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Review IJPSE

Sulfur-Based Copolymers: Current Status and New Opportunities in Synthesis and Product Applications

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Abstract

Sulfur-based copolymers are fascinating materials with a wide range of applications. This review article delves into the synthetic aspects of sulfur copolymers, their characteristics, and their applications. Sulfur is a byproduct of refineries, produced in large quantities worldwide. Various sulfur-based copolymers have been synthesized through inverse vulcanization, catalyst-induced low-temperature inverse vulcanization, and polycondensation reactions. Researchers have studied a variety of monomers, including benzoxazine moieties and sulfur-based systems with allylic or vinylic functionalities. The article discusses the characterization of sulfur copolymers, such as sulfur quantification in copolymers, solubility, microstructure, molecular weight, processability, and self-healing properties. Further, it highlights the current challenges associated with large-scale applications of sulfur-based copolymers. Applications discussed include Li-S batteries, IR transparent lenses, concrete, controlled-release fertilizers, removal of toxic metals from water, biomedical applications, and environmental remediation.

Keywords: Sulfur, lithium-sulfur batteries, inverse vulcanization, polysulfide

INTRODUCTION

Sulfur is one of the most abundant materials on earth and the 16th most abundant element in the lithosphere. Up until the 19th century, the major source of sulfur was the volcanic soil on the island of Sicily [1]. After the Industrial Revolution, the demand for sulfur increased significantly, mainly to produce sulfuric acid. In the 20th century, the Frasch process enabled the extraction of large volumes of molten sulfur from the salt domes of North America [2]. The Frasch process dominated the world's sulfur production until 1971, when it became necessary to eliminate sulfur from petroleum feedstock, and an excessive amount of sulfur as a by-product raised environmental concerns. Elemental sulfur is produced in large quantities as a by-product of the hydrodesulfurization process during petroleum refining [3]. Elemental sulfur has been used for diverse applications since ancient times. In 1600 B.C.E., Egyptians used it to bleach cotton fabric, while Greeks and Romans used sulfur in topical pharmaceuticals for its antimicrobial properties. The Chinese first used sulfur for making explosives for the military. In the mid-19th century, the method of sulfur incorporation known as vulcanization was discovered [4–7]. Since then, it has become an essential additive for tire formulation. Sulfer is used to produce both commodity and specialty chemicals, such as sulfuric acid and fertilizers. It is widely consumed in antimicrobial agents, chemical dyes, petroleum refining, mining, pulp and paper processing, rubber production, and construction [7–9].

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Despite an oversupply, most sulfur is stored as powder or solid blocks. Extensive research is being conducted to find uses for sulfur, particularly in polymeric forms. Polymeric sulfur is attractive because it addresses ecological concerns from excess sulfur and can reduce reliance on existing synthetic polymers. The incorporation of S–S bonds within a polymer can generate unique properties, such as being redox-active, highly polarizable, and exhibiting dynamic covalent character. Sulfur polymers have been studied for a wide variety of applications, including Li-S batteries, antimicrobial materials, controlled -release fertilizers, stabilization of metal nanoparticles, oil-water separations, water purifiers, environmental remediation, and IR transparent lenses [10–18]. An overview of sulfur-based copolymers used for different applications is listed in Table 1.

Table 1. Different sulfur-based copolymers and their applications.

S. N.	Application	S-Based Polymer	Comonomer I	Comonomer II	Reference
1	High refractive index and semiconductor application	Polythioamide	m-xylylenediamine, 1,6-hexanediamine, ethylenediamine and 1,4-cyclohexanediamine	Sulfur	[19]
2	Polymeric 1D photonic crystal as distributed Bragg reflector	Chalcogenide hybrid organic/inorganic polymer	Selenium/diisopropenyl benzene	Sulfur	[20]
3	High refractive index material	Sulfur rich diblock polymeric nanoparticles	Polynorbornene derivative	Cyclic polysulfanes	[21]
4	Polymeric distributed Bragg reflectors	Sulfur copolymer by inverse vulcanization	2,5-diisopropenylthiophene	Elemental sulfur	[22]
5	Curable soft benzoxazine films	Polybenoxazine based sulfur copolymer	Diallyl benzoxazine (B-ala)	Di-functional thiol compound, 1,2-ethanedithiol	[23]
6	UV-curable high refractive index oligomers	Sulfur-containing melamine and urethane acrylates	melamine acrylate	Thiophenol/ 2-mercaptothiazoline/2-mercaptobenzothiazole/triphenyl methanethiol/p-thiocresol	[24]
7	Active materials for Li–S batteries	Sulfur copolymer by inverse vulcanization	Sustainable algae oil, Botryococcene (unsaturated hydrocarbon)	Elemental sulfur	[25]
8	Infrared imaging camera lenses Li–S battery component, absorbents for water purification/ oil spill clean-up, slow-release fertilizers	High sulfur-content materials by radical aryl halide–sulfur polymerization	2,4-dimethyl-3,5-dichlorophenol	Elemental sulfur	[26]

9	Mercury capture and removal	Sulfur based copolymer through inverse vulcanization	Limoene/diisopropenyl benzene/ dicyclopentadiene/Myrcene/ farnecene/ farnesol	Elemental sulfur	[27]
10	Mercury capture and removal from soil and water	Sulfur based copolymer through inverse vulcanization	Limonene	Elemental sulfur	[16]
11	Amine functional prepolymer	Inverse vulcanization using nucleophilic activator, such as 1,3-metaphenylene diamine	Styrene	Sulfur	[28]
12	Li-S battery for fabrication of 2032 type coin cell battery	Sulfur copolymer by inverse vulcanization at kg scale	Diisopropenyl benzene	Sulfur	[29]
13	Cathodic material for Li-S cell	Sulfur copolymer by inverse vulcanization	Diallyl disulfide/ myrcene	Elemental sulfur	[30]
14	Cathodic material for Li-S cell	Sulfur copolymer by Inverse vulcanization	Divinyl benzene	Elemental sulfur	[31]
15	Cathodic material for Li-S battery	Sulfur copolymer by inverse vulcanization	Cardanol benzoxazine monomer	Elemental sulfur	[32]
16	UV-curable high refractive polymer resin	photopolymerization under UV irradiation	Sulfur-containing aromatic acrylates 2,7-Bis[(2-acryloylethy(l)[sulfanyl]thianthrene/ 4,4'-Bis[(acryloyloxyethylthio)diphenyl] sulfide	No elemental sulfur	[33]
17	Curing agents for rubber	Sulfur-organic copolymer by inverse vulcanization	Dicyclopentadiene/ terpentine/styrene/limonene/furfural/liquid rubber Thiokol lP23	Elemental sulfur	[34]
18	Construction material	Sulfur copolymer by inverse vulcanization	Dicyclopentadiene	Elemental sulfur	[35]
19	Concrete application	Sulfur copolymer through inverse vulcanization	Divinyl sulfone/Divinyl terminated polydimethylsiloxane/Divinyl adipate/Vinyl crotonate/Diallyl phthalate/Diallyl isophthalate	Elemental sulfur	[36]
20	Self-healing material	POSS-sulfur hybrid through inverse vulcanization	Multifunctional methacrylated POSS	Elemental sulfur	[37]

Different nomenclatures have been used to designate sulfur copolymers like organic polysulfide, inorganic polysulfide, and sulfur allotropes. In sulfur chemistry, the term polysulfide generally refers

to both organic and inorganic sulfur containing covalently bonded sulfur chains (–S_n–), ionic compounds (S_n^{2-}, n > 2) and organosulfur compounds. To avoid the ambiguities, Steudel [38] suggested that the name polysulfide should be used to describe inorganic ionic compounds based on sulfur**.** The term organic polysulfane should be used for sulfur-based systems designated as R-Sn-R where n > 2, R=organic residue (alkyl or aryl) linked to sulfur chain via a carbon atom. Polysulfide polymers are polymeric materials that have hydrocarbon in the backbone with multiple sulfur units [39, 40]. Organo sulfur-based materials include polyalkylene sulfides, polyarylenesulfides, polythioureas, polysulfoxides and polysulfones. All of them contain single C–S linkage in one repeating unit. Organo disulfide copolymers contain S–S linkage per repeating unit. Apart from this, polymers containing thioesters, thiocarbonates, thiocarbamates and thioamides are reported in the literature, which comprises multiple C–S bonds per repeating unit, incorporated by thiocarbonyl based functional group [41]. Polymers derived from polymerization of elemental sulfur having a random or statistical sequence of –S_n– units, fall under a distinctive category termed as chalcogenide hybrid inorganic/organic polymers (CHIPs) [42]. Generally, the reaction between elemental sulfur and organic comonomers lead to the formation of CHIPs, also known as organic polysulfides. The different structures of sulfur copolymers are shown in Figure 1.

