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Proposal to Reuse Rubber Waste from End-Of-Life Tires Using Thermosetting Resin

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Abstract: Due to the increasing production of motor vehicles, a large amount of waste with different characteristics and compositions is generated, notably end-of-life tires, which are harmful to the environment when not properly disposed. Their composition contains contaminating chemical elements, resulting in negative impacts on the environment. This research aims to present a process that favors the recycling of rubber waste from end-of-life tires. For the construction of the state of the art and state of the technique, a review of the literature on end-of-life tire rubber, and a search on Google Patents and Espacenet was done using Methodi Ordinatio. For the experimental work, samples were made using concentrations of 20%, 40%, and 60% of end-of-life tire rubber particles, with the addition of thermoset polymeric matrix of isophthalic polyester resin, catalyst, and dyes. In order to evaluate the quality of the mixture, some tests with the material resulting from the mixture were performed: Izod impact strength, Shore D hardness, immersion density determination, flexural strength, and scanning electron microscopy analysis. The results from the tests indicate that the composition with 60% of rubber particles had better mechanical results than samples containing 20% and 40%. The tests also show that end-of-life tire particles promote chemical adsorption (interaction) with the thermoset polymer matrix, favoring the mechanical properties. The final results of this research are: the literature review and the search on granted patents showed that this study is original; the experimental work suggests that practical applications are possible, generating a new product, harder with a proportion of 60% of rubber particles, as indicated by the tests, with a smooth surface that does not require polishing. Thus, this research is characterized as innovative as well as having sustainable characteristics.

Keywords: end-of-life tires; rubber particles; tire rubber; tire recycling; sustainable materials

1. Introduction

Each year, the generation of polymeric waste has been growing. Mostly originating from motor vehicles [1], notably from end-of-life tires.

The production of motor vehicles has been growing over the years as a result of consumption patterns in industrialized countries [2]. In the last decade, there was an increase of 85% in relation to world production of cars. In 2016 alone, around 97 million vehicles were produced, which represents a 7% increase over the previous year [2]. This accounted for approximately 25.6 million tons of end-of-life tires (ELTs) generated in 2016, according to the World Business Council for Sustainable Development (WBCSD) [3].

ELTs are used to define the maximum wear stage a tire can achieve [3]. According to the European Tire and Rubber Manufacturers Association (ETRMA) [4], "when tires are removed from vehicles, they become partially worn tires, or ELTs". These tires are unsuitable for use and should be suspended as their parameters and specifications or manufacturing characteristics may be condemned at this stage [4].

In 2012, there were one million ELTs, and it is expected that by 2030 there will be around 500 million discarded, originating from motor vehicles. Only a small part of that waste is recycled and millions are destined to landfills or simply buried, where they take up a lot of storage space [1,5]. Tire waste recycling is a serious environmental problem, because its chemical structure is very complex [1], as described in Landi [6].

The WBCSD's study [3] points out that the main generator of ELTs was China (10.3 million tonnes, 40.2%), followed by the United States (3.5 million tonnes, 13.7%) respectively. New Zealand was the least influential country in the generation of ELTs (0.04 million tons, 0.2%) among the group of countries analyzed in the period [3]. Rubber wastes, which composition is described in Landi [6], release toxic substances and chemical elements that contaminate the local environment: the air, soil, and even groundwater.

In order to minimize the environmental impacts related to ELTs, some tire recovery practices are adopted by companies, such as monitoring tire recycling status, overseeing recycling processes, and avoiding improper disposal in the environment, among others [7]. However, the world average percentage of unrecovered material is 31% [3].

Thus, final disposing of tires is still a worldwide problem, and burning them is a risk to the environment and human health. Disposal in landfills is considered inappropriate as they are not suitable places, allowing the proliferation of insects and rodents [1,8]. The extant literature in this field has studies that aim to minimize the negative impacts caused by toxic substances from ELTs rubber waste, indicating contributions to the redirection and use of ELTs. For instance, Saleh's study [9] highlights the relevant role of surface chemical reactivity control in order to improve the possibilities of chemical reactions by contact, or chemical adsorption process. In Saleh [10], silica nanocomposites incorporated with carbon and activated carbon nanotubes were synthesized and characterized; the purpose was to investigate the efficient removal of mercury ions in aqueous solutions.

There are studies using activated carbon prepared from ELTs, where their surface functional groups have been improved by chemical oxidation with nitric acid, indicated for a better investigation in industrial use [11]. Danmaliki [12] report that the use of activated carbon with the presence of nickel nanoparticles solves the problems of waste management and desulphurization simultaneously, thus acting as a chemical adsorption promoter. Saleh [13] studied manganese oxide-treated activated carbon for further improvement of its surface properties for adsorption desulphurization. Saleh [13] addresses the adsorption facilitated by the action of activated carbon, with tungsten oxide and iron, and is also applied in the cleaning and decontamination of water. Saleh [14] used activated carbon derived from diethylenetriamine tire residues to increase the adsorption efficiency. Specifically, in that study the objective of the experiment was to remove phenol from water. Saleh [15] comments that "sulfur removal from petroleum products is an important step in the refining process".

Several techniques have been developed to address the limitations of hydrodesulfurization, including adsorption desulfurization. One of the requirements of the adsorption desulphurization process is the use of efficient, economical materials and the search for a simple process. The study in Adio [16] discusses the "use of poly (amidoxime) modified magnetic activated carbon as an efficient approach for chromium and thallium adsorption. Activated carbon was synthesized from rubber tire waste, further enhanced with magnetic properties and modified by poly (amidoxime), providing more functional groups and thus improving adsorption efficiency".

Turning to the aspect of ELTs recycling methods and processes, Gonzalez [17] studied their use in construction and pointed out that there is good stability of modified hot bitumen with ELTs and polymeric additives, stating that its rheological and technological properties improve with all polymeric additives near the binder. Blessen [8] conducted a study noting that the use of ELTs mixed in building concrete makes it highly resistant to harsh environments and it is recommended for use in areas where there is a greater possibility of acid attack. Siddik [18] concluded that the use of polymers mixed with building concrete improves the final properties mainly in relation to durability and tensile strength.

