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# Natural Rubber Composites and Nanocomposites: State-of-the-Art, New Challenges, and Opportunities

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***Abstract***

In this chapter, the we are providing a short versions of all the chapters related to different topics such as natural rubber-bamboo composites for noise control applications, natural rubber-based bio-composites and bio-nanocomposites, mechanical, dynamical/mechanical, electrical, and thermal properties of natural rubber-carbon nanotube nanocomposites and their applications, biodegradation of natural rubber and their composites and nanocomposites, radiative protective qualities of natural rubber-based polymer composites, the use of green additives in eco-friendly compounds based on natural rubber, natural rubber recycling: advances, limitations and applications, elastocaloric effect of natural rubber, and natural-rubber based composites and nanocomposites.

***Keywords*:** Natural-rubber, composites, nanocomposites, elastocaloric, rubber-bamboo, eco-friendly compounds

## 1.1 Natural Rubber–Bamboo Composites for Noise Control Applications

Rubber can be produced in two ways: naturally from the latex of the *Hevea brasiliensis* tree, which is mostly grown in the Far East, or artificially by

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utilizing several processes on petroleum. The *H. brasiliensis* tree is cultivated in tropical parts of Southeast Asia, mostly in Malaysia and Indonesia. It produces latex, which is used to make natural rubber (NR), which is economically marketed [1]. The lengthy entwined coils that make up the natural rubber's polymer chains are always in motion at room temperature. Carbon black has been the most popular reinforcing filler in the rubber industry, particularly tires, for many years. Crude oil is the source of carbon black, which is a non-renewable resource that can eventually run out. As a result, a natural alternative source is required for carbon black in the rubber industry as a reinforcing agent without significantly altering the final products' mechanical and physical qualities. For damping applications, Praveen *et al.* [2] created a styrene butadiene rubber (SBR) compound that is loaded with carbon black (CB) and organo-modified nanoclay.

They discovered that when the filler was loaded, the mechanical characteristics and storage modulus increased significantly, leading to a low damping ratio. Yurkin *et al.* [3] investigated the vibration damping of three viscoelastic composites. The findings indicate that butyl rubber, EPDM, and EVA had damping ratios of 1.38, 0.6, and 0.42, respectively, suggesting that they could be used as viable options for damping applications. A filler is required to improve the mechanical, chemical, and physical qualities of elastomers when they are used in vibration damping for vehicles, railroads, and aircraft. Fillers have a significant impact on how rubber composites behave in a viscoelastic manner. NR completely satisfies the requirements for cut resistance, flex-fatigue resistance, and tensile qualities of final goods [4]. Except for rubber, all materials are specified as part per hundred rubber (PHR) or the quantity needed for 100 rubbers. A tire rubber compound should offer the best possible performance. For the best grip, the largest coefficient of friction must exist between the wheel and pavement. Simultaneously, the rolling resistance can be decreased to enhance fuel efficiency [5]. Materials with extremely small particle sizes are added to the RB mixture in powdered form as fillers or reinforcement additives [6]. Fillers are used to strengthen rubber, make it easier to process, and lower the cost and color of the material. Fillers can be either organic or inorganic and can be dry powders. Fillers are typically utilized to provide elastomers with the desired characteristics in commercial applications. The primary motivation for this is to lower costs and enhance compositional qualities. Fillers can be divided into two categories based on their color and impact. They can be separated and categorized into three types of fillers: semi-active, inactive, and active (reinforcing). Carbon blacks are known as black fillers, including silica, talc, calcium carbonate, talc, and zinc oxide, are known as white fillers [7].

In 2014, 32 million tons of wood and textile waste and 68 million tons of paper waste were produced in the United States, accounting for

approximately 39% of the country's annual municipal solid waste burden [8]. The Central Pollution Control Board (CPCB) in New Delhi conducted research that indicated that the proportion of trash generated in India comprises components of several materials ranging between 3%–5% and 1%–5%. Overall, the unfavorable noise resulting from improvements in mechanical tools has proven to be a more complicated issue. Following this principle, waste products from the processing of fabrics and corn can be mixed with waste products from the processing of paper to produce a substance that absorbs sound and reduces noise pollution [9]. With time and living progress, noise contamination and mechanical oscillations have become inevitable problems in human existence. The need for a better living environment is growing, and people can no longer be exposed to mechanical vibrations and the noise they produce. Furthermore, mechanical vibration shortens machine life and reduces precision [10]. Global bamboo production is estimated to be 20 million tons (MTs) per year, with 10 MTs originating from China, Japan, and India [11]. Bamboo finds its use in a wide range of industries, including apparel, food, furniture, flooring, and interior design. Over the past few decades, there has been increased interest among researchers in the thermochemical conversion of waste bamboo into products rich in carbon and biochar. Researchers have developed a spectrum of damping materials using various methods. The two most common modification strategies are the addition of functional reinforcing fillers to the IIR matrix or their mixing with other fillers to generate composite damping materials. Nanofillers have a large specific surface area that allows them to penetrate deeply into the rubber matrix. Carbon nanotubes, talc, and carbon black are joint-strengthening fillers. To improve the mix of filler and rubber from an environmental perspective, Tang *et al.* [12] substituted waste recycled red brick powder with the conventional filler carbon black and silica in styrene-butadiene rubber (SBR). The production costs were reduced, while the tensile characteristics were improved.