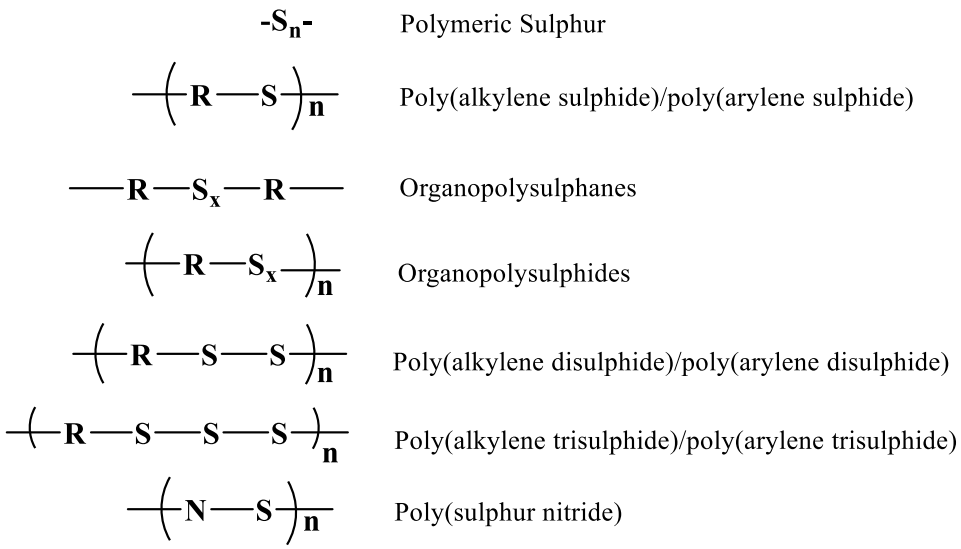

Figure 1. General structures of sulfur-based polymers.

This review discusses the synthesis of various sulfur-based polymeric systems. Inverse vulcanization, the most used method, reacts elemental sulfur with monomers having allylic and vinylic functionalities. Developments in sulfur chemistry include low-temperature catalyst-induced inverse vulcanization, high sulfur content polymers, and polysulfides. Innovative applications include new self-healing materials and heat-recast cycles. Characterization of sulfur copolymers involves quantifying sulfur content, determining microstructure, estimating molecular weight, and assessing thermal properties and stability. Restricted solubility of sulfur-based copolymers poses characterization challenges.

SYNTHETIC ASPECTS

Free radical polymerization or inverse vulcanization methods are used for the synthesis of sulfur copolymer. The homolytic cleavage of sulfur starts at 159°C, which is called the floor temperature (T_f). Upon continuous heating at this temperature, the homolytic cleavage of the S–S bond takes place, generating sulfur radicals (thiyl radicals) which can attack another S_8 to open the ring. Further polymerization proceeds by repeated ring-opening and bond formation between S_8 and the polysulfide chain. The polymeric sulfur is unstable due to the terminal sulfur radical of the polysulfide chain, which promotes depolymerization, forming monomeric cyclic sulfur. Therefore, sulfur radicals should be quenched by reacting with other monomers before depolymerization.

Sulfur-containing polymers with one polysulfide component and another organic or inorganic are often called CHIPs. Many organic compounds with unsaturation (e.g., benzoxazines, norbornenes, and various vinylic comonomers) form polymers with sulfur through inverse vulcanization [43, 44]. This process is further modified to synthesize sulfur-based polymers at lower temperatures, called dynamic covalent polymerization, and accelerated or catalytic inverse vulcanization. Recently, functionalized CHIPs have gained attention for post-polymerization modification, step-growth polymer transformations, and crosslinking to form thermosets [45–48]. The different monomers that undergo inverse vulcanization are discussed below.

Sulfer Copolymer by Conventional Inverse Vulcanization

Dicyclopentadiene

Temperature plays a significant role in controlling the reaction during inverse vulcanization between sulfur and dicyclopentadiene (DCPD). At temperatures >140°C, the reaction mechanism becomes more complex, involving free radical and cationic pathways, polymer degradation, and H_2S generation. At <140°C, the reaction produces a linear polymer where only one double bond from the norbornene ring participates. High temperatures produce a highly cross-linked polymer involving both double bonds from norbornene and cyclopentene in DCPD. At high temperatures, DCPD can dissociate into two molecules of cyclopentene, which react with sulfur and undergo ring-opening metathesis polymerization (ROMP). This ROMP can be metal-free or metal-catalyzed. Initially, in inverse vulcanization with DCPD, the reaction proceeds with the double bond in the norbornene ring, and as the temperature increases, crosslinking occurs through the remaining double bond in cyclopentene. Low temperature is preferred for the reaction between DCPD and sulfur. The reaction takes place without any solvent, with both co-monomers in a molten state. In the absence of solvent, an increase in viscosity during polymerization initiation and propagation steps inhibits the termination step, leading to an auto-accelerated exothermic reaction and the formation of solid foam [49–54].

Diisopropenylbenzen

Small-scale reactions of sulfur with 1, 3-diisopropenylbenzene (DIB) at 185°C (10 g, 25 g, and 100 g) achieved high conversion within minutes without copolymer degradation. However, scaling up to 1 Kg failed due to auto-acceleration or Trommsdorff effect. To address this, large-scale synthesis was preferred at 130°C with 90 wt.% or 50 wt.% sulfur. Solution polymerization using 1, 2-dichlorobenzene at 185°C was successful for a 50% sulfur feed ratio but inhibited at 90 wt.% [29]. Recent studies have used DIB as a crosslinking agent for nanocomposites with polystyrene and sulfur. Poly (sulfer-co-1, 3-diisopropenylbenzene) nanoparticles were prepared in a polystyrene matrix via in-situ inverse vulcanization at 230°C [55].

Divinylbenzene

The inverse vulcanization of elemental sulfur with low concentrations of dienes has been successfully used to create new cathode materials. One of the crosslinkers, 1, 3-diisopropenyl benzene, is expensive and reacts slowly. Other crosslinkers include diethynyl benzene, which crosslinks with sulfur at high temperatures, 1, 4-diphenylbutadiyne, used for high sulfur content materials, and thiophene monomers with allyl groups. The reaction of sulfur with divinylbenzene (DVB) has been studied to synthesize sulfur-inorganic polymers with good chemical stability and easy processability. The sulfur-DVB reaction, carried out at 185°C under an inert atmosphere, completes in 5 minutes with low DVB content and 15 minutes with high DVB content, which is faster than most inverse vulcanizations that take 1–2 h [56–60].

Renewable Resources

Sulfur and limonene are used to synthesize a low molecular weight polysulfide with potential to remove toxic metals from water. Besides limonene, renewable olefinic co-monomers like myrcene, farnesol, farnesene, perillyl alcohol, and squalene has copolymerized with sulfur via inverse vulcanization [27, 30, 44, 61]. The copolymers are prepared by heating sulfur with co-monomers at 160–175°C for 45 minutes and curing at 140°C for 12 h [27, 44, 61]. Myrcene, identified in algae oil from Botryococcus Braunii (Race B) as Botryococcene (BT), reacts with sulfur at 185°C in various

ratios (Figure 2). Polymers with sulfur to BT ratios of 5:5 and 7:3 are soluble in organic solvents, like $C_2H_2Cl_4$ at 50°C, but higher sulfur content (9:1) results in insolubility. Samples with a 5:5 ratio show partial solubility after 15 minutes due to residual sulfur [25].

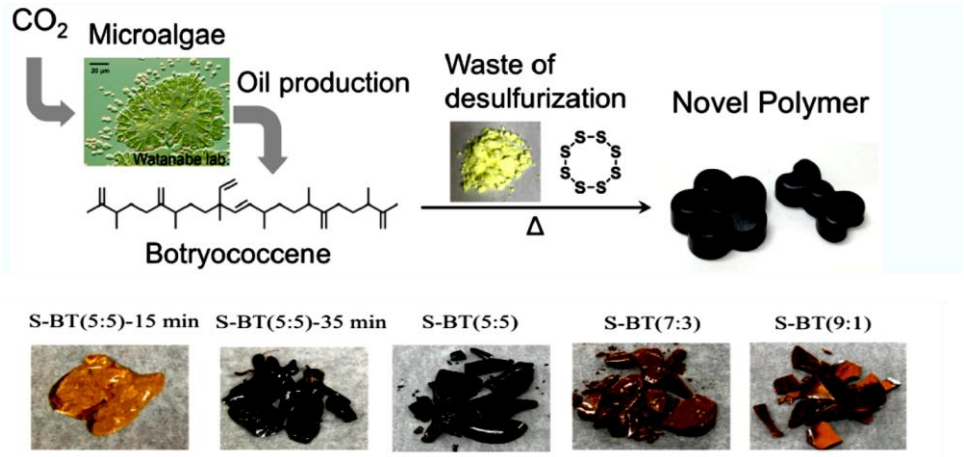

Figure 2. Sulfer copolymer from algae *Botryococcus braunii* and elemental sulfur [25].

Supercritical carbon dioxide and salt templating techniques are used to create porous copolymers. These materials have a high surface area, allowing efficient absorption of mercury from aqueous solutions. The S–S bonds in the copolymers can oxidize Hg(I) to Hg(II). Additionally, canola oil has been copolymerized with sulfur for applications in metal scavenging, crude oil remediation, and slow-release fertilizers [27].