The study by Blessen [8] is also relevant when analyzing the polymer-modified asphalt mixture at room temperature using cryogenic broken ELTS, but it does not indicate a significant difference in the performance of binders found in laboratory tests. Landi [6] conducted a tire life cycle analysis, focusing on the viability of the textile material; such material is not recommend as a reinforcement material in the asphalt, since there is no proven economic viability in this study.

Faced with the need to manage ELTs, environmental and governmental entities have established policies and actions to promote its proper destination [18]. These policies establish legal mechanisms to reduce the volume of ELTs and their impacts.

Due to many sustainability-focused environmental laws, countries are looking to use ELTs, and one of the most targeted means is to apply granular tire rubbers as energy resources, such as for furnace burning or oil extraction, for instance [18]. Table 1 sets out the key ELT management systems, as well as their characterization, and lists the countries that have their systems-based actions to manage the proper disposal of those wastes.

Table 1. ELTs management systems.

System	Definition	Countries	
"Free market system"	The legislator approves the objectives to be fulfilled. However, there is only the existence of an industrial association in charge of promoting the management of ELTs.	Argentina Germany Switzerland Great Britain Austria China India Indonesia Japan Malaysia Mexico	New Zealand Saudi Arabia Thailand U.S Bosnia Herzegovina Serbia Albania Macedonia Montenegro
"Tax system"	The government is responsible for the recovery of ELTs and remunerates the operators in the recovery chain. ELT management is financed through taxes levied on tire manufacturers and importers, which are passed on to consumers.	Denmark Croatia	

Source: Adapted from the World Business Council for Sustainable Development [3] and European Tire and Rubber Manufacturers' Association (ETRMA) [4].

European Tire and Rubber Manufacturers' Association (ETRMA) [4] and the European Union (EU) are precursors to all rules and decisions related to the disposal practices of ELTs in Europe. The European ELT management systems are the "Extended Producer Responsibility System (EPR)", "Tax System", and "Free Market System" [3,4,19].

In Brazil, the responsibility for the environmentally appropriate collection and disposal of ELTs lies with tire manufacturers and importers [20], under the regulation of Resolution 416/2009 of the Brazilian National Environmental Council [20]. According to Lagarinhos [21], in addition to the responsibility of manufacturers and importers, other agents (dealers and resellers) are responsible for collecting damaged or non-standard tires for use in vehicles.

There are countries that do not have specific regulations on ELT management, such as Indonesia, Malaysia, Morocco, and Thailand. Other countries—such as South Korea, Russia, Ukraine, China, Saudi Arabia, Argentina, and Japan—do not have specific legislation, but use basic guidelines for managing ELTs [3].

In order to reuse ELTs waste, it is first necessary to change the tire into rubber particles using one of the following processes: (a) pyrolysis, (b) microwave, (c) cryogenic, or (d) microbiological [22–24].

The pyrolysis process is described as the thermal degradation of the organic components of ELTs, performed at high temperatures without the presence of oxygen [25–27]. Pyrolysis is a costly process due to the presence of carbon black, and its final product is of inferior quality than that extracted directly as a primary oil item [8]. However, as a complement to civil construction and concrete, the presence of carbon black favors the replacement of some agglomerates, resulting in interesting material properties [8]. According to Misik [28], in the process by pyrolysis there are barriers to its successful application, both economic and technical. The pyrolysis process is known for low emissions on the environment but carries with it the disadvantage of high cost in its manufacturing. The pyrolysis products do not have sufficient added value, since the result of the process is based on the extraction of different oils. The value of the barrel of oil in the international market determines the viability of the pyrolysis process.

The recycling process by microwave is carried out using sufficient energy to break the chemical bonds of the vulcanized material at temperatures between 260 °C and 350 °C. The major disadvantage in the microwave process is the cost of the energy used and the existence of tailings such as carbon black, which is difficult to recycle [29]. The microwave process has its best results when the microstructure results in finer particles, leading to improved mechanical properties. The latest potential microwave applications involve steel production, recycling of used tires and alternative sources for energy recovery [30].

The cryogenic process consists in reducing the rubber temperature of the tires to a temperature below the glass transition temperature, which leaves the chemical bonds more rigid, and soon thereafter the grinding of this rubber in impact mill, fragmenting into smaller pieces and in different granulometries, which are separated by sieving [22].

The microbiological recycling process is a method that uses bacteria as microorganisms to promote the decomposition of the chemical structure of the ELTs, usually attacking the crosslinking of the vulcanization process. This breaks down vulcanized currents and generates smaller rubble particles and is intended for various purposes in the market [22–24].

In our study, in order to obtain the rubber particles, the process used is the scrapping of the tires. The scrapping is done without having to apply any of the process previously described, which implies that no substance or residues, like smoke on the air, or pollution into the ground or water, will be disposed as required by the process. A machine will do the scrapping, and the particles are deposited in a recipient for later use. The particles will be, then, mixed to other components to form a mixture. This mixture can turn into specific design, further described in this paper.

The aim of this paper is to propose the reuse of rubber waste from end-of-life tires using thermosetting resin. As a complementary objective, we analyze the mixture of end-of-life rubber tire particles, together with isophthalic thermosetting resin, inferring possible practical applications of this material, of which final design of the pieces has as a strong characteristic a smooth surface that does not require further polishing.

2. Materials and Methods

This section presents two subsections: Section 2.1 describes the theoretical background, and Section 2.2 describes the experimental work.

2.1. Theoretical Approach

The theoretical approach was done on the literature and on patents granted. The systematic review on the extant literature was performed using the Methodi Ordinatio methodology [31,32] as described in Stadler [33], Campos [34], Cunha [35], and Muller [36]. The purpose of this methodology is to select articles according to their scientific relevance, taking into consideration the main factors to be considered in a scientific article: the impact factor of the journal in which the document was published, the number of citations, and the year of publication. The phases were:

Phase 1—Establishing the research focus: "Tire recycling".
Phase 2—Preliminary exploratory keyword research in databases: the databases linked to the researched theme were Science Direct, Scopus, and Web of Knowledge.
Phase 3—The definition of keyword combinations, as well as the bibliographic databases, as presented in Table 2.
Phase 4—The final database search: for this phase, the reference managers Mendeley® and JabRef® were used. Gross results are shown on Table 2.
Phase 5—Filtering Procedures: to eliminate duplicate documents; articles not related to the theme; conference papers and books and/or book chapters—the latter were used as complementary material on theoretical background.
Phase 6—Impact factor (metrics) identification, year and number of citations: the impact factor was obtained from the Scopus and Science Direct website; following this order of preference: JCR, CiteScore, SJR (SCimago), and SNIP. The number of citations was obtained from Google Scholar. This information—metrics, number of citations—together with the year of publication, is critical to calculating InOrdinatio.
Phase 7—To classify articles according to their scientific relevance, using the index InOrdinatio Equation (1). The equation was applied using an electronic spreadsheet.

$$\text{InOrdinatio} = (\text{IF}/1000) + \alpha \times [10 - (\text{ResearchYear} - \text{PublishYear})] + (\text{Ci}) \quad (1)$$

Table 2. Gross results from final search of Phase 4.