Lignin is a possible reinforcing material for polymeric materials because of its high stiffness, which is attributed to its aromatic portion and intramolecular solid/intermolecular contacts [13]. The butyl rubber's qualities can be enhanced by curing IIR with phenolic resin modified by lignin. Butyl rubber is a hydrophilic substance that absorbs moisture during use because it contains polar functional groups. Owing to their low thermal stability, classic damping materials typically have a limited-service life. Therefore, the development of damping materials with good moisture resistance and thermal stability is crucial. Rubber is a common material found in various products. Several common rubber products that we encounter daily are rubber bands, shoes, and gloves. Because rubber products may return to

their original shapes after being stretched or twisted, they are classified as elastomers. Rubber is an elastic substance that can be produced both naturally and artificially. Given that NR is an organic material, its characteristics are dictated by the biochemical mechanism by which the plant produces resin. Unlike synthetic rubber, NR polymerization cannot be changed. Natural rubber cannot be altered after it is removed from the plant. The modified forms of natural rubber that are considered significant are epoxidized natural rubber, poly (methyl methacrylate)-grafted natural rubber, hydro-halogenated natural rubber, cyclized natural rubber, depolymerized liquid natural rubber, resin-modified natural rubber, and poly (methyl methacrylate)-grafted natural rubber.

Mechanical oscillations and noise pollution have become unavoidable issues in human life as time and life have evolved. People are increasingly in need of improved living conditions, and they are unable to tolerate the noise and vibrations caused by machinery. Moreover, mechanical vibrations decrease the precision and shorten the life of the equipment. Sound-absorbing materials exhibit excellent dampening properties and a wide range of possible applications. Rubber-like materials offer excellent viscoelasticity, friction, and damping capabilities. These rubbers usually have a high relative molecular mass and strong molecular chain interactions, including polar, hydrogen, and ionic interactions. These RBs are used as dampers in various industries, including trains, aircraft, and cars. This study analyzed and highlighted natural bamboo rubber composite materials for successful noise and vibration control.

## 1.2 Natural Rubber-Based Bio-Composites and Bio-Nanocomposites

Sustainable materials, alternatively known as "green" or eco-friendly materials, are currently receiving a lot of attention and are characterized as inexpensive renewable resource materials that are locally produced without causing any kind of harm to living beings [14]. Bio-composites and bio-nanocomposites are not regarded as sustainable if one or more of their parent materials are regarded as eco-unfriendly or if their production process poses serious harm to the environment and human health [15]. Examples include composites that contain synthetic fillers such as carbon black (CB), silica, and carbon fiber, and/or synthetic polymers such as polyethylenes, polybutadienes, polypropylenes, polystyrenes, polyesters, butyls, nitriles, nylons, epoxies, vinyls, and acrylated, chlorinated,

fluorinated, and sulfonated polymers [16]. In contrast to bio-composites, which are composed of natural fiber particles that are not on the nanoscale, bio-nanocomposites consist of particles with one, two, or three dimensions of less than 100 nm [17, 18]. Furthermore, composites are generally divided into different classes, with *class 1* comprising composites reinforced with a specific filler and *class 2* encompassing structural composites [19].

Bio-composites and bio-nanocomposites can also be prepared using natural rubber (NR), which is mainly harvested as latex from rubber trees (*H. brasiliensis*), as their base polymer. There are two types of natural rubber: *cis-1,4-polyisoprene* and *trans-1,4-polyisoprene*. The former is a typical bio-based elastomeric matrix for bio-composites and bio-nanocomposites. Moreover, although they are currently in the research and development stage and do not have many applications except in the automotive sector, these composites are expected to play a significant role in the future, particularly in building and construction, sports equipment, agriculture, aerospace, marine, and several other sectors that manufacture goods related to engineering [20–22]. The primary goal is to provide an overview of natural rubber-based bio-composites and bio-nanocomposites, with a particular emphasis on their preparation, properties, as well as long-established and possible applications. Despite being a type of natural fiber (particularly mineral fiber), asbestos is also associated with health concerns owing to its carcinogenic properties [23]. Nevertheless, a variety of plant and animal fibers as well as minerals (such as chalk, limestone, talc, silica (silicon dioxide), and montmorillonite) are still easily accessible. In contrast to the production of avian fibers and silk fibers by birds and chickens, as well as the domestic silk moth, other mammals' hair and fur are sources of cashmere, shearling, Persian, shahtoosh, angora, mohair, and bison wool [24, 25]. Among these, cashmere wool is the most popular owing to its comparatively low density and extremely plush and sumptuous texture [26]. Eggshells, seashells, and cuttlebones have recently been proposed as possible sustainable sources of animal fibers. Therefore, it is possible that the exploration of animal fibers for composites would considerably depend on the presence of protein-based constituents.