Oligomeric Polyhedral Silsesquioxane (POSS)

An interesting example is the formation of a POSS-sulfur hybrid when POSS with vinylic or acrylate functionality reacts with elemental sulfur. A multifunctional methacylated POSS has been reacted with elemental sulfur above T_f following inverse vulcanization process. Diglyme solution used for the reflux process. These S-MMA-POSS have potential as a useful precursor for preparation of materials with high transparency in midinfrared region [37]. Various sulfur-based copolymers have been prepared using elemental sulfur and diene monomers i.e. divinyl sulfone, divinyl terminated polydimethylsiloxane, adipic acid divinyl ester, vinyl crotonate, diallyl phthalate, and diallyl isophthalate through thermal ring-opening polymerization [36]. Different monomers with allylic or vinylic moieties having proficiency towards inverse vulcanization with elemental sulfur have shown in Figure 3.

Further, the inclusion of reactive moieties, such as electropolymerizable thiophenes [62] and alcohols [63] are reported. Amine functionalized CHIPs are capable of post-polymerization reactions with acid chlorides and isocyanates. The reaction between sulfur and 4-vinyl aniline by inverse vulcanization is demonstrated to produce CHIP. The reaction mechanism of 1, 3 meta phenylene diamine with sulfur and poly(sulfur random styrene) has been investigated. The final product obtained is oligomeric, miscible with a wider range of organic solvents and comonomers [63].

Synthesis of High Sulfur Polymer

High sulfur content materials (HSM) are conventionally prepared by reaction of sulfur containing comonomer like thiols, allyl disulfides, allyl trisulfides, and elemental sulfur. The reaction between alkyl thiol and sulfur proceeds via free radical mechanism conducted in the temperature range 130–160°C and end products of the reaction are hydrogen terminated polysulfides or sulfanes. The efficiency of diethylamine as a catalyst in the temperature range of 20–50°C for copolymerization between elemental sulfur and dithiols has been discussed [64, 65]. Further, HSM has been developed by copolymerization of elemental sulfur with 2, 2-dimethyl-3, 5-dichlorophenol (DPP) through radical aryl

halide-sulfur polymerization route (RASP) as shown in Figure 4 [26]. The developed product contains 70–81 wt. % elemental sulfur and 19–30 wt. % DPP. Other examples for HSM are reported for inverse vulcanization of sulfur with cellulose and lignin [66, 67].

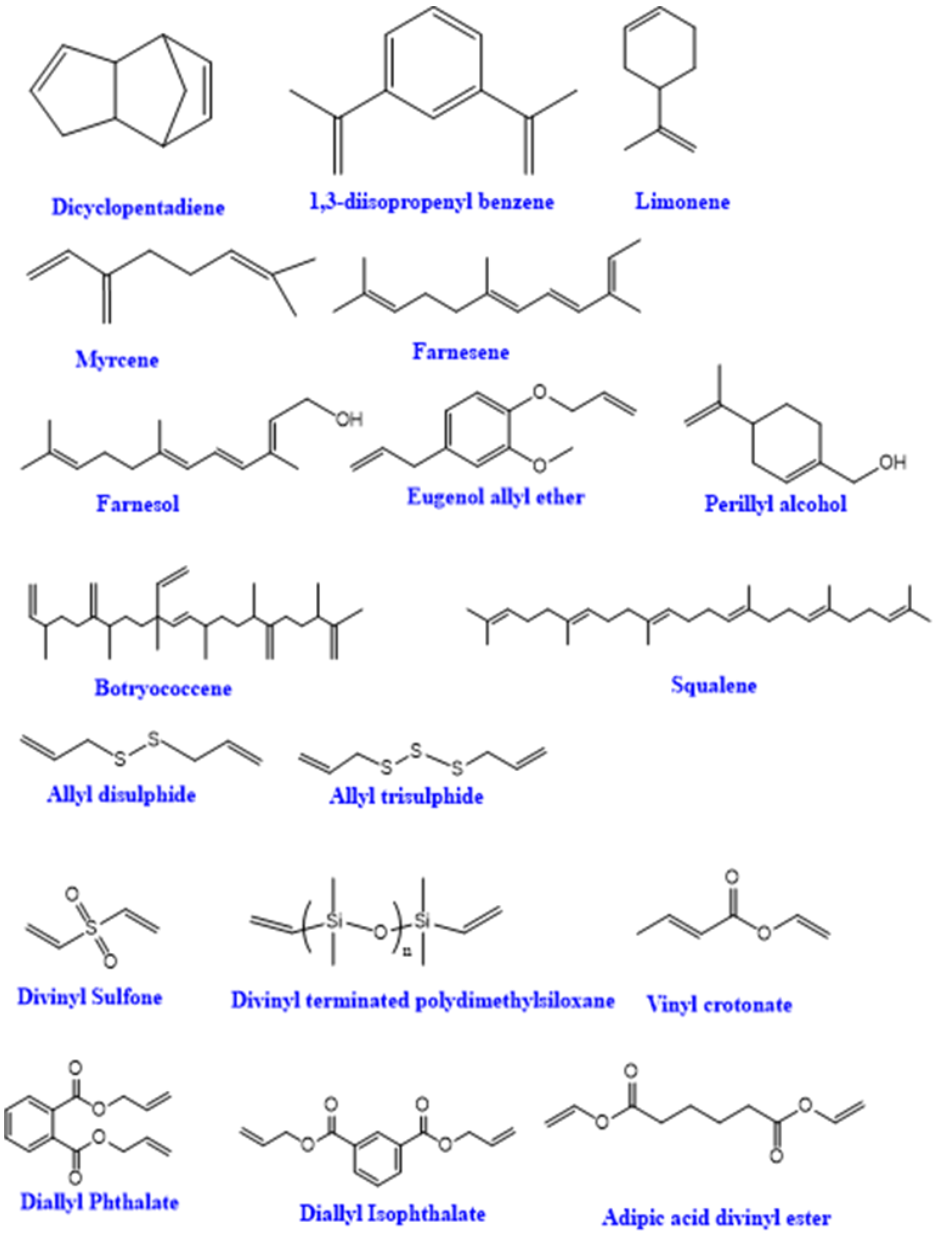

Figure 3. Different monomers for inverse vulcanization with sulfur [12, 25, 27, 38, 61].

Catalytic Synthesis of Sulfur Copolymer at Low Temperature

Inverse vulcanization has been used to polymerize elemental sulfur with vinylic monomers. Sulfur (S_8) polymerizes above 159°C, when sulfur radicals are generated through homolytic cleavage. At higher temperatures, there is a chance of forming hydrogen sulfide, thiols, and dehydrogenated olefins [68, 69]. The use of a catalyst can auto-accelerate the reaction via the Trommsdorff–Norrish effect, lowering the reaction temperature and reducing H_2S generation. Two organic accelerators, 4-vinyl aniline and n-methylimidazole, have been reported. 4-vinyl aniline enhances the reaction rate through polarity reversal, while n-methylimidazole acts as a nucleophilic activator. The efficiency of nucleophilic activators in organocatalytic pathways has been discussed [47, 48]. The copolymerization of sulfur and styrene has been studied in the presence of 4-vinyl aniline and n-methylimidazole. In the

presence of n-methylimidazole, S_8 dissolves metal, such as Cu and Zn producing $Cu_4(S_5)(NMI)_4$ and $ZnS_6(NMI)_2$ [70, 71]. This indicates the activation of sulfur in presence of n-methylimidazole. In the presence of amine base catalysts can accelerate the reaction rate between thiol and sulfur [64].

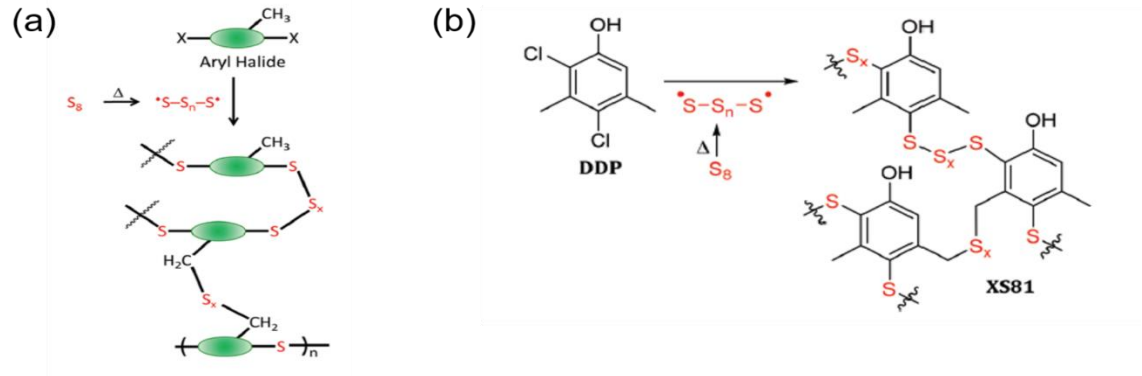

Figure 4. (a) Radical induced aryl halide-sulfur polymerization (b) Preparation of high sulfur containing material using DPP [26].

