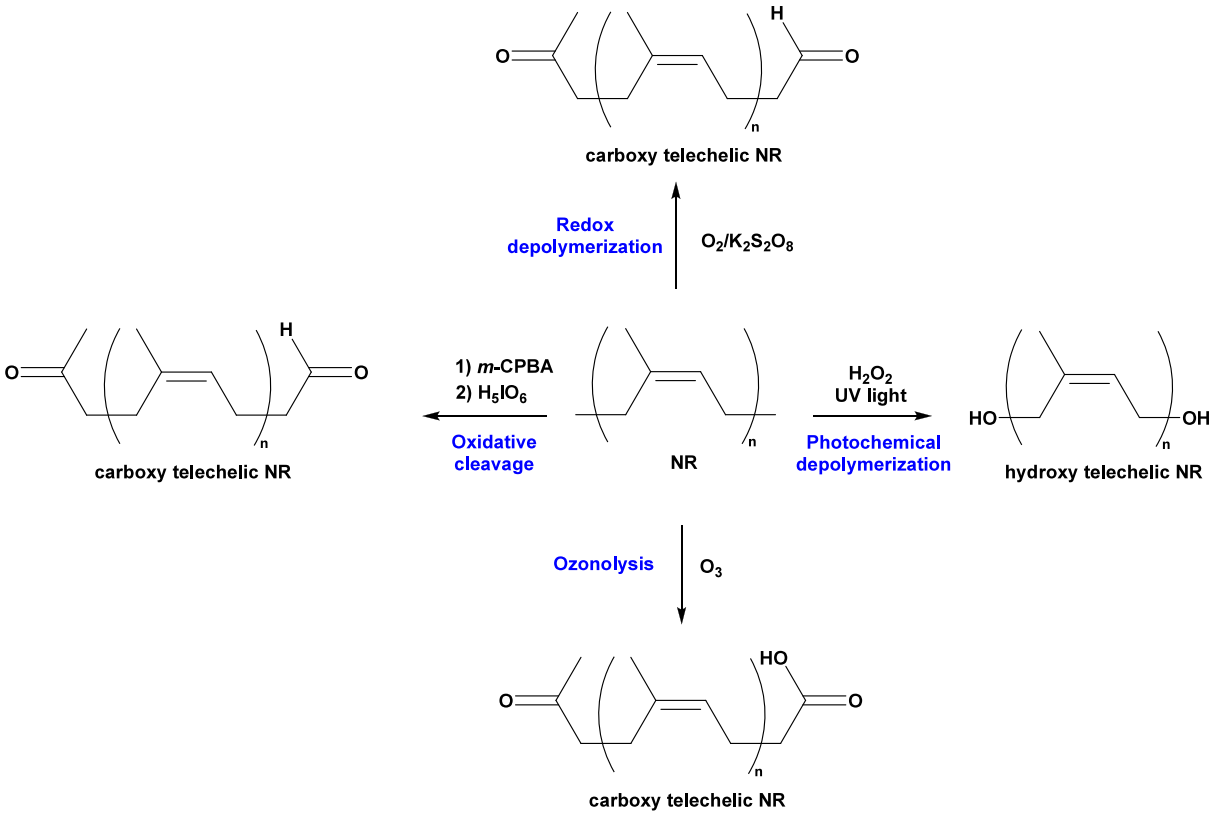

Figure 10. NR depolymerization strategies.

composed by potassium persulphate, $K_2S_2O_8$, and propanal can degrade NR at 60 °C. The proposed mechanism involves the oxidation of chain by a radical initiator, followed by a reaction of propanal with aldehyde terminal group. The obtained telechelic liquid natural rubber contained aldehyde and ketone groups.

2.4.1.3. Specific Oxidative Cleavage of Double Bonds. Specific oxidative cleavage of double bonds is a chemical reaction where the double bond in an alkene is broken, and the carbon atoms involved in the double bond are converted into carbonyl compounds. This process is particularly useful in organic synthesis for fragmenting larger molecules like polymers into more functionalized units.[156]

2.4.1.3.1. Ozonolysis. The term ozonolysis indicates a treatment with ozone, which leads to the double bonds' cleavage of rubbers, like polyisoprene, polybutadiene, polyisobutylene, with the consequent formation of a mixture of shorter functionalized polymers or oligomers. This oxidative technique brings to the formation of ketones, aldehydes, carboxylic acids and peroxide compounds on polymer chains, with a lower molecule weight with respect to the starting polydienic compound.[153] This is a promising approach, which still needs effort to increase the selectivity towards a specific functional group. Ozone is a highly toxic gas for concentrations higher than 0.1 ppm, with a boiling point of −111 °C and a melting point of −192 °C. Its reactivity should be modulated throughout the setting of process time (not too long), concentration and flow rate. The chosen solvent has an important role as well. The mechanism of interaction between ozone and C═C was studied by Cringè,[155] who proposed a path of reaction passing through unstable intermediates (molozonides), reaching stable carbonyl compounds or unstable carbonyl oxide, called zwitterion. The unstable carbonyl oxides tend to stabilize in a following step. The nature of the rubber will influence the preferred path.

Recently, the effect of humid atmosphere during ozonolysis has been analyzed, supposing the existence of a new route of cleavage in addition to the already known mechanism, which implies the formation of hydroxyl radicals.[157]

2.4.1.3.2. Oxidative Cleavage With Periodic Acid. According to literature,[155,158,159] *m*-CPBA (*meta*-chloroperbenzoic acid) is added to the polydienic rubber to form epoxides in random positions, in correspondence of C═C of the chain, which can be broken in a second step of reaction with periodic acid in its dihydrate form. *m*-CPBA can transform C═C into a tensionate ring with O that could be easily attacked by periodic acid. After oxidative cleavage, a bi-functionalized polymer or oligomer is obtained, with an aldehyde in chain end position and a ketone in beta position on the other side.

The percentage of epoxide is directly linked with the weight of the produced oligomers.

2.5. CRITICAL REMARKS

Table 1 summarizes the main advantages and disadvantages of most diffused techniques discussed above.

Considering the requirement for sustainability and circularity, living anionic polymerization remains the gold standard for producing model polymers with nearly absolute control over architecture, with well-established industrial processes to

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Table 1. Comparative Evaluation of Functionalization Strategies: Trade-Off, Performance Gains vs Environmental Burdens, and Current Debates

Strategy	Precision vs Scalability Trade-Off	Performance Gains vs. Environmental Burdens	Current Debates
Living Anionic Polymerization	High precision. Control of molecular weight and architecture.[164] Industrial maturity. Needed removal of polar impurities (special equipment at lab scale).	Performance: enables "natural-like" precision.[165] Burden: High reliance on toxic organic solvents (e.g., cyclohexane) and energy-intensive cryogenic conditions.	Use of unconventional media such as deep eutectic solvents (DES).[161]
Radical Thiol-Ene Click	Moderate precision.[162] Rapid kinetics and solvent-free processing. Scalability.	Performance: robust, fast and generally water-resistant.[166] Burden: High odor and toxicity of low-M.W. thiols.	Side by-products from competitive homopolymerization.[167]
Nucleophilic Thiol-Michael Addition	High precisionModerate scalability. in a narrower range than from radical pathways. $_{g}T$More uniform functionalization and[168] Restricted to electron-deficient "enes".	Performance: better ductility due to the step-growth nature of the process.[149] Burden: High catalyst concentrations.	Prevention of disulfide formation.[169]
Oxidative Depolymerization	Low precision.Industrial maturity.[170] Economically viable for producing liquid natural rubber: broad molecular weight distributions (3,000−35,000 g/mol).	Performance: conversion of waste into functional oligomers.[171]-CPBA). *m*Burden: Use of highly toxic gases (e.g., ozone), or reagents	Enzymatic pore formation and chemical cleavage for vulcanized rubber degradation.[163]

produce styrene-butadiene copolymers. While the process is industrially mature, it is accompanied by significant sustainability issues. The utilization of toxic solvents and energy-intensive conditions, such as low-temperature control and rigorous purification to remove polar contaminants, drives the search for more robust and eco-friendly synthetic alternatives.[160] Unconventional media like deep eutectic solvents (DES) are a novel opportunity.[161] They are a new class of green, tunable, and biodegradable liquids formed by mixing solid hydrogen bond donors and acceptors to achieve significant freezing point depression.

Thiol-ene reaction offers a valid alternative, particularly for cross-linking and surface modification. Its ability to proceed rapidly in bulk (solvent-free) under ambient conditions makes it a favorite for large-scale manufacturing.[162] Provided that issues related to odor, toxicity, and network heterogeneity are addressed through the adoption of nucleophile-initiated thiol-Michael addition where appropriate.[98]

Functionalized depolymerization has the potential to transform the field by enabling true "polymer-to-polymer" recycling, provided that innovations in enzymatic and chemodivergent catalysis continue to enhance selectivity and energy efficiency.[163]

3. EFFECTS OF FUNCTIONALIZED ELASTOMERS ON THE COMPOSITES' PROPERTIES

The effects of polymer functionalization on silica-based compounds are discussed in the scientific literature, which addresses themes such as change in the nature of dangling chains, melt viscosity and elasticity, and filler networking.

The removal of dangling chain has been shown to decrease internal friction.[172−176] Nevertheless, it is well established that functionalized elastomers affect the processability of the compound:[177,178] the filler-polymer interaction during compounding causes the melt elasticity, a phenomenon defined as the ability of molten polymer to recover from elastic deformation.[179] This is the main factor responsible for die swell of (tyre) compounds.[180] This property is effectively measured through Mooney viscosity measurements, which reveal the increase of Mooney viscosity and Mooney relaxation.[181−185]

Increasing the polymer-filler interactions by using end-functionalized polymers inhibits the filler flocculation, resulting in less extensive filler networking (reduced magnitude of Payne effect).[186−188] Furthermore, end-functionalized polymers have been demonstrated to effectively trap the chain ends at the interface with the filler, reducing hysteresis.

Analysis of scientific and patent literature was carried out, to investigate the correlation between the structure of the functionalized elastomers and the properties of the composites, also on a quantitative basis.

3.1. Data From Scientific Literature

The data reported in the scientific literature are summarized in Table 2, which shows the functionalization method, the functionalizing agent, the functional group introduced into the elastomers and its effect on the silica-based composites.

Data are organized as a function of the position and of the type of the functional group: as chain end or in chain as the position, and silane, amine, hydroxy, epoxy, carboxylic acid as the functional groups.

Functionalization of polymers at the chain-end via living anionic polymerization was mostly used to introduce silane groups or amino groups. The use of silanes, such as APTES,[189] resulted in an increase of viscosity (24%), and a reduction of Payne effect (23%). The tan delta profile was modified, with a slight increase at low temperature and reduction at high temperature. Increase of tensile strength and slight reduction of elongation at break were observed.

With an amino,[196] DPE-$(NMe_2)_2$[190] and carbamate groups,[91] reduction of Payne effect was observed. With the latter two functional groups tan delta was observed also at low temperature, and simultaneous increase of tensile strength and elongation at break were obtained, up to 60% with the former modifier.

When amines were combined with alkoxysilyl groups, as in the case of the initiator formed from a functional styrene derivative (*N*-(dimethyl(vinylbenzyl)silyl)-*N*,*N*-bis(trimethylsilyl)amine) and either *n*- or sec or tert-butyllithium,[191] an increase in the reinforcement index (up to 88%) and tensile strength (up to 14%) was obtained, and tan delta at 70 °C decreased by 25%.

When a coupling agent as TEOS was used,[192] viscosity increased by 36%, with a reduction of Payne effect by 23%. The elongation at break worsened by 29% with respect to the reference compound.