Group	Keywords and Combinations	Article Journals
1	"Tire* recycling" or "Tyre* recycling"	46
2	"Rubber waste"	39
3	"Knowledge and Technology Transfer"	16
4	("Tire* recycling" or "Tyre* recycling") and "Rubber waste"	12
5	("Tire* recycling" or "Tyre* recycling") and "Knowledge and Technology Transfer"	12
6	"Rubber waste" and "Knowledge and Technology Transfer"	0
	Total	125

The elements of the equation are: IF—impact factor; α—alpha value, ranging from 1 to 10, to be defined by the researcher according to the importance of the novelty of the theme. For this study, the value of α was set as 10, since the theme is the object of study in very recent articles; ResearchYear—year in which research was developed; PublishYear—Year the article was published; and Ci—number of times the article was cited.

Phase 8—Downloading the papers in full format.
Phase 9—Systematic reading and analysis of the articles: bibliometric mapping and content analysis, with the focus theme of the study.

In order to verify the state of the technique in ELTs recycling, a search on patents granted under this theme was performed. Searches were conducted on Google Patents [37] and Espacenet [38] as they have extensive and up-to-date databases containing the world's largest patent grants, and present up-to-date and easily accessible data.

The filtering criteria used for patents search are described in Figure 1.

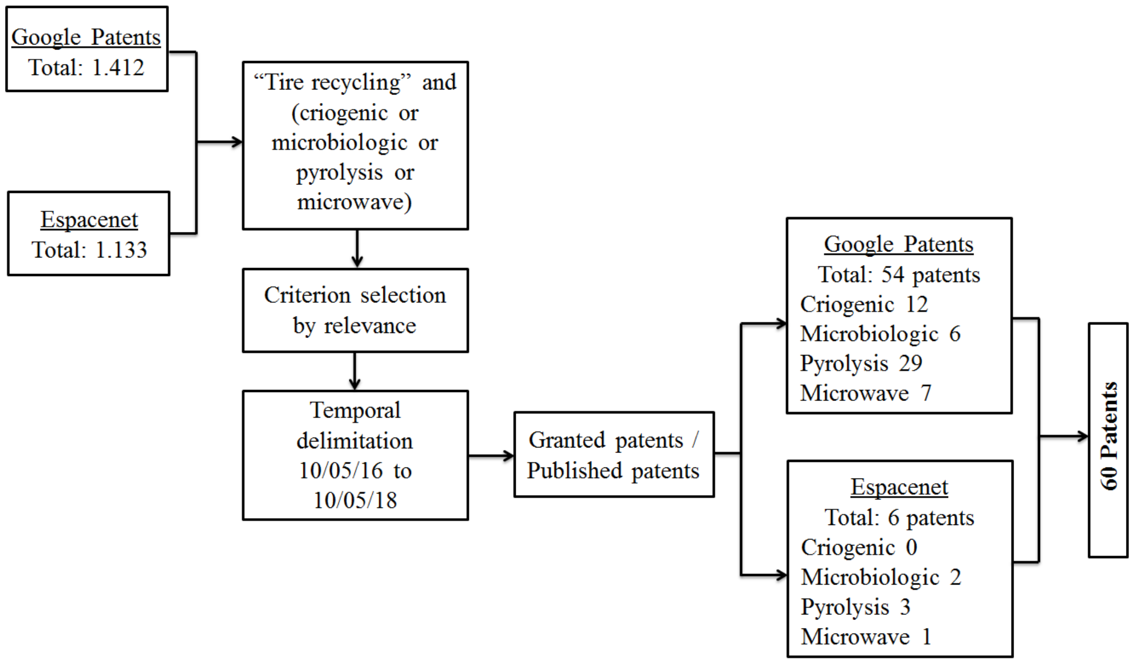

Figure 1. Filtering criteria used in patents searching.

As shown in Figure 1, patent searches were carried out using the keyphrase “Tire Recycling”. When analyzing the set of patents, we perceived that there are four large distinct groups as ELT recycling methods, which were focal points as filter criteria for this study: “cryogenic”, “microbiological”, “pyrolysis”, and “microwave”. Other filtering criteria were: patents granted, accredited, and published on Google [37] or Espacenet [38] systems, respectively; the temporal factor (patents registered in the last two years, between May 2016 and May 2018, were priority for the study) and; patent status (we eliminate patents under review).

On Espacenet [38] patent database, the filtering process consisted in eliminating duplicate patents, already in Google Patents [37].

A total of 2,545 patents had ’granted’ status considering both databases. However, only 60 patents had been accredited and published. For this reason, from 2,545 patents analyzed, 60 were selected for detailed analysis, as their content focused on the subject of this study (as in Appendix A), and the remaining 2,485 were unrelated to research, and thus eliminated.

The temporal analysis was determined considering that a patent has a validity period of 20 years. Therefore, when analyzing the patents granted until 2018, it is possible to infer that the data collection is substantial and consistent, and no similar patent was proposed previously to this study.

2.2. Experiments

The following subsection presents the steps for performing the experiments, which include sample material production and mechanical testing. In the sequence, the steps for carrying out the experiments, which include the production of the sample pieces material and the mechanical tests, are described.

2.2.1. Preparation of Sample Pieces and Prototyping

Samples pieces were used for the flexural strength tests, following the specific standard for this test, according to the American Society for Testing and Materials (ASTM). The prototypes were made in two dimensions: 200 × 200 mm and 100 × 150 mm.