Further Ito, et al. demonstrated the absolute rate constants for the addition reactions of the benzenethiyl radical and its para-chloro derivative to various substituted styrenes and α-methylstyrenes using flash photolysis, finding that the polar effects and reaction constants of these radicals vary significantly, with *p*-$ClC_6H_4S^{\cdot}$ having larger polar effects compared to $C_6H_5S^{\cdot}$ [72]. In another example, dynamic covalent polymerizations have been used to prepare sulfur polymers at lower temperatures. Initially, the oligomer or pre-polymer is synthesized at a higher temperature to activate the sulfur radicals. In this study, an accelerator or catalyst is used to reduce the reaction temperature or time. Sulfur polymers prepared at lower temperatures with a catalyst (sodium diethyldithiocarbamate (NaDTC) exhibit varying colors based on the reaction degree and sulfur chain length, becoming darker with more catalyst (Figure 5) [68].

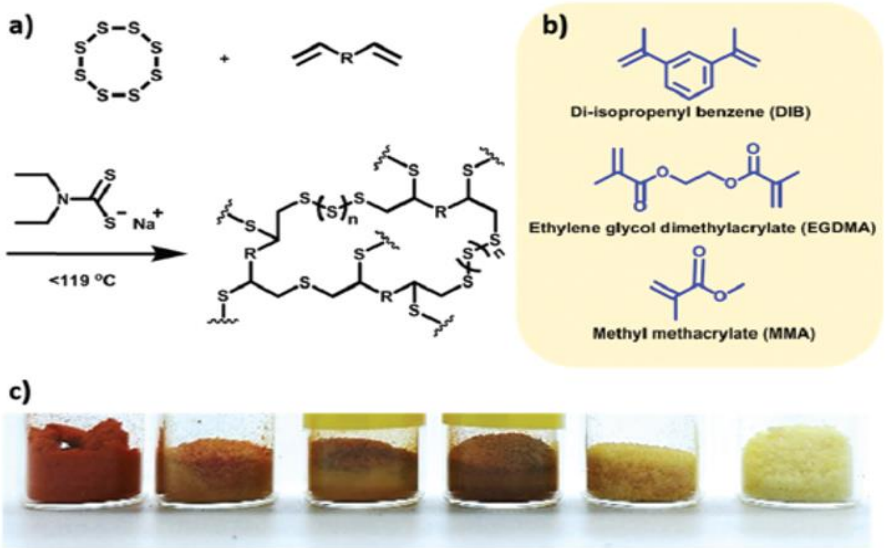

Figure 5. Low temperature inverse vulcanization using DIB, EGDMA, and MMA with elemental sulfur in presence of NaDTC as catalyst [68].

Synthesis of Benzoxazine Based Sulfur Copolymer

The synthesis of 1, 3-benzoxazines involves a two-step Mannich reaction and subsequent ring closure using primary amines with formaldehyde and phenol. Polymerization occurs via a cationic mechanism

at 150–250°C, stabilized by N and O atoms in oxazine rings, or through radical formation with initiators. Phenolic impurities lower the cure temperature, while pure benzoxazines require temperatures above 300°C. Methods to address high cure temperatures include precursor synthesis, monomer functionalization, and reactions with other polymers or fillers [72–85]. Beyazkilic et al. demonstrated that soft benzoxazine films can be prepared through simultaneous photoinduced thiolene and COLBERT reactions using difunctional thiol and diallyl benzoxazine. The obtained precursors contain benzoxazine and allyl groups for subsequent curing. During heat treatment, both ring-opening polymerization and thiol crosslinking reactions occurred. The double-cured polymers achieved comparable thermal stability to classical polybenzoxazines due to higher crosslink density [23]. Other types of benzoxazines, such as those derived from cardanol, show high thermal stability and low viscosity and are synthesized using cardanol and bisphenol A [32, 86].

Synthesis of Polysulfides

Polysulfides, also known as polythioethers or thiokols, are chemical compounds containing chains of sulfur atoms. They are used in various applications, such as sealants, caulks, and adhesives in the building, construction, aircraft, and automobile industries [87]. The polysulfide can be broadly divided into two classes inorganic and organic polysulfides. Inorganic polysulfides can be dianions or radical anions with the general formula, $[Sx]^{2-}$ or $[Sx]^{2\bullet-}$, respectively, where $x \geq 2$ [38]. Moreover, different hydrophobic compounds derived from garlic, such as allicin, vinyldithiins, thioenes, diallyl sulfide, diallyl trisulfide, diallyl tetrasulfide, etc. are having multiple sulfur atoms and exhibit broad-spectrum antimicrobial activities [88]. The synthesis methods of organo-tetra-sulfides (R–S–S–S–S–R') and Poly-organo-tetra-sulfides are described in below section.

Synthesis of Organo-Tetra-Sulfides

Organotetrasulfides can be synthesized by reacting alkyl or aryl thiol with sulfur monochloride in the presence of a suitable base like pyridine in a suitable solvent. Bis-aryltetrasulfide and bis-alkyltetrasulfide were synthesized by treating aryl thiol and alkyl thiol, respectively, with sulfur monochloride in the presence of pyridine at –78°C [89]. The substituted tetrasulfides were prepared by treating various benzylamine derivatives with tetrasulfur tetranitride for different reaction times [90]. The unsymmetrical tetrasulfides, such as substituted benzyl-2-hydroxyethyl tetrasulfides, were synthesized by treating substituted benzyl mercaptan with 2-mercaptoethanol and sulfur monochloride in ether at 0–4°C for 4 h [91]. The symmetrical aromatic trisulfides and tetrasulfides were prepared by reacting aromatic thiols with sulfur dichloride and sulfur monochloride, respectively, in the presence of pyridine at –78°C for 2 h [92]. Kim et al. synthesized diallyl tetrasulfide by treating allyl mercaptan with sulfur monochloride in the presence of triethylamine using diethyl ether as the solvent at –78°C for 2 h [93]. Panzella et al. prepared di-, tri-, and tetra-sulfide derivatives of 5-S-lipoylhydroxytyrosol by vigorously stirring 5-S-lipoylhydroxytyrosol with elemental sulfur in methanol in the presence of phosphate buffer (pH 7.4) at room temperature for different time intervals [94]. 3, 3'-Diindolyl-2, 2'-tetrasulfide (an organo-cyclic tetrasulfide) was synthesized by treating indole and sulfur in dimethylformamide under nitrogen in an oil-bath maintained at 145°C for 3 h [95].

Synthesis of Poly-Organo-Tetra-Sulfides

The poly (ethylenetetrasulfide) was prepared by treating ethylene dichloride and sodium tetrasulfide using methyltributyl ammonium chloride as a phase transfer catalyst at 70–80°C, with a reaction time of 2 h and a high conversion rate [96]. Further, Kalaee et al. synthesized poly (methylenetetrasulfide) from methylene dichloride and sodium tetrasulfide by the interfacial polycondensation technique, using methyltributyl ammonium chloride at 55–60°C, with a reaction time of 2 h [97]. Sheydaei et al. implemented the interfacial polycondensation technique for synthesizing poly(*p*-xylenetetrasulfide) using 1,4-bis(chloromethyl)benzene and sodium tetrasulfide, and studied the effect of methyltributyl ammonium chloride, tetrabutyl ammonium bromide, and benzyltriethyl ammonium chloride as phase transfer catalysts [98]. Polyphenylene tetrasulfide polymer can be synthesized through the condensation reaction of 1,4-benzenedithiol with elemental sulfur in an appropriate solvent [99]. Poly(phenoxy

methyl) ethylene polysulfides (mono, di, and tetrasulfide) were synthesized by treating dihalides with Na_2S_x (generated in situ from $Na_2S{\cdot}9H_2O$ and sulfur, x = 1, 2, 4) in the presence of tetra-n-butylammonium bromide as PTC, using chloroform as a solvent for 24 h [100].

CHARACTERISTICS OF SULFUR COPOLYMERS

Sulfur polymers derived from inverse vulcanization exhibit unique thermomechanical and electrical properties, which are influenced by their structure, synthesis method, and conditions. The phase composition and transition of polysulfides depend on the hetero-chain characteristics, with desired polysulfidity generated by the metal sulfide used in the polycondensation reaction. Increased polysulfidity affects the phase transition temperature. The chemical and thermal properties also depend on the C–S and S–S bond strengths, which vary widely. The S–S bond strength is ~70 kcal/mole in disulfides but reduces to 33 kcal/mole in polysulfides. The C–S bond strength is about 70 kcal/mole but decreases with electron-accepting substituents. Sulfur copolymers are intriguing materials that need further understanding and control to realize their potential applications [101, 102]. An overview of characterization techniques used for sulfur-based copolymer is given in Figure 6.