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Table 2. Functionalization Methods and Effects on Silica-based Composites, Data from Scientific Literature[a]

Polymer (M.W.)	Functionalization method	Functionalization agent/functional group	Viscosity index (%)[b]	Payne effect (%)	tanδ (%)[c]	Reinforcement index (%)[d]
chain-end functionalization						
S-SBR (142 kg/mol)	living anionic	3-aminopropyl)triethoxysilane (APTES) (in α, ω) / silane	+24 %	−23 % (ΔG′)	+12 % (at 60 °C) −2 %(at 0 °C)	+12 %
S-SBR (280 kg/mol)	living anionic	tetraethoxy silicate (TEOS) (in ω) / silane	+36 % (minimum torque M_L)	−22 % (G′)	−4 % (60 °C) −16 % (at 0 °C)	N/A
S-SBR (262 kg/mol)	living anionic	N/A (in α)/ amine	−5 % (minimum torque ML)	−31 % (ΔG′)	−0.6 % (at 70 °C)	−3 %
S-SBR (116 kg/mol)	living anionic	1,1-bis(4-N,N-dimethylaminophenyl) ethylene (in α) DPE-$(NMe_2)_2$/amine	N/A	−36 % (ΔG′)	−12 % (at 60 °C) −5 % (at 0 °C)	N/A
Polybutadiene (162 kg/mol)	pseudo living (CCTP)	hexamethylene diisocyanate (in ω) / carbamate	−7 %	−26 % (ΔG′)	N/A	−4 %
in chain functionalization						
S-SBR (196 kg/mol)	radical thiol-ene	3-(triethoxysilyl)propane-1-thiol (MPTES) / silane	+86 % (minimum torque ML)	−89 % (ΔG′)	+161 % (at 7 % of strain) −50 % (at 0 °C)	N/A
S-SBR	radical thiol-ene	3-mercaptoethanol / hydroxy	N/A	−10 % (G′)	+21 % (at 60 °C) −33 % (at 0 °C)	N/A
S-SBR (185 kg/mol)	radical thiol-ene	3-mercaptopropanol / hydoxy	−14 % (minimum torque ML)	−74 % (ΔG′)	+112 % (at 7 % of strain) −21 % (0 °C)	N/A
S-SBR	oxidation of double bonds	H_2O_2 / epoxy	N/A	−27 % (G′)	+184 % (at 60 °C) −52 % (at 0 °C)	+8 %
E-SBR	oxidation of double bonds	*m*-CPBA / (10 % mol)epoxy	N/A	−14 % (ΔG′)	+25 % (at 60 °C) −6 % (at 0 °C)	+2 %
S-SBR (186 kg/mol)	radical thiol-ene	11-mercaptoundecanoic acid / carboxylic acid	+68 % (minimum torque ML)	−89 % (ΔG′)	+161 % (at 7 % of strain) −27 % (at 0 °C)	−38 %

[a]All % data reported are relative to unmodified elastomer/silica nanocomposites. [b]Calculated from ML 1+4 at 100 °C. [c]Calculated from axial measurements. [d]C

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In chain functionalization, achieved primarily through thiol-ene reactions or the oxidation of double bonds, exhibited considerably more pronounced effects.

In the case of S-SBR functionalized with 3-(mercaptopropyl)triethoxysilane, 86% increase of viscosity and 89% decrease of Payne effect were observed.[57] Grafting of triethoxysilane was also shown[193] to reduce rolling resistance by 30%, and abrasion by 38%, and to improve the wet-skid resistance by 88%.

Primary hydroxy group[57] reduced the compound viscosity by 14% and the rolling resistances by 21%, with an improvement of wet skid resistance of 112%.

In chain epoxidation,[194,195] showed an increase of tan delta at 0 °C by up to 184%, with a reduction by 52% at 60 °C. In addition, the reinforcement index, the tensile strength and elongation at break increased with respect to the reference compound.

Mercaptoundecanoic acid[57] reduced Payne effect by 89% and provided a major increase in tensile strength up to 73%, with a reduction of elongation by 25%.

As a summary, common effects of the functional groups were the reduction of Payne effect and hysteresis at high temperature. In most cases, the reinforcement index was not remarkably modified, the tensile strength was enhanced and the elongation at break was reduced.

3.2. Data from Patent Literature

In Table 3 were collected patents which refer to the functionalization of elastomers, both chain-end and in chain. The aim of the research activity covered by the patents was to achieve a better balance between wet grip, rolling resistance and abrasion resistance. Comments in the following refer to the prevailing effects brought about by the functional groups.

A good number of patents are available on living anionic polymerization and many of them report the introduction of silanes as chain ends.[198−201] Silanes led to the increase of composites' viscosity, to the reduction of Payne effect and to a better hysteresis profile, higher at low temperature and lower at high temperature. A clear increase of the M300/M100 ratio was also observed, in most cases. The ultimate tensile properties were not remarkably affected, but an appreciable reduction of elongation at break was also reported.

Functional groups such as hydroxy,[202,203] or carboxy groups[204] led to similar results, but with a larger increase of viscosity. Better abrasion was also claimed.

When a coupling agent as TEOS was used,[205] the increase of viscosity was more than 100%, with a reduction of the M300/M100 index.

The metathesis reaction led to the formation of oligomers with chain end functional groups, which promoted a substantial reduction of viscosity, together with remarkable reduction of Payne effect (80%) as well as tan delta at 60 °C (52%).[206]

The in-chain functionalization was characterized by the remarkable increase of viscosity and the large reduction of Payne effect. It is worth observing that, in most cases, the tan delta values were reduced both at high and low temperature, hence failing to meet the target of improving the wet grip of a tire compound. For example, functionalization with carboxylic acid led to the reduction of tan delta at low temperature[149,150,206] up to 57%.[149] Imidazole functionalization[147] led to the reduction of tan delta by 39% and 38% at 23 °C and 100 °C respectively. Notably, grafting on the polymer chain of imidazole[147] or tetrazole,[148] via 1,3-dipolar cycloaddition, was performed *in-situ* during compounding. Grafting with tetrazole increased the tensile strength by 89% and the elongation at break by + 17%.

The effects of functional groups, which arise from the data reported in Table 2 and Table 3, from scientific and patent literature respectively, are substantially in line. However, it is worth observing that the grating of polar groups, either through radical process of 1,3-dipolar cycloaddition led to the mentioned reduction of tan delta at low temperature, whereas the addition, through thiol-ene reaction, of silane, OH, COOH groups and the oxidation to epoxide, reported in the scientific literature, led to the increase of tan delta at low temperature, thus suggesting a key role of the functionalization technique.

3.3. Simultaneous Optimization of Processing and Composites' Properties

Values reported in Table 2 and Table 3 reveal that functionalized elastomers lead to superior mechanical and hysteretic properties. However, processing can be challenging. The functional group *per se* does not affect the rheological behavior, but the adduct of the functionalized chain with the filler does it. This issue can be resolved by targeting controlled molecular architecture during polymerization.

According to White and Tokita,[207] Tokita and Pliskin,[208] and Cotten,[209] raw elastomers, when processed, must be investigated through a nonlinear viscoelastic approach, including the Mooney and Mooney Stress relaxation test.

In this frame, commercially available elastomers are characterized by very complex structures, and the nonlinear viscoelastic response is strongly affected by changes in the relaxation time spectrum of the polymer matrix, when for example, branched chains are involved. Introducing branched chains directly affects the relaxation dynamics of the entanglement network, resulting in a change in the distribution of relaxation times. Variations in well-known parameters such as the Mooney stress relaxation plot and the dynamic modulus crossover point are observable effects. Given the configuration of the processing equipment, the variation in relaxation time introduced by branching points translates directly into a different dimensionless parameter, such as the Deborah number, and modified processability.[210,211]

E-SBR, for example, is widely used in rubber mixing due to its good filler incorporation and to the favorable processing of E-SBR based compounds. In emulsion copolymerization of butadiene and styrene using a free-radical initiator, an inherent chain transfer mechanism results in long branch formation. Broad molecular weight distribution and long branches promote filler incorporation and processability. However, this polymerization mechanism shows poor flexibility in terms of molecular architecture. As discussed above, the anionic solution polymerization is thus used to have better control of the microstructure of SBR, for optimum vulcanizate properties (namely mechanical reinforcement and hysteresis). However, the resulting nearly linear structure and the narrower molecular weight distribution do not benefit processability, as indicated by the higher Mooney viscosity.

S-SBR containing a controlled amount of long-chain branching can be designed to optimize processing and performance simultaneously.

In a recent patent the macromolecular architecture of functionalized polybutadiene was designed to achieve good processability. This was done by controlling the branching of the polymer. A degree of branching equal to or greater than 2 was

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Table 3. Functionalization Methods and Effects on Silica-Based Composites, Data from Patent Literature[a]

Polymer (M.W.)	functionalization method	Functionalization agent/functional group	Main effects[b]	Viscosity index (%)[c]	Payne effect (%)	tanδ (%)[d]	R
chain-end functionalization							
Polybutadiene (219 kg/mol)	pseudo-living	3-glycidoxypropylmethyldiethoxysilane/ silane	reduced hysteresis	+20 %	−35 %(G′ at −20 °C)	+16 % (at 0 °C) −25 % (at 60 °C)	+
Polybutadiene (300 kg/mol)	pseudo living	*N,N*-diethyl-1,1-dimethyl-1-(2-methylenebut-3-en-1-yl) silanamine /silane	reduced hysteresis, better balance of low rolling resistance and high wet grip	+6 %	N/A	+15 % (at 0 °C) −12 % (60 °C)	N
S-SBR	living anionic	trimethoxysilane /silane	wet/dry traction, handling, wear resistance	+15 %	−40 % (G′ at 10% strain)	+18 % (at 0 °C) −30 % (at 100 °C)	N
S-SBR (200-300 kg/mol)	living anionic	3-(aminopropyl)triethoxysilane/ silane	improved processability and wet grip, reduced rolling resistance	- 8 %	−39 %(ΔG′)	+11% (at 0 °C) −12 % (at 60 °C)	+
S-SBR (300 kg/mol)	living anionic	bis(trimetilsylil)ammide/ star-shaped	improved grip and reduced hysteresis	+9 %	−24 %(G′ at minimum strain)	+30 % (at 0 °C) −28 % (at 60 °C)	+
Polybutadiene	living anionic	trimethoxy(4-vinylphenyl)silane (branching agent) + aminoalkoxysilane (coupling agents)	improved processability and bale stability even without process oils	+80 %	N/A	−30 % (at 50 °C)	N
S-SBR(161 kg/mol)	living anionic	TEOS(coupling agents)	reduced rolling resistance	+115 %	N/A	−3 % (at 0 °C) −24 % (at 60 °C)	- 2
Polybutadiene (121 kg/mol)	living anionic	4,4'-bis(N,N-diethylamino) benzophenone/amine	Improved abrasion resistance and lower hysteresis.	+80 %	−18 % (ΔG′)	−25 % (at 50 °C)	+
Butadiene- styrene-acrylonitrile	living anionic	glycidyl methacrylate /hydroxy	improved rolling resistance, wet grip, and abrasion resistance	+60 %	N/A	−9 % (at 0 °C) +6 % (at 60 °C)	+
S-SBR (279 kg/mol)	living anionic	1,3-dimethyl-2-imidazolidinone/ hydroxy	reduced hysteresis	+64 %	−60 % (ΔG′)	+15 % (at 0 °C) −18 % (at 60 °C)	N
S-SBR (130 kg/mol)	living anionic	CO_2 /carboxy	reduced hysteresis and good reinforcement	+30 %	−90 % (ΔG′/G′)	−60 % (at 23 °C)	+
Polydiene and S-SBR (1-500 kg/mol)	living anionic	Epoxy-TEMPO /nitroxide	improved abrasion resistance and prevention of molecular weight reduction during mechanical action	+14 %	N/A	−9 % (at 60 °C)	+
Polyisoprene (50-600 kg/mol)	metathesis depolymerization	1,4-diacetossibut-2-ene/ acetate	better filler dispersion, low hysteresis, lower rolling resistance	−40 %	−80 % (ΔG′)	+25 % (at 0 °C) −52 % (at 60 °C)	+
in chain functionalization							
Natural rubber	radical grafting	phenylaminopropyltriethoxysilane/ PETA[f] (2:1) /silane	improved filler dispersion, decreased rolling resistance, better tread wear, and improved wet skid performance	+28 %	−70 % (ΔG′)	+38 % (max) −57 % (6% second sweep)[d1]	+
S-SBR	grafting reaction (1,3-dipolar cycloaddition)	imidazole	reduced hysteresis, increased stiffness	N/A	−76 % (ΔG′)	−39 % (at 23 °C) −38% (at 100 °C)	+
Polybutadiene	grafting during mixing (1,3-dipolar cycloaddition)	2,5-disubstituted tetrazole[g]	improved filler dispersion, static and dynamic mechanics	N/A	−30 % (ΔG′)	N/A	−