In order to obtain the material, the following procedures were performed:

(a) The scraped particles of ELTs rubber residues were purchased from a vehicle tire picker. The particles collected were found in different sizes and formats, since the process, due to the characteristic of the scraping machine, produce uneven particles.
(b) The ELT residue particles are selected through sieving in order to separate the particles according to the granulometry between 20 and +60 meshes, following the technical standard [39]. The equipment used was the Vibrotec CT 025.
(c) The ELT particles are placed into three separate containers, in the amounts of 20%, 40%, and 60%, respectively. The mixture derived from ELTs and isophthalic polyester resin was laid in molds. It is important to clarify that the three mixtures were done simultaneously only because the tests were performed in sample pieces with different percentage amounts of ELTs rubber residues (20%, 40%, and 60%).
(d) In each of the containers other components were added, such as colorant in the desired color (between 1% and 3%); and polyester isophthalic resin in the inverse proportion of the quantity of ELTs.
(e) The mixing must be done slowly to avoid formation of air bubbles within the material; it must become a homogeneous blend.
(f) After this process, the catalyst (methyl ethyl ketone peroxide) is added in each of the containers, and may range from 5% to 10% concentration, depending on the desired final texture in the part.
(g) The mixing is again done slowly and homogeneously, forming a blend that will be cast in the desired format for the samples, according to the respective technical standards for each test.
(h) After the preparation of the blend, if intended to add decorative material such as such as metal powder particles, a new mixing must be done. For instance, in our research, the metal resulting from the scraped tire was added, resulting in shining pieces. They were then laid in molds of 200×200 mm proportions to obtain plaques, the prototype.
(i) After curing and drying the blender, the unmolding is done, and the pieces can then be applied for the desired purpose.

2.2.2. Mechanical Tests

The scrap tire rubber residues were sieved according to ASTM D6913-2017 [39], using rubber particles with grain size between 20 and 60 mesh and 20%, 40%, and 60% sample load concentrations. Bogdal [40] reports that, with 2% initiator, the cure temperature of the isophthalic resin is 152 °C and may reach 160 °C at the exothermic temperature in the curing process of the polymer. The components (isophthalic resin and treated rubber residues) were mixed, obtaining test bodies for the mechanical tests and also to make the prototypes with addition of dye (entre 1% a 3%) in the form of glass plates with 200×200 mm.

Subsequently, Izod impact strength tests, Shore D hardness, immersion density and flexural strength determination were performed according to ASTM: 41, 42, 43, and 44, respectively. All assays were performed at 23 °C at 50% humidity.

Izod Impact Resistance

This testing method is used in plastic materials to determine its shock resistance of a pendulum standardized according to ASTM D256-2010 [41], during the impact. The notch serves to concentrate the stresses involved and act as a central point for material breakage. By releasing the pendulum, it acquires a falling energy, where part of it is absorbed by the polymeric material that is notched, during impact. The notch serves to concentrate the stresses involved and to act as a center. The pendulum must have a 180° movement to move freely. However, when there is a shock with a proof body, the absorption of the energy is measured by the equipment denoting its loss by the difference of the resulting final height, which will not complete the 180°.

The conditions for the impact test obeyed the technical standard [41]. The equipment used for this purpose was the NZ Philpolymer, model XJC—25D and pendulum of 1 J. Only sample pieces with complete breakage were considered, classified in a category of type C. As established by technical standard, ten bodies are required to evidence the results. The tests of flexural strength (Izod impact) were performed with 10 test bodies; all specimens with a square cross-section of 12.7 mm (width) and 63.5 mm (length) [41] technical standard.

Hardness Shore D

This test indicated for thermoplastic and/or vulcanized elastomer polymer material as thermosets. The International System (SI) of measures is considered in this test. For this test, the Maynard durometer M-701 DG, which measures the resistance of the test bodies to the penetrator D type indenter, was applied with an angle between 30° and 35°, pressed against the sample piece by the action of a spring under standard load, with a time of application of the load of 15 s. The sample test piece is 6 mm thick, with lateral dimensions sufficient to allow measurements of at least 12.0 mm from each edge. Hardness testing conditions are outlined in ASTM D2240-2015 [42]. The standard cited in this test requires at least five specimens to obtain a test average.

Determining the Density of the Test Bodies by Immersion

Density is the ratio of mass sample to volume occupied by i, in a given ambient condition [43]. This density was determined by Equation (2).

$$d = (m/v) \tag{2}$$

where: d is the density; m is the mass, and; v is the volume.

The test conditions followed the technical standard [44], having as immersion fluid ethyl alcohol, whose density its density is 0.8020 g/cm^3. The standard for this assay requires that there be at least the average of three specimen readings.

Flexural Strength

A load cell of 5 KN steadily, according to the ASTM D790-2010 [45] technical standard, with test speed of 2 mm/min and Instron Emic equipment, model 23–30, was applied to the test bodies in three points. Five sample pieces were tested.

The calculation is performed according to the thickness of the test piece (according to the norm) by means of Equation (2).

$$\sigma = [(3 \times P \times L)/(2 \times b \times d^2)] \tag{3}$$

where σ is the tension in the bending (MPa); P is the load or force applied (N); L is the distance between two fixed supports (mm); d is the mean thickness of the specimens used in mm; b is the width of the specimen in mm.

This test covers the determination of the flexural strength of polymeric materials with reinforcement or without reinforcement and can be applied in either in rigid or semi-rigid materials. However, this test may only be used on materials that break or exhibit a surface failure during the test. The procedures adopted follow the International System (SI) standard.

Scanning Electron Microscopy (SEM)

Two equipment, model FEI Inspect S 50 and model Vega3 TeScan were used. In this test, the adhesion of scrap tire rubber residues to the polymer matrix, especially their inference was investigated in the test bodies ruptured by the flexural strength tests.

The investigated samples were those ruptured in the IZOD impact resistance test. The ruptured surfaces analyzed underwent the metallization process with gold at 25 KV, and 60 s of exposure, with the distance of the electron beam cannon from the 15 mm sample, facilitating SEM visualization at different ocular increases.