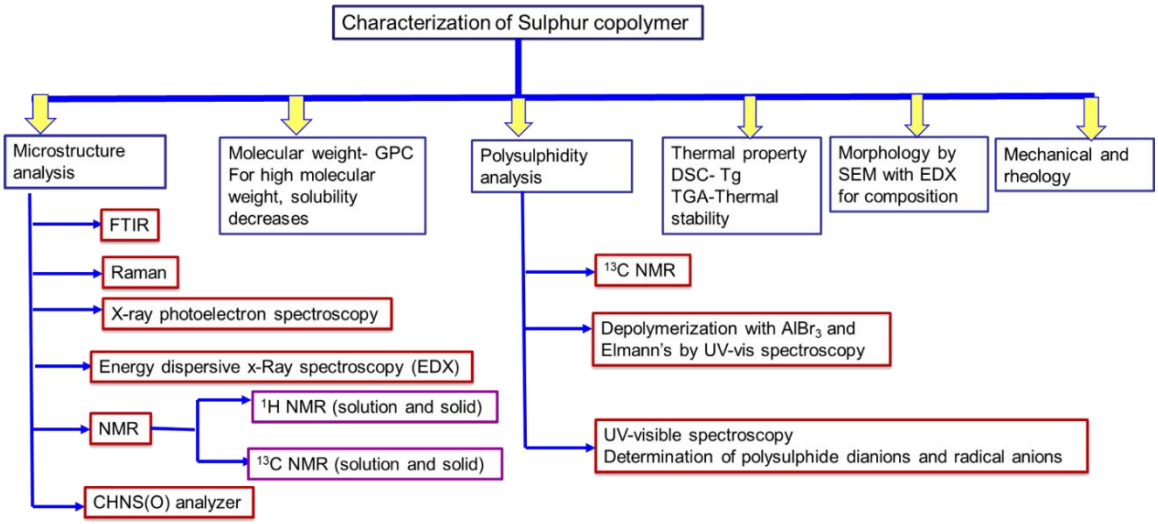

Figure 6. Different characterization methods for sulfur copolymer.

Solubility

Solubility is a crucial parameter for determining the characteristics of sulfur polymer by different characterization methods like NMR, GPC, and UV-visible techniques. A copolymer with high S–S linkages is insoluble in common solvents, such as THF, chloroform, dichloromethane, 1, 2-dichlorobenzene, dimethylformamide, dimethyl sulfoxide, acetone, and conc. H_2SO_4 [102]. Copolymers containing DVB with low and equal amounts of sulfur exhibit good solubility in THF, dichloromethane, chloroform, and 1, 2-dichlorobenzene. Limonene-based polysulfide is sparingly soluble in methanol, insoluble in water, and completely soluble in dichloromethane, chloroform, and tetrahydrofuran [16].

Sulfur Content Quantification

Sulfur-containing materials from inverse vulcanization can be homogeneous copolymer networks or composites with free sulfur in voids. Free sulfur is soluble in CS_2, while crosslinked networks are insoluble, allowing for the extraction and quantification of non-covalently bonded sulfur. The extent of S–C aryl bonds in HSM XS81 is determined using $AlBr_3$, with thiol concentration quantified by Ellman's reagent. UV-vis spectroscopy and ^{13}C NMR are used to identify polysulfide linkages, providing detailed insights into sulfur polymer properties [26, 103–106]. Further, UV-visible spectroscopy is used to identify polysulfide dianions and radical anions. Polysulfide dianions $(S_n)^{2-}$ have colors ranging from pale yellow for disulfide to orange red for longer chains, with absorption

maxima around 400 nm. In electron pair-donating solvents, like DMSO, DMF, and THF, these dianions exist in equilibrium mixtures. Radical anions like $(S3)^-$ show bright blue color with absorption bands in the range of 595–620 nm. UV-absorption spectra for polysulfide copolymers, such as polysulfide-co-divinyl sulfone (DVS) and polysulfide-co-divinyl terminated polydimethylsiloxane (DV-PDMS) show absorption maxima at 320 nm due to polysulfide linkages [36, 107].

Microstructure

^{1}H NMR studies of copolymers are challenging due to poor solubility in organic solvents, depending on the amount of organic comonomer in the sulfur polymer. The sulfur-diallyl disulfide-based copolymer with 40 wt.% diallyl disulfide is solubilized in CS_2, with deuterated chloroform. 50 wt.% myrcene-based copolymer is soluble in chloroform. NMR of poly (sulfur–DAS) 40% shows disappearance of allyl protons at 6.2 and 5.5 ppm, signals at 1.0 and 2.5 ppm for protons of an alkyl group not bonded to polysulfide chains, and a broad signal between 2.5 and 4 ppm for alkyl protons close to the polysulfide chain [27]. The Poly(S-DVB) synthesized from sulfur and divinylbenzene shows the disappearance of the vinylic protons at 5.5–6.0 ppm and the appearance of signals at 2.5 and 4.5 ppm, assigned to methylene group protons near the polysulfide chain, and at 1–2 ppm for alkyl protons from vinyl group copolymerization. The copolymer used for NMR analysis contains more than 40 wt.% DVB, enhancing its solubility in organic solvents [31].

Advanced NMR and EPR spectroscopy have been used to elucidate the role of DIB in copolymer formation. Solid-state CP MAS NMR study, including CP/TOSS, CPPI, and cross polarization kinetics, identifies multiple peaks in S-DIB copolymers. CPPI distinguishes carbon signals based on polarization inversion time, while cross polarization kinetics controls polarization transfer, affecting carbon peak intensities. Dynamic CP and ^{13}C T1 experiments predict ^{13}C spin lattice relaxation behavior. Solution NMR with HSQC-DEPT supports microstructure analysis and thiol proton identification. EPR spectroscopy confirms radicals from tertiary carbon in the DIB copolymer, with no sulfur-centered radicals (thiyl RS**)** detected (Figure 7) [108].

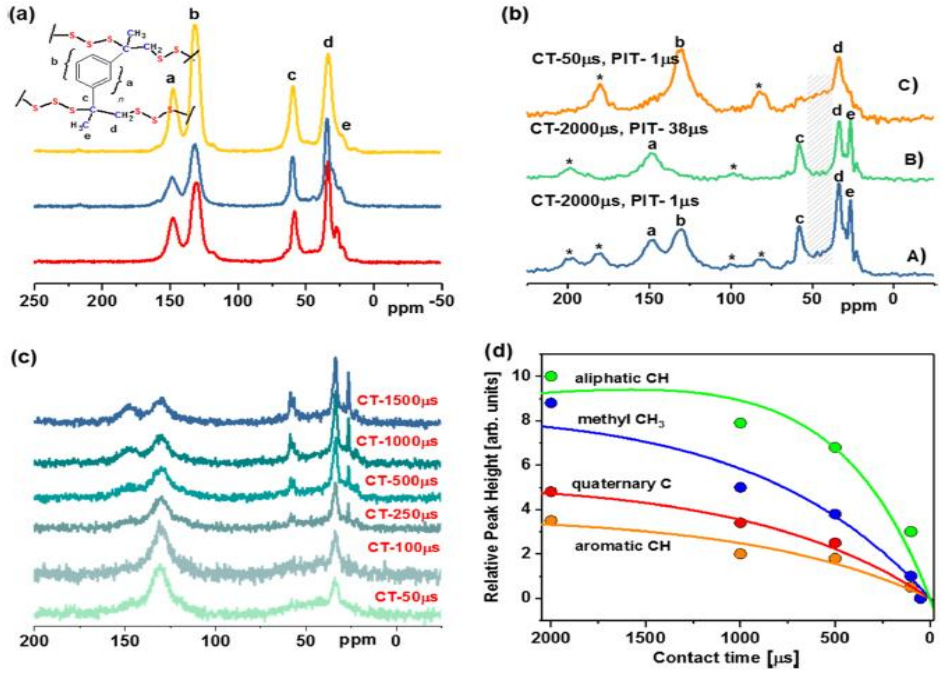

Figure 7. Advanced spectroscopy studies for S-DIB copolymers [108].

The FTIR spectrum of sulfur and divinyl benzene-based copolymer with 50 wt.% DVB shows a peak at 2950 cm^{-1}, indicating methylene stretching in $S–CH_2$ and $CH–CH_2$ units. C–S bond presence is confirmed by signals at 705 cm^{-1}, 1015 cm^{-1}, and 1042 cm^{-1}. As copolymerization utilizes vinylic

unsaturation, the intensity of the band at 900 cm^{-1} for $CH=CH_2$ in DVB decreases. This information helps in understanding the structural changes during the copolymerization process [58, 109]. The FTIR spectra of DCPD and sulfur-based copolymer show a reduction in signals at 3047 cm^{-1} and 1620 cm^{-1} for C=C–H and C=C vibrations, and at 700 cm^{-1} for cis-disubstituted alkene C–H bending, indicating mostly crosslinked material. No signal is detected at 2550–2620 cm^{-1} for thiol groups. This suggests that thiol groups are absent or not significantly present in the copolymer [110].

Raman analysis of sulfur and divinyl benzene-based copolymers shows a decrease in S–S vibrational stretching (239–483 cm^{-1}) and an increase in aromatic stretching (1001 cm^{-1} and 1625 cm^{-1}) with higher divinyl benzene content. A peak at 492 cm^{-1} indicates sulfur presence in Poly(S-r-DVB) with 80 wt.% DVB [102]. X-ray photoelectron spectroscopy is used for microstructure analysis of poly (sulfur-divinyl benzene) copolymer. The elemental composition is assessed with peaks at 285.4 eV and 290.5 eV, where the small peak at 290.5 eV represents the sp^2 carbon of divinyl benzene. The curve shift by ~1 eV at 165 eV indicates a reduction in binding energy for sulfur as it binds to the carbon atom [31].