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ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

Table 3. continued

Polymer (M.W.)	functionalization method	Functionalization agent/functional group	Main effects[b]	Viscosity index (%)[c]	Payne effect (%)	tanδ (%)[d]	R
S-SBR (134 kg/mol)	radical grafting	3-mercaptopropionyc acid/ carboxylic acid(80 meq/kg)	reduced rolling resistance while maintaining processability	+51 %	−93 % (ΔG′)	−57 % (at 23 °C)	+
Polybutadiene (200 kg/mol)	radical grafting	methacrylic acid/carboxylic acid	stable high modulus at high temperatures and decreased Payne effect	+1 %	−47 % (ΔG′)	−6 % (at 0 °C) −9 % (at 50 °C)	N
Poly(cis-1,4-isoprene) (900 kg/mol)	radical grafting	maleic anhydride/carboxylic acid	improved static/dynamic mechanical properties and tear resistance without negatively affecting processability	+80 %	N/A	−30 % (at 23 °C) −20 % (at 70 °C)	−

[a]All % data reported are relative to unmodified elastomer/silica nanocomposites. [b]Claimed by the inventors. [c]Calculated from ML 1+4 at 100 °C. [d]Calculated fr
from shear stress measurements. [e]Calculated by M300/M100. [f]PETA is Pentaerythritol tetraacrylate. [g]Without TESPT with respect to the reference.

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obtained during the synthesis, by adjusting the type, quantity and the 'timing' of the addition of branching and coupling agents, containing nitrogen and silicon atoms. For example, the utilization of trimethoxy(4-vinylphenyl)silane as branching agent and an aminoalkoxysilane as coupling agents led to the synthesis of a branched polymers which resulted in an increase in Mooney viscosity by 80%, a decrease of Payne effect by 30% and Mooney shear rate maintained within a specific range of 0.10 to 0.40, measured at 100 °C.[212]

4. FUTURE PERSPECTIVES IN ELASTOMERS FUNCTIONALIZATION AND SWOT ANALYSIS

Despite significant advancements in elastomer functionalization, there are still some important challenges to overcome before it can be considered industrially viable and sustainable. Nevertheless, these challenges present opportunities for future research.[217]

The modern elastomer functionalization landscape must address three key issues: scalability, economic feasibility and environmental sustainability.[218−220]

It is a significant technical challenge to transfer functionalization reactions demonstrated in the laboratory to an industrial scale.[221] While much useful functionalization chemistry takes place under highly controlled laboratory conditions, this does not consider reaction homogeneity and heat dissipation in large reactors. For instance, anionic polymerizations necessitate extremely dry and oxygen-free conditions, which are difficult to guarantee in industrial-scale reactors.[222] Similarly, although radical thiol-ene reactions are efficient, they can generate large exotherms and require precise control over initiation and termination to prevent runaway reactions or the formation of unwanted by-products.[135] Recently, the functionalization landscape is continuously expanding through the integration of highly efficient synthetic methodologies, such as advanced click chemistry platforms. Revived by Sharpless group, SuFEx, the sulfur (VI) fluoride exchange, stands as a promising new option for widely expanding the toolbox for polymers' post-polymerization modification.[141]

In addition to technical scaling up, the economic aspects are subjects of significant academic and industrial interest. Incorporating functionalized steps into the elastomer production process complicates it and makes it more expensive.[223] This often involves using expensive functionalized reagents, initiators, or noble metal catalysts (e.g., ruthenium for ROMP reactions).[224] These additional costs must be justified. In short, functionalized elastomers must offer significant performance benefits, such as longer tyre life, improved grip or reduced rolling resistance for better fuel economy, which are worthwhile for manufacturers and consumers alike.[225]

Finally, environmental issues and the increasingly urgent need to develop more sustainable chemistries are dictating research agendas.[226] Most established functionalization methods utilise volatile organic compounds (VOCs), such as toluene or THF, which pose severe environmental and health risks.[227] These approaches result in the formation of unwanted by-products or entail the use of toxic metal catalyst residues that must be removed from the end material, creating disposal issues. Therefore, regulatory bodies and society are increasingly pushing for more sustainable production processes to be created.[228]

Using bio-based feedstocks is one of the most significant moves towards greater sustainability.[229,230] This involves shifting from using fossil fuels to using renewable feedstocks to produce monomers, initiators and functionalizing reagents. This process can dramatically reduce the carbon footprint and reliance on non-renewable petroleum resources.[231] Examples include using bio-based terpenes,[232] vegetable oils,[233,234] or sugars[235] as feedstocks for new elastomers or functionalizing agents, or as direct bio-based monomers for polymerization. This approach affects not only the functionalizing agent, but also the entire elastomer value chain.[236]

A future milestone will be to incorporate the self-healing function into elastomers. Developing self-healing polymers that can repair low-order damage, such as micro-cracks, would significantly enhance tyre life and reduce waste.[237,238] This involves inserting functional groups capable of forming reversible bonds, such as reversible hydrogen bonding, disulfide bridges[239] or reversible Diels−Alder adducts,[240] which rupture under stress and are reversible under relaxation or specific stimuli. Integrating self-healing sites into the silica-rubber interface with the utilization of Diels-Alder chemistry is a promising technology. By functionalizing the silica surface with silanes carrying specific moieties, the filler particles themselves become reversible cross-linking nodes.[241] Another possible application is creating adaptive reinforcing filler-polymer matrix interfaces.[242−244] These interfaces would dynamically respond to environmental stimuli, such as temperature variations or mechanical loads, by changing their interaction strength.[245,246] These interfaces would be capable of dynamically adjusting the tyre's characteristics (e.g., traction and rolling resistance) based on driving conditions, offering a degree of performance tuning that was previously unimaginable.[247]

Lastly, due to limited resources, it is crucial to recycle and reuse elastomers, since their mechanical performance and safety are affected by their end-of-life disposal methods.[248] A truly circular economy requires the creation of materials with inherent characteristics that enable their recyclability at the end of their life, such as controllable de-crosslinking or the introduction of easily breakable and reformable bonds.[249] Addressing these challenges requires a focused research agenda, demanding the development of new materials with improved self-healing properties, as well as low-cost, large-scale production methods and the wider application of these materials.[250] Adopting this multidisciplinary approach is essential for managing sustainable materials and significantly reducing our environmental impact. This approach is in line with global efforts to protect the environment and utilise resources more efficiently.[251]

To provide a clear picture of the current situation and suggest future research directions, a SWOT analysis of the main functionalization strategies discussed in this review was conducted. This assessment, the details of which are presented in Figure 11, considers the strengths of current methodologies, the weaknesses that limit performance or industrial applicability, the opportunities provided by emerging needs and technology, and the external threats that could hinder progress in this field.

There are many **strengths** in the field of functionalized elastomers for tyres, particularly in developing new products with low rolling resistance, better grip and a longer lifetime. They are even more important in silica-based nanocomposites, where modifications with polar groups enable better dispersion of the filler and improve processability and performance.[252] This

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ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

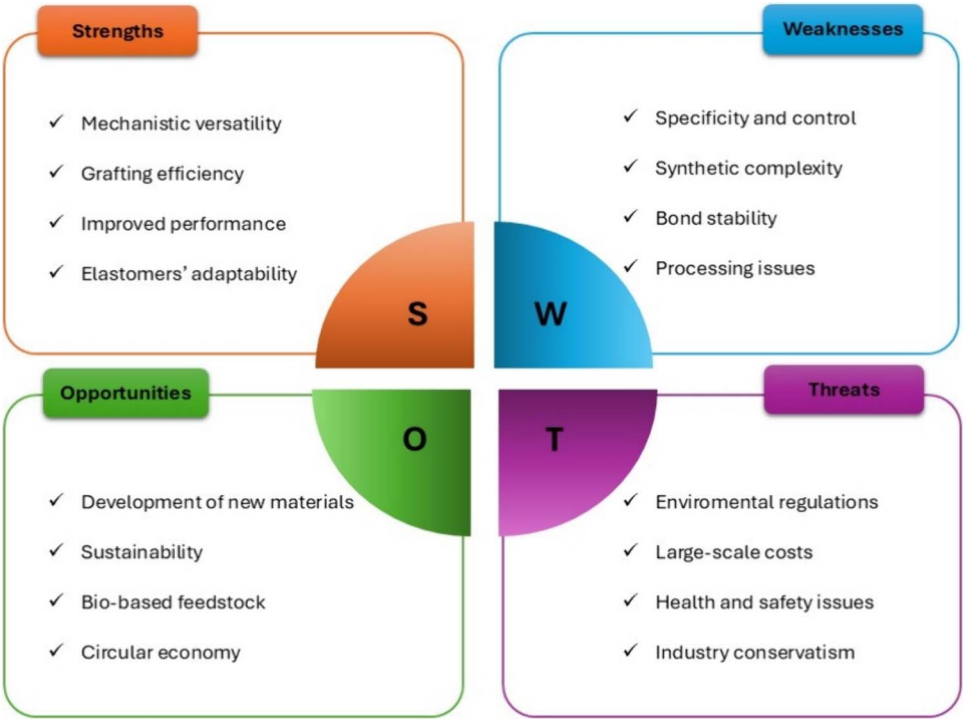

Figure 11. SWOT analysis of *elastomers' functionalization* topic.

meets today's market requirements. One of the most important **opportunities** lies in committing to sustainability through green chemistry. This involves using fewer toxic reagents and solvents and implementing cost-saving, atom-efficient reactions. Other prospects include incorporating bio-based feedstock to generate functional or monomeric units from renewable resources and adhering to the principles of the circular economy by creating elastomers that allow tyre recycling or repair.[253] Among **weaknesses**, synthesis has several drawbacks. Selectivity and control over the position and quantity of functional groups are issues resulting from specificity and reaction control. Furthermore, the synthetic complexity of some functionalized elastomers or single initiators, which often require harsh conditions (e.g., anaerobic conditions for anionic polymerization) or costly reagents/catalysts (e.g., ruthenium or palladium), may hinder commercial scaling up. In terms of performance, the long-term stability of bonds under operational stresses (e.g., heat and oxidation) and processing issues (e.g., rheology modification as a function of functional groups) require careful optimisation of manufacturing processes. Furthermore, recent studies undertaken by Blume *et al*. demonstrated that the release of ethanol in silica/silane systems is elevated in the presence of certain functional groups for S-SBR, such as amine, due to the significant acceleration of the silanization process they can affect. This finding is not consistent with the current trend of reducing VOCs emissions. This is attributable to the fact that such a reduction has implications for emission management (i.e., cost and environmental issues) and process efficiency.[196] Numerous external pressures, so-called **threats** also need to be considered, such as increased environmental standards demanding a reduction in the carbon footprint and the phasing out of toxic chemicals.[254,255] The cost-benefit ratio is a key barrier to uptake: the additional cost and complexity of functionalization must be offset by a significant improvement in performance. Competition from other materials, health and safety issues arising from handling some reagents and the conservatism inherent in the long-established tyre industry all hinder the adoption of new technologies.[256]

5. CONCLUSIONS

Chemical functionalization of elastomers remains a fundamental strategy to overcome the polarity gap between hydrophobic polymer matrices and hydrophilic reinforcing fillers such as silica, a prerequisite for producing high-performance, sustainable tyres. This review outlines the main chemical approaches for the functionalization of elastomers, including polymerization-based methods (e.g., smart functional initiators in living anionic polymerization), post-polymerization modifications (e.g., efficient thiol−ene "click" reactions), and depolymerization strategies. Together, these techniques provide a robust toolkit for designing elastomers with tailored reactivity and compatibility, directly improving filler dispersion and interfacial adhesion.