3. Results and Discussion

Pacheco-Torgal [5] show that it is necessary to recycle rubber tires and indicate that the most current means are linked to civil engineering techniques, where ETL particles are added in asphalt or concrete with favorable results in their mechanical and chemical properties when they become resistant to acid attack, for example.

The studies of Dong [46] and Flores-Medina [47] proved that tire rubber particles, when chemically treated, have a change in their properties by potentiating the surface chemical bonds. For instance, one can verify this condition by using NaOH to treat ELTs; they also washed the ELTs particles and used them in the concrete. ELT rubber residues increase the absorption of impact energy. This asphalt reduces noise and the cracking by freezing and thawing, due to the elastic properties of rubber [48]. However, when in contact with excessive heat, the result might not be so satisfactory due to the softening.

A study by Sienkiewicz [1] proved that there is chemical reaction subsequently there is chemical interaction between ELTs and thermoplastic polymeric matrix, which is responsible for the mechanical properties of the promoted material of the reactions coming from.

The mechanical properties of chemical adsorption between ELTs and the polymeric compound will depend on aspects such as the amount of ELT concentration, their distribution, and the nature of chemical interactions such as the type and size of rubber grains [1].

The tests showed mechanical properties of the composition in different concentrations of scrap rubber waste, 20%, 40%, and 60%, in all tests performed. The results of these tests are discussed in sequence.

3.1. Analysis of Granted Patents

According to the Table A1 in Appendix A, it can be observed that patents are distributed in four large blocks, those of the processes using cryogenics, pyrolysis, microbiologic, and microwave. In the different patents via cryogenic process there is a quest to break tire rubber, giving rise to smaller particles and this is in general sifted and separated in different granulometry.

Through the process of pyrolysis, the patents on the Appendix A demonstrate that the result of this process is different oils, used by industries. The residue of this process is carbon black, which might represent a danger to the environment.

The microbiological process seeks the breaking of the vulcanized rubber chain of tires using microorganisms, as can be seen in the patents described in Appendix A.

The microwave process results in breaking the vulcanized chains, originating ELT particles in different sizes.

In the Appendix A, in the field sub product generated, there is a clearer description of the waste or sub products of each process. However, some patents do not clarify their sub product and there are cases in which the patent refers to equipment, and not a sub product.

3.2. Izod Impact Resistance

Ten test bodies were evaluated for each composition with ELTs addition. Table 3 shows the results of the variation of the impact resistance and energy absorbed as a function of the particle charge concentration used. Thirty specimens were used, 10 with 20% addition of tire rubber, 10 with 40%, and 10 other specimens with 60% tire rubbers.

It was observed that the average of the impact resistance increased as the amount of ELTs rubber residues were added in the composition of the sample pieces. All test bodies had type C fracture, that is, complete rupture during the tests performed.

Table 3. Results from Izod tests (impact resistance), with 20%, 40%, and 60% of ELTs rubber particles.

Test Bodies	Absorbed Energy (J)			Resistance Impact (J/m)			Resistance Impact (Kj/m^2)		
	20%	**40%**	**60%**	**20%**	**40%**	**60%**	**20%**	**40%**	**60%**
1	0.047	0.059	0.066	9.23	7.73	9.99	0.90	0.76	0.98
2	0.034	0.058	0.063	6.93	7.42	9.42	0.68	0.73	0.92
3	0.044	0.059	0.056	8.78	7.39	9.24	0.86	0.72	0.97
4	0.034	0.059	0.058	6.96	7.26	9.24	0.69	0.72	0.94
5	0.033	0.052	0.060	6.69	8.02	9.52	0.66	0.80	0.95
6	0.041	0.061	0.064	8.26	9.14	10.20	0.82	0.93	1.02
7	0.036	0.066	0.057	7.46	9.21	9.00	0.72	0.95	0.90
8	0.099	0.064	0.058	9.83	8.09	9.20	0.98	0.82	0.92
9	0.032	0.065	0.071	6.52	8.25	10.36	0.65	0.82	1.04
10	0.040	0.060	0.064	7.85	8.45	9.96	0.78	0.84	1.00
Average	**0.044**	**0.060**	**0.062**	**7.85**	**8.10**	**9.61**	**0.77**	**0.81**	**0.97**

The average of samples of test bodies with 60% of ELTs presented higher value (0.97 KJ/m^2) when compared to the other test bodies with 20% and 40%. Also, a higher energy level could be absorbed during the impact (0.062 J) in the test bodies with 60% of ELTs.

It is worth mentioning no other work, regarding the proportions of ELTs rubber residues addition, was found in the literature that could be compared to this research.

Studies on the addition of ELTs to concrete indicate that there is an improvement in the absorption of the impact when the amount of ELT in the mixture is larger [45–47].

3.3. Hardness Shore D

The tests were run on five test bodies for each of the three addition amounts of tire rubber residues (20%, 40%, and 60%, respectively). The results obtained are shown in Table 4.

Table 4. Results of Shore D hardness tests with 20%, 40%, and 60% of ELTs rubber particles.

Samples with Different Amount of Residues	Measures					Average
	1	**2**	**3**	**4**	**5**	
20%	77.5	77.0	80.5	76.5	78.0	78.0
40%	76.0	73.0	68.0	73.0	74.5	72.9
60%	75.5	76.0	74.5	70.5	70.5	73.4

The hardness Shore D with 0% addition of tire rubber residues was 70 Shore D, as indicated by the manufacturer [49]. The concentration of 60% of ELTs obtained a similar result with 40%, and also showed a hardness of less than 20% of ELTs.

One important aspect for analysis is that the presence of ELTs in the composition of the test bodies absorbed part of the stress deposited on the polymer matrix due to its adhesiveness.

3.4. Determination of Immersion Density

Three specimens were made for each addition of tire rubbers (20%, 40%, and 60%), with the average for each ELT concentration.

The results obtained in these tests are described in Table 5.

Table 5. Results of immersion density tests with 20%, 40%, and 60% of ELTs rubber particles.

Test Body	Immersion Density (g/cm^3)		
	20%	**40%**	**60%**
1	1.229	1.191	1.184
2	1.220	1.191	1.171
3	1.229	1.192	1.133
Average	**1.226**	**1.191**	**1.163**

The density of the resin without addition of tire rubber residues is of 1600 g/cm^3 [49]. The analysis of the results in Table 5 infers that the greater the presence of tire rubber residues, the lower the density could be. The study by Blessen [8] confirms the reduction of density with the addition of the ELT concentration to the chemical mixture. This is due to the low density of naturally existing tire rubber. This research reveals that the density of specimens with 60% ELTs is lower than the 20% concentration.