In contrast, polysaccharides, particularly crystalline cellulose, semicrystalline chitin, amorphous hemicellulose, and lignin, are the primary chemical components of plant fibers for composite use [27]. The literature indicates that the presence of cellulose, chitin, hemicellulose, or lignin in plant fibers is the key reason why they are substantially beneficial for composite application. Natural rubber (NR)-based bio-composites are an important example of rubber composites that have recently attracted considerable interest in both academia and industry, particularly in terms

of their properties, performance, applications, and sustainability [28–31]. These composites, in which NR is mainly *cis-1,4-polyisoprene*, are generally referred to as "green" or eco-friendly materials, where a mechanically and/or chemically transformed natural fiber, serving as a reinforcing filler, is dispersed efficiently in a solid or latex NR matrix [32]. Both NR and natural fibers, which are derived from natural systems, contribute to the outstanding properties and high performance of NR-based bio-composites [33, 34]. Moreover, as various natural fibers and rubbers usually have varied properties, it is expected that the properties (and performances) of NR-based bio-composites will vary for different NR-based bio-composites. This is because the way the matrix transfers stress to the employed fiber determines the mechanical properties of the NR-based bio-composites. NR-based bio-composites comprising plant fibers have been investigated more frequently than those comprising animal fibers, minerals, or mineral fibers. In addition, solid NR has been investigated more for NR-based bio-composites than NR latex. As a result, additional research on the reinforcement of NR-based bio-composites using mineral and animal fiber-sourced fillers, as well as related studies with NR latex, is necessary. Currently, the second most researched bio-filler sources for NR-based bio-composites are palm oil and chitosan. Sugarcane bagasse (also known as megass or bagasse) is another source of key fibers that are widely used as bio-fillers worldwide, with nearly 23,000 and 48.84 lakh registered sugarcane growers in South Africa and India, respectively. The long-established and potential applications of NR-based bio-composites include soles, belts, straps, gloves, hoses, furniture, caskets, sports equipment, brush bristles, architectural elements, and point-of-sale displays, as well as various storage, packaging, and gadget materials [35].

Nonetheless, studies published thus far makes it abundantly evident that the automotive sector is comparatively the one that has made the greatest use of NR-based bio-composites [36]. For instance, the utilization of natural fibers has increased by 73% at Mercedes-Benz, in addition to approximately 10,000 tons of bio-composites that Bayerische Motoren Werke (BMW) utilized in 2004. The C-, S-, E-, and A-class cars of the 164/251 2004 model from Mercedes-Benz had their dashboard support, as well as the surface of the seats and backrests made of NR/coconut fiber bio-composites. Moreover, Shahril *et al.* [37] suggested the use of NR/Kenaf fiber bio-composites to create rubber mounts for automotive engines, whereas Patil *et al.* [38] suggested the use of NR/Coir bio-composites to manufacture insulations, mattresses, toys, and automobile tires. NR latex foam/chitin bio-composites, according to Zhang *et al.* [39], offer strong

practical value for future applications and may be broadly utilized in home products, including pillows, beds, and cushions.

The development of natural-based bio-nanocomposites, incorporating nanometer-scale reinforcing bio-fillers such as nanocelluloses, shows their potential to impart improved properties at lower volume fractions compared to macro- or micro-sized fillers [40, 41]. It provides an excellent matrix for studying filler reinforcement effects, allowing the tailoring of properties through the addition of reinforcing fillers with diverse surface chemistries and aggregate size/aspect ratios [42, 43]. Bio-based polymer nanocomposites represent a novel class of sustainable materials derived from bio-renewable sources. There is a growing demand for reinforcing fillers sourced from renewable materials in the research field, owing to their biodegradability, superior mechanical properties, cost-effectiveness, environmental friendliness, biocompatibility, ease of processability, and low density. To develop sustainable polymer nanocomposites, bio-fillers such as chitin, cellulose, and lignin have garnered significant attention among scientists. As highlighted earlier, NR is a biopolymer, and the incorporation of bio-derived nanofillers into NR holds promise for producing environmentally friendly polymer nanocomposites with exceptional properties.