Significant progress has been achieved, particularly in controlling polymer architecture and end-group chemistry in unsaturated elastomers such as SBR. However, challenges remain: synthetic complexity, stringent reaction conditions, byproducts and VOCs emission and unfavourable cost-to-benefit ratios still limit industrial scalability.

Functional groups like alkoxysilanes have proven highly effective in enhancing silica-based composites properties: lower Payne effect, better tan delta profile, higher at low temperature and lower at high temperature, higher reinforcement index and tensile strength, lower abrasion. These composites can thus improve the trade-off of wet grip, rolling and abrasion resistance, the well-known magic triangle. Issues such as increase of viscosity and melt elasticity are the subject of continuous research.

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Future research must embrace a retrosynthetic and circular approach to material design, rethinking elastomer chemistry from origin to end-of-life. This means prioritizing greener, atom-efficient, and solvent-free reactions, integrating bio-based feedstocks, and engineering polymers that are not only high-performing but also inherently recyclable and regenerable.

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ABBREVIATIONS

ADMET	Acyclic diene metathesis polycondensation
AIBN	Azobisisobutyronitrile
APTES	(3-aminopropyl)triethoxysilane
CQ	camphorquinone
CCTP	Coordinative Chain Transfer Polymerization
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DES	Deep eutectic solvent
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DMTHFA	N,N-dimethyltetrahydrofurfurylamine
DPE-(NMe2)2	1-(4-dimethylaminophenyl)-1-phenylethylene
E-SBR	Emulsion styrene butadiene rubber
EVMG	Ethylene-vinyl acetate-glycidyl methacrylate terpolymer
ITX	Irgacure thioxantone
LPO	Lauroyl peroxide
m-CPBA	*Meta*-chloroperbenzoic acid
MPL	3-mercaptopropanol
MPTES	3-mercaptopropyltriethoxysilane
MUA	Mercaptoundecanoic acid
M.W.	Molecular weight
NR	Natural rubber
PEG-PDMS	poly(ethyleneglycol)-poly(dimethylsiloxane)-block copolymer
PETA	Pentaerythritol tetraacrylate
ROMP	Ring-opening metathesis polymerization
SBR	Styrene butadiene rubber
S-SBR	Solution styrene butadiene rubber
SWOT	Strengths, weaknesses, opportunities, threats
TEMPO	2,2,6,6-Tetramethylpiperidine 1-oxyl, 2,2,6,6-Tetramethyl-1-piperidinyloxy, free radical
TEOS	Tetraethoxy silicate
TES	Triethoxysilane
TESPD	Bis-(triethoxysilylpropyl)disulfide
TESPMA	3-(triethoxysilyl)propyl methacrylate
TESPT	Bis-(triethoxysilylpropyl)tetrasulfide
T_g	Glass transition temperature
TPO	2,4,6-trimethylbenzoyldiphenylphosphine oxide
TRIs	Thermal radical initiators
VOCs	Volatile organic compounds

REFERENCES

(1) Noordermeer, J. W. M. Recent developments in rubber processing, leading to new applications such as the "green tyre". *Macromol. Symp.* **1998**, *127* (1), 131–139.

(2) Fan, Y.; Fowler, G. D.; Zhao, M. The past, present and future of carbon black as a rubber reinforcing filler – A review. *J. Cleaner Prod.* **2020**, *247*, No. 119115.

(3) Sizirici, B.; Fseha, Y.; Cho, C.-S.; Yildiz, I.; Byon, Y.-J. A Review of Carbon Footprint Reduction in Construction Industry, from Design to Operation. *Materials* **2021**, *14* (20), No. 6094.

(4) Shoul, B.; Marfavi, Y.; Sadeghi, B.; Kowsari, E.; Sadeghi, P.; Ramakrishna, S. Investigating the potential of sustainable use of green silica in the green tire industry: a review. *Environ. Sci. Pollut. Res.* **2022**, *29* (34), 51298–51317.

(5) Lee, D.; Song, S. H. A Study of Silica Reinforced Rubber Composites with Eco-Friendly Processing Aids for Pneumatic Tires. *Macromol. Res.* **2019**, *27* (9), 850–856.

(6) Biswal, T. *Biogenic Silica as Filler Material for Elastomers*. **2025**, https://books.rsc.org/books/edited-volume/2259/chapter/8190617/Biogenic-Silica-as-Filler-Material-for-Elastomers.

(7) Cichomski, E. M. Silica-silane reinforced passenger car tire treads: effect of silica morphology, silica-polymer interface structure and rubber matrix network on tire-performance indicators. Ph. D. Thesis, University of Twente, **2015**.

(8) Kim, M. C.; Adhikari, J.; Kim, J. K.; Saha, P. Preparation of novel bio-elastomers with enhanced interaction with silica filler for low rolling resistance and improved wet grip. *J. Cleaner Prod.* **2019**, *208*, 1622–1630.
(9) Lolage, M.; Parida, P.; Chaskar, M.; Gupta, A.; Rautaray, D. Green Silica: Industrially scalable & sustainable approach towards achieving improved "nano filler − Elastomer" interaction and reinforcement in tire tread compounds. *Sustainable Mater. Technol.* **2020**, *26*, No. e00232.
(10) Hall, D. E.; Moreland, J. C. Fundamentals of Rolling Resistance. *Rubber Chem. Technol.* **2001**, *74* (3), 525–539.
(11) Zhang, P.; Morris, M.; Doshi, D. Materials Development for Lowering Rolling Resistance of Tires. *Rubber Chem. Technol.* **2016**, *89* (1), 79–116.
(12) Zhuravlev, L. T. The surface chemistry of amorphous silica Zhuravlev model. *Colloids Surf., A* **2000**, *173* (1−3), 1–38.
(13) Luhmer, M.; d'Espinose, J. B.; Hommel, H.; Legrand, A. P. High-resolution 29Si solid-state NMR study of silicon functionality distribution on the surface of silicas. *Magn. Reson. Imaging* **1996**, *14* (7), 911–913.
(14) Yatsuyanagi, F.; Suzuki, N.; Ito, M.; Kaidou, H. Effects of secondary structure of fillers on the mechanical properties of silica filled rubber systems. *Polymer* **2001**, *42* (23), 9523–9529.
(15) Gui, Y.; Zheng, J.; Ye, X.; Han, D.; Xi, M.; Zhang, L. Preparation and performance of silica/SBR masterbatches with high silica loading by latex compounding method. *Composites, Part B* **2016**, *85*, 130–139.
(16) Ghosh, J.; et al. Cradle-to-cradle approach to waste tyres and development of silica based green tyre composites. *Resour., Conserv. Recycl.* **2020**, *154*, No. 104629.
(17) Dillon, J. H.; Prettyman, I. B.; Hall, G. L. Hysteretic and Elastic Properties of Rubberlike Materials Under Dynamic Shear Stresses. *J. Appl. Phys.* **1944**, *15* (4), 309–323.
(18) Fletcher, W. P.; Gent, A. N. Nonlinearity in the Dynamic Properties of Vulcanized Rubber Compounds. *Rubber Chem. Technol.* **1954**, *27* (1), 209–222.
(19) Payne, A. R. The dynamic properties of carbon black-loaded natural rubber vulcanizates Part I. *J. Appl. Polym. Sci.* **1962**, *6* (19), 57–63.
(20) Warasitthinon, N.; Genix, A.-C.; Sztucki, M.; Oberdisse, J.; Robertson, C. The Payne Effect: Primarily Polymer-Related or Filler-Related Phenomenon? *Rubber Chem. Technol.* **2019**, *92*, 599.
(21) Bouasse, H.; Carrière, Z. Sur les courbes de traction du caoutchouc vulcanisé. *Ann. Fac. Sci. Univ. Toulouse Sci. Math. Sci. Phys.* **1903**, *5* (3), 257–283.
(22) Mullins, L. Softening of Rubber by Deformation. *Rubber Chem. Technol.* **1969**, *42* (1), 339–362.
(23) Diani, J.; Fayolle, B.; Gilormini, P. A Review on the Mullins Effect. *Eur. Polym. J.* **2009**, *45*, 601–612.
(24) Zhong, X.; Song, Y.; Zheng, Q. Payne effect and Mullins effect of silica filled butadiene rubber nanocomposites vulcanizates and their unextractable gels. *Polymer* **2023**, *267*, No. 125634.
(25) Robertson, C. G.; Roland, C. M. Glass Transition and Interfacial Segmental Dynamics in Polymer-Particle Composites. *Rubber Chem. Technol.* **2008**, *81* (3), 506–522.
(26) Bohm, G. A.; Tomaszewski, W.; Cole, W.; Hogan, T. Furthering the understanding of the non linear response of filler reinforced elastomers. *Polymer* **2010**, *51* (9), 2057–2068.
(27) Heinrich, G.; Klüppel, M. Recent Advances in the Theory of Filler Networking in Elastomers. In *Filled Elastomers Drug Delivery Systems*, Advances in Polymer Science, Berlin, Heidelberg: Springer Berlin Heidelberg, **2002**, vol. 160, pp. 1−44.
(28) Maier, P. G.; Goritz, D. Molecular interpretation of the Payne effect. *Kautsch. Gummi, Kunstst.* **1996**, *49* (1), 18–21.
(29) Funt, J. M. Dynamic Testing and Reinforcement of Rubber. *Rubber Chem. Technol.* **1988**, *61* (5), 842–865.
(30) Chazeau, L.; Brown, J. D.; Yanyo, L. C.; Sternstein, S. S. Modulus recovery kinetics and other insights into the payne effect for filled elastomers. *Polym. Compos.* **2000**, *21* (2), 202–222.
(31) Sternstein, S. S.; Zhu, A.-J. Reinforcement Mechanism of Nanofilled Polymer Melts As Elucidated by Nonlinear Viscoelastic Behavior. *Macromolecules* **2002**, *35* (19), 7262–7273.
(32) Montes, H.; Lequeux, F.; Berriot, J. Influence of the Glass Transition Temperature Gradient on the Nonlinear Viscoelastic Behavior in Reinforced Elastomers. *Macromolecules* **2003**, *36* (21), 8107–8118.
(33) Gauthier, C.; Reynaud, E.; Vassoille, R.; Ladouce-Stelandre, L. Analysis of the non-linear viscoelastic behaviour of silica filled styrene butadiene rubber. *Polymer* **2004**, *45* (8), 2761–2771.
(34) Zhu, Z.; Thompson, T.; Wang, S.-Q.; von Meerwall, E. D.; Halasa, A. Investigating Linear and Nonlinear Viscoelastic Behavior Using Model Silica-Particle-Filled Polybutadiene. *Macromolecules* **2005**, *38* (21), 8816–8824.
(35) Kalfus, J.; Jancar, J. Elastic response of nanocomposite poly(vinylacetate)-hydroxyapatite with varying particle shape. *Polym. Compos.* **2007**, *28* (3), 365–371.
(36) Jancar, J.; et al. Current issues in research on structure−property relationships in polymer nanocomposites. *Polymer* **2010**, *51* (15), 3321–3343.
(37) Parent, J.; Mrkoci, M.; Hennigar, S. Silica agglomeration and elastomer reinforcement: Influence of surface modifications. *Plast. Rubber Compos.* **2003**, *32*, 114–121.
(38) An, D.; Wang, Z.; Zhao, X.; Liu, Y.; Guo, Y.; Ren, S. A new route to synthesis of surface hydrophobic silica with long-chain alcohols in water phase. *Colloids Surf., A* **2010**, *369* (1), 218–222.
(39) Abutalib, N.; Karnati, S. R.; Oldham, D.; Zhang, L.; Fini, E. Surface Modification of Silica Fume with Amine Groups to Reduce Agglomeration and Improve Asphalt Resistance to Oxidation. *Res. Rev. J. Mater. Sci.* **2017**, *4* (4), 1065–1072.
(40) Boonrasri, S.; Thipchai, P.; Sae-Oui, P.; Thanakkasaranee, S.; Jantanasakulwong, K.; Rachtanapun, P. Property Improvements of Silica-Filled Styrene Butadiene Rubber/Butadiene Rubber Blend Incorporated with Fatty-Acid-Containing Palm Oil. *Polymers* **2023**, *15* (16), No. 3429.
(41) Scurati, A.; Hergenrother, W. L.; Lin, C. J. Hysteresis temperature dependence in filled rubbers II Mechanical mixing, filler microdispersion, and polymer−filler interactions. *J. Appl. Polym. Sci.* **2008**, *108* (3), 1722–1736.
(42) Wolff, S. Silanes in Tire Compounding After Ten Years — A Review. *Tire Sci. Technol.* **1987**, *15* (4), 276–294.
(43) Debnath, S. C.; Datta, R. N.; Noordermeer, J. W. M. Understanding the chemistry of the rubber/silane reaction for silica reinforcement, using model olefins. *Rubber Chem. Technol.* **2003**, *76* (5), 1311–1328.
(44) Vilmin, F.; et al. Reactivity of Bis[3-(triethoxysilyl)propyl] Tetrasulfide (TESPT) Silane Coupling Agent over Hydrated Silica: Operando IR Spectroscopy and Chemometrics Study. *J. Phys. Chem. C* **2014**, *118* (8), 4056–4071.
(45) Sho, S.; Arefazar, A.; Khosrokhavar, R. Silane Coupling Agents in Polymer-based Reinforced Composites: A Review. *J. Reinf. Plast. Compos.* **2008**, *27*, 473–485.
(46) Neethirajan, J.; Parathodika, A. R.; Hu, G.-H.; Naskar, K. Functional rubber composites based on silica-silane reinforcement for green tire application: the state of the art. *Funct. Compos. Mater.* **2022**, *3* (1), 7.
(47) Goerl, U.; Hunsche, A.; Mueller, A.; Koban, H. G. Investigations into the Silica/Silane Reaction System. *Rubber Chem. Technol.* **1997**, *70* (4), 608–623.
(48) Ten Brinke, J. W.; Debnath, S. C.; Reuvekamp, L. A. E. M.; Noordermeer, J. W. M. Mechanistic aspects of the role of coupling agents in silica−rubber composites. *Compos. Sci. Technol.* **2003**, *63* (8), 1165–1174.
(49) Locatelli, D.; et al. Biosourced Janus Molecules as Silica Coupling Agents in Elastomer Composites for Tires with Lower Environmental Impact. *ACS Sustainable Chem. Eng.* **2023**, *11* (7), 2713–2726.
(50) Li, Q.; Lin, G.; Zhang, S.; Zhang, L.; Geng, C.; Borah, J. Enhanced mechanical properties and interfacial interaction of ESBR composites by introducing silica decorated with epoxy functionalized elastomer. *Polym. Test.* **2022**, *112*, No. 107632.

