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Review

Rubberized Geopolymer Composites: Value-Added Applications

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Abstract: The discovery of an innovative class of inorganic polymers has brought forth a revolution in the history of construction technology. Now, no energy-intensive reactions at elevated temperatures are essential, as found in the case of contemporary cement production. In addition to their attributes of low energy and a mitigated carbon footprint, geopolymeric composites can incorporate diversely originated and profound wastes in their manufacturing. As of today, profoundly accessible landfills of rubber tyre waste negatively impact the environment, water, and soil, with many health hazards. Their nonbiodegradable complex chemical structure supports recycling, and toxic gases are emitted by burning them, leading to aesthetic issues. These, altogether, create great concern for well-thought-out disposal methods. One of the achievable solutions is processing this waste into alternative aggregates to thus generate increased economic value whilst reducing primary aggregate consumption through the incorporation of these vast automobile solid wastes in the manufacturing of geopolymer construction composites, e.g., binders, mortar, concrete, etc., produced through the process of geopolymerization as a replacement for natural aggregates, providing relief to the crisis of the degradation of restricted natural aggregate resources. Currently, tyre rubber is one of the most outstanding materials, extensively employed in scores of engineering applications. This manuscript presents a state-of-the-art review of value-added applications in the context of rubberized geopolymer building composites and a review of past investigations. More significantly, this paper reviews rubberized geopolymer composites for their value-added applications.

Keywords: rubberized geopolymer composites; waste of rubber tyres; synthetic aggregate; disposal; recycling; pyrolysis

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1. Introduction

Even though portland cement is an excellent and vital binder for construction composites, its present production process is highly energy-consuming [1] and, moreover, approximately one ton of CO_2 is emitted in the production of each ton of portland cement [2,3]. Not only that, but the said process also uses up limited natural resources of limestone as a raw material, as well as coal, which is used to obtain the elevated temperatures essential for calcination [3]. All these challenges have compelled researchers around the world to look for new user- and eco-friendly alternative construction materials with reduced energy and low carbon footprints that can be integrated with diverse types of waste while achieving performances that are as high as or even higher than ordinary portland cement [4].

Nowadays, innovative green geopolymer technology is garnering attention for the outstanding performance of geopolymer construction composites, which have nine-times lesser CO_2 emissions and six-fold lower energy consumption [2], preventing the degradation of natural limited resources and providing relief to global warming [5].

The significance of natural rubber for mankind is undoubted and, to date, its use has risen globally. In accordance with the International Rubber Research Group, the total global consumption of rubber in 2018 was predicted to escalate by 3.4% and total 29.39 million tonnes. In 2018, the expected rise was 2.5%, to 30.12 million tonnes in the year 2019 [6]. In harmony with the data of the [7] Association of Natural Rubber Producing Countries (ANRPC), the consumption of rubber, both synthetic and natural, was 29.2 million tonnes in the year 2018, including 13.72 million tonnes of natural rubber. Another report, from July 2018, found the worldwide production of natural rubber was 7.37 million tonnes, with an expansion of 3.7% in the initial 7 months of 2018 [6]. Natural rubber utilization has grown by 5.2% and reached 8.16 million in seven months. The total world production of rubber during 2013 was estimated to be over 27 million tonnes, rising at a yearly average rate of 3%, from 22.44 million tonnes in 2006 [7]. The total production of Malaysian rubber in 2013 was 0.933 million tonnes. [8]. This rubber production is useful for producing tyres and other industrial and consumer products [9]. The history of rubber tyres shows that they have been the subject of research and technological upgrades for one century, more or less. In 2019, the ongoing demand for tyres is predicted to touch the mark of 3 billion units, which demonstrates a yearly rise of 4% and estimated sales of USD 258 billion [10,11]. The constant developments and improvements make the tyre a well-designed and elegant piece of technology, rather than simply a piece of rubber. The number of vehicles augments day by day and worldwide, due to the improvement of economics and the necessity of transportation. That is why, over the years, an escalating and vast quantity of discarded rubber tyres, both as waste generated during new production and end-of-life rubber tyres [12], has accumulated globally. Tyres are mostly unsystematically disposed of into landfills as a solid waste, which is a major and alarming threat to the environment [13,14]. This huge accumulation of rubber tyre waste is a dilemma for waste-disposal management [15]. Some of them are buried, but that is an impractical approach since they are not bio-degradable. Moreover, they contain toxic and soluble components [16]. Burning tyres is the easiest, simplest, and most cost-effective route of disposal, but it is unfeasible and hazardous to mankind and the fauna and flora of the planet. Moreover, the leftover residue powder subsequent to burning creates soil pollution, and discarded tyres may cause fires (as they are susceptible to fire), especially during summer. These fires are particularly difficult to put out, since the 75% free space in them can amass lots of free oxygen. Not only that, but they also emit toxic gases upon burning, creating aesthetic problems, and this is prohibited, too, in some nations. For these reasons, the said wastes that have not undergone recycling must be scientifically disposed of. Rubber tyre waste covers extensive open spaces that might be otherwise useful for other fruitful purposes. Wasted rubber tyres are bulky, and 75% of a tyre is the central hole. This shape, and the impervious nature of tyres, can hold water and provide breeding habitats for mosquitoes and various pests, e.g., mosquitoes, insects, rats, mice, vermin, etc., thus creating health hazards [17–19]. Stockpiled rubber tyre waste exhibits off-putting impacts on health and creates environmental and water pollution [18]. Their non-biodegradable nature is an obstacle for decomposition below the surface of the earth after burial [20]. This is because of the cross-linking of vulcanized rubber with sulphur bonds, and the degradation is further hindered by antiozonants and antioxidants [21]. This is the root cause for the creation of "black pollution", which is a menace to the environment [22].

Looking at the statistics of these wastes, it has been reported that the annual global generation of tyre waste is estimated to be, more or less, 4 billion tonnes. Globally, according to one estimate, there are 1.5 billion tyres discarded every year, and roughly the same quantity of tyres reach the end of their service life annually [23]. While in accordance with the other assessments, it comes to almost 1000 million tyres every year reaching the end of their useful service lives [18,24], and out of that, over half, i.e., more than 500 million per year, are disposed of in landfills as waste, with no treatment or any secondary use [25–30], and are accountable for water and soil pollution in addition to being a cause of deadly diseases and fire [21]. In a developed nation such as the UK, the annual usage of tyres during 2002 was found in the region of 37 million and it is still growing [31]. Estimates, for Brazil, of waste tyre generation range between 17 and 20 million units per annum. In the case of the USA, the figure is in the vicinity of 275 million scrap tyres each year [32]. The report of the European Tyre & Rubber Manufacturers' Association (ETRMA) [11] says that 1.4 billion tyres are produced each year in order to meet the exigencies of the industry worldwide, and the quantity of rubber tyre waste that is generated in European Union member states is, single-handedly, 3.5 million tonnes.

Expectedly, the amount of wasted tyres might reach 5 billion per annum, and that of motor vehicles might touch 1200 million by 2030. As of today, gargantuan amounts of tyres are stockpiled already, either as "whole tyres" or shredded landfilled tyres, in the quantity of 3000 million within the European Union and 1000 million in the USA. [19]. The states of the European Union generate greater than three million tonnes of rubber tyre waste per annum and, more or less, 600 tonnes of rubber tyres are stockpiled [33,34]. Additionally, discarding rubber tyres in landfills is an eco-adversary, since tyres are prone to return to the surface by breaking layer covers, damaging the land settlement and their rehabilitation in the long term. Concerns for the contamination of air, water, and soil, together with health perils owing to landfills full of rubber tyres, have piloted the rummaging around for reuse technologies for leftover tyres. Without a doubt, globally, scrapped tyre disposal is regarded as one of the most crucial predicaments to the environment, on account of its manifold disadvantages and difficulties.

Consequently, the energetic valorisation of tyres is initiated along with the introduction to their application as a raw or aggregate material in structural construction in buildings, in asphalt surfacing processing, or in the footwear industry, etc. Undoubtedly, a modest amount of non-recycled end-of-life tyres are employed to provide shock fortifications for marine platforms against the influence of waves or ships [35], as well as for sports ground and binders in asphalt [36]. Moreover, the wasted tyres can be reused and recycled in novel fresh-rubber products, and in some applications of civil engineering, doormats, wheel chocks, gaskets, and railroad crossing mats, but these are not enough against the piles of discarded tyres. This is why the disposal of rubber tyre waste has cropped up as a hot ecological crisis in the world [37,38]. Over and over again, colossal quantities of tyres are disposed of, either being thrown away or buried throughout the planet. Still, however, wasted tyres are emerging as a very grave peril to the environment [39–41]. The Directive [42], opened in 2006, has announced that the disposal of tyre waste exposed to the environment is forbidden, subsequent to the consideration of the fact that the quantity of rubber tyre waste has augmented drastically. Often, it is found that tyre waste piles are accountable for spreading unfamiliar contagious diseases. Taking the above facts into consideration, it is highly necessary to dispose of this hazardous waste of rubber tyres methodically and in an eco-friendly way for a good cause.