3.5. Flexural Strength

Three specimens were made for each concentration of ELT tire rubbers (20%, 40%, and 60%) for the flexural strength test.

The flexural strength had its highest average, 15.63 MPa, with 60% of ELTs, and 15.45 MPa with 20% of ELTs (Table 6).

Table 6. Results of flexural strength tests with 20%, 40%, and 60% of ELTs rubber particles.

Test Body	Flexural Strength (MPa)			Modulus of Elasticity (GPa)		
	20%	**40%**	**60%**	**20%**	**40%**	**60%**
1	16.15	10.83	14.41	1.59	0.61	1.12
2	15.95	15.32	15.08	1.42	1.17	1.31
3	14.26	11.63	17.40	1.54	0.66	1.15
Average	15.45	12.59	15.63	1.52	0.81	1.19

The flexural strength with 60% of ELTs was the most significant. In the study by Davallo [50], free of particles of tire rubber residues ELTs, the isophthalic resin presented 78 MPa of flexural strength, superior to the results obtained in the tests.

The work by Blessen [8] shows that flexural strength and compressive strength increases when ELTs are added up to 25%. This study corroborates our research by indicating that the best results with 60% ELTs totaling 15.63 MPa against 15.45 MPa with 20% and 12.59% with 40% ELTs. The compressive tensile strength increases by 10% to 20% than when the addition of tire rubbers (ELTs) is not used, as stated by Blessen [8].

The study by Blessen [8] shows that flexural strength and compressive strength increase when there is addition of ELTs rubber residues up to 25%. This study corroborates our research when indicating that the best results occur with 60% ELTs rubber residues, being 15.63 MPa versus 15.45 MPa with 20% and 12.59% with 40% ELTs. The compressive tensile strength increases by 10% to 20% more than when the addition ELTs rubber residues is not used [8].

3.6. Scanning Electron Microscopy (SEM)

In Figures 2 and 3, we can see pieces of a sample, with load of 60% of ELTs rubber residues. The sample was submitted to the impact test (Izod). After the rupture of the sample, the fracture surface was analyzed in SEM. What can be observed in the result of the broken pieces are:

- Figure 2 shows the polymer matrix of unsaturated polyester Isophthalic resin with ELT particles. We highlight in the circumference of the figure adsorption points between the matrix and the particular rubber. It is possible to observe that the process of radical reaction occurs between the means, that is, between the matrix and the particle. The sample of Figure 4 was visualized in the scanning electron microscope (SEM), magnified 200×.

- In Figure 3 we highlight two adsorption points of the ELT particle and the polymer matrix. It can be seen that the particle is in adherence in the structure and that part of it has been ruptured during the impact resistance test.

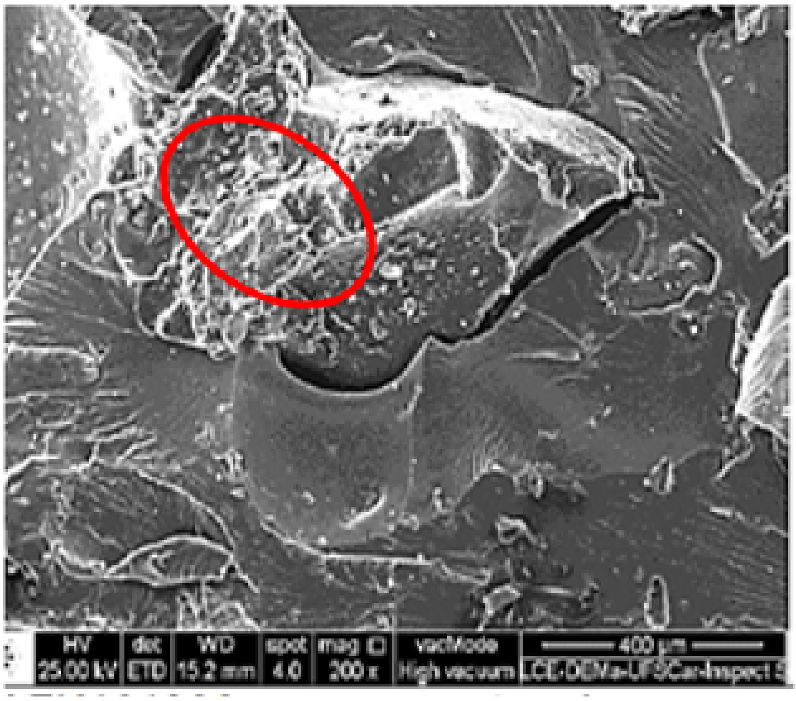

Figure 2. Sample SEM 25.00 KV, magnified 200×. WD of 15.2 mm (EspectroScan UFSCar).

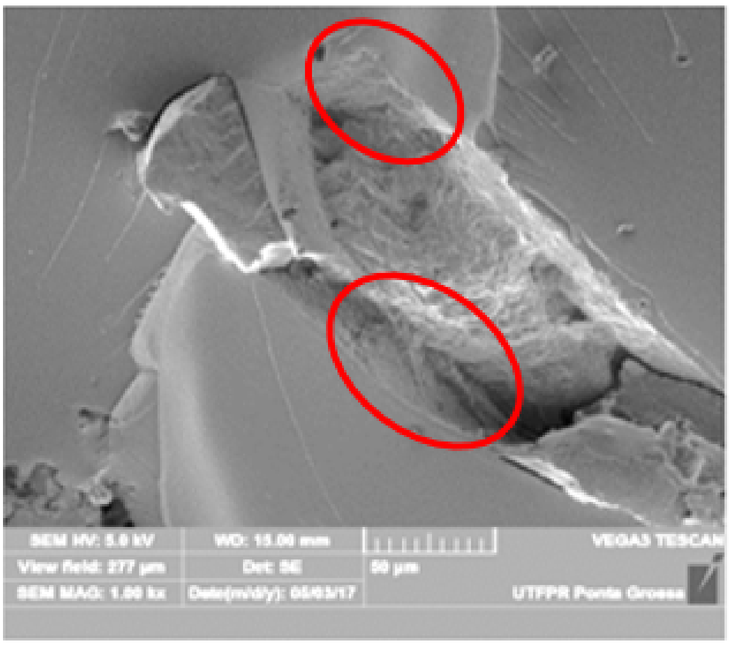

Figure 3. Sample SEM 5 KV. Magnified 400×. WD of 15 mm. (VegasTescan UTFPR).