## 1.3 Mechanical, Dynamical/Mechanical, Electrical, and Thermal Properties of Natural Rubber-Carbon Nanotube Nanocomposites and their Applications

NR has attracted significant scientific and industrial interest owing to its excellent elasticity, flexibility, high tear, general fatigue resistance, low heat build-up, high resilience, retention of strength at elevated temperatures, and superior mechanical and dynamic properties [44]. Owing to its elasticity, resilience, and toughness, NR is used in transportation (e.g., tires), industrial (sealants), consumer (rubber boots, sports materials), hygienic, and medical sectors, and several others. NR was subjected to different modifications to form maleated natural rubber (MNR) and epoxidized natural rubber (ENR). NR in the vulcanization process in the presence of sulfur, an accelerator, and other compounding ingredients, and exhibits excellent mechanical properties owing to the strain-induced crystallization phenomenon [45]. The exceptionally high tensile strength compared to other carbon materials makes them suitable for developing high-performance composite materials for their applications as efficient vibration and shock

absorbers [46], biomedical applications [47, 48], tires for cars, buses, and even airplanes [49]; automotive parts, such as bearings, seals, o-rings, oil filter gaskets, manifold gasket brake pads, airbags, drive couplings, springs and window seals, and toys [50]. Mensah *et al.* [51] observed the important role of morphology, dispersion, and functionalization of CNTs in the preparation of NR/CNT nanocomposites in achieving the desired mechanical properties. Thomas *et al.* [52] studied the effect of 1-octadecanol functionalization on acid-treated carbon nanotubes. Subsequently, NR/CNT composites were prepared by adding sonicated CNT (in toluene) to rubber already dissolved in toluene, followed by compounding in a two-roll mill. These findings showed better dispersion of functionalized CNT in the natural rubber matrix compared to the non-functionalized CNT in the NR matrix, as evident from the TEM images. Conductive nanocomposites of NR/CNT by solvent-cast suspensions followed by vulcanization [53] and solution mixing using an ultrasonicator [54] also produced a homogeneous dispersion of CNT.

Investigations have also been conducted to study the effects of *in situ* functionalization of MWCNT with bis(triethoxysilylpropyl) tetrasulfide (TESPT) and 3-aminopropyltriethoxysilane (APTES) as silane coupling agents on the properties of the corresponding ENR/CNT composites. Anand and his co-workers [55] used SDS to enhance the dispersion of SWCNTs in water and this stabilized aqueous solution of SWCNTs was used in the preparation of NR nanocomposites through the latex compounding method. In addition, it resulted in a 4% enhancement in the 300% modulus and a 5% decrease in the Akron abrasion loss compared with those of the NR/CNT composites. The observed enhancement in the mechanical properties could be attributed to the dispersion of CNT in NR and the bonding between the WPRP and the NR matrix. The tensile strength and tensile modulus of the NR/SWNT (2 phr) nanocomposite prepared by latex compounding through surfactant-assisted sonication were significantly enhanced compared to those of NR. Guo *et al.* [56] improved the dispersion of CNT in NR by using waterjet-produced rubber powder (WPRPP) as a carrier. The resulting composite comprising 5 phr of WPRP exhibited an approximately 3% oncrease in the tensile strength. Mohamed *et al.* [57] measured the mechanical properties of MWCNTs in NR latex nanocomposites following the enhanced dispersion of surfactants bearing phenyl groups. Rubber nanocomposites were prepared by incorporating CNT in addition to carbon black into the NR, which significantly improved the tensile strength, hardness, and tear strength of the NR system up to a threshold CNT content of 2 phr [58]. A possible reason for

this is the homogeneous dispersion and effective interaction between the CNT and the NR. Wang *et al.* [59] fabricated CNTs@CNC (cellulose nanocrystal)/NR nanocomposites with a 3D hierarchical conductive network following a latex assembly approach.

Jahed *et al.* [60] reported mechanical properties of NR/ethylene propylene diene monomer (EPDM)/ MWCNT composites were prepared in an internal and a two roll-mill mixer in two steps. They observed that the tensile strength and modulus at 300% of NR/EPDM/MWCNT nanocomposites were enhanced by the filler content, functionalized MWCNT, and compatibilizer; however, the elongation at break decreased. Abdullateef *et al.* [61] observed a reduction in the volume resistivity of CNT incorporated in the NR matrix (~5 Ω·m). In contrast, the surface-modified CNT-based NR composite showed an increase in resistivity (~13 Ω·m). In another study, Nakaramontri *et al.* [62] investigated the electrical conductivity of epoxidized NR filled with 1 phr of CNT (1 phr), CNT functionalized with bis(triethoxysilylpropyl) tetrasulfide (CNT-TESPT), and 3-aminopropyltriethoxysilane (CNT-APTES) prepared by *in situ* functionalization. Aguilar-Bolados *et al.* [63] measured the electrical properties of hybrid nanocomposites comprising a combination of few-layer thermally reduced graphite oxide (TRGO) and multiwall carbon nanotubes (MWCNTs) mixed with NR. They observed an increase in the electrical conductivity of the polymer by approximately 13 orders of magnitude for a combination of 2 wt.% TRGOs and 2 wt.% MWCNTs hybrid filler. This is ascribed to the can be attributed to the formation of a highly interconnected percolation network. Nanocomposites have made major contributions in the field of flexible and stretchable electronics such as sensing, aerospace, non-metallic flexible capacitors, and robotic arms. It is anticipated that these carbon-nanotube-reinforced natural rubber nanocomposites may have major contributions in the aerospace sectors, robotic arms, sensors, nonmetallic flexible capacitors, and many other fields. Natarajan *et al.* [64] investigated the sensing performance of natural rubber nanocomposites filled with MWCNT, CB, and their combinations operating from 50% to 150% strain depending on the ratios of the two-filler system. They concluded that these elastic materials could be used in structural health monitoring and sensors in different dynamic elastomeric parts such as tires, valves, gaskets, and engine mounts. In another study, piezoresistive CNT-filled rubber-based composites were used to determine the strain sensing application and main mechanisms underlying the conductivity of NR/CNT composites at different strains [65].