FA is the key solid waste generated as a by-product from coal-firing power plants, and thermal electricity stations are seeking ways to dispose of it in an economical and environmentally beneficial way, along with CO_2 sequestration [43]. More understanding of the physicochemical and mechanical properties of fly ash is therefore essential to review in both its natural and modified forms. Coal represents 25 to 30% of the total global energy production. This is the core reason for the generation of roughly 800 million tonnes of fly ash by the power plants of the world; however, only 50% of it is being recycled [44]. Concerning the management of sustainable raw materials, it is vital to recycle wastes from the industry for as long as is feasible, and to develop brand-new technology that results in novel added-value materials [45–48]. The application of rubber tyres as artificial aggregates will lend a hand to the relieving of the shortage of natural aggregate resources in the rising construction and infrastructure industries since the problem of depleting natural resources is a great challenge to environmentalists. Fortunately, artificial aggregates from rubber tyres, e.g., fibres, crumb rubber, rubber ash, etc., which were formerly regarded as waste and as pollutants to the environment, are now emerging as supporters to the environment, becoming a natural sand replacement in order to prevent the degradation of natural restricted aggregates for brand-new building materials, thereby facilitating a means for sustainable development and promoting the growth of eco-sustainable buildings through eco-construction [49,50].

This review manuscript aims to assess the impact of the incorporation of fly ash and rubber tyre waste to produce a geopolymer composite product, as well as their synergetic applications as cost-effective raw materials and artificial aggregates, respectively. Nevertheless, the recent consciousness of the environment in the field of construction and infrastructure industries promotes the bringing-into-play of alternative binders to partly or wholly replace portland cement and/or natural aggregates. Moreover, a summary of the most important studies that have been carried out on geopolymer composites, especially fly ash-based rubberized geopolymer concrete and crumb-rubberized concrete, establish them as sustainable eco-friendly building materials for the future. The literature study found only restricted data on the properties of rubberized construction composites. The current state-of-the-art knowledge of rubberized geopolymer composites delves into fresh and hardened-state characteristics, classification, composition of rubber tyres, mix design, and its value-added applications as a partial substitute for natural aggregates; the mechanical strength, durability, etc., has been comprehensively reviewed.

2. Tyre Production from Rubber

Globally, in the year 2017, the estimated growth of the demand for tyres was about 4.3 percent annually, touching 2.9 billion units, whereas tyre waste disposal in 2015 reached roughly 1 billion units [51–53]. According to the data of the Brazilian Pneumatic Industry Association, the historical record of Brazilian production from the rubber tyre sector was eye-catching in the year 2013 and 2014, and the total Brazilian industry units were 70.8 million [54,55]. Furthermore, 7 million tyres were imported and 12.4 million were exported in 2013, which is a 0.6% growth concerning total manufactured tyres. Except for the years 2009 and 2012, during which the global economic crisis prevailed, Brazilian tyre production presented a sustained rising behaviour [56–58]. By and large, the life cycle of a tyre comprises five key stages, namely, raw material mining, production, utilization, collection of the waste tyre, and recycling progression or dumping, relying upon locally prevailing conditions in every country or province where the same are produced or marketed [59]. Nationwide statistics of waste for rubber tyre generation in 2013 were 4.4 million metric tonnes in the USA, 3.4 million metric tonnes in Europe, 1.02 million metric tonnes in Japan, 1 million metric tonnes in the Russian Federation, and 365 thousand tonnes in Brazil, together with 3.31 million metric tonnes produced in the rest of the world. Parallel to this, the EU stands with an over 1.43 billion tonnes per year generation of this waste and is escalating at rates akin to those for economic growth [60–63]. Worldwide, 1.4 billion fresh tyres, more or less, are sold annually, which is rather less than those produced globally, and afterwards, just as many make up the number of end-of-life tyres when used. Among units sold, passenger car tyres make up more than 90%, whereas the remaining 10% are truck tyres [64]. The estimation is made that, in developed nations, one car tyre per person per year is discarded, figuring to a total of 1 billion tyres in the form of wastes that are dumped annually in the world, while 4 billion used rubber tyres are resting in landfills and stockpiles globally [65]. The used tyres in EU countries were approximated at 3.6 million tonnes in 2013, whereas in the U.S.A., the estimate was made of about 4 million tonnes in 2015 [66,67]. The EU and Turkey have generated in the region of 4.5 million tonnes of tyres in 2010, representing 26.5% of the total tyre production on the planet, out of which more than 3.2 million tonnes are dumped annually. Considering an average, single new and scrapped car tyres weigh 11 kg and 9 kg, respectively, and analogously, heavy tyres of trucks and buses weigh 54 kg for pristine and 45 kg for discarded tyres, in that order. Their disposal in open lands is banned in the EU; minimizing use and reuse are alternatives with narrow applicability, and recycling is not capable enough of addressing the disposal quandary fully [68–71].

For that reason, energy recovery appears to have a higher potential to practice and to valorise wastes of rubber tyres. Thermo-chemical processes, e.g., pyrolysis, gasification, and combustion, extend imperative benefits, from an energetic approach, to get rid of this confrontation.

3. Chemistry/Composition of Rubber Tyres

Chemically, modern rubber tyres are manufactured from known petrochemical feedstock, i.e., styrene and butadiene. The production process of rubber tyres necessitates raw materials, their mixing, component manufacturing for reinforcement, their assembly, and vulcanizing. The main raw materials for tyre production is mainly natural (60 to 65 wt.%) rubber, and at times, synthetic rubber also; carbon black (25 to 35 wt.%) and the rest of the materials are some other chemicals. Materials added during the tyre-producing process entail vulcanization accelerators and retarders, fillers, fabric, and wire, along with other car compounds, softeners, extenders, plasticizers, activators, and protectants [72]. Nylon tyre cord and rubber chemicals, along with oil, are also useful. Carbon black and silica are regarded as significant materials which facilitate tyre mechanical reinforcement and ensure a superior safeguard against abrasion [10]. Presently, Si compounds are more preferable to carbon black for the manufacturing of "greener" tyres [10]. Textiles in tyre composition exist as natural rayon, polyester, and nylon. However, there are fewer textiles used in the tyres of trucks, owing to reinforcement necessities, but they are employed more often as a replacement for metals, resulting in lighter tyres [10,73]. Metal components, e.g., steel and alloys, play a role as reinforcing materials and can be incorporated into the belts or in the beads of wires in diverse proportions, depending upon the vehicle type and the particular application of the tyre. The rubbery materials are marking their presence in the form of C_xH_y, in association with some fibrous materials [74], and they are regarded as thermoset polymers. The tyres of both passenger and truck-type vehicles are mostly a mixture of natural and synthetic rubber-like butyl rubber and styrene-butadiene copolymer rubber. These tyres consist of a tread and a body, whereby the former extends traction and the latter furnishes containment for the amount of compressed air. The structures, shapes, and sizes of these compounds may be at variance, depending on their location in the structure. Smaller-sized particles are employed in treads and carcasses, whereas greater particles are utilized in inner liners. The "Hevea brasiliensis" or the "Pará rubber tree" or "Sharinga tree" or "Seringueira tree", or more popularly, a "rubber tree", categorized as a "flowering plant", is the key source of natural rubber in form of a runny, milky white liquid, known as "latex", which oozes from the bark when cut, while synthetic rubber is by and large extracted from products of a petroleum kind. [10]. The latex is then blended with acids in order to facilitate its solidification. Natural rubber possesses distinctive elasticity—an essential attribute for a tyre to go on the road. Even though rubber is made up of elastomeric polymers characterised by the existence of a network structure, it can be deformed temporarily when exposed to external forces.

The IRSG (International Rubber Study Group), [75] has accounted 24.37 million tonnes of the total rubber production in 2010, including 10.38 million tonnes, about 42% of which was natural, and a remaining 13.99 million tonnes (roughly 58%) of synthetic rubber. An amorphous carbon with quasi-graphitic structure, i.e., carbon black, is produced largely by partial combustion of fossil hydrocarbons, which strengthens and provides abrasion resistance to the rubber. Approximately 7 wt.% of organic and about 3 wt.% of inorganic fillers constitute the remaining percentage through the supplement of an extender oil, which is a blend of aromatic, naphthenic, and paraffin hydrocarbons, to make the rubber softer and to enhance its workability. Possibly, greater than 100 dissimilar compounds, in general, can be supplemented in the production of tyres, depending upon the definite trademark and on the precise duty to be allotted to a particular tyre [76]. In normal practice, the accelerators are added towards the end of the mixing cycle, when the mill or internal mixer temperature is plunging [77]. During tyre production progression, the course of vulcanisation takes place, whereby an irrevocable reaction between the elastomer, sulphur, and some other chemicals results in cross-links amongst the chains of elastomer molecules and the formulation of a 3D chemical network. The referred-to cross-linked elastomers are solid, insoluble, and infusible thermo-set materials, resulting in a higher strength and elasticity, making the tyre trickier to decompose [78]. More often than not, the additives and vulcanisation agents, i.e., sulphur groups, zinc oxides (ZnO), and stearic acids ($C_{18}H_{36}O_2$), are employed to make a few easy manufacturing processes to form and speed up the development rate of 3D networks in the tyre [10,79]. However, the content of organic sulphur in rubber tyres as an accelerator is only added up to or in the vicinity of 1.5 wt. % in the form of a catalyst, which does not merely control the reaction kinetics of vulcanisation but also boosts the physical attributes of the rubber [76,80–82].