Molecular Weight

Gel permeation chromatography was used for copolymers soluble in chloroform, calibrated with polystyrene standards. GPC analysis of soluble copolymers S-DIB, S-limonene, S-farnesene, S-farnesol, and S-myrcene reveals varying molecular weights and polydispersity indices (PDI). S-DIB-based copolymer has an M_w of 8000–8450 g/mol and PDI of 8.6–9.5. S-farnesene's M_w is 2290 g/mol with a PDI of 3.0. S-farnesol and S-myrcene are not fully soluble, affecting accuracy. S-farnesol's M_w is 9,770–10,000 g/mol with a PDI of 8.0–8.5. S-myrcene's M_w is 960–1000 g/mol with a PDI of 2.4. S-limonene's polymer has an M_w of 890–900 g/mol with a PDI of 1.8. Increased polydispersity and molecular weight are due to branched molecular architecture [111].

Thermal Properties

Thermal behaviors of sulfur copolymers are used to analyze by DSC studies. For poly(S-DAS) with 10 wt% DAS, the crystallization peak is noticeable. This peak persists until myrcene content reaches 40 wt% in the sulfur copolymer. The lack of a melting peak in other copolymers implies that the sulfur distribution in the polymer chains exhibits a strong random character [111]. DSC study of the copolymer synthesized from sulfur and Botryococcene (BT) reveals a glass transition temperature (T_g) of around 32°C for an S: BT ratio of 5:5. This T_g is higher compared to that of the S-myrcene copolymer [25]. Poly(S-DIB) was synthesized at different weight ratios (30% and 50% DIB), temperatures (110°C and 180°C), and catalyst concentrations (0, 5, 1, and 10%). DSC, performed under nitrogen flow with heating and cooling rates of 5°C/min from –50 to 150°C, showed a T_g around 10°C without a melting peak for sulfur. The T_g increased with higher catalyst amounts. Powder X-ray diffraction patterns for poly(S-DIB) differed significantly from sulfur polymorphs indicating complete ingestion of elemental sulfur [67].

The DSC analysis of benzoxazine and sulfur copolymers reveals that the ring-opening polymerization of benzoxazines occurs between 150°C and 260°C. In the presence of sulfur, the onset temperature for ring-opening decreases to 157°C, with the curing maximum at 182–184°C. Sulfer does not participate in crosslinking but increases the copolymer mass. Higher sulfur content (70 wt% and above) leads to detectable melting endotherms, indicating unreacted sulfur. T_g of the copolymers ranges from 52°C to 66°C, with higher sulfur content resulting in lower T_g. Degradation starts at 210°C, and higher sulfur content leads to greater char yield at 800°C, although the presence of weak S–S bonds lower thermal stability. The char yield is higher for copolymers with 50 wt%, 60 wt%, and 70 wt% sulfur compared to cured polybenzoxazine. No residual sulfur is detected in the copolymer, and the drop in char yield is attributed to the dilution effect of sulfur [112].

Self-Healing Properties

The S-MMA-POSS hybrid material serves as a reactive building block for crosslinked nanocomposites and exhibits self-healing properties. When the cured film is cut and thermally treated

at 120°C for 1 h and 3 h, complete healing is observed after 3 h. At 120°C, the S–S bond breaks, partially disrupting the crosslinked structure and allowing molecular chains to heal the cut. Upon cooling to room temperature, the crosslinked structure is restored [37]. The self-healing behavior is shown in Figure 8.

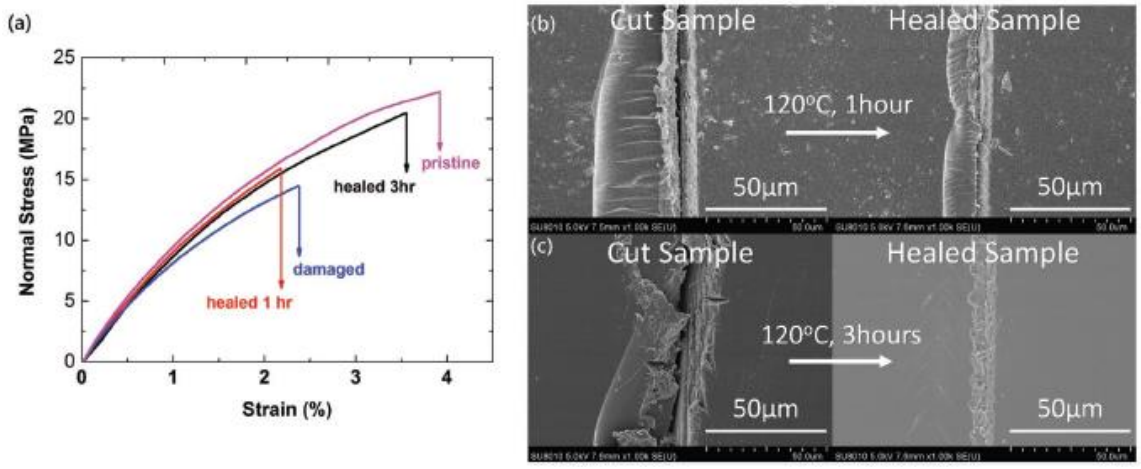

Figure 8. Thermally induced self-healing of S-MMA-POSS sample (a)Stress-strain behavior, (b) SEM images showing healing at 120°C for 1h and (c) SEM images showing healing at 120°C for 3h [37].

Processability

High sulfur-content materials can undergo melt-recast cycles due to the thermal reversibility of S–S bond formation [103]. Recyclability of the material with retention of mechanical strength is achieved in a high sulfur material XS81 [26]. The re-processibility of the material is shown in Figure 9.

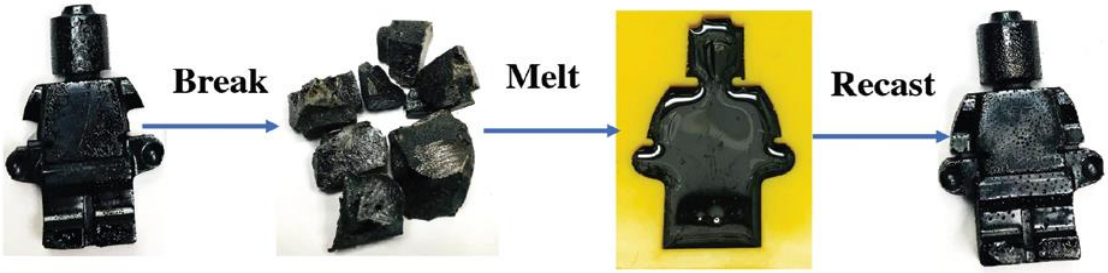

Figure 9. Recyclable high sulfur polymer-breaking and melt processing [26].

Epoxy-based disulfide crosslinked systems have been utilized as re-processable materials. Through hot-pressing experiments at 200°C and 100 bar for 5 minutes, the re-processibility of the dynamic epoxy network was demonstrated. The material, which was broken down to powder, was successfully reshaped [113].

APPLICATIONS

Lithium-Sulfur Battery

Elemental sulfur is an appealing cathode material for high-specific-energy rechargeable lithium cells due to the Li/S couple's high theoretical specific energy (~2600 Wh/kg), as well as sulfur's affordability and nontoxicity. Sulfur can electrochemically react with lithium to form various lithium polysulfides. However, using sulfur as a cathode material in rechargeable lithium cells has been challenging because of rapid capacity fading, attributed to the dissolution of several lithium polysulfides in the electrolyte [114–116].

The cycling behavior and electrochemical characteristics of the sulfur electrode in lithium/sulfur rechargeable cells were studied using galvanostatic cycling and cyclic voltammetry in different solvents. Higher molecular weight solvents resulted in lower capacity fade rates, and the best cell achieved 600 deep cycles above 100 $mAhg^{-1}$ and 400 cycles above 160 $mAhg^{-1}$ (80% of original capacity) at room temperature [116]. Griebel et al. successfully scaled up the production of poly(S-r-DIB) copolymer using a single-step, low-temperature (130°C) inverse vulcanization process, yielding one kilogram of the material. Thermal property studies confirmed that the scaled-up copolymer had identical properties to those prepared on a smaller scale. As a cathode material in Li-S batteries, the copolymer exhibited good capacity and cycle stability [29]. To sequester active sulfur within the electrode and prevent polysulfide dissolution, nanocomposite materials are used to encapsulate the S_8 active phase. Various nanomaterials, such as carbon black with microporous structures (<2 nm), have been explored. Ji et al. demonstrated the feasibility of achieving high capacities by creating highly ordered interwoven composites. The mesoporous carbon framework constrains sulfur nanofiller growth, maintains essential electrical contact, and traps polysulfides formed during redox. Polymer modification of the carbon surface further aids in controlling diffusion and ensures more complete reactions, leading to reversible capacities up to 1,320 $mAhg^{-1}$ [117]. To enhance the mechanical integrity and electrical transport within cathode composites, various materials, such as ordered carbonaceous fillers, high aspect ratio nanomaterials (e.g., nanotubes, hollow nanotubes, solid nanofibers), mesoporous hollow carbon spheres, graphene oxide, and graphene sheets have been employed to create hybrid nanocomposites with sulfur [118–131]. Xiao et al. demonstrated the effectiveness of poly (aniline) nanotubes as reactive reservoirs for sulfur, resulting in partial vulcanization during infusion and improved capacity retention. The electrode maintained a discharge capacity of 837 mAh/g after 100 cycles at 0.1 C and showed stable cycling capacity up to 500 cycles at 1 C [132, 133].