https://doi.org/10.1021/acssusresmgt.5c00668
ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

(51) Sęk, M.; Kaewsakul, W.; Anyszka, R.; Schultz, S.; Bandzierz, K.; Blume, A. Insight into the interactions of functionalised rubber-modified silica in tyre tread compounds. *Eur. Polym. J.* **2025**, *236*, No. 114144.
(52) Anyszka, R.; Beton, K.; Szczechowicz, M.; Bielinski, D. M.; Blume, A. Velcro-inspired supramolecular system for silica−rubber coupling. *Rubber Chem. Technol.* **2020**, *93* (4), 672–682.
(53) Galimberti, M.; et al. Elastomeric Compounds with Silica Lower Hysteresis in the Presence of Functionalised Isoprene Oligomers. *Macromol. Symp.* **2006**, *234* (1), 203–210.
(54) Zhang, S.; et al. The effect of functionalization in elastomers: Construction of networks. *Polymer* **2021**, *213*, No. 123331.
(55) Kumar, V.; Schneider, U.; Rose, V.; Giese, U. Nanocomposites based on epoxidized poly(styrene-co-butadiene) rubber and graphene nanoplatelets. *J. Appl. Polym. Sci.* **2019**, *136* (30), No. 47802.
(56) Rezelman, S. A. *Compounding and characterization of tire tread compounds using funtionalized rubber*. **2024**, https://essay.utwente.nl/96281/.
(57) Gao, W.; Lu, J.; Song, W.; Hu, J.; Han, B. Interfacial interaction modes construction of various functional SSBR−silica towards high filler dispersion and excellent composites performances. *RSC Adv.* **2019**, *9* (33), 18888–18897.
(58) Agostini, G.; Bergh, J.; Materne, T. New Compound Technology. In *Proceedings of the 146th Spring Technical Meeting of the Rubber Division*; American Chemical Society: Akron, Ohio, **1994**.
(59) Thurn, F.; Burmester, K.; Pochert, J.; Wolff, S. Rubber compositions containing silica and an organosilane. US3873489A, **1975**.
(60) Wolff, S. Chemical Aspects of Rubber Reinforcement by Fillers. *Rubber Chem. Technol.* **1996**, *69* (3), 325–346.
(61) Ahmad, S.; Schaefer, R. J. Energy saving tire with silica-rich tread. CA1204374A, **1986**.
(62) Rauline, R. Rubber compound and tires based on such a compound. EP0501227B1, **1995**.
(63) Szwarc, M.; Levy, M.; Milkovich, R. Polymerization Initiated by Electron Transfer to Monomer a New Method of Formation of Block Polymers1. *J. Am. Chem. Soc.* **1956**, *78* (11), 2656–2657.
(64) Quirk, R. P.; Zhuo, Q.; Jang, S. H.; Lee, Y.; Lizarraga, G. Principles of Anionic Polymerization: An Introduction. In *Applications of Anionic Polymerization Research*, ACS Symposium Series, American Chemical Society, **1998**, vol. 696, pp. 2−27.
(65) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem., Int. Ed.* **2001**, *40* (11), 2004–2021.
(66) Posner, T. Beiträge zur Kenntniss der ungesättigten Verbindungen II Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe. *Ber. Dtsch. Chem. Ges.* **1905**, *38* (1), 646–657.
(67) Picchioni, F.; Broekhuis, A. A. Method for reclaiming rubber, and renewed rubber compositions obtainable thereby. WO2018093260A1, **2018**.
(68) Quirk, R. P.; Jang, S. H.; Kim, J. Recent Advances in Anionic Synthesis of Functionalized Elastomers Using Functionalized Alkyllithium Initiators. *Rubber Chem. Technol.* **1996**, *69* (3), 444–461.
(69) Quirk, R. P.; Pickel, D. L. 6.10 - Controlled End-Group Functionalization (Including Telechelics). In *Polymer Science: A Comprehensive Reference*; Elsevier: Amsterdam, **2012**, 351-412.
(70) Hong, K.; Uhrig, D.; Mays, J. W. Living anionic polymerization. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4* (6), 531–538.
(71) Hirao, A.; Loykulnant, S.; Ishizone, T. Recent advance in living anionic polymerization of functionalized styrene derivatives. *Prog. Polym. Sci.* **2002**, *27* (8), 1399–1471.
(72) Quirk, R. P.; Chavan, V.; Janoski, J.; Yol, A.; Wesdemiotis, C. General Functionalization Method for Synthesis of α-Functionalized Polymers by Combination of Anionic Polymerization and Hydrosilation Chemistry. *Macromol. Symp.* **2013**, *323* (1), 51–57.
(73) Jagur-Grodzinski, J. Functional polymers by living anionic polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (13), 2116–2133.
(74) Schulz, D. N.; Halasa, A. F. Anionic polymerization initiators containing protected functional groups II. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15* (10), 2401–2410.
(75) Stewart, M. J. N, Shepherd, and DM Service, Brit. *Polym. J.* **1990**, *22*, 319.
(76) Pispas, S.; Pitsikalis, M.; Hadjichristidis, N.; Dardani, P.; Morandi, F. Anionic polymerization of isoprene, butadiene and styrene with 3-dimethylaminopropyllithium. *Polymer* **1995**, *36* (15), 3005–3011.
(77) *U.S. Patent for Soluble anionic polymerization initiators and method of preparing same Patent (Patent # 5,578,542)*. **1996**, https://patents.justia.com/patent/5578542.
(78) Kwag, G.; Lee, H.; Kim, S. First in-Situ Observation of Pseudoliving Character and Active Site of Nd-Based Catalyst for 1,3-Butadiene Polymerization Using Synchrotron X-ray Absorption and UV−Visible Spectroscopies. *Macromolecules* **2001**, *34* (16), 5367–5369.
(79) Nuyken, O. *Neodymium Based Ziegler Catalysts − Fundamental Chemistry*; Advances in Polymer Science, Springer: Berlin, Heidelberg, **2006**, 204.
(80) Olonde, X.; Mortreux, A.; Petit, F.; Bujadoux, K. A useful method for the synthesis of neodymocene homogeneous catalysts for ethylene polymerization. *J. Mol. Catal.* **1993**, *82* (1), 75–82.
(81) Pelletier, J.-F.; Mortreux, A.; Olonde, X.; Bujadoux, K. Synthesis of New Dialkylmagnesium Compounds by Living Transfer Ethylene Oligo- and Polymerization with Lanthanocene Catalysts. *Angew. Chem., Int. Ed. Engl.* **1996**, *35* (16), 1854–1856.
(82) Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative Chain Transfer Polymerization. *Chem. Rev.* **2013**, *113* (5), 3836–3857.
(83) Mundil, R.; Bravo, C.; Merle, N.; Zinck, P. Coordinative Chain Transfer and Chain Shuttling Polymerization. *Chem. Rev.* **2023**, *124*, 210.
(84) Kwag, G.; Kim, P.; Han, S.; Choi, H. Ultra high cis polybutadiene by monomeric neodymium catalyst and its tensile and dynamic properties. *Polymer* **2005**, *46*, 3782–3788.
(85) Ozawa, Y. et al. Functionalized High Cis-1,4-Polybutadiene Prepared Using Novel Functionalizing Agents. US20150259452A1, **2003**.
(86) Ozawa, Y. et al. Modified polymers prepared with lanthanide-based catalysts. US7750087B2, **2010**.
(87) Robert, P.; Thuilliez, J. Method for preparing a functionalised diene elastomer such as polybutadiene. EP2376544A1, **2011**.
(88) Ozawa, Y. F. et al. Functionalized high cis-1,4-polybutadiene prepared using novel functionalizing agents. US8618199B2, **2013**.
(89) Luo, S. Polymers functionalized with imide compounds containing a protected amino group. EP2307461B1, **2017**.
(90) Zhang, X.; et al. Facile strategies for green tire tread with enhanced filler-matrix interfacial interactions and dynamic mechanical properties. *Compos. Sci. Technol.* **2021**, *203*, No. 108601.
(91) Zhang, X.; et al. Facile and efficient in-situ end-functionalization of neodymium-based polybutadiene by isocyanate via a coordinative chain transfer polymerization strategy. *Polymer* **2024**, *305*, No. 127166.
(92) Liu, L.; Zhao, W.; Wang, F.; Zhang, X.; Liu, H. End-Functionalization in Coordination Chain Transfer Polymerization of Conjugated Dienes. *Catalysts* **2026**, *16* (2), 121.
(93) Zhang, X. H.; et al. Synthesis and Performance Study of High-molecular-weight Amide End-functionalized cis-Polybutadiene Rubber. *Acta Polym. Sin.* **2025**, *56* (9), 1633–1643.
(94) Zhang, H.; Zhang, X.; Zheng, H.; Wang, F.; Wei, X.; Zhang, X.; Liu, H. Synthesis of α, ω-end hetero-functionalized polyisoprene via neodymium-mediated coordinative chain transfer polymerization. *Polym. Chem.* **2025**, *16* (14), 1556–1567.
(95) Wang, W.-X.; et al. Polyisoprene Bearing Dual Functionalized Mini-Blocky Chain-Ends Prepared from Neodymium-mediated Coordinative Chain Transfer Polymerizations. *Chin. J. Polym. Sci.* **2023**, *41* (5), 720–727.
(96) Leimgruber, S.; Trimmel, G. Olefin metathesis meets rubber chemistry and technology. *Monatsh. Chem.* **2015**, *146* (7), 1081–1097.
(97) Hérisson, P. J.-L.; Chauvin, Y. Catalyse de transformation des oléfines par les complexes du tungstène II Télomérisation des oléfines cycliques en présence d'oléfines acycliques. *Makromol. Chem.* **1971**, *141* (1), 161–176.
(98) Mol, J. C. Metathesis of functionalized olefins. *J. Mol. Catal.* **1982**, *15* (1), 35–45.