The vulcanisation or curing entails sulphur bond development with the rubber [83]. Admirably, vulcanised materials are found to be long-lasting with outstanding attributes, such as a greater resistance against deformation because of cross-linking. Devulcanization is the reverse step from vulcanisation, consisting of the scission of sulphur cross-links to reinstate the early characteristics of the rubber. Crumb rubber regroups all the rest of the rubbers or elastomers tainted by metals and fibres [84]. Additives, i.e., antioxidants, antiozonants, extender oils, and waxes, augment the performance of the tyre and favours the vulcanisation. Improvement can be brought about, with respect to the rubber attributes, by a smaller-quantity addition of some inorganic compounds, such as silicates, clayey fillers, carbonates of Ca, and Mg together with Na, K, Cl, [83], and several pigment materials [85]. The characteristics of rubber compounds rely directly upon its microstructure, which is developed normally through elastomeric chains—named also natural rubber, polymer, or resin—and fillers or add-ons. This, in turn, formulates a constant and homogeneous polymer composite. There exists two chief kinds of products of plastics, namely, thermo-plastics and thermo-settings [86]. The thermoplastics are polymers comprised of monomers ordered in self-governing big chains, which alter their attributes with an augment in temperature without a linked phase modification [87]. The molecular weight or the degree of polymerization of the rubber is confirmed through the number of monomeric units in a macromolecule. The elevated mechanical strength, together with the high density of a thermo-plastic, corresponds to superior values for the polymerization level of rubber. Whereas chemical covalent forces bond powerfully a single chain, dissimilar chains are bonded with feeble secondary van der Waals forces that entail attraction and repulsion among atoms, molecules, surfaces, and some other inter-molecular forces that differ from covalent and ionic bonding, in which they are the reason for correlations in the variable polarisations to neighbouring particles. Three dimensional zigzag molecular structural designs of the referred-to chains possess freely rotating bonds that make possible the stretching and shortening of the rubber molecule without any alteration to its in-house energy [86]. This provides thermo-plastics with a higher deformability but inferior strength, owing to the van der Waals forces. In order to improve the strength of the rubber compounds, vulcanizing agents or sulphur is supplemented to unsaturated rubbers for linkage of the chains utilizing primary strong bonds, which create thermo-set polymers. Contrasting thermo-plastics, the characteristics of thermo-sets are not influenced by temperature, and for that reason, they are extensively employed to produce tyres so that the tyres can resist severe mechanical and/or environmental states. The physical-plus-chemical attributes of thermo-set rubbers can be influenced by vulcanisation course, period, and temperature for curing, as well as by filler type [88,89]. Even so, the overall stress–strain behaviour and microstructural alterations of thermo-set rubbers exposed to tensile stress pursues common patterns, as portrayed through the schematic in Figure 1. In the beginning, the strains build swiftly on account of the feeble van der Waals forces bonding amongst the filler and polymer (see stage 1 in Figure 1). Subsequently to when the Van der Waals bond is overcome, the response becomes rigid in the second stage because of (a) the work of covalent bonds for a few aligned chains, and (b) friction amongst the fillers and the polymer chains in the course of the chain's repositioning in the direction of the applied tensile load. During the ultimate third stage, the response becomes more rigid since the bulk of the polymer chains have stretched and aligned with the direction of the applied force [89,90]. The rubber tyre chemistry affects not merely its mechanical behaviour, but also its grip and service span. At the same time, the chemical composition of rubber tyres exhibits a discrepancy following diverse manufacturers. The raw materials utilized for the European Union's tyre manufacturing are analogous, as summed up in Figure 2 [91]. Generally speaking, the characteristics of rubber are defined by (i) the kind and/or quantity of the elastomer employed as a binder, (ii) the course of cross-linking, and lastly, (iii) the size, quantity, and kind of filler that is used. Consequently, the chemistry of tyres impacts the thermal decomposition mechanisms under a variety of conditions that, in turn, influence the mathematical model types, which can be utilized to portray the progression of pyrolysis.

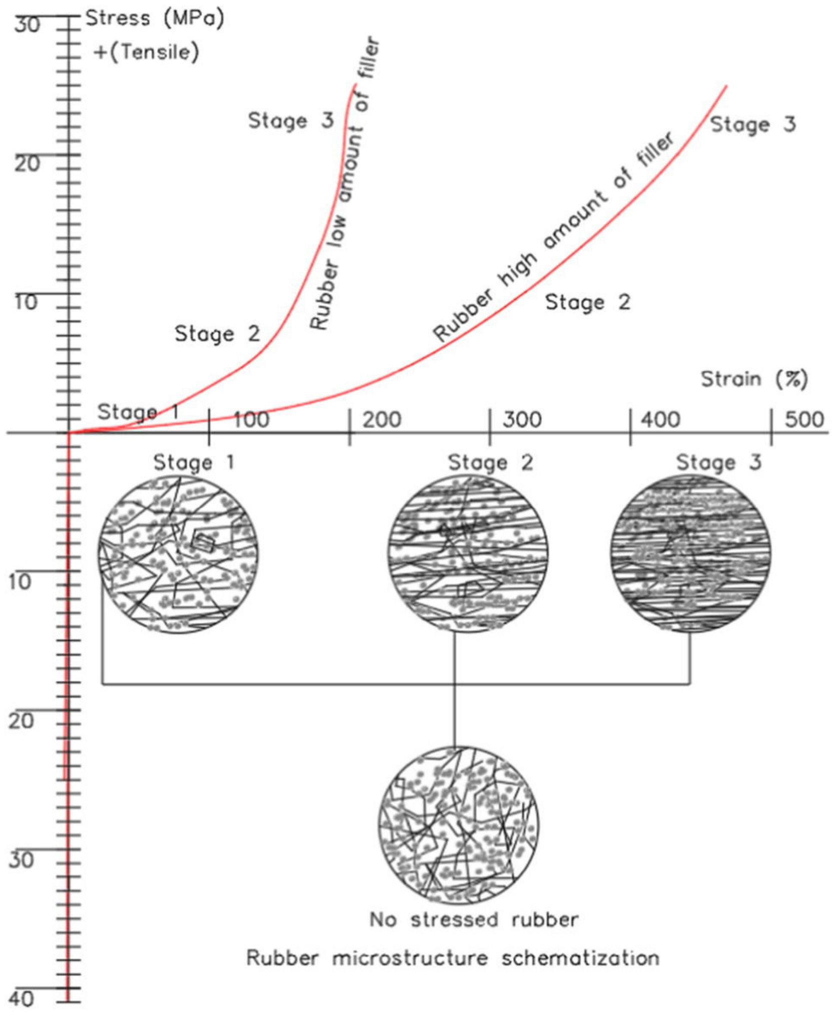

Figure 1. Schematic representation of stress–strain and microstructural behaviours of two thermoset rubbers.

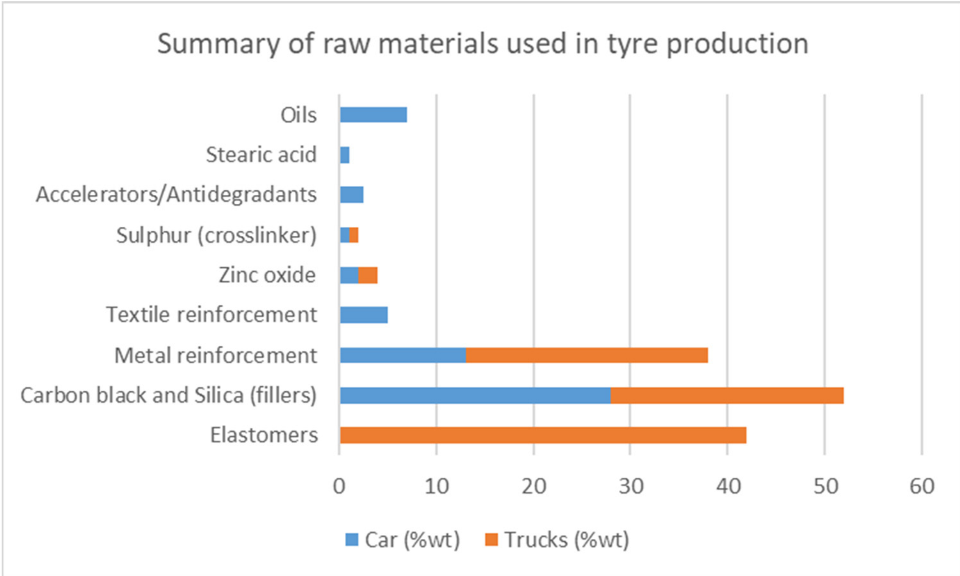

Figure 2. Summary of raw materials in tyre production.