Pyun et al. explored poly (sulfur-random-1, 3-di-isopropenyl benzene) (poly(S-*r*-DIB)) copolymers as active materials. These copolymers possess electrochemical properties like elemental sulfur, making them suitable for use as the active material in Li-S batteries. These copolymers achieve a high specific capacity of 823 $mAhg^{-1}$ at 100 cycles and display improved capacity retention [56]. Simmonds et al. successfully created a poly (sulfur-random-1, 3-diisopropenylbenzene) copolymer through the inverse vulcanization process using DIB. The study examined the performance of Li-S batteries with these copolymers, showing that higher DIB concentrations (5–50% by mass) affected the voltage profiles. Specifically, increased DIB content led to a shift toward lower voltage in charge and discharge profiles. This research demonstrated for the first time that high-capacity polymeric electrodes could be fabricated while also reducing capacity fading, maintaining performance for up to 500 cycles (Figure 10) [134].

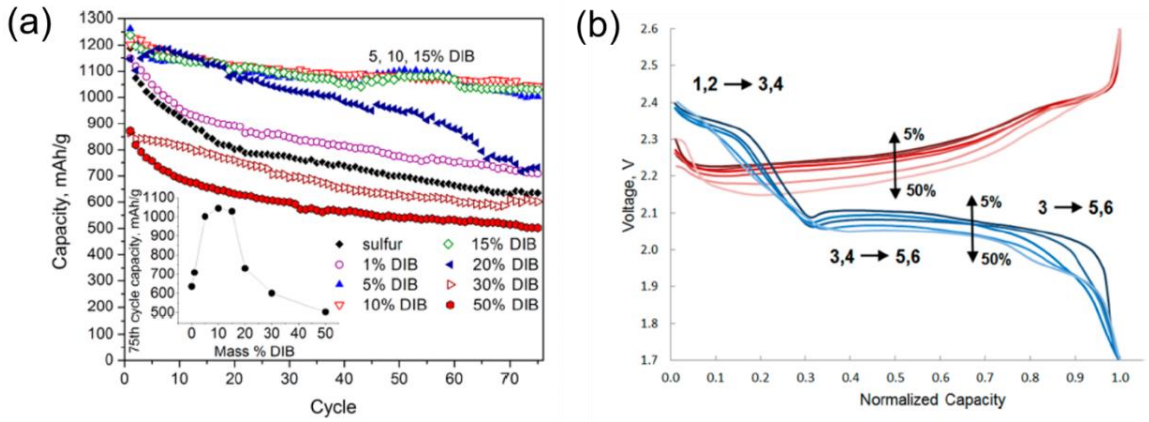

Figure 10. (a) Cycling performance of Li-S batteries from Sulfur copolymers with varying composition 0–50% by mass of DIB and (b) Normalized charge and discharge cycles for copolymer cathodes with different DIB composition [134].

Sulfur-rich polymeric materials with a semi-interpenetrating network (semi-IPN) structure have been developed as a novel lithium-sulfur cathode. These materials are synthesized through copolymerization of elemental sulfur with 1,3-diethynylbenzene (DEB), resulting in a cage-like structure that effectively suppresses polysulfide dissolution and diffusion. This leads to excellent cycling stability and high coulombic efficiency, with an initial discharge capacity of 1143 mA h g^{-1} and capacity retention of 70% after 500 cycles [57].

Wei et al. developed a soluble inverse vulcanized hyperbranched polymer (SIVHP) using a modified inverse vulcanization method. Post-functionalization of poly(S-*r*-DIB) via thiol-ene and menschutkin click reactions yielded a water-soluble copolymer. These were combined with graphene oxide to create polymeric nanocomposite materials for Li-S batteries. The SIVHPs-based cells achieved high initial specific capacities of >1200 $mAhg^{-1}$ and maintained good cyclability after 90 cycles. They also exhibited excellent rate capability, significantly reduced shuttle effect, and maintained stable coulombic efficiency around 100% [59]. Kang et al. synthesized a series of copolymers using sulfur and different allyl ether comonomers. Among these, poly(S-tetra(allyloxy)-1,4-benzoquinone) (poly(S-TABQ)) demonstrated excellent cycling capability, retaining a specific capacity of 833 mAh g^{-1} and a cycling rate of 10°C. This performance is highly beneficial for the fabrication of Li-S batteries [135].

Bhargav et al. studied polyphenylene tetrasulfide polymer as a flexible cathode material for rechargeable lithium batteries. This polymer can be molded into a membrane or cathode by infusing it into a flexible, porous, and conductive scaffold like CNT paper. Both membranes show excellent flexibility and stretching ability. The cathode material exhibits favorable electrochemical performance, including reversibility, high capacity, rate capability, and high Coulombic efficiency, even under strained conditions, meeting the requirements for high-capacity and energy cathode material for flexible lithium batteries [99]. Renewable resources, like cardanol and eugenol, have been used to develop Li-S batteries. Cardanol benzoxazine reacts with sulfur to form a random copolymer with over 80 wt% sulfur content, suitable as a cathode material. Similarly, eugenol-phosphazene monomer reacts with sulfur to create a covalently linked polymer with 83 wt% sulfur, offering flame retardancy and safe cathode material. Additionally, sulfur and squalene-based copolymer has been incorporated into 3D graphene and carbon nanotube networks to fabricate cathodes for Li-S batteries [136–138].

High Refractive Index Material

Inorganic or organometallic monomers have been reacted with sulfur through inverse vulcanization to create materials with a high refractive index (RI). Anderson et al. synthesized Poly(S-r-Se-r-DIB) for the first time in a one-pot process, incorporating Se units via cracking grey selenium precursor and solubilizing liquid sulfur radicals. The resulting CHIP increases the RI above n = 2.0 from 633 to 1554 nm. This material is used to fabricate one-dimensional photonic crystals/Bragg's reflectors, allowing for the selection of desired RI values and creating a large RI contrast [139]. These ultrahigh refractive index (RI) CHIPs have been used to design highly reflective all-polymer Bragg reflectors. This is achieved through the solution fabrication of alternating CHIPs and cellulose acetate films, which generates a high RI contrast [140]. Boyd et al. reported the incorporation of Se in the crystalline sulfur-Se compound at 400°C, followed by polymerization with diisopropylbenzene (DIB). They synthesized poly(S-r-TVSn) by introducing high atomic weight metal Sn with sulfur and the organometallic comonomer tetravinyl tin (TVSn) via inverse vulcanization. These materials exhibited a high refractive index (n) and transmission in the IR region [141, 142]. Poly(S-*r*-DIT), a copolymer from sulfur and 2, 5-diisopropenylthiophene, is a high RI polymer used for fabricating photonic crystals and polymeric distributed Bragg reflectors. It is blended with poly (N-vinyl carbazole) (PVK) to enhance processability [22]. The high RI thin film from the copolymer of sulfur and divinyl benzene (DVB) is produced through sulfur chemical vapour deposition. In this method, polymerization occurs in the gaseous form of sulfur and vinyl monomer [143].

Metal Ion Absorption

Sulfer polymers can effectively absorb metals like mercury, gold and arsenic, etc. The materials used to create sulfur polymers are often low-cost and readily available, making them an economical option

for heavy metal remediation. For environmental remediation, removing various mercury forms from industrial waste is challenging. Inverse vulcanization with unsaturated triglycerides, like canola oil, produces reactive polysulfide sorbents, oxidizing mercury metal to mercury sulfide. Increased temperature improves mercury gas binding rates. Polymer particles milled with contaminated soil effectively remove mercury metal [144]. A method for effectively removing mercury (II) ions from aqueous solutions using poly (BA-ala-co-sulfur) copolymers has been demonstrated by Akay et al. This method is appealing due to the easy synthesis of the sorbent and its strong affinity for mercury (II) ions, supported by solid analytical data. The adsorption capacity of this material is like other non-porous adsorbents. Synthesizing porous poly (BA-ala-co-sulfur) or similar materials can enhance mercury sorption [145]. Sulfur copolymers demonstrate mercury vapor and organomercury compound binding. Gold mining sectors encounter toxic anthropogenic mercury, where copolymer affinity for ionic gold offers a solution [146, 147]. Vojoudi et al. studied silica-based mesoporous SBA-15-S4, synthesized via template method, modified with bis (3-triethoxysilylpropyl) tetrasulfide, effectively removing arsenic As(III) ions from aqueous samples [148].

Controlled Release Fertilizer

A porous polymer was fabricated using canola oil and sulfur with nitrogen, phosphorus, and potassium nutrient salts (NPK) as porogen. The composites, prepared with 50%, 60%, and 70% NPK by mass, showed slow nutrient leaching in soil tests. This slow-release mechanism prevents nutrient waste, even under heavy rain and irrigation. Another study found that sulfur-soybean oil copolymers degraded by soil fungus Aspergillus niger are biodegradable and can act as fertilizers. Spent cooking oil used in these copolymers contributes to the circular economy. Fertilizers released nutrients after 60 days in initial tests, with controlled-release composites reducing nutrient loss compared to free NPK salt. Canola & soyabean oil-sulfur copolymers are also effective for metal scavenging, crude oil remediation, and slow-release fertilizers [13, 15, 27, 149].