## 1.4 Biodegradation of Natural Rubber and their Composites and Nanocomposites

Aerobic biodegradation uses oxygen in chemical reactions that break down degrading substances [66–69]. The end product of the degradation process is carbon dioxide or methane. Anaerobic digestion, on the other hand, is a series of processes in which microorganisms break down biodegradable materials in the absence of oxygen. Anaerobic biodegradation is widely used to treat wastewater sludge and biodegradable waste because it provides volume and mass reduction of the input material [70–73]. Recent research has focused on improving the properties of biopolymer composites, including starch-based materials, cellulose-derived polymers, bacterial polyesters, and natural rubber composites [74]. The blending process, which involves the addition of biofillers (such as agricultural waste, cellulose, and ash), can be used to modify the properties of biopolymer composites. Biodegradable polymers have a wide range of applications in electronics, including in dielectric material, electronic packaging, insulators, and (semi) conductors [75]. Diverse biodegradation environments, such as soil, aquatic settings, landfills, and compost, present unique conditions, and host distinct microorganisms. For instance, fungi assume a pivotal role in soil, predominantly facilitating the degradation of organic matter, including polymers. In aquatic environments, two types of bacteria, surface and sediment bacteria, dominate, and their concentration diminishes as depth increases [76].

Research on bio-nanofillers made from biomass has accelerated because of the need for fillers other than petroleum-based fillers. Bio-based nanocomposites occasionally exhibit special benefits over conventional inorganic nanoparticles [77]. NR are frequently used in cellulose whiskers, chitosan, starch nanocrystals, and other bio-nanofillers. The goal of these filler investigations is to produce them at a production cost that is comparable with other petroleum-based fillers while maintaining equivalent qualities [78]. Furthermore, it is anticipated that the bio-based fillers' biocompatibility and biodegradability will be preserved after their dispersion in the NR matrix [79]. While cellulose nanocrystals are 100% crystalline, starch nanocrystals contain approximately 45% crystalline content. To produce starch nanocrystals from waxy maize starch, starch granules were mixed with a known concentration of $H_2SO_4$ solution and stirred at a specific speed with orbital shaking. Following various durations of hydrolysis, the resulting suspension was washed with distilled water until neutral pH was achieved [80]. Angellier *et al.* [81] synthesized nanocrystal platelets

from waxy maize starch, characterized by dimensions of 6–8 nm thickness, 40–60 nm length, and 15–30 nm width. These starch nanocrystals, present in an aggregated form, exhibit an average size of 4.4 mm. This study also examined the properties of unvulcanized natural rubber (NR) reinforced with these nanocrystals. The resulting films were conditioned at 0% relative humidity (RH).

The elongation at break of the NR filled with starch nanocrystals decreased with increasing nanocrystal content, dropping from 1960% (unfilled) to 920% (30 wt.%). Conversely, the tensile modulus experiences almost exponential growth with starch content, rising from 0.64 MPa for the unfilled NR matrix to 77.8 MPa for composite films filled with 30 wt.% of starch nanocrystals. However, at higher filler contents (e.g., 20 wt.%), there is a reduction in tensile modulus when exposed to 43% RH compared to the same loading at 0% RH. Furthermore, the elongation at break decreases to 1,500% for filler loadings of 5–20 wt.% at 43% RH. This deterioration in the properties of starch nanocrystal-filled NR at a high moisture content or RH is attributed to the hydrophilic nature of the starch nanocrystals. According to Ismail *et al.* [82], who studied the incorporation of chitosan as a new type of filler in rubber compounds, one of the most important requirements for chitosan to be successfully employed as a filler is ensuring good interaction with rubber at a reasonable loading level, with the loading level being the amount or concentration of chitosan added to the composite. The hydrophobicity of rubber and the hydrophilicity of chitosan were cited as reasons why the rubber–filler interaction weakened with the addition of chitosan and further weakened with higher chitosan loading.