4. Characteristics of Rubber Tyre

Rubber is a versatile product material on account of its combination of attributes. Physical characteristics of rubber tyres include, e.g., specific gravity, abrasion resistance, tear resistance, compression set, resilience, elongation, tensile modulus, and tensile strength. The recycled aggregate derived from rubber tyres is utilizable in various sizes to make the correct gradation. In the main, chipped rubber can be employed to substitute coarse aggregates, whereas unevenly shaped crumb rubbers can be used as fine aggregates. Not only that, but the rubber powder can also be used as a filler, binder, or sometimes even as a fine sand in the manufacturing of concrete [92]. Rubber tyre fibres are comparatively competent in the context of the enhancement of the strength attributes of the resultant concrete [15,93]. The appearance of diverse kinds of recycled aggregates derives from rubber tyres. Looking to the density of recycled rubber tyres, it is found ranging between 0.5 and 0.55 g/cm^3 [94]. The lower absorption of water competence and the density of recycled rubber tyres as an aggregate goes well with the prerequisite of light-weight aggregates. The broad-spectrum chemical composition of crumb rubber unveils the presence of natural and synthetic rubbers, carbon black, zinc (Zn), silicon (Si), and some other components. Significantly, the key component of carbon black plays a role in reinforcement. Due to the complex chemical structure of a rubber tyre, it scarcely degrades over time [95–97]. That means the tyres are non-biodegradable, even after an extensive time period following landfill treatment. Moreover, it is prone to potential accidental auto-fire, especially during summers, which are tricky to extinguish with water or by cutting off the supply of oxygen, because tyres are bulky with a 75% voided volume, which helps to provide fresh O_2 for burning horrifically, producing= a dark and dense black smoke, which impairs visibility, and highly toxic gas emissions enclosing mutagenic and carcinogenic chemicals [72,98–100]. This uplifts the temperatures to elevated levels, causing the tyres to melt, producing oil that pollutes soil and water. The referred-to enclosed content of oil may generate from the melting of tyres when buried in landfills, causing them to float up to the surface, owing to the pressure of entrapped gases breaking the upper landfill cover. Thus, the incineration of rubber tyres necessitates expensive air emissions control systems. In 1990, a fire at Tire King Recycling, Hagersville, Ontario, Canada, was long-lasting, taking 17 days to put out [101].

5. Wastes of Rubber Tyres

Out of the blue, a dramatic growth in the quantity of used rubber tyres around the world was witnessed on account of an ever-increasing quantity of vehicles on the roads, creating the dilemma of the disposal of this solid automobile waste when the end of their life comes. Sienkiewicz et al. [102] have unearthed that the yearly worldwide production of rubber tyres is approximately 1.4 billion units; that corresponds to an approximate 17 million tonnes of end-of-life tyres each year, whereas roughly 800 million tyres are found discarded every year around the globe, in accordance with van Beukering and Janssen [60], which is estimated to increase by 2% on a yearly basis. The key source of rubber tyre waste is broadly classified into automobile and truck tyres. Their physical characteristics and chemistry, on the whole, vary as to various sources, and that is why they exhibit dissimilar impacts on the strength properties of rubberized composites when used. Most often, the ingredients of tyres are synthetic as well as natural rubbers, carbon black, metals, textile fabrics, and additives. Recycled aggregates can be produced from rubber tyres through mechanical grinding, either at ambient or pyrolytic or cryogenic temperatures [103]. Rubber constituents are vulcanized to acquire the precise attributes of tyres. In the meantime, the integration of a variety of additives, such as antioxidants, antiozonants, and stabilizers in the production of rubber tyres give them their non-biodegradable nature and makes them resistant to photochemical decomposition, chemical reagents, and elevated temperatures. In consequence, disposal management of tyre waste happens to be technically, ecologically, and financially more challenging. Even so, the tyres of cars and trucks are made up of a unique blend of constituents; the majority of them enclose a practically equal quantity of synthetic and natural rubbers. More or less, 14% to 55% rubber can be extracted from any sort of tyre, depending on the authentic compositions. Here, for the most part, the rubber share arrives from the sidewall and tread parts of the tyres. Rubber tyres can be employed in civil and non-civil engineering applications such as geotechnical works, agriculture (to seal silos), road construction, on- and off-shore break walls, estuaries (to buffer the impact of ships), retaining walls in harbours, artificial reefs (to pick up fishing), incineration for the production of electricity, fuel in cement kilns, reefs in marines, or as synthetic aggregates in building materials. Regrettably, still, millions of tyres are being thrown away, buried, or burnt globally.

6. Disposal Management of Rubber Tyre Waste

The disposal of rubber tyre waste has turned out to be a foremost environmental crisis all over the world. However, at this time, reuse is the superlative choice for rubber tyre waste recycling. Apart from this, the disposal of these solid wastes is being managed mostly through three key techniques, namely, landfills, incineration, and pyrolysis. Re-treading allows for the reuse of rubber tyres by supplementing a new tread, which slims down both the rubber consumption for the "new" tyres and also the costs of production. Rubber tyres waste is generated either by the substitution of old tyres with newer ones or by removing them from vehicles prior to scrapping. These wasted rubber tyres can be separated into partly worn-out tyres or end-of-life tyres. Partly worn-out tyres can still be considered as fit for the on-the-road use, but end-of-life tyres cannot be reused for their original function. Further, they can be categorized into two groups as per the ability to re-tread and reuse them. Re-tread-able rubber tyres are those wasted tyres which can be newly treaded if they have still a good-quality casing. Most probably, rubber tyre casings scarcely weaken during their first life [104]. For this reason, well-handled tyres are suitable enough for re-treading for a minimum of two times before being discarded. Reusable tyres, however, have a noteworthy tread still left behind on the tyre making them fit for reuse on the road [60]. At this time, in Brazil, the waste of rubber tyres is used as an optional fuel in producing cement, granulated manufacturing and rubber powder for rubber products, rubber, or asphalt, etc. Lamination uses 6.0% of the total waste tyres as a raw material for shoe soles, inland pipelines, etc. Figure 3 represents the life cycle of a tyre [55].

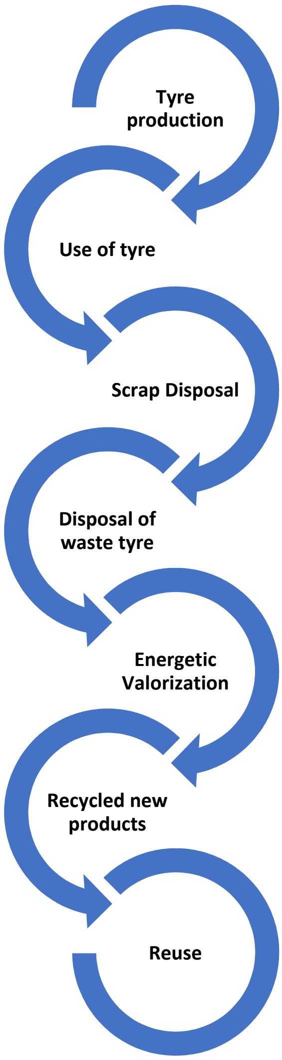

Figure 3. Life cycle of tyres.

Recycling methods and energy recoveries are the leading consumers of a wasted rubber tyre. The estimation of about 1.5 billion tyres is made as the annual world production [39]. Worldwide, approximately 1000 million tyres are discarded every year; out of that, more than 50% are thrown away or buried in landfills as garbage without any treatment, impacting environments pessimistically. The Rubber Manufacturer's Association [105] reported that, each year, more than 230 million scrap tyres are generated in the US only, and around 75 million are stockpiled. Expectedly, by the year 2030, the quantity will touch 1200 million per annum, and there will be 5000 million rubber tyres wasted regularly, accounting for stock-piled tyres too [25–30]. Globally, the covering-up of open land spaces by turning them into piles of landfills for discarded rubber tyres and tyre mono filling are among the most primitive approaches to tyre disposal. However, these erroneous disposals of wasted tyres can pilot rainwater gathering, due to the particular type of shape, creating a paradise for the proliferation of disease-transporting pests. Auto-inferno of large tyre piles may take place, and lighter-end gases are emitted during the decomposition process as well as the contamination of surface and ground waters. The lighter gases can build up inside the interior of the tyre, slowly but surely compelling it to "float" to the surface, smashing up the design integrity of landfills. For that reason, some tyres might not stay buried, cropping up ecological quandaries. This is why landfilling is one of the most unwelcome techniques for used rubber tyre disposal. At this time, the most excellent alternative for waste tyre recycling is "reuse". However, recycling rubber tyre waste to create novel products is an attractive route for wasted tyre disposal. Looking, at a glance, at the Indian scenario, the estimation of the total quantity of leftover tyres comes to 112 million annually, subsequent to double re-treading [26]. Perilously, stockpiled tyres are the root cause for economic and health hazards and for polluting the environment, water, and soil as well [27]. The particular shape and impervious nature of rubber tyres help to store water for the long sheltering and breeding of mosquitoes, various pests, mice, etc. Moreover, they are prone to auto-ignition while resting in landfills and release lighter-end gases in the course of decomposition, which can build up inside the interior forcing upwards step by step and eventually to "float" to the surface, impacting the landfill design integrity unfavourably. Normally, so far, the discarded tyres are disposed of by a variety of methods, such as landfilling, burning, using them as fuel, pyrolysis to produce carbon black, etc. Despite being the simplest and cheapest method of disposal, tyre burning causes a grave fire jeopardy because of the poisonous smoke with panic-stricken emissions of a potentially injurious nature and the enclosing of styrene and several benzene compounds that negatively affect living humans, animals, and plants on the planet. Butadiene is an extremely carcinogenic four-carbon chemical compound discharged from the styrene-butadiene polymer for the duration of combustion. Among the toxic gas emissions, the key compounds are polyaromatic hydrocarbons, CO, SO_2, NO_2, and HCl. The air pollutants also emit a dense black smoke, impairing visibility and painting soil surfaces black, polluting them with powdered residue leftovers. Even though scores of these residues are non-biodegradable and are dumped, owing to a deficiency in precise and stringent regulations and/or due to the unappealing high-priced recycling. The discarded rubber tyres are categorized into these sorts of solid residues and managed as waste, even though they could undergo recycling or re-manufacturing, being considered a burden that adds noteworthy charges over disposal, and often play the role of an obstacle to advancing resource efficiency. Most phenomenally, in recent times, construction and infrastructure industries are taking this challenge of the systematic disposal of rubber tyres by incorporating these solid waste materials as synthetic aggregates, replacing natural ones in the manufacturing of diverse sustainable green concretes. This fantastic, economically viable, and eco-benevolent approach helps not only to dispose of the waste tyres methodically but also helps protect environments and the degradation of costly restricted natural aggregate resources. An auto-fire at Tire King Recycling, Hagersville, Ontario, (1990), which lasted for as long as 17 days, is evidence of the danger of disposing waste rubber tyres in landfills [101]. Moreover, the leaching of metals and additives, such as stabilizers, colourants, plasticizers, and flame retardants, may take place from the tyre waste contaminating the soils, which is an eco-adversary because these substances can likely retard or kill the beneficial colonies of bacteria in the soils [106]. To get rid of this complex solid waste of discarded rubber tyres, the best options is reutilization.