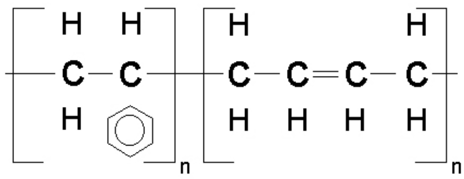

Figure 4. Chemical structure of styrene butadiene rubber (SBR).

In Figure 3 the rubber particle is visible inside the matrix, making the interface stickiness clear in the highlighted region. This is due to the temperature promoted during the cure of the isophthalic resin (152 °C) with a 5% initiator, reached the temperature of the vulcanization of the rubber, favoring the adhesiveness in this interface. Such a process does not occur in every interface (rubber/matrix) because the curing of the matrix occurs very quickly, given the time required to promote the vulcanization process, with only greater adhesion and with it a greater adhesion between the interfaces involved.

3.7. Chemical Interaction

Saleh's different studies show that the adsorption between ELT particles and polymeric compounds is possible. Saleh's focus is on removing metals from their surroundings, such as the work of removing metals from water, for example. Below is a brief narrative of these works by Saleh, which help to ground and understand the research of this article with ELTs and isophthalic polyester resin.

Multi-walled carbon nanotubes (MWCNTS) have been studied for very demanding applications. These MWCNTS are activated by oxidative process with the purpose of inserting functional groups to satisfy special needs [9]. Carboxylic groups (-COOH) are formed on the surface, and these functional groups promote the chemical reactivity of MWCNTS. These carboxyl groups increase regularly with increasing concentration of the percentage of the medium that surrounds them [9].

The chemical interaction is relevant to promote the adsorption and removal of heavy metals. The study by Saleh [51] shows that there is ion exchange methods for biosorption, membrane techniques, precipitation, among others, which show low adsorption performance to remove aluminum. The research by Saleh [13] indicates better results with nanocomposite of activated carbon/magnetic tungsten.

However, Saleh [15] mentions that sulfur concentrations promote contamination in industrial catalysts and as in oils, reducing the useful life drastically. In addition, organic sulfur compounds are converted to sulfur oxides, having a negative effect on nature.

Sienkiewicz [1] states that ELTs can be used together with polymeric matrices as thermoplastics to form new rubber–polymer composites.

In the process of chemical interaction that occurs between the unsaturated polyester isophthalic resin matrix and the rubber particle of ELTs, whose base is styrene butadiene (SBR), can be analyzed below. In Figure 4 it is possible to observe that the chemical structure of SBR has only one double bond occurring between carbons.

Figure 5 shows that the chemical structure of unsaturated polyester isophthalic resin, which has four carbon-oxygen double bonds (C=O), and a carbon-carbon double bond (C=C).

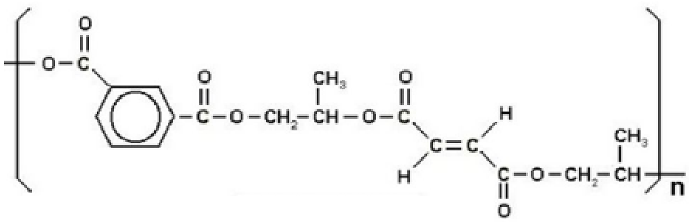

Figure 5. Isophthalic polyester resin chemical structure.

When the tire is prepared for the retreading or re-molding process, there are particles of different sizes originating from the scraping process of SBR [52]. It is observed that this SBR (Figure 4) is vulcanized and, when scraped, the crosslinking is broken. There is the disengagement of the SBR particle, which immediately undergoes oxygen action (O_2) present in the medium (Figure 6), confirming the rupture in the sulfur present in the cross chain by the vulcanization process [15,29].

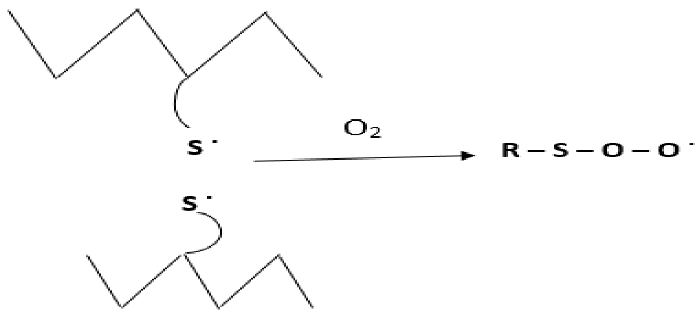

Figure 6. Opening of sulfur crosslinking and the action of oxygen in the environment.

In this free radical in oxygen (O˙), we can have the reaction occurring with the addition (R-S-O-O-R) of another free radical of the SBR rubber.

Another chemical bonding process is with the addition of methyl ethyl ketone peroxide interacting with R-S-O-O˙, of the carbon chain of SBR; having the formation of a carboxylic acid (O = C-OH) + R-S-O˙. This oxidation promotes radicalization and the chemical reaction process [15,45]. It can be seen that in both cases of reactions described there is a free radical, which will accelerate the reaction process, leading to a more intense exothermic reaction. The free radical (R-S-O˙) on contact with isophthalic polyester resin tends to promote a radical reaction (Figure 7).

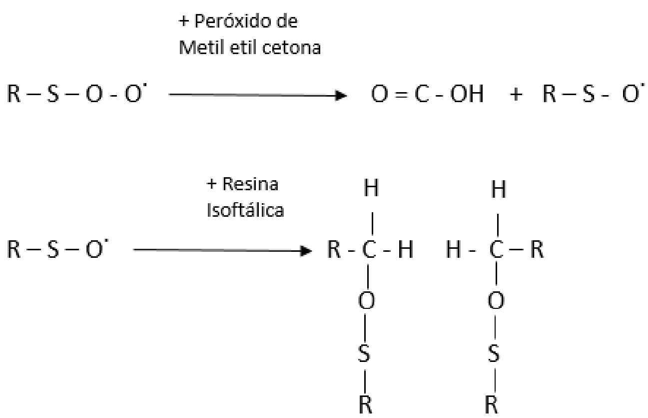

Figure 7. Reaction of the free radical of SBR with methyl ethyl ketone peroxide and isophthalic resin.