(99) Fürstner, A. Olefin Metathesis and Beyond. *Angew. Chem., Int. Ed.* **2000**, *39* (17), 3012–3043.
(100) Trnka, T. M.; Grubbs, R. H. The Development of L2X2RuCHR Olefin Metathesis Catalysts: An Organometallic Success Story. *Acc. Chem. Res.* **2001**, *34* (1), 18–29.
(101) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. A General Model for Selectivity in Olefin Cross Metathesis. *J. Am. Chem. Soc.* **2003**, *125* (37), 11360–11370.
(102) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. Synthesis of molybdenum imido alkylidene complexes and some reactions involving acyclic olefins. *J. Am. Chem. Soc.* **1990**, *112* (10), 3875–3886.
(103) France, M. B.; Grubbs, R. H.; McGrath, D. V.; Paciello, R. A. Chain transfer during the aqueous ring-opening metathesis polymerization of 7-oxanorbornene derivatives. *Macromolecules* **1993**, *26* (18), 4742–4747.
(104) Chatterjee, A. K.; Grubbs, R. H. Synthesis of Trisubstituted Alkenes via Olefin Cross-Metathesis. *Org. Lett.* **1999**, *1* (11), 1751–1753.
(105) Natta, G.; Dall'asta, G.; Mazzanti, G.; Pasquon, I.; Valvassori, A.; Zambelli, A. Crystalline alternating ethylene-butadiene copolymers. *Macromol. Chem. Phys.* **1962**, *54*, 95–101.
(106) Schuster, M.; Blechert, S. Olefin Metathesis in Organic Chemistry. *Angew. Chem., Int. Ed. Engl.* **1997**, *36* (19), 2036–2056.
(107) Grubbs, R. H. Olefin-metathesis catalysts for the preparation of molecules and materials (Nobel Lecture). *Angew. Chem., Int. Ed.* **2006**, *45* (23), 3760–3765.
(108) Bielawski, C. W.; Grubbs, R. H. Living ring-opening metathesis polymerization. *Prog. Polym. Sci.* **2007**, *32* (1), 1–29.
(109) Wagener, K. B.; Patton, J. T. Acyclic diene metathesis (ADMET) polymerization Synthesis of unsaturated polycarbonates. *Macromolecules* **1993**, *26* (2), 249–253.
(110) Opper, K. L.; Wagener, K. B. ADMET: Metathesis polycondensation. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (4), 821–831.
(111) da Silva, L. C.; Rojas, G.; Schulz, M. D.; Wagener, K. B. Acyclic diene metathesis polymerization: History, methods and applications. *Prog. Polym. Sci.* **2017**, *69*, 79–107.
(112) Abdellatif, M. M.; Nomura, K. Acyclic Diene Metathesis Polymerization Approach for Synthesis of Biobased Polyesters: Summary of Recent Reports. *Eur. J. Lipid Sci. Technol.* **2025**, *127* (7), No. e70009.
(113) Devaraj, N. K.; Finn, M. G. Introduction: Click Chemistry. *Chem. Rev.* **2021**, *121* (12), 6697–6698.
(114) Moses, J. E.; Moorhouse, A. D. The growing applications of click chemistry. *Chem. Soc. Rev.* **2007**, *36* (8), 1249–1262.
(115) Lowe, A. B.; Hoyle, C. E.; Bowman, C. N. Thiol - yne click chemistry: A powerful and versatile methodology for materials synthesis. *J. Mater. Chem.* **2010**, *20* (23), 4745–4750.
(116) Lowe, A. B. Thiol-ene "click" reactions and recent applications in polymer and materials synthesis. *Polym. Chem.* **2010**, *1* (1), 17–36.
(117) Machado, T. O.; Sayer, C.; Araujo, P. H. Thiol-ene polymerisation: A promising technique to obtain novel biomaterials. *Eur. Polym. J.* **2017**, *86*, 200–215.
(118) Sinha, A. K.; Equbal, D. Thiol−Ene Reaction: Synthetic Aspects and Mechanistic Studies of an Anti-Markovnikov-Selective Hydrothiolation of Olefins. *Asian J. Org. Chem.* **2019**, *8* (1), 32–47.
(119) Singha, N.; Schlaad, H. Thiol-ene Based Functionalization of Polymers. In *Functional Polymers by Post-polymerization Modification*; Wiley, **2013**, 65-86.
(120) Fairbanks, B. D.; Love, D. M.; Bowman, C. N. Efficient Polymer-Polymer Conjugation via Thiol-ene Click Reaction. *Macromol. Chem. Phys.* **2017**, *218* (18), No. 1700073.
(121) Prieto-Castañeda, A.; et al. Photoinitiated thiol−ene mediated functionalisation of 4,5-enoses. *Org. Biomol. Chem.* **2025**, *23* (22), 5332–5338.
(122) Binder, W.; Sachsenhofer, R. "Click" Chemistry in Polymer and Material Science: An Update. *Macromol. Rapid Commun.* **2008**, *29*, 952–981.
(123) Scanlan, E. M.; Corcé, V.; Malone, A. Synthetic Applications of Intramolecular Thiol-Ene "Click" Reactions. *Molecules* **2014**, *19* (11), 19137–19151.
(124) Yagci, Y.; Jockusch, S.; Turro, N. J. Photoinitiated Polymerization: Advances, Challenges, and Opportunities. *Macromolecules* **2010**, *43* (15), 6245–6260.
(125) Uygun, M.; Tasdelen, M. A.; Yagci, Y. Influence of Type of Initiation on Thiol−Ene "Click" Chemistry. *Macromol. Chem. Phys.* **2010**, *211* (1), 103–110.
(126) Scott, G. Mechanisms of photophysical processes and photochemical reactions in polymers: Theory and applications J. F. Rabek, John Wiley and Sons, Chichester, 1987. pp. xix + 756, price £9900 ISBN 0-47 1-9 11 80-1. *Br. Polym. J.* **1988**, *20* (5), 449–449.
(127) Yin, J.; et al. 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TPO) analog: a non-cytotoxic type-I photoinitiator for free radical photopolymerization. *Green Chem.* **2025**, *27* (5), 1451–1461.
(128) Randolph, L. D.; et al. Photopolymerization of highly filled dimethacrylate-based composites using Type I or Type II photoinitiators and varying co-monomer ratios. *Dent. Mater.* **2016**, *32* (2), 136–148.
(129) Allushi, A.; Kutahya, C.; Aydogan, C.; Kreutzer, J.; Yilmaz, G.; Yagci, Y. Conventional Type II photoinitiators as activators for photoinduced metal-free atom transfer radical polymerization. *Polym. Chem.* **2017**, *8* (12), 1972–1977.
(130) Lima, A. F.; et al. Increased rates of photopolymerisation by ternary type II photoinitiator systems in dental resins. *J. Mech. Behav. Biomed. Mater.* **2019**, *98*, 71–78.
(131) Eibel, A.; Fast, D. E.; Gescheidt, G. Choosing the ideal photoinitiator for free radical photopolymerizations: predictions based on simulations using established data. *Polym. Chem.* **2018**, *9* (41), 5107–5115.
(132) Leprince, J. G.; et al. Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins. *Dent. Mater.* **2011**, *27* (2), 157–164.
(133) Sasaki, H.; Nagayama, M. Thermal decomposition of additive polymerization initiators I Azobisisobutyronitrile. *J. Appl. Polym. Sci.* **1967**, *11* (11), 2097–2108.
(134) Qu, B.; Liu, S.; Guo, R.; Chiang, C.-L. Using dynamic and adiabatic methods for thermal hazard evaluation of styrene bulk polymerization initiated by AIBN. *J. Therm. Anal. Calorim.* **2023**, *148* (11), 4791–4799.
(135) Zoller, A.; Gigmes, D.; Guillaneuf, Y. Simulation of radical polymerization of methyl methacrylate at room temperature using a tertiary amine/BPO initiating system. *Polym. Chem.* **2015**, *6* (31), 5719–5727.
(136) Wilson, G. O.; et al. Evaluation of peroxide initiators for radical polymerization-based self-healing applications. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (12), 2698–2708.
(137) Hoyle, C. E.; Lee, T. Y.; Roper, T. Thiol−enes: Chemistry of the past with promise for the future. *J. Polym. Sci., Part A:Polym. Chem.* **2004**, *42* (21), 5301–5338.
(138) Cramer, N. B.; Bowman, C. N.Thiol−Ene Chemistry. In *Chemoselective and Bioorthogonal Ligation Reactions*; John Wiley & Sons, Ltd, **2017**, 117-145.
(139) Koo, S. P. S.; et al. Limitations of radical thiol-ene reactions for polymer−polymer conjugation. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (8), 1699–1713.
(140) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem. Soc. Rev.* **2010**, *39* (4), 1355–1387.
(141) Bultema, L. A.; Huang, X.; Brauer, D. D.; Theato, P. Polymer Functionalization. In *Functional Polymers*; Springer: Cham, **2018**, pp. 1−51.
(142) Chan, J.; Hoyle, C.; Lowe, A.; Bowman, M. Nucleophile-Initiated Thiol-Michael Reactions: Effect of Organocatalyst, Thiol, and Ene. *Macromolecules* **2010**, *43*, 6381.
(143) Smith, L. I. Aliphatic Diazo Compounds, Nitrones, and Structurally Analogous Compounds Systems Capable of Undergoing 1,3-Additions. *Chem. Rev.* **1938**, *23* (2), 193–285.

https://doi.org/10.1021/acssusresmgt.5c00668
ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