At present, recycling and recovery are the most-employed techniques for utilization. Quite a lot of endeavours have been made to consume end-of-life tyres through reclamation, devulcanization, elevated temperature and higher pressure sintering, pyrolysis energy recovery, etc. [107–110]. Advantageously, the techniques for the utilization of rubber tyre waste have been found accounted for deeply in the literature. Taking into consideration the environmental concerns, economical and geopolitical issues and oil price instabilities have motivated the development of new technologies for energy generation. The sustainable utilization of resources for energy is highly indispensable for not only the correct management of the limited natural resources, but also for the lessening of the pollution of the environment. That is why the issue of obtaining renewable fuels is amongst the foremost contemporary challenges. However, it should be affordable and financially doable to reduce emissions of CO_2, NOx, particulate matter, as well as C_xH_y. Rubber tyre waste must be correctly disposed of to lessen its impact on the environment; nonetheless, the disposal method that takes place, in the majority of the cases, is incineration, which is considered the swiftest and simplest way of to get rid of tyres waste. The incineration of rubber tyre waste generates huge emissions with a broad set of halogen-chlorinates, hydro-carbon compounds, etc. Moreover, this produces pyrolytic oils that enclose noxious chemicals together with compounds enclosing heavy metals, causing health hazards.

6.1. Recycling

The recycling of rubber tyres, or rubber recycling, is the line of action to recycle end-of-service tyres to manage their value-added systematic disposal, otherwise covering a lot of open land spaces as landfills. The general recycling of rubber tyre waste from a wasted tyre can be made through recovering engineering materials, reconstruction, or gaining energy from them [21]. Briefly, "recycling" means any recovery tactic to reprocess wastes into advantageous products, whether for the original or some other objective. However, it entails processing organic materials, but it neither engages the energy recovery nor the reprocessed materials for back-filling or as fuels. The need for the recycling of end-of-life rubber tyres is escalating significantly, owing to the emergent exigency and increasing use of tyres [21,111,112]. A wasted tyre can be recycled through a variety of routes and by a range of techniques for separating rubber and steel fibres which play a role in replacing engineering raw materials.

These discarded rubber tyres with non-biodegradable attitudes are a challenging source of waste, keeping in view not only their gargantuan volume but also their higher durability and nature of enclosing components that impact environments pessimistically. The improvements in tyre-production technology have brought about novel materials to add to tyres [11,111] with more a momentous proportion than before, which makes recycling trickier. One recycling method, called "cryogenic", is when rubber tyres are frozen with superbly cold fluids, or "cryogens". The subsequent breakdown converts them into "crumb rubber", which is useful for truck bed liners, beds for asphalt roads, hoses for agriculture, etc. Recycling is a more preferred disposal method, in comparison with the recovery technique, since the latter one is merely competent for recovering 30 to 38% of the energy embedded in newer rubber tyres [106]. Not only that, but rubber tyre de-recycling is also a momentously interesting route for the disposal of cut or shredded tyre waste by converting them to newer products, such as liquids reservoirs, higher-performance road bases, sports fields, playground covers and other equipment, artificial reefs, erosion controllers, highway crash barriers, break walls and floatation devices, athletic tracks, asphalt mixes, and most importantly, in civil engineering applications, etc. [113].

6.2. Pyrolysis

Pyrolysis is a significant newer technique for recycling discarded tyres suitably, despite their resilience and great volume. Simply speaking, "pyro" means heat, and 'lysis" means to break down. That means "pyrolysis' is an irreversible chemical decomposition brought about by way of elevated temperatures, normally in the range of 400° to 500° C, i.e., heat, in a reactor vessel in an N_2 atmosphere without oxygen (O_2), thereby avoiding oxidation [114]. In other words, pyrolysis is a course of action whereby bigger and complex molecules break down into smaller and simpler ones, due to the high thermal impact in the absence of O_2. The pyrolysis of rubber tyre waste relies greatly on tyre chemistry and the inter-molecular as well as intra-molecular bonding type found present amongst the polymers constituting the tyres. Usually, the by-products of pyrolysis are found with four output streams, while intact discarded tyres are processed, releasing pyro-gases, liquids in the form of tyre-pyrolysis oils, solids in the form of pyro-char, and steel. The yields are the fundamental chemical compounds employed to produce tyres, i.e., carbon black, Zn, sulphur, steels, oils, and gases. The chemical composition of every fraction highly relies upon the conditions utilized for pyrolysis and on the composition of the tyre. Elevated temperatures of, more or less, 500 °C are regarded as optimal for the course of tyre pyrolysis. The solid pyrolysis residue is a mesoporous material with an average heating value of 30 MJ/kg, made up of reinforcing carbon black employed in tyre manufacturing and other inorganic compounds formulated in the pyrolytic course. The production of pyro-char ranges, roughly, from 35 to 55 wt.%, enclosing an extremely high carbon content, which can be employed to make porous activated carbon utilized for investigations into dangerous gas adsorption and in energy storage utilizations, such as Na, K, and Li-ion-containing batteries, supercapacitors, and catalysts for the production of biodiesel [115]. The liquid-phase, i.e., pyrolysis oil chiefly encloses xylenes, tri-methyl-benzenes, di-methyl-styrenes, di-methyl indene, limonenes, and some hetero atom-possessing compounds [116]. The products of pyrolysis oil are found in the range of 38 to 56 wt.%, while the heating value of pyro-gas is around 40–43 MJ/kg [117]. This rubber tyre pyrolysis oil is a very complex mix, enclosing aromatics, aliphatic hetero atoms, and polar fractions chemically, and is useful as an optional fuel engines and also for the synthesis of carbon nanotubes [118]. On the other hand, pyro-gas from pyrolysis varies in the region of a few (say 5) percent to greater than 10 and maybe up to 20 Wt.% of the total yields, with a towering heating value of up to, roughly, 84 MJ/Nm^3 or 42 MJ/kg [119]. In general, gas-phase yields of rubber tyre pyrolysis are a mix of paraffin and olefins, with the appearance of other hydrocarbons, carbon oxides, hydrogen, and smaller quantities of compounds of sulphur and nitrogen. These pyro-gaseous products are useful as fuel in pyrolysis and the highest amount of the gas is in hydrogen. The gaseous fraction is comprised of non-condensable gases, namely, H_2, CO, CO_2, C_2 H_4, and C_3 H_6, etc., whereas the pyro-char found is very highly carbon-containing and can be cost-effective and a waste precursor to synthesize porous activated carbon materials for further use in energy storage devices [120]. Normally, the pyrolysis of rubber tyre waste is aimed at maximizing the liquid-phase product since it gifts valuable chemicals. Analogously, the gaining of activated carbon from char is one more means of enhancing its economy. What is more, the higher calorific value of pyrolysis gas meets the energy needs of the procedure and permits extra electricity production too. Technically, the course of pyrolysis is a viable approach to mining expensive yields, such as combustible gases, activated carbon, fuels, chemicals, etc., from the waste of rubber tyres. However, still, pyrolysis has not come out to be commercially successful, despite the numerous endeavours made to make it viable in this regard [121]. For this reason, the process for tyre waste pyrolysis has been explored in depth by researchers over time, who have even used several approaches to comprehend its mechanisms and reaction kinetics. Moreover, rubber is recycled through a pyrolysis method for carbon black powder production, but this can contaminate the atmosphere. Carbon black harvesting through rubber pyrolysis is found to be more costly and is of inferior quality, compared to petroleum oils. That is why a call for synthesis, both qualitative and quantitative, has cropped up and, once more, increasing interest for and attention to dealing with this solid waste rubber tyre disposal dilemma, while also extending energy recovery, is the objective. In this connection, recently, active research for unearthing a novel mode to recycle waste rubber tyres, comprising grinding, crumbling, re-treading, combustion, and pyrolysis, is in the pipeline. Recycling based on the pyrolysis method is eye-catching, owing to its lesser eco-impacts [122].