## 1.5 Radiative Protective Qualities of Natural Rubber-Based Polymer Composites

Natural Rubber (NR) is known for its flexibility and good resistance to extreme temperatures. As such, NR is not recommended as EMI shielding because of its poor conductivity and SE value. However, composites of natural rubber with some metals as fillers can enhance the conductivity and SE of the NR composite materials. Many researchers worldwide are conducting experiments to develop better EMI shielding materials using NR as part of their composite matrix. Zhan *et al.* [83] attempted to enhance the EMI shielding properties of natural-rubber-based supercritical $CO_2$ foams. The authors have developed an EMI Shielding material comprising NR/

CNT composites. In addition, the authors concluded that the addition of CNT to the NR matrix enhanced the EMI Shielding effectiveness and electrical conductivity of the NR/CNT composites. Wang *et al.* [84] developed $Ti_3C_2T_x$ MXene/NR composite to have a better EMI Shielding material. In the study, authors modified the structure of the matrix from brick-mortar to honeycomb structure by the help of vulcanization reaction. It is observed that the SE value of the composite matrix with a honeycomb structure is 63.5 dB when compared to that of 57.1 dB. Jeevakumari *et al.* [85] investigated the role of conductive graphene nano platelet and cobalt nano wire in the natural rubber matrix in enhancing the mechanical property of the composite material.

This proves that, the addition of graphene nano platelet and cobalt nano wire to NR matrix enhances the SE and mechanical properties of shielding material. Rashid *et al.* [86] studied the EMI shielding effect by adding PANI (polyaniline) and NiFe (nickel ferrites nanoparticles) to the natural rubber. The authors attempted to prepare three combinations (NBR/PANI, NBR/NiFe, and NBR/PANI/NiFe) of the composite to understand the effect of additives on the NBR matrix. The electromagnetic interference shielding effectiveness of Natural Rubber (NR) and Ethylene Vinyl Acetate (EVA) with conductive short carbon fibers (SCF) and carbon black was studied by Das *et al.* [87]. In this study, an attempt was made to compare the shielding effectiveness (SE) of two different composites. Kanking *et al.* [88] have developed the NR polymer composite in which bagasse fiber ash (BFA) was used as filler along with carbon black or precipitated silica. The authors attempted to replace carbon black or precipitated silica in polymer composites. However, the study shows that the mechanical properties of both BFA:CB/NR and BFA:Psi/NR composites are reduced by the addition of BFA to the polymer matrix. Ninyong *et al.* [89] have used lead as filler particles in natural rubber (NR) based polymer composites. The study revealed no significant improvements in the curing characteristics upon adding lead to the natural rubber matrix as lead does not interact chemically with the rubber matrix, whereas wood/natural rubber composites were found to be better than natural rubber composites.

## 1.6 The Use of Green Additives in Eco-Friendly Compounds Based on Natural Rubber

In a study by Dasgupta *et al.* [90], natural rubber (NR) compounds containing various vegetable oils (soybean oil, castor oil, etc.) were compared

to compositions of aromatic, naphthenic, and paraffinic oils with low levels of polycyclic aromatic compounds (PCA). The addition of these oils affected the action of the vulcanization system, resulting in low ML, MH, and optimum vulcanization time ($t_{90}$) in relation to the compounds containing conventional petroleum-derived oils. Da Costa *et al.* [91] conducted a study on castor oil used as an activator in the process of NR vulcanization using compositions containing silica. They observed that neat castor oil did not show a significant improvement in vulcanization characteristics. However, when castor oil was combined with stearic acid, better performance was achieved. This effect was attributed mainly to the castor oil lubricant, which promoted an improvement in the vulcanization characteristics. Gujel *et al.* [92, 93] studied the effect of the incorporation of soybean oil in ethylene-propylene diene monomer rubber (EPDM). The results showed that vulcanization properties were affected, and there was a reduction in vulcanization and, consequently, a reduction in the processing time. Another conclusion was that the incorporation of 10 phr of soybean oil (MD600) reduced the amount of lubricant oil required by approximately 60%. Jayewardhana *et al.* [94] analyzed the reason for a better dispersion of fillers such as carbon black on NR matrix containing vegetable oils.

In this case, the interactions between the long chains of unsaturated fatty acid esters of vegetable oil with the polar groups present on the surface of carbon black (phenol, carboxyls, and lactones) and the non-polar interaction of these oils with the molecules of NR provided such a result. Some additives that are used are unsafe to human health and may cause illnesses. NR latex is widely used as medical items like gloves, catheters, among others. Dithiocarbamate accelerators, commonly used in NR latex, are likely to cause allergies, which can be avoided by changing the sulfur vulcanization by radiation vulcanization [95–97] or by peroxide curing. Concerning the environmental problems related to zinc, water pollution by the zinc contained in rubber formulations mainly occurs indirectly because the disposal of waste in the soil (mainly due to the natural wear of tires) is of great concern to the environment because of the contamination of surface water bodies or groundwater. Human health, aquatic fauna, and flora are polluted by inorganic pollutant residues. Organisms may also be sensitive to toxic actions, such as bioaccumulation, affecting the food chain and endangering the organisms located at the top of the chain [98, 99].