(144) Huisgen, R.; Seidel, M.; Sauer, J.; McFarland, J.; Wallbillich, G. Communications: The Formation of Nitrile Imines in the Thermal Breakdown of 2,5-Disubstituted Tetrazoles. *J. Org. Chem.* **1959**, *24* (6), 892–893.
(145) Huisgen, R.; Seidel, M.; Wallbillich, G.; Knupfer, H. Diphenylnitrilimin und seine 13-dipolaren additionen an alkene und alkine. *Tetrahedron* **1962**, *17* (1), 3–29.
(146) Huisgen, R. 13-Dipolare Cycloadditionen Rückschau und Ausblick. *Angew. Chem.* **1963**, *75* (13), 604–637.
(147) Ugolinnikov, O.; Ivanov, S.; Lannox, C.; Salit, A. -F.; Gander, S.; Twilye, A. -L. 1,3- dipolar compounds with imidazole functionalities. CN105683165B, **2018**.
(148) Giannini, L.; Tadiello, L.; Papagni, A.; Monti, M. Compositions for elastomeric compounds comprising tetrazole compatibilizing agents and tyres comprising the same. US20230257552A1, **2023**.
(149) Galimberti, M. et al. Tire comprising an elastomeric polymer including a functional group and crosslinkable elastomeric composition. WO2005118695A1, **2005**.
(150) Lin, C.-C.; Hergenrother, W.; Graves, D.; Bohm, G. Tire components having improved modulus. WO2002081233A1, **2002**.
(151) Mcneill, I. C. Thermal Degradation. In *Comprehensive Polymer Science and Supplements*; Elsevier, **1989**, 451-500.
(152) Miao, Y.; von Jouanne, A.; Yokochi, A. Current Technologies in Depolymerization Process and the Road Ahead. *Polymers* **2021**, *13* (3), 449.
(153) Nor, H. M.; Ebdon, J. R. Telechelic liquid natural rubber: A review. *Prog. Polym. Sci.* **1998**, *23* (2), 143–177.
(154) Gupta, S. K.; Kurup, M. R.; Devadoss, E.; Muthiah, R.; Thomas, S. Development and evaluation of a novel binder based on natural rubber and high-energy polyurethane/composite propellants. *J. Appl. Polym. Sci.* **1985**, *30*, 1095.
(155) Anancharoenwong, E. Synthesis and characterization of cis-1, 4-polyisoprene-based polyurethane coatings ; study of their adhesive properties on metal surface. Ph.D. Thesis, Le Mans Université, **2011**, https://theses.hal.science/tel-00649080.
(156) Mecozzi, F.; Dong, J. J.; Angelone, D.; Browne, W. R.; Eisink, N. N. H. M. Oxidative Cleavage of Alkene C=C Bonds Using a Manganese Catalyzed Oxidation with H_2O_2 Combined with Periodate Oxidation. *Eur. J. Org. Chem.* **2019**, *2019* (42), 7151–7158.
(157) Sazali, N.; Ibrahim, H.; Jamaludin, A. S.; Mohamed, M. A.; Salleh, W. N. W.; Abidin, M. N. Z. Degradation and stability of polymer: A mini review. *IOP Conf. Ser.: Mater. Sci. Eng.* **2020**, *788* (1), No. 012048.
(158) Gillier-Ritoit, S.; Laguerre, A.; Singh, R. Telecheliccis-1,4-oligoisoprenes through the selective oxidolysis of epoxidized monomer units and polyisoprenic monomer units incis-1,4-polyisoprenes. *J. Appl. Polym. Sci.* **2003**, *87*, 42–46.
(159) Sadaka, F.; Campistron, I.; Laguerre, A.; Pilard, J.-F. Controlled chemical degradation of natural rubber using periodic acid: Application for recycling waste tyre rubber. *Polym. Degrad. Stab.* **2012**, *97* (5), 816–828.
(160) Ntetsikas, K.; Ladelta, V.; Bhaumik, S.; Hadjichristidis, N. Quo vadis carbanionic polymerization? *ACS Polym. Au* **2022**, *3* (2), 158–181.
(161) Sánchez-Condado, A.; Carriedo, G.; Soto, A.; Rodríguez-Álvarez, M.; García-Álvarez, J.; Hevia, E. Organolithium-Initiated Polymerization of Olefins in Deep Eutectic Solvents under Aerobic Conditions. *ChemSusChem* **2019**, *12*, 3134.
(162) Hoyle, C.; Bowman, C. Thiol-Ene Click Chemistry. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540–1573.
(163) Rovaletti, A.; et al. Recent Theoretical Insights into the Oxidative Degradation of Biopolymers and Plastics by Metalloenzymes. *Int. J. Mol. Sci.* **2023**, *24* (7), No. 6368.
(164) Hadjichristidis, N.; Hirao, A. *Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications*; Springer: Japan, **2015**.
(165) Clarke, C. J.; Tu, W.-C.; Levers, O.; Bröhl, A.; Hallett, J. P. Green and Sustainable Solvents in Chemical Processes. *Chem. Rev.* **2018**, *118* (2), 747–800.
(166) Kim, Y.-H.; Baek, J. J.; Chang, K. C.; Park, B. S.; Koh, W.-G.; Shin, G. Effect of Synthetic Low-Odor Thiol-Based Hardeners Containing Hydroxyl and Methyl Groups on the Curing Behavior, Thermal, and Mechanical Properties of Epoxy Resins. *Polymers* **2023**, *15* (13), No. 2947.
(167) Konuray, O.; Fernández-Francos, X.; Ramis, X.; Serra, À. State of the Art in Dual-Curing Acrylate Systems. *Polymers* **2018**, *10* (2), 178.
(168) Konuray, O.; Fernández-Francos, X.; De la Flor, S.; Ramis, X.; Serra, À. The Use of Click-Type Reactions in the Preparation of Thermosets. *Polymers* **2020**, *12* (5), No. 1084.
(169) Chan, J.; Yu, B.; Hoyle, C.; Lowe, A. The nucleophilic, phosphine-catalyzed thiol−ene click reaction and convergent star synthesis with RAFT-prepared homopolymers. *Polymer* **2009**, *50*, 3158–3168.
(170) Bahruddin; Fadhillah, I.; Septian; Wiranata, A.; Zahrina, I. Molecular Weight of Liquid Natural Rubber (LNR) Product from the Chemical Depolymerization Process of High Molecular Weight Narutal Rubber Latex. *J. Phys.: Conf. Ser.* **2020**, *1655* (1), No. 012091.
(171) Schiaffo, C. E.; Dussault, P. H. Ozonolysis in Solvent/Water Mixtures: Direct Conversion of Alkenes to Aldehydes and Ketones. *J. Org. Chem.* **2008**, *73* (12), 4688–4690.
(172) Medeiros, B. *Principles of Polymer Chemistry*. **2026**, https://www.academia.edu/43782174/Principles_of_Polymer_Chemistry (Accessed May 7, 2026).
(173) Ferry, J. D. *Viscoelastic Properties of Polymers*; Edition, John Wiley & Sons Inc.: New York, **1980**, https://www.scirp.org/reference/referencespapers?referenceid=274271.
(174) Mark, J. E. Molecular aspects of rubberlike elasticity. *Acc. Chem. Res.* **1985**, *18* (7), 202.
(175) Curro, J. G.; Pearson, D. S.; Helfand, E. Viscoelasticity of randomly crosslinked polymer networks Relaxation of dangling chains. *Macromolecules* **1985**, *18* (6), 1157–1162.
(176) Morita, H.; Toda, M.; Honda, T. Analysis of the end-segment distribution of a polymer at the interface of filler-filled material. *Polym. J.* **2016**, *48* (4), 451–455.
(177) Tokita, N.; White, J. L. Milling behavior of gum elastomers: Experiment and theory. *J. Appl. Polym. Sci.* **1966**, *10* (7), 1011–1026.
(178) White, J. L. Elastomer Rheology and Processing. *Rubber Chem. Technol.* **1969**, *42* (1), 257–338.
(179) Hill, R. Elastic Liquids. By AS Lodge. Academic Press, 1964. 389 pp. 75s. *J. Fluid Mech.* **1965**, *21* (4), 764–765, https://www.cambridge.org/core/journals/journal-of-fluid-mechanics/article/abs/elastic-liquidsby-a-s-lodge-academic-press-1964-389-pp-75s/5C3DF9884AD9608160E8E25440746A01.
(180) White, J. L. *Rubber processing: technology, materials, and principles*. Munich; New York: Hanser Publishers; Cincinnati: Hanser/Gardner Publications, **1995**, http://archive.org/details/rubberprocessing0000whit.
(181) Leblanc, J. L. Rubber−filler interactions and rheological properties in filled compounds. *Prog. Polym. Sci.* **2002**, *27* (4), 627–687.
(182) Mooney, M. A Shearing Disk Plastometer for Unvulcanized Rubber. *Ind. Eng. Chem. Anal. Ed.* **1934**, *6* (2), 147–151.
(183) Mooney, M. A Theory of Large Elastic Deformation. *J. Appl. Phys.* **1940**, *11* (9), 582–592.
(184) *Mooney Viscosity - an overview*. **2026**, https://www.sciencedirect.com/topics/engineering/mooney-viscosity (Accessed May 7, 2026).
(185) Lin, C.; Hergenrother, W. L.; Hilton, A. S. Mooney Viscosity Stability and Polymer Filler Interactions in Silica Filled Rubbers. *Rubber Chem. Technol.* **2002**, *75* (2), 215–245.
(186) Randall, A. M.; Robertson, C. G. Linear-nonlinear dichotomy of the rheological response of particle-filled polymers. *J. Appl. Polym. Sci.* **2014**, *131*, No. 40818.
(187) Baeza, G. P.; Oberdisse, J.; Alegria, A.; Couty, M.; Genix, A.-C. A high-temperature dielectric process as a probe of large-scale silica filler structure in simplified industrial nanocomposites. *Phys. Chem. Chem. Phys.* **2014**, *17* (3), 1660–1666.
(188) Baeza, G.; Oberdisse, J.; Alegria, A.; Saalwächter, K.; Couty, M.; Genix, A.-C. Depercolation of aggregates upon polymer grafting in

https://doi.org/10.1021/acssusresmgt.5c00668
ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