Figure 4 represents the schematic diagram for pyro-products obtained from the pyrolysis of rubber tyre waste, along with their applications [123].

Lower energy needs, higher liquid yields, and primary devices for volatile product condensation are some of the positive sides of the pyrolysis process [124]. The solid carbonaceous residues, a non-condensable fraction of gases, and a condensable fraction of pyrolytic oil can be reduced through pyrolysis. This is a well-organized technique for recycling rubber tyres waste, and that is why, recently, it has gained attention as a rubber tyre waste-disposal method. Except for the likelihood of recovery of carbon black, the discharged volatile compounds are capable of renewable energy recovery. The liquefaction of them to liquid fuel is quite remarkable, since they can be manipulated, transported, and stored with ease, facilitating a higher flexibility for power utilization. In reality, rubber tyre waste pyrolysis oil is entirely miscible with diesel and petroleum, or with blends of both fuels, fuelling active compression ignition engines [125,126]. The reaction kinetics of the process of pyrolysis can be classified as (i) a primary reaction for pyrolysis at 250° to 520 °C, (ii) a secondary pyrolysis of volatiles contents at 600° to 800°C, and (iii) char gasification with CO_2, H_2O, and O_2 at 750° to 1000 °C [127]. Williams et al. [128] have carried out pyrolysis experiments on tyre waste at temperatures in the range of 300° to 720 °C, using rates of heating between 5° and 80 °C/min^{-1}.

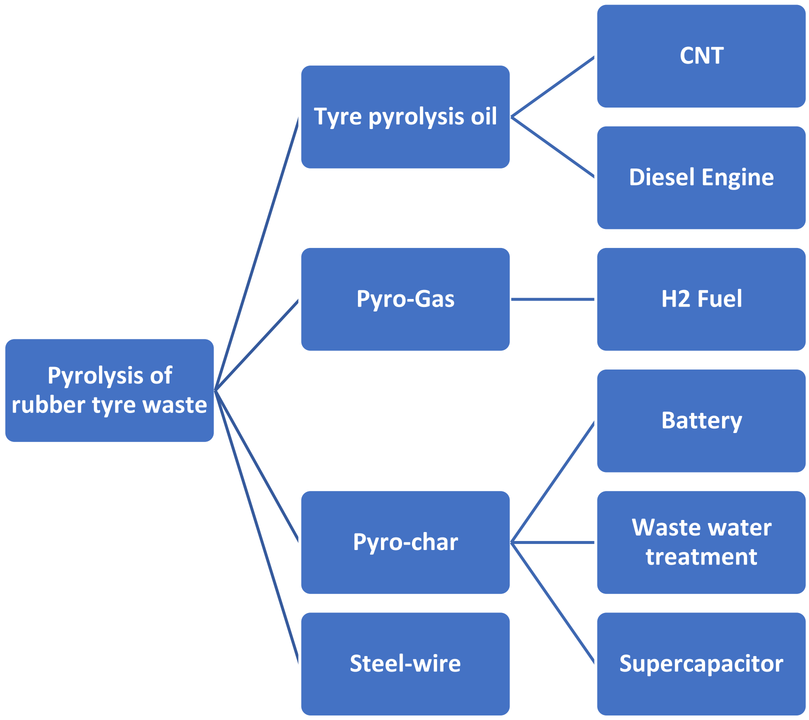

Figure 4. Waste tyre pyrolysis products and their applications.

Temperature elevations over 500 °C do not impact the char and gas yields of pyrolysis; however, in the opinion of Laresgoiti et al., temperature disparities sensibly influence the ultimate gas composition [129]. The energy for pyrolysis, described as pyrolysis heat or pyrolysis enthalpy, is the requisite energy to augment the temperature of feed-stock from the ambient to the reaction temperature and the energy to conduct the pyrolysis reactions. As studied by Dodds, the net energy balance for pyrolysis of rubber tyre waste indicates that the energy recovery varies from 75% to 82% of the heat of tyre combustion. Laird et al. [130] reported that pyrolysis energy efficiency entails the chief progression yields as a function of commercial ability. Conspicuously, rubber tyre waste pyrolysis furnishes promising outcomes for plants of both pilot and industrial scale with distinctive process technologies.

Numerous investigations on rubber tyre waste pyrolysis have been carried out to estimate the operating parameters' impact on, for example, heating rate, pressure, temperature, solid and volatiles residence times on product yields, together with their attributes, making use of poles apart from pyrolysis reactor kinds. An efficient heat transfer for a homogeneous temperature distribution is the key predicament of across-the-board applications to drive the pyrolysis. This is a significant hindrance for large-scale plants that affects its economic and technical feasibility, as well as its endorsement, pessimistically [131]. Moreover, the pyrolysis yields of discarded rubber tyres are more physicochemically complex than products of the substituted thermo-chemical conversion progressions of these wastes, such as combustion or gasification. Murillo et al. [132] accounted that the pyrolysis of rubber tyre waste is feasible not only technically, but also ecologically, and that the economic stability of the process depends highly on the potential applications of its derived yields. Gasification seems to be an optional practice with quite a lot of benefits over rubber tyre waste combustion and pyrolysis.

7. Energy Recovery

The "energetic valorisation of waste rubber tyres" cannot be categorized as recycling; however, it is a value-added application of waste tyres owing to their higher bouncy content of more than 90% organic materials, with a heat value (32.6 MJ/kg) greater even than that of coal (18.6 to 27.9 MJ/kg) [133]. Looking at the strategies of tyre recovery, a range of technologies and treatments have been set up to reuse or reclaim the materials that tyres are enclosing. The execution of the technologies can be classified into three most-important categories, such as civil engineering, whereby the structural benefits of discarded tyres are being used as water retention basins, safety barriers, etc., and as back-fillers in mining and land-site filling, etc., whereas the second category of energy recovery is energy from end-of-life tyres through their direct application as fuel replacements in cement kilns or via additional processing to yield fuel by pyrolysis. The third category of material recovery involves the components of chiefly rubber and steel to be recovered. The material recovery varies from size diminution to devulcanization to produce rubber beans or powder, in that order, and rubber analogous to the original product or that can be reprocessed. The referred-to size-reduced yields are utilized in energy recovery and civil engineering works or can be processed ahead of time. Devulcanization processes are those whereby the polymer attributes of vulcanization are reversed, which differs from other reclamation and recycling treatments since the intention is to recover materials akin to the virgin product by scission of the poly-sulphide bonds. Shulman [10] has suggested that there are four basic treatment levels linked by a rising process complexity, and that they can be successive. The first level represents the devastation of the tyre structure using simple mechanics, destroying one or more of their physical features, such as shape, rigidity, weight-bearing capacity, etc., together with bead, sidewall, and tread removals, along with cutting, compressing, and baling for use in engineering applications such as thermal insulation, as feedstock or as light-weight fillers for other recycling levels. In the second level, the release and separation of the elements of the tyre through treatments takes place, processing the tyre to be segregated into key components such as rubber, textiles, and metals. Here, the most widespread is cryogenic and ambient size-reduction technologies, including shredding, chipping, ambient grinding, and cryogenic progression, e.g., pyrolysis. Level three denotes successive treatments and technologies which are capable of bringing about mechanical, thermo-mechanical, chemical, or mechano-chemical changes to a minimum of one structural attribute of the material, e.g., devulcanization, surface modification, pyrolysis, and reclamation. The fourth and last level designates the technologies necessary to improve certain definite attributes, such as the preparation of thermoplastic elastomers, enhanced reclamation, and advanced carbon yields [133–135].

8. Benefits

Looking at the benefits of recycled rubber, it is accounted by John Dunham that, economically, a boost in rubber recycling pilots will give the rubber tyre recycling industry USD 1.6 billion per annum and many more opportunities for related jobs. Not only that, but it will also provide roughly 8000 highly paid employments in all 50 states, creating greater than USD 500 million in worker compensation and USD 182 million in federal, state, and neighbourhood charge incomes. On the other hand, noteworthy environmental benefits are also found in rubber tyre waste recycling [133–135]. The key international waste recycling organizations are operational, augmenting the rate of rubber tyre recycling beyond 90%. This mission will trim down a few of the pessimistic impacts of this waste on the environmental conditions.

9. Value-Added Applications

The value-added structural applications of rubberized concrete have drawn attention as valuable ways for diminishing environmental jeopardy. The rubberized geopolymer concrete is found with higher strengths, ductility, and impact resistance, and hence is valuable as a structural element and can be exposed to impacts and loads of a dynamic kind, such as bridge approach slabs, railway buffers, airport runways, etc. The rubber tyre waste's utilization indicates that recovered tyre waste can be regarded as a "rich" material, on account of its chemistry and attributes, proving to be a source of value-added raw material [136,137]. The effectiveness of rubber tyre waste-recovery models has led to the valuable transformation of rubber tyre waste into energy or materials. These "rich" wasted rubber tyres are useful for producing brand-new goods of utilitarian or practical importance.