Sulfer Copolymer for Concrete Application

Research into incorporating sulfur in concrete has faced durability issues due to sulfur's solid-state transition from monoclinic (S_β) to orthorhombic (S_α) form, causing internal stress. Using chemical modifiers to polymerize sulfur eliminates these transitions, improving concrete performance. Sulfer-based cement is created by mixing sulfer with stabilizers and fillers, like fly ash, furnace slag, talc, and mica, which enhance strength and hardness. Chemical modifiers, like dicyclopentadiene, olefinic polysulfide, and 5-ethylidene-2-norbornene, are used to improve durability. ENB is beneficial due to its lower toxicity, lower melting temperature, and light color, enabling further customization. Modified sulfur maintains stable monoclinic crystals, confirmed by X-ray spectroscopy. Recent research has explored using oleic acid to enhance the mechanical strength of sulfur-based polymeric cements, especially in strong oxidizing acid solutions. These advancements in sulfur-modified concrete hold potential for commercial applications in industries dealing with mercury contamination. The use of sulfur and olefinic plasticizers improves resistance to acids and alkalis, offering a durable and cost-effective solution for construction in challenging environments. Overall, incorporating sulfur and innovative chemical modifiers presents a promising approach to developing more resilient and versatile concrete materials [36, 150–161]. The modified sulfur concrete is known as sulfur polymer concrete (SPC). The moulded object for concrete application is shown in Figure 11.

Bio-Medicinal Application

Munchberg et al. studied the biological activities of garlic polysulfides, including diallyl sulfide, diallyl disulfide, diallyl trisulfide, and diallyl tetrasulfides. These polysulfides demonstrated antibacterial, antifungal, antimicrobial, and antioxidant properties. Preliminary studies showed that diallyl trisulfide exhibited selective activity towards cancer cells [162]. Viry et al. studied the antiproliferative effects of natural tetrasulfides on human breast cancer cells, finding that these effects are mediated through the inhibition of cell division cycle 25 (Cdc25) phosphatases. Diallyl tetrasulfides (from garlic) and dipropyl tetrasulfides (from onion) emerged as effective irreversible inhibitors of the Cdc25 isoforms A and C in vitro. These tetrasulfides significantly decreased the growth of both

sensitive (MCF-7) and resistant (Vcr-R) human breast carcinoma cells [163]. Mossa et al. developed a garlic (Allium sativum L.) essential oil nanoemulsion and studied its acaricidal activity against eriophyid olive mites. GC-MS analysis identified major components of garlic oil, including diallyl sulfide (8.6%), diallyl disulfide (28.36%), dimethyl tetrasulfide (15.26%), di-2-propenyl trisulfide (10.41%), and di-2-propenyl tetrasulfide (9.67%). The nanoemulsion, created via 35 minutes of ultrasonic emulsification, had a droplet size of 93.4, demonstrated high acaricidal activity against eriophyid mites, with LC50 values of 298.225 and 309.634 μg/ml [164]. Panzella et al. studied the antioxidant properties of 5-S-lipoylhydroxytyrosol and its disulfide, trisulfide, and tetrasulfide derivatives. The study found that all four derivatives are efficient hydroxyl radical scavengers, non-toxic, and provide significant protection against reactive oxygen species (ROS) generation and cell damage induced by 400 μM tert-butyl hydroperoxide. These compounds demonstrated greater overall antioxidant activity than hydroxytyrosol [94]. Deng et al. studied the antibacterial activity of a copolymer of sulfur and 1, 3-diisopropenyl benzene (DIB) prepared by inverse vulcanization. The copolymer containing 50 wt% sulfur exhibited good resistance against E. coli, with a 28% bacteria survival rate [12]. The antibacterial activity of the copolymer is explained by the thiolation theory. According to this theory, DIB crosslinked polysulfides react with intercellular thiols like cysteine and glutathione. Bacteria need glutathione to protect against oxidative damage. After deprotonation, glutathione or cysteine becomes nucleophilic and can attack S–S bond polysulfide linkages, forming disulfide, trisulfide, persulfide (RSSH), and hydropolysulfides. Glutathione deficiency occurs as it is consumed during the polysulfide reaction, leading to bacterial death. The DIB crosslinked polysulfide retains its antibacterial properties for a longer time and is more cost-effective than contact-active cationic antimicrobial polymers [165–167].

Figure 11. Molded concrete products from sulfur-based copolymer [36].

Corrosion Resistance

Wen et al. demonstrated that bis-(3-triethoxysilyl propyl) tetrasulfide enhances the super-hydrophobicity and corrosion resistance of self-assembled monolayers (SAM) on 6061 aluminum alloys. SAMs showed good corrosion resistance at 0.10 mol/L concentration and effectively protected the aluminum alloy [168]. Arisawa et al. reported efficient synthesis of diaryl sulfides using a rhodium-based catalyst system. In the presence of RhH(PPh3)4, 1,2-bis(diphenylphosphino) benzene, and tributylsilane, substituted pentafluorobenzenes react with sulfur to generate bis(4-substituted-2,3,5,6-tetrafluorophenyl) sulfides. Di-tert butyl tetrasulfide reacts with reactive aryl monofluorides and substituted pentafluorobenzenes, with reactivity explained by S–S bond energy differences [trisulfide (46 kcal/mol) > tetrasulfide (37 kcal/mol) > sulfur (33 kcal/mol)]. Organo tetrasulfides can be used as metal coatings to increase hydrophobicity and corrosion resistance [169].

Antioxidant

Chauvin et al. studied the use of tetrasulfides as radical-trapping antioxidants (RTA). The RTA activity of polysulfides varies with chain length. Di-tertbutyl tetrasulfide, among the series of mono, di, tri, and tetrasulfide, is particularly reactive towards peroxyl radicals, inhibiting the autoxidation of 1-hexadecene at 100°C and n-hexadecane at 160°C [170].

Chain Transfer Agent

Murthy et al. reported that polyv(styrene tetrasulfide) serves as a chain transfer agent and retarder in radical polymerization of styrene [171]. Ganesh et al. studied the thermal degradation of poly (methyl methacrylate) (PMMA) in the presence of poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST) using thermogravimetry (TG) and direct pyrolysis-mass spectrometric (DP-MS) analysis. Both PSD and PST were found to stabilize PMMA degradation. These polyorgano tetrasulfides can be used as chain transfer agents and thermal stabilizers in radical polymerization [172].

CURRENT CHALLENGES AND FUTURE DIRECTIONS

Inverse vulcanization enables the development of a wide range of sulfur-based copolymers, which can be tailored for specific applications, increasing thermal stability and expanding their use. However, solubility is a significant obstacle for these copolymers. Low molecular weight copolymers are soluble, facilitating characterization, but as molecular weight increases, solubility decreases, complicating characterization with solution NMR and gel permeation chromatography. High sulfur content copolymers may have unreacted sulfur that can leach over time, limiting their application. These factors hinder the commercialization of inverse vulcanized polymers, with only a few systems progressing to commercial scale. Recent developments include sulfur-based composites created through melt mixing in a micromixer, entrapping polysulfur in a nylon matrix via alkyl ammonium polysulfide complex formation [173]. These composites can be processed into threads, sheets, and molded articles. Polystyrene-sulfer nanocomposites using 1,3-diisopropenyl benzene as a crosslinker show high refractive index and antibacterial properties, offering commercial potential. Another class of sulfur-based polymers is polysulfides, formed by reacting sulfur with sodium sulfide to produce sodium polysulfides, which then react with aryl halides via condensation polymerization [60]. The sulfur rank (n=2 to n=9) is crucial for determining structure and properties, with various methods, like ^{13}C NMR, UV-visible spectroscopy, and depolymerization with $AlBr_3$ used for analysis. Advanced NMR techniques and other methods have improved the characterization of inverse vulcanized sulfur copolymers. Most literature focuses on synthesizing new sulfur-based copolymers, their microstructure, and application, with limited information on mechanical strength and rheology for commercial feasibility.

CONCLUSIONS

This review highlights the synthetic aspects of sulfur-based copolymers, showing that various copolymers can be synthesized through inverse vulcanization. Accelerated or catalytic inverse vulcanization is promising for lowering reaction temperatures. The presence of unsaturation (vinylic and allylic) in the monomer is essential for reacting with sulfur, often requiring modification of organic molecules to introduce unsaturation. The main goal of inverse vulcanization is to entrap sulfur molecules within the polymer chain, enhancing thermal stability and reducing sulfur leaching over time. The major applications of sulfur-based copolymers are in Li-S batteries and high refractive index materials. However, solubility remains a challenge, as crosslinking during the reaction can render the material insoluble, restricting its applications. Characterizing the composition and molecular weight of sulfur copolymers can also be difficult, limiting large-scale commercial applications. Improving the thermal stability and solubility of sulfur-based copolymers presents an opportunity for the scientific community to develop highly efficient and novel materials.

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