simplified industrial nanocomposites studied with dielectric spectroscopy. *Polymer* **2015**, *73*, 131.
(189) Ahn, B.; Park, N.; Kim, D.; Kim, W. Influence of end-functionalized solution styrene−butadiene rubber on silica-filled vulcanizates with various silica−silane systems. *Rubber Chem. Technol.* **2019**, *92* (2), 364–377.
(190) Sun, C.; et al. Improvement of Silica Dispersion in Solution Polymerized Styrene−Butadiene Rubber via Introducing Amino Functional Groups. *Ind. Eng. Chem. Res.* **2019**, *58* (3), 1454–1461.
(191) Babula, P.; Kozak, R.; Schab-Balcerzak, E. Synthesis and characterization of anionic polymerization initiator from functional styrene derivative. *J. Appl. Polym. Sci.* **2025**, *142* (4), No. e56409.
(192) Hassanabadi, M.; Najafi, M.; Nikazar, S.; Garakani, S. S.; Motlagh, G. H. Impact of Placement of Aminopropyl Triethoxy Silane and Tetraethoxy Silicate on SSBR Chains: Analysis of Rolling Resistance, Wet Grip, and Abrasion Resistance. *Adv. Polym. Technol.* **2022**, *2022* (1), No. 1566042.
(193) Li, H.; Liu, L.; Zhang, Y.; Zhang, L. Nanocomposites of Triethoxysilane Functionalized Solution Polymerized Styrene-Butadiene Rubber by Hydrosilylation as High-Performance Green Tire. *Polym. Compos.* **2026**, *47* (4), 3879.
(194) Ansari, A.; Mohanty, T. R.; Sarkar, S.; Ramakrishnan, S.; Amarnath, S.; Singha, N. K. Epoxy modified styrene butadiene rubber (SBR) in green tire application. *Eur. Polym. J.* **2024**, *213*, No. 113069.
(195) Hui, J.; Liu, L.; Yu, Z.; Wu, Q.; Zhang, L. Silane coupling agent 3-aminopropyltriethoxysilane modified silica/epoxidized solution-polymerized styrene butadiene rubber nanocomposites. *Polym. Compos.* **2023**, *44* (10), 6957–6968.
(196) Yamada, C.; Yasumoto, A.; Matsushita, T.; Blume, A. Influence of functionalized S−SBR on silica−filled rubber compound properties. *Funct. Compos. Mater.* **2022**, *3* (1), 6.
(197) Xu, Y.; Liu, Y.; Gao, Y.; Liu, L.; Zhang, L. Designing high-performance green tire treads by reinforcing the styrene-butadiene rubber/silica interface with chain difunctionalization. *Composites, Part B* **2025**, *290*, No. 111887.
(198) Cicerchi, J. A.; Hogan, T. E.; Kuhel, I. J. J. Modified high-cis polybutadiene polymer, related methods and rubber compositions. EP3966259B1, **2024**.
(199) Park, N.; Rossle, M.; Thiele, S.; Heidenreich, D.; Gutschank, B. Aminosilane-functionalized dienes for use in functionalization of elastomeric polymers. US10421767B2, **2019**.
(200) Ryba, J. L.; Sandstrom, P. H.; Cronin, S. W.; Marts, B. H. Tire with rubber tread containing combination of resin blend and functionalized elastomer. US8459319B2, **2013**.
(201) Kyomiki; Sekigawa Modified conjugated diene polymer, modified conjugated diene polymer composition, and rubber composition. CN110684154A, **2020**.
(202) Wendling, P.; Reif, L.; Trimbach, J.; Rawlinson, A., Peter, R.; Engehausen, R. Quaterpolymers with functional hydroxyl or epoxy groups. US20020120052A1, **2002**.
(203) Steinhauser, N. 1-amino-3- (oxyalkylalkoxysilyl) -2-propanol terminated diene rubber. CN114026140B, **2023**.
(204) Robert, P. ; Favrot, J.-M. ; Laubry, P. ; Barbotin, F. Composition for tyre running tread and method for preparing same. WO2001090237A1, **2001**.
(205) Takeichi, H. et al. Diene polymers and copolymers incorporating partial coupling and terminals formed from hydrocarboxysilane compounds. US6228908B1, **2001**.
(206) Gandon-Pain, S. Method for obtaining an elastomer graft with functional groups along the chain and rubber compositions. WO2004096865A2, **2004**.
(207) White, J. L.; Tokita, N. Elastomer processing and application of rheological fundamentals. *J. Appl. Polym. Sci.* **1967**, *11* (3), 321–334.
(208) Tokita, N.; Pliskin, I. The Dependence of Processability on Molecular Weight Distribution of Elastomers. *Rubber Chem. Technol.* **1973**, *46* (5), 1166–1187.
(209) Cotten, G. R. Significance of Extensional Flow in Processing of Rubbers. *Rubber Chem. Technol.* **1981**, *54* (1), 61–71.
(210) Bacchelli, F. Rheological Implications of the Reduction in Viscosity of SBR Copolymers During Mixing. *Kautsch. Gummi Kunstst.* **2008**, *61*, 188, https://www.semanticscholar.org/paper/Rheological-Implications-of-the-Reduction-in-of-SBR-Bacchelli/ed670197d14edff629bfb38923b9663c7a061dd6.
(211) Bacchelli, F.; Grasso, F.; Pellizzari, B.; Coppola, S. Matching processability, Performance and Sustainability in SBR Compounds. *Kgk-Kautsch. Gummi Kunstst.* **2019**, *72*, 45.
(212) Hisamura, K.; Ishikaza, T.; Kondo, T. Modified conjugated diene polymer, bale, method for producing modified conjugated diene polymer, rubber composition, and tire. WO2025028621A1, **2025**.
(213) Siolek, M.; Kozak, R.; Weda, P.; Bogacz, R.; Skrok, T.; Walenia, M. Bissilylamino-functionalized conjugated dienes, their preparation and their use in the production of rubbers. WO2020152332A1, **2020**.
(214) Ozawa, Y. et al. Functionalized high cis-1,4-polybutadiene prepared using novel functionalizing agents. WO2002038615A1, **2002**.
(215) Ashiura, M.; Chino, K.; Kawazura, T. Radical-modified polymer and polymer composition containing the same. US6653409B2, **2003**.
(216) Backer, M.; Chaussee, T.; De Buyl, F.; Deheunynck, D.; Habimana, J. D. L. C.; Smits, V. Modified diene elastomers. WO2011083050A2, **2011**.
(217) Adu, P. C. O.; et al. Challenges and advancements in Elastomer/CNT nanocomposites with mechanochemical treatment, reinforcement mechanisms and applications. *Smart Mater. Manuf.* **2024**, *2*, No. 100053.
(218) Yang, L.; Ou, Z.; Jiang, G. Research Progress of Elastomer Materials and Application of Elastomers in Drilling Fluid. *Polymers* **2023**, *15* (4), 918.
(219) Thomas, J.; Patil, R. The Road to Sustainable Tire Materials: Current State-of-the-Art and Future Prospectives. *Environ. Sci. Technol.* **2023**, *57*, 2209.
(220) Zhang, G.; Guo, B.; Zhang, L. Significant Trends in Rubber Research Driven by Environment, Resource, and Sustainability. *Macromolecules* **2025**, *58* (12), 5883–5903.
(221) Kumar, A.; Rathee, J.; Mehta, S. Functionalization and industrial-scale fabrication of nanoemulsion with relevant application in pharmaceutical, food, and agricultural sector. In *Industrial Applications of Nanoemulsion*; Elsevier, **2024**, pp. 17−47.
(222) Ishizone, T.; Sugiyama, K.; Hirao, A. Anionic Polymerization of Protected Functional Monomers. *Polymer* **2012**, *3*, 591–621.
(223) Alam, M. N. Advances in Functional Rubber and Elastomer Composites. *Polymers* **2024**, *16* (12), No. 1726.
(224) Novak, B. M.; Risse, W.; Grubbs, R. H. The development of well-defined catalysts for ring-opening olefin metathesis polymerizations (ROMP). *Adv. Polym. Sci.* **1992**, *102*, 47.
(225) Magaletti, F.; et al. Adducts of Carbon Black with a Biosourced Janus Molecule for Elastomeric Composites with Lower Dissipation of Energy. *Polymers* **2023**, *15* (14), No. 3120.
(226) Sarkar, P.; Bhowmick, A. K. Sustainable rubbers and rubber additives. *J. Appl. Polym. Sci.* **2018**, *135* (24), No. 45701.
(227) Mangotra, A.; Singh, S. K. Volatile organic compounds: A threat to the environment and health hazards to living organisms − A review. *J. Biotechnol.* **2024**, *382*, 51–69.
(228) Kamran, F.; Afshar, H.; Shahi, F. Recent Advances and Applications of Sustainable and Recyclable Polymers. *Polym. Eng. Sci.* **2025**, *65* (8), 3845–3879.
(229) Gonçalves, R.; et al. Biobased polymers for advanced applications: Towards a sustainable future. *Prog. Polym. Sci.* **2025**, *162*, No. 101934.
(230) Sampath, M.; Konikkara, N.; David, S.; Ramakrishnan, S.; Rath, J. P.; Amarnath, S. K. P. Advancements in sustainable materials for environmentally responsible tyre production: a comprehensive review. *RSC Sustainability* **2025**, *3* (10), 4336–4363.
(231) Hahladakis, J. N.; Velis, C. A.; Weber, R.; Iacovidou, E.; Purnell, P. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *J. Hazard. Mater.* **2018**, *344*, 179–199.

https://doi.org/10.1021/acssusresmgt.5c00668
ACS Sustain. Resour. Manag. 2026, 3, 1253−1275

(232) Noppalit, S.; Simula, A.; Ballard, N.; Callies, X.; Asua, J. M.; Billon, L. A renewable terpene derivative as a bio-sourced elastomeric building block in the design of functional acrylic copolymers. *Biomacromolecules* **2019**, *20*, 2241.
(233) Miao, S.; Wang, P.; Su, Z.; Zhang, S. Vegetable-oil-based polymers as future polymeric biomaterials. *Acta Biomater.* **2014**, *10* (4), 1692–1704.
(234) Jašek, V.; Figalla, S. Vegetable Oils for Material Applications − Available Biobased Compounds Seeking Their Utilities. *ACS Polym. Au* **2025**, *5* (2), 105–128.
(235) Gregory, G. L.; López-Vidal, E. M.; Buchard, A. Polymers from sugars: cyclic monomer synthesis, ring-opening polymerisation, material properties and applications. *Chem. Commun.* **2017**, *53* (14), 2198–2217.
(236) Rigo, E.; Ladmiral, V.; Caillol, S.; Lacroix-Desmazes, P. Recent advances in radical polymerization of bio-based monomers in aqueous dispersed media. *RSC Sustainability* **2023**, *1* (4), 788–813.
(237) Jain, A.; Goswami, S.; Banerjee, S. Advances in Self-Healing Polymers: Mechanisms, Applications, and Future Perspectives. *Macromol. Chem. Phys.* **2025**, *226* (14), No. e00159.
(238) Utrera-Barrios, S.; Verdejo, R.; López-Manchado, M. Á.; Hernández Santana, M. Self-Healing Elastomers: A sustainable solution for automotive applications. *Eur. Polym. J.* **2023**, *190*, No. 112023.
(239) Das, M.; Parathodika, A. R.; Maji, P.; Naskar, K. Dynamic chemistry: The next generation platform for various elastomers and their mechanical properties with self-healing performance. *Eur. Polym. J.* **2023**, *186*, No. 111844.
(240) Ratwani, C. R.; Kamali, A. R.; Abdelkader, A. M. Self-healing by Diels-Alder cycloaddition in advanced functional polymers: A review. *Prog. Mater. Sci.* **2023**, *131*, No. 101001.
(241) Low, D. Y. S.; et al. Nano-reinforced self-healing rubbers: A comprehensive review. *J. Ind. Eng. Chem.* **2024**, *139*, 18–35.
(242) Tang, Z.; Liu, Y.; Guo, B.; Zhang, L. Malleable, Mechanically Strong, and Adaptive Elastomers Enabled by Interfacial Exchangeable Bonds. *Macromolecules* **2017**, *50* (19), 7584–7592.
(243) Bernal-Ortega, P.; Anyszka, R.; di Ronza, R.; Aurisicchio, C.; Blume, A. Dynamic Imine Bonds in Tire Tread Compounds: A Pathway to a Circular Economy and Reduced Waste. *ACS Sustainable Chem. Eng.* **2025**, *13* (8), 3209–3221.
(244) *Polymer−filler interactions in a tire compound reinforced with silica*. **2025**, https://www.ielrs.org.br/documentos/polymer-filler-interactions-tire-compound-reinforced-silica.
(245) Nadzharyan, T. A.; Kramarenko, E. Y. The Effect of Particle−Matrix Interface on the Local Mechanical Properties of Filled Polymer Composites: Simulations and Theoretical Analysis. *Polymers* **2025**, *17* (1), 111.
(246) Dolui, T.; et al. Stimuli−Responsive Mechanoadaptive Elastomeric Composite Materials: Challenges, Opportunities, and New Approaches. *Adv. Eng. Mater.* **2023**, *25* (20), No. 2300584.
(247) Sridharan, K.; Sivaramakrishnan, R. Dynamic Behavior of Tyre Tread Block. *Am. J. Eng. Appl. Sci.* **2012**, *5* (2), 119–127.
(248) Kim, H. J. Current Advances and Challenges in Chemical Recycling of Polymeric Materials. Preprints **2023**.
(249) Cui, L.; Zeng, G.; Yuan, C.; Xiong, Y.; Huang, G.; Zhang, P. Recyclable Hydroxyl-Terminated Polybutadiene Based Polyurethane Composites via Interfacial Dynamic Cross-Linking. *ACS Appl. Polym. Mater.* **2025**, *7* (15), 9947–9959.
(250) Dasgupta, A.; Sen, B.; Dutta, P. Development of a sustainable polymer composite: enhancing properties of waste plastic with ground tire rubber reinforcement. *Phys. Scr.* **2024**, *99* (9), No. 095013.
(251) Liu, C.; Fang, W.; Cheng, Q.; Qiu, B.; Shangguan, Y.; Shi, J. Revolutionizing Elastomer Technology: Advances in Reversible Crosslinking, Reprocessing, and Self-Healing Applications. *Polym. Rev.* **2025**, *65* (2), 483–526.
(252) Scacchi, M.; Nichetti, D. The Nonlinearity Index: A New Fingerprint for Polymer−filler Interactions In Functionalized SBR. *Rubber Chem. Technol.* **2025**, *98* (4), 643.
(253) Mohammad, A. S. Chapter 15 - Redesign and reduce: Rethinking rubber recipes for sustainable elastomer production. In *Rubber Materials*; Santana, M. H.; Utrera-Barrios, M. H.; Elsevier, **2025**, 429-452.
(254) Singh, P.; et al. A review of rubber tyre derived micro- and nanoplastics: fate, impact and risks. *Environ. Geotech.* **2025**, *12*, 691–708.
(255) Kang, J.; et al. Tyre Wear Particles in the Environment: Sources, Toxicity, and Remediation Approaches. *Sustainability* **2025**, *17* (12), No. 5433.
(256) Sakao, T.; Bocken, N.; Nasr, N.; Umeda, Y. Implementing circular economy activities in manufacturing for environmental sustainability. *CIRP Ann.* **2024**, *73* (2), 457–481.

https://doi.org/10.1021/acssusresmgt.5c00668
ACS Sustain. Resour. Manag. 2026, 3, 1253−1275