## 1.7 Natural Rubber Recycling: Advances, Limitations, and Applications

The application of granulated vulcanized elastomer in equestrian soils [100] has been shown to be promising. The granules, incorporated into other materials and sand, provide horse cushioning during the race and impulse in jumps, due to the elasticity and flexibility of the material, so muscle and joint problems can be minimized in the animals. Unlike pure sand, the compound does not produce such an amount of dust during the exercise of the horses, in addition to avoiding excessive wear of horseshoes. The same can also be applied to the comfort of other large animals such as cattle. Similarly, athletes of different sports have demonstrated the advantages of recycled rubber in multi-sport courts because of characteristics such as elasticity, shock absorption, drainage, and high strength [101]. Rattanasom *et al.* [102] studied the vulcanization characteristics and mechanical properties of polymeric blends raw NR/recycled NR (rubber powder). The results indicated that the scorch time and optimum vulcanization decreased with an increase in the incorporated residue content. Regarding the mechanical properties, an increase in the modulus at 100% and 300% elongation was observed because of the increase in elastomeric stiffness resulting from the increase in the residue concentration. In rubbers such as NR, SBR, and EPDM, this capacity is low and can be improved by the incorporation of another material in the formulation with a higher microwave absorption capacity. Carbon black, a filler widely used in rubber goods such as tires, can be used as a conductive filler [103, 104], which induces a phenomenon known as Maxwell–Wagner polarization [105]. According to De *et al.* [106], a large number of chemical reclaiming agents such as diphenyl disulfide, dibenzyl disulfide, diamyl disulfide, bis(alkoxy-aryl) disulfides, butyl mercaptans, thiophenols, xylene thiols, other mercaptans, phenol sulfides and disulfides, iron oxide phenyl hydrazine-based catalysts, and copper chloride-tributyl amine catalyst have been used for the treatment of scrap ground rubber crumbs or powders at elevated temperatures. Desulfurization of ground rubber is performed by bacteria and fungi, which can convert cross-linked sulfur to simple sulfur compounds or inorganic sulfate [107]. This method is considered ecofriendly because it does not use chemicals or energy. On the other hand, some disadvantages are that the process is slow, only superficial devulcanization/desulfurization occurs, and some additives may inhibit the function of bacteria [108] and reduce the culture responsible for the process due to toxicity.

## 1.8 The Elastocaloric Effect of Natural Rubber

Refrigeration technology is considered as one of the most transformative engineering achievements of the 20th century [109, 110]. Despite its enormous social benefits, its use in various applications incurs significant environmental costs [111]. For this reason, there has been growing interest in developing alternative refrigeration technologies over the last few decades [112]. Natural rubber (NR), a promising elastocaloric material, is a natural polymer comprising isoprene as its main component. NR has a high strength [113, 114] and resistance to crack expansion [115–117]. It is environmentally-friendly, recyclable, low cost and non-toxic [118–120]. Its most notable physical property is its low modulus of elasticity [121, 122]. Moreover, it condenses under normal ambient conditions, whereas it is rarely studied at low temperatures. Sebald *et al.* [123] investigated the effect of fatigue on the thermal effects of NR elasticity. The engineering strain cycles at different amplitudes were investigated experimentally, and it was observed that the number of natural rubber fracture cycles in the experiment was limited (approximately 800 cycles). This indicates an extremely short fatigue life. The experiments mainly investigated the fatigue dependence of the elasto-thermal effect in three small-amplitude strain states with strain amplitudes of 3 for strains 0–3, 2–5, and 4–7.

British physicist Gough [124] first discovered the elastocaloric effect of NR in the early 19th century and proposed related concepts. Gough's theory was confirmed 50 years later by Joule [125].

Gerlach *et al.* [126] proposed that a heat pump or refrigeration system operating with rubber as the elastic thermal mass is divided into four paths: adiabatic stretching, isothermal stretching, adiabatic shrinkage, isothermal shrinkage. Tianying [127] independently constructed a cyclic stretching experimental bench. The elastocaloric effects of different rubber materials were investigated in experiments where the Mullins effect was eliminated. The lab bench consisted of two main parts. The first part was an FLS40 series screw linear module with a controller, drive, and DC power supply. The second part is a self-designed fixture fixed on the module, which is composed of an aluminum plate that is tightened by nuts to fix the rubber. Farris [128] designed a small rubber fiber engine. Confirmation of the high-power potential of these engines when using modern elastane fiber designs. A specific cooling power of 1 W/g was applied at a temperature difference of 30 K between the heat source and heat sink. This demonstrates the high-power potential of engines using elastane fibers. Lyon *et al.* [129] performed thermomechanical cycling experiments on two polyurethane

elastomers at different strains and temperature differences. The two elastic fibers used in the experiments were commercially available polycondensate yarns. Zhongjian *et al.* [130] investigated the effect of pre-stretching on the thermal effect of NR elasticity. Compared to deformation without pre-stretching, pre-stretching can skip the low elastic heat coefficient region and move directly to the high elastic heat coefficient region induced by the SIC. In particular, the elastic thermal coefficient reaches its maximum value when pre-stretching is applied before SIC. The elastic thermal coefficient decreased again when pre-stretching was applied to the SIC. In addition, the stress input is maximum when pre-stretching is applied at the beginning of SIC.