Analogously, recycled rubber is useful after the mechanical treatment courses for recycling, namely, shredding, granulating, and crumbling. Every single progression has a specific usefulness, from civil engineering and use as a fuel, to used products and asphalt ground-aggregation procedures, such as: brand-new tyre manufacturing; applications for athletics and recreation; products of cut, punctured, and stamped rubber; as a tyre-extracted fuel; in industries like cement, paper or pulp, utility and industrial boilers; molded and derived products; in civil engineering; in landfill construction and operations; back-filling for bridge abutments and water; sub-grade insulation for roads; septic drain systems; rubber-modified asphalt; ground rubber; producing crumb rubber powder; in horticulture; for animal bedding; etc. Tyres can be recycled in four kinds of forms, as a whole, cut, shredded, or chipped, as well as in a crumb form. Whole-rubber tyres are accumulated for resale while rubber tyres cut into pieces are employed in the yields of clothes, shoes, etc. Shredded or chipped rubber tyres are low-priced progressions of recycling, whereby the rubber tyre is shredded and shrunk in size to make it useful for incorporation with construction composites, whereas crumb tyres are slimmed in size through cryogenic freezing or mechanical grinding. The tyres are then granulated and separated from other materials, such as fibres and steel, during this course of action. The tyres then undergo several more grinding progressions, to achieve the smallest essential size, using a miller. The tyres are frozen with the addition of nitrogenic material in the cryogenic process, and after that, a miller is employed to separate the rubber from any supplementary materials. Crumb rubber is made up of finer particles of up to 0.1 mm in size, providing a superior-quality rubber powder; however, it is not a cheaper one. The utilization of crumb rubber recycled from scrapped rubber tyres in concrete mixtures was initiated in the past couple of years to trim down another ecological impact of concrete caused by the consumption of limited natural resources. Firstly, the cement industry is one of the most-consuming industries of rubber tyre waste. Whole and shredded tyres are employed as fuel in cement kilns, which require temperatures beyond 1200 °C for the calcification of limestone. This ensures the entire combustion of every bit of the tyres' components. The steel cord and ash are everlastingly fastened to a clinker, which is eco-safe on account of many reduced emissions of destructive gases in comparison with coal combustion. Currently, in Brazil, the most widespread disposal route of discarded tyres is its application as an optional fuel for the production of cement, which was recorded as 69.7% of the total in 2014. Likewise, waste rubber tyres are also utilized as fuel in lime, steam, paper, pulp, electrical energy, and steel industries [138]. Not only that, but recycled tyres are also employed for the production of various new products, such as liquids reservoirs, higher-performance road bases, playground covers, sports fields, etc. Secondly, the granulated manufacturing and rubber powder have attractive consumption in making rubber products, rubbery or asphalt, figuring to 17.8% of the allotment. The lamination process, wherein 6% of the rubber tyre waste is accumulated as raw material, is used for shoe soles, inland pipelines, etc. In 1990, crumb rubber was produced in the US, which is competent enough to be blended with concrete in manufacturing. This novel product has exhibited excellent performance during the later stages of employment. Subsequently, Han Zhu [139] has erected several test-structure sites with this kind of building material, in collaboration with the Arizona government, providing a praiseworthy experience for the promotion of crumb rubber concrete as a structural material in engineering. In 2003, the world's first crumb-rubberized concrete-paved road was built in the state of Arizona, with the help of the state government. The research outcomes were in favour of using crumb-rubber concrete in road engineering. However, so far, concerning structural engineering, the ductility and dynamic performance of crumb-rubber-amalgamated concrete had to be enhanced to a great extent by adding the rubber. The research, in the context of strength, has reported that the strength loss can be slimmed down by optimizing the mixture ratio and by surface-treating rubber particles, and that the strength of crumb-incorporated rubberized concrete can even achieve identical intensity to ordinary concrete. An application of crumb rubber in the manufacturing of geopolymer bricks/blocks is quite doable. The crumb-rubberized concrete demonstrated many superior attributes over conventional concrete, namely, light-weight, higher resistance to cracking, superior impact behaviour, anti-aging, low permeability, enhanced sound absorption, and excellent thermal characteristics [140–142]. Given the brilliant referred-to attributes, employing crumb-rubberized concrete for pavements and barriers that may undergo grave dynamic impacts, sound absorbers, and foundation pads for railway stations [142–144] is promising. Astonishingly, it was unearthed that geopolymers containing crumb rubber can even be utilized as structural elements under dynamic loading. Moreover, the strength loss in crumb-rubberized concrete can be lowered when crumb rubber is treated with the solution of sodium hydroxide before being added, on account of a diminished porosity, implying that the application of crumb-rubberized concrete activated by alkaline activators can, in turn, address the crisis of strength mitigation for conventional crumb-rubberized concrete. Nowadays, wasted rubber tyres are expansively utilized in many energy applications, namely, power plants, cement kilns, tyre manufacturing facilities, etc. These value-added applications have exhibited the potential to mine energy from the waste rubber tyres in an eco-acceptable mode. Buekens [145] has opined that the chief route for wasted rubber tyres is their employment as a supplementary fuel in cement kilns. The rubber tyre transformation, especially the combustion of carbon black (CB), is encouraged by the elevated temperatures and long-lasting time in a cement kiln. Furthermore, the progression of cement production can consume the iron enclosed in the rubber tyres, belts, and steel beads without altering the quality of the cement. Many investigations were carried out in the past on the application of rubber tyre waste in cement kilns as a "tyre-derived fuel" and as gasifiers, and also as a direct fuel for bubbling fluidized bed reactors functioning as combustors. Following Singh et al. [146], employing tyre-derived fuel as a resulting fuel in thermal power plants to trim down the consumption of coal and emissions of NOx is viable. Giugliano et al. [147] put forward blends of rubber tyre waste with coke in cement kilns, which does not necessitate chief alterations in the layout or function of the plant. In the same manner, the American Environmental Protection Agency (EPA) recognizes the application of tyre-derived fuel as a feasible option to the utilization of fossil fuels and supports the bringing into play of rubber tyres in portland cement kilns and some other industrial services, such as pulp and paper mills, industrial or institutional boilers, and electric utilities, so long as they can cope with the managing and ecological needs framed by the authorities. The tyre-derived fuel has presented 54%, i.e., roughly 2.5 million tonnes, of the entire discarded rubber tyre generation in the USA in 2007, out of a total of approximately 4.6 million tonnes. The key advantages in employing rubber tyres in cement kilns include the preservation of non-renewable fuels, energy recovery, drops in production costs for cement, and the utilization of previously active facilities, etc. In addition to applications of rubber tyre recycling in civil engineering, it is useful for concrete and asphalt manufacturing and roofing as well. The waste of rubber tyres can be employed as fuel with an elevated heat value, steel fibres, and the residual products of rubber ash, and can also be used to manufacture concrete. Waste rubber tyres are employed majorly for energy recovery and building materials and are being reused as fuel in developed nations. The recycled rubber and steel fibres make concrete tougher and stronger, displaying enhanced post-cracking attitudes and elevated fatigue lives [148]. Not only that, the recycled fibres also entail monetary advantages in construction. Nowadays, greener, inorganic geopolymeric construction composites are appearing to be a most promising substitute for OPC-based systems, with an exhibition of excellent properties, such as higher mechanical attributes, lower creep, less shrinkage, and extraordinary resistance to chemicals such as acid [149–153]. The exothermal process of geopolymerization among alkali solutions and the silica- and alumina-rich source materials of geological or industrial origin at low temperatures is competent enough for manufacturing geopolymer pastes, binders, mortar, and concrete, and for incorporating rubber tyre waste as a replacement for fine and/or coarse natural aggregates to form the rubberized geopolymer construction composites [153,154]. The raw materials with geological origin, such as calcined kaolin or metakaolin or other industrial by-products, namely, coal fly ash, coal bottom ash, blast furnace slag, etc., are the leading examples of possible raw materials for geopolymerization. Hydroxides and silicates of sodium or potassium are more commonly used as activators. The process symbolizes mitigated CO_2 emissions and a reduced operational energy, in comparison with the present course of portland cement production [152–154]. Not only that, geopolymerization produces added-value construction products by means of reusing the industrial residues enclosing alumino-silicates [155]. Most eye-catching of all, however, are fly ash-based geopolymers exhibiting higher early strengths, brilliant resistances to attacks of sulphate, acid, and corrosion-causing factors, as well as outstanding resistances to fire and high temperatures [156,157]. Using tyre rubber waste as an aggregate in concrete was introduced to manufacture a brand-new kind of concrete produced by the substitution of natural aggregates and is coined as rubberized concrete, or elastic concrete, or crumb rubber concrete, or rubber tyre concrete, or rubber concrete, or concrete with ground waste tyre rubber, or rubber create. The key objective behind the integration of rubber was to add a definite quantity of flexible components with the original multi-constituent concrete to enhance the concrete performance [153,157]. Synthetic rubber aggregates can be derived not only from waste rubber tyres, but also from cables, rubber belts, wires, industrial rubber products, hoses, and some other kinds of waste rubber, etc. The plain rubberized concrete can also be regarded as conventional-strength-grade concrete with coarser and/or finer synthetic rubber aggregate substitutions. As a semi-rigid material, crumb-rubberized concrete has performed between normal and asphalt concrete. The rubber tyre waste employed in developing rubberized concrete can be classified into three main categories, emphasizing particle size: crumb rubber, chips, and powder rubber [158].

The crumb-containing rubberized concrete formulated through rubber particles as synthetic finer aggregates has been investigated expansively.

On the other hand, vulcanized rubber is awfully strong, durable, and flexible while maintaining volume, even under loads, suggesting its fittingness for employment as an aggregate for edifice materials. Looking to the chemistry, it consists of long-chain polymers which are cross-linked with sulphur bonds protected by antioxidants and antiozonants, making them competent for resisting degradation. The techniques for recovery influence the appropriateness of recycled rubber for application in the new composite productions. For illustration, smaller rubber granulates possess a greater contact surface than bigger rubber chips, and hence, the former shows a better adhesion to the matrix.

Constructions and Infrastructures Sector

For the past couple of years, the constructions and infrastructures industries have been reacting to the challenge of integrating sustainability into manufacturing that was made possible via the application of solid wastes as artificial aggregates in concrete or by means of a search for more eco-benign raw materials. One of the doable solutions for the use of worn tyres is in concrete-making technology as man-made aggregates [159,160]. What is more, the fundamental nature of the dissimilar kinds of rubbers and compositions necessitate comprehension to wholly exploit their attributes in high-valued uses in the construction industry. The application of rubber into concrete has eye-catching attractions. Preceding research has accounted for the substitution of natural aggregates with synthetic waste tyre ingredients in concrete mixes, piloting a noteworthy boost in the context of ductility and stiffness [161]. The research investigations on the application of waste rubber tyres as artificial aggregates in concrete demonstrates that concrete with enhanced strength and sound insulation can be manufactured. Research has uncovered that supplementing fibrous rubber into concrete production enhances the shockwave abrasion and resistance to acid rain, while trimming down noise levels and heat conductivity. The utility of rubber as a supplementary material in making concrete formulates a composite and is appropriate to partly substitute the natural aggregate. Upon replacing the aggregates with crumb rubber, the compressive strength of concrete was mitigated appreciably. Nevertheless, a huge quantity of energy under tensile and compressive loads can be absorbed by rubberized concrete [162–164]. It is supposed that the augmentation in impact resistance was obtained from the boosted aptitude of the material to absorb energy. The rubberized concrete was proposed to be utilized under conditions where vibration-damping is necessitated, such as in the construction of highways as shock absorbers and in structures as earthquake shockwave absorbers [165–167]. The addition of shredded rubber into concrete manufacturing lends a hand to make concrete softer and generates larger plastic deformations on impact, along with inferior deceleration forces. The rubberized concrete, whereby the sand is partially replaced with tyre rubber, is apposite for employment in utilizations where mechanical attributes are less important but higher resistances to chloride ion infiltration is needed, as suggested by Chou et al. [166]. This change can save a passenger's life and simultaneously mitigate the rubber quantity that frequently finishes in stockpiles or landfills. At present, a mere 5% of recycled waste rubber tyres are employed, even though their potential in construction is superior. To achieve rubber aggregates from waste rubber tyres, the waste rubber tyres have to be diminished in size before recycling [168]. Two dissimilar technologies can be employed, namely, a mechanical type of grinding at ambient temperatures to manufacture chipped rubber substituting coarser ingredients, and a cryogenic type of grinding at a temperature lower than the temperature of glass transition to yield crumb rubber, which replaces finer aggregates. Currently, the rubber utilized in concrete entails shredded and crumb rubbers.

The fibres of shredded rubber can viaduct the cracking in concrete and boost the interaction among the artificial rubber aggregates and cement paste. Consequently, the concrete incorporated with shredded rubber exhibits greater flexural strength, ductility, and damping attributes than the rubberised concrete without fibres [169–171]. What is more, the free water absorption by textile fibres augments the water absorption of fresh rubberized concrete, in that way ensuing from a decline in a slump. The second technique yields, more often than not, crumb rubber to be used as a substitute for finer natural aggregates [172]. The stages in yielding crumb rubber entail shredding, separation of textile and steel fibres, granulation, and classification. Subsequent to shredding, the textiles and steel fibres are taken away through air separators and magnetic screens, correspondingly [173,174].

On account of the supplement of particles of rubber, the rubberized concrete has gained lower density, superior acid resistance, good-quality sound absorption, excellent freeze–thaw resistance, boosted damping capabilities and flexibility, impacting toughness and strength, as well as a brilliant chloride-permeability resistance. The referred-to benefits make the rubberized concrete attention-grabbing for utilizations such as light-weight concrete, pavements, noise screening, rubberized concrete beams with higher impact resistance, and reinforced columns for resistance to earthquakes in structures. Nevertheless, numerous investigations have exhibited that making use of rubber in concrete normally pilots a drop in the strength of the concrete. The abridged strength of the rubberized concrete is, for the most part, owing to the following reasons: (A) the hydrophobic attitude of rubber creates the hydraulic phase to move out of the rubber and yields a less dense matrix at the interfacial transition zone. (B) (a) In shredded rubber, i.e., tyre waste chips, and (b) crumb rubber, the lower elastic modulus of a softer rubber than its neighbouring media, i.e., cement paste and aggregates, causes the artificial rubber aggregate to play the role of a "soft core" in the rubberized concrete. In the course of the loading progression, higher stress concentrations form around the synthetic rubber aggregates and ultimately pilot escalated cracking of the rubberized concrete. (C) Because of the lower specific gravity of the particles of rubber, compared to conventional natural aggregates, and the pitiable interfacial bonding among the particles of rubber and cement matrix, the particles of rubber are inclined to move towards the outer surface of concrete for the duration of the vibration treatment. The heterogeneous distribution of the particles of rubber within the rubberized concrete finally leads to a fall in the concrete's strength [174–176]. For that reason, to alleviate the mechanical strength decrease of the concrete due to the integration of the particles of the rubber, the artificial aggregates from rubber can be surface-changed, making use of physical or chemical treatments. The surface treatment of the particles of the rubber can enhance the interfacial bond among the particles of the rubber and the matrix of the cement, as well as boost the bonding strength among them, which is advantageous for improving the mechanical attributes and durability of rubberized concrete.

10. Discussion

As a natural resource-conserving and eco-benevolent approach, the integration of rubber tyre waste in the building and infrastructure industries can lend a hand to the mitigation of pollution whilst contributing to the design of not only more cost-effective but also more sustainable buildings with acceptable norms. Consequently, the use of rubber tyre aggregates in concrete has happened to be progressively more popular, creating an earth-shattering research interest in this 21st century. This is why the replacement of restricted natural fine and coarse aggregates with a variety of recycled rubber synthetic aggregates has made momentous progress globally, thereby sinking the call for quarried virgin restricted natural aggregates. As the best way to get rid of the profuse automobile solid rubber tyre waste is by reusing them in a recycled form with concrete, using recycled synthetic aggregates from the scrapped tyres to produce useful rubberized geopolymeric construction products appears to be a viable solution to use in place of natural ones. Rubberized geopolymers can also solve a social and environmental problem, due to the large accumulation of tyres in landfills. Confined studies have piloted the impact of incorporating crumb rubber with geopolymer concrete mixes despite the reality that it has a much-amplified consideration in structural exercises in the range of empirical explorations accomplished in the literature references. However, the findings of this review indicate that rubberized concrete enhances ductility and impact resistance, but reduces compressive, tensile, and flexural strengths to a slightly low extent. However, clear and added proofs to verify the likelihood of establishing crumb rubber as a partial replacement for fine and/or coarse natural aggregate materials are necessitated because merely restricted data is on hand for the mechanical characteristics of rubberized geopolymer concrete integrated with rubber or crumb rubber as synthetic aggregates. Even though there is still inadequate data on the interaction among rubber and some other constituents in rubberized geopolymer concretes, its mixes are found with acceptable outcomes regarding strengths, ductility, and impact resistance when employed in structural elements that are exposed to not only impact but also the dynamic loads of bridge approach slabs, airport runways, railway buffers, etc. The replacement of natural sand with crumb rubber has proven to enhance the ductility, impact resistance, insulation attributes of thermal conductivity, and acoustic impedance of cement-based crumb-rubberized concrete. Nevertheless, there is still a very limited amount of accessible information on crumb rubber applications in geopolymer mortar and concrete. The SWOT analysis explores the strengths of rubberized geopolymers, showing a higher compressive strength than the conventional rubberized cement concrete, but the weakness is that rubber waste decreases the flow tendency and, as a result, increases the water requirements. Evocatively, rubberized geopolymer composites are a sustainable alternative to cement systems and require roughly 60% less energy with 80% less CO_2 emissions, compared to the OPC production process, proving them more eco-friendly and energy-effective, with the added benefits of safeguarding natural mineral resources and reducing the number of wasted tyres entering landfills. Predictably, the production of bricks or blocks, whereby no higher compressive strength is obligatory, can be promoted with the full replacement of natural aggregate crumb rubber; however, no study has yet been accounted for in the literature on this kind of research work on crumb rubber as a 100% replacement for natural aggregates to manufacture geopolymer mortar and/or concrete.

For this reason, recycling discarded tyres as crumb rubber integrated with concrete has turned out to be one of the options in sustaining the environmental balance with value-added profitable significance. The potential predicaments of end-of-life tyres seem to have with a systematic solution for their disposal by incorporating recovered materials from rubber tyre waste into cementitious materials as one of the recent innovative approaches. To date, most of the rubber extracted from tyres is burnt as fuel-producing perilous gas, while recovering merely 25% of the energy employed to produce rubber that is useful as aggregates.

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