Aprea *et al.* [131] studied the application of thermal effects in heat pumps: application of acetoxy silicone rubber and vulcanized natural rubber to active thermal storage heat pump systems. A comparison between electrothermal, piezothermal, and magnetothermal materials was performed. The system consists of a cold heat exchanger (in contact with the outdoor environment), hot heat exchanger (in contact with the indoor environment), parallel-plate heat accumulator made of thermophysical material, and auxiliary fluid (water).

## 1.9 Natural Rubber-Based Composites and Nanocomposites

Natural Rubber as a polymer matrix for applicational level composites are important because of its wide applications, but it generates vast amounts of waste. At the same time, special consideration is given to NR composites made with natural fillers, such as cellulose and starch. Natural fillers are particularly significant in the realm of environmentally friendly composite applications owing to their widespread availability, low cost, and straightforward manufacturing processes [132]. The abiotic degradation of NR involves hydrolysis of rubber by water. Hydrolysis in rubber refers to the chemical breakdown of the polymer and the resulting physical breakdown or crumbling of rubber. This process was accelerated by warmth and high humidity. NR can undergo hydrolysis in water under certain conditions. One methods for degrading NR by hydrolysis is hydrous pyrolysis [133]. The biodegradation of NR is influenced by several factors, including the properties of the polymer (such as molecular weight, crystallinity, presence of functional groups, substituents, or additives), the specific microorganisms involved, and any pretreatment applied to the polymer [134].

NR degrades slowly in nature because of certain microorganisms, and natural environments contain a few bacteria and fungi that can degrade NR as a carbon and energy source. The degradation of rubber by fungi was initially examined by De Vries through the utilization of several strains of Penicillium and Aspergillus in a liquid medium consisting of 10% (wt/vol) NaCl. The results revealed a 6% increase in biomass and a weight reduction of 15.5% to 30.9% in the rubber material over an incubation period ranging from 19 months to 5 years [135].

However, in 2013, an investigation into the isolation of two fungal species, Penicillium and *Aspergillus niger*, degraded the NR sample by 20% and 25.9% of its weight loss, respectively, over a two-month period [136]. Many researchers have verified the substantial potential of natural fillers as alternative reinforcements, due to their advantages including low cost, low density, eco-environmentally friendly, biodegradability, and large availability in nature, in addition to their ability to improve the mechanical properties of composite materials [137–139].

NR composites consist of an NR matrix and various fillers or reinforcements such as carbon black, silica, clay, cellulose, and starch. The addition of these fillers can improve the mechanical, thermal, and electrical properties of NR, and reduce its costs. However, the presence of fillers can also affect the biodegradability of NR composites, depending on their nature, amount, and interaction with the rubber matrix. A biodegradable NR composite is formed by blending NR with other natural or biodegradable materials, resulting in an environmentally friendly composite that can naturally decay or disintegrate over time by microorganisms, such as bacteria and fungi [140]. Biodegradable fillers can include natural fibers, such as like cellulose, jute, hemp, or sisal, as well as other biodegradable materials, such as starch-based components, chitosan, or other plant-derived materials. The biodegradation of NR composites is an important process that can contribute to sustainable and eco-friendly rubber product development and is a potential solution for reducing the environmental impact of the disposal of rubber waste. Recently, a study produced biodegradable composite sponges of NR and cellulose fibers (NR-C) using the Dunlop process has been reported [141]. Microcellulose fibers from eucalyptus pulp were used as reinforcement fillers, while sodium alginate was utilized as a dispersing agent to improve the compatibility between cellulose and NR. The NR-C sponges exhibited a higher compressive stress, modulus of elasticity, and efficient water absorption capacity. Starch is a natural polymer fiber that is classified as a carbohydrate and is composed of repeating glucose units. Starch is abundant in nearly all plants because of photosynthesis, and serves as the primary energy storage compound. Its abundant supply,

renewable nature, affordability, and capacity for decomposition make it a valuable resource to produce bioplastics. Starch contains an integral protein that resides in its granular structure. This protein synthesizes a complex carbohydrate chain consisting of amylose and amylopectin, which is consumed by soil bacteria to generate an enzyme that breaks down the matrix, similar to the NR latex backbone chain.

Another NR/starch-based biodegradation study reported biopolymer sheets comprising a combination of maleated epoxidized natural rubber (MENR) and natural rubber-g-cassava starch (NR-g-CSt) [142]. There is an abundance of biodegradable NR rubber research utilizing natural fibers [68]; for example, sisal/oil palm hybrid fiber that also reinforced NR composites and their biodegradability and aging were studied by Jacon *et al.* [143]. The degradation of the composites was found to be dependent on the fiber content and chemical treatment. Degradation of the composites was discovered owing to the fiber content and chemical treatment.

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