The methyl ethyl ketone peroxide in contact with the oxidized SBR particle tends to remove O_2. The reaction is now radical of the peroxide with the isophthalic resin, promoting the breaking of the double bond between C = C.

Figures 6 and 7 prove that there is a chemical interaction, and the reaction should be adsorption of the ELTs with the polyester isophthalic resin.

In the literature we can mention Davallo [50] who studied the blends: (a) unsaturated polyester resin added to the epoxy; and (b) the mixture of isophthalic polyester resin added to the polystyrene. The authors make comparisons of the tests for compression and flexion.

Rajan [29] used 15% rubber waste added to the hydrocarbon rubber. They do the rubber vulcanization process analysis. They do not make tests but present the chemical process: in terms of oxidation, the presence of free radicals and the chemical bonds coming, proving similarity of the process of chemical reaction, with the principle of this research. Its process shows the breaking of the vulcanized rubber chain. This process leaves a positive radical and makes the other negative in the rubber bond. These radicals, in turn, undergo oxidation as a result of the environment itself, with a chemical stabilization.

However, the parameters used in the tests by the two authors are different from the parameters proposed in this research. Thus, it was not possible to establish a complete reliable comparison between the two papers and this research.

Other considerations are regarding the process of chemical reaction and, subsequently, its drying: Bogdal [40] reports that with 2% of catalyst addition, the temperature of the cure in isophthalic polyester resin reaches between 152 °C and 160 °C in the exothermic process. For the prototyping of our samples, 5% to 10% of catalyst was used.

Another consideration is that the material with the highest amount of catalyst addition (10%) will promote a very rapid exothermic reaction, with abrupt withdrawal of the oxygen from the interior, with the formation of bubbles, which upon bursting at the surface generate a high roughness. With 5% addition of the catalyst, the curing process of the resin is slower than the above described process; however, there is the formation of a smoother textured surface.

4. Practical Results After Tests

After the tests with the sample pieces, some prototypes were made (Figures 8–11), all of them using 60% of ELTs, and drying process in an environment with 50% humidity and 20 °C temperature.

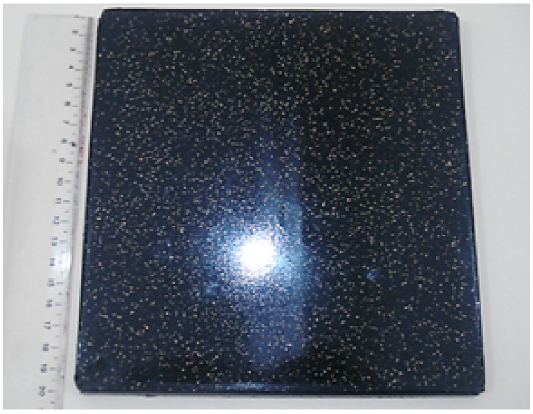

Figure 8. Slab measuring 200 × 200 mm with 60% ELTs in black color.

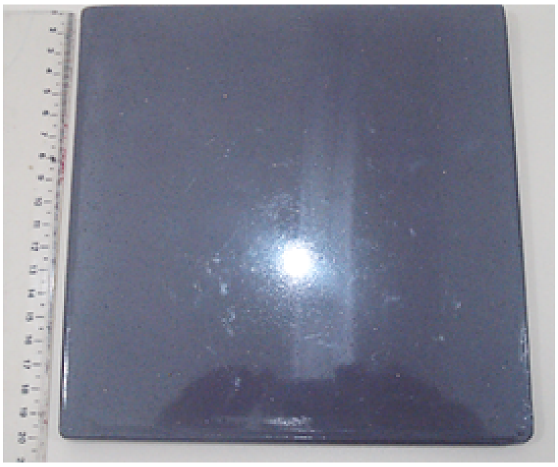

Figure 9. Slab with the same characteristics, in a different color.

Figure 10. Slab measuring 200 × 200 mm with 60% load of rubber in gold color with a differentiated surface.

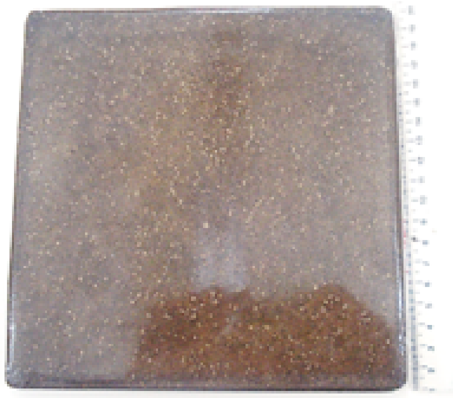

Figure 11. Slab with the same characteristics mentioned, but with a smooth texture and shiny surface.

The components (isophthalic resin com ELTs) were mixed, obtaining test bodies for the mechanical tests and also to make the prototypes with addition of dye (1% of the 3%) on glass plates with 200 × 200 mm.

After the results of the mechanical tests and their analysis, the material was made for prototypes with a concentration of 60% of ELTs, in black and gray colors (Figures 8 and 9, respectively) and different textures on the surfaces (Figures 10 and 11, respectively).

By means of the temperature control in steps of the slabs production process it is possible to obtain differentiated finishes, as presented.

Sienkiewicz [1] comments that it is necessary to have a good interaction between the surfaces of the ELTs and the polymeric matrix to obtain a good result in the material properties. Chemical adsorption between ELT particles and the polymer matrix is possible and will be responsible for the characteristics of the resulting material [1]. Our research, on its turn, shows that there is a chemical adsorption between the surfaces of the ELTs particles and the isophthalic thermosetting resin matrix, favoring the material properties; may have possible practical applications. In the Conclusion section, you can read the originality of this article and the possible applications of this research.

5. Conclusions

The generation of polymeric waste from tire rubbers is noticeable worldwide where the use of vehicles is in large scale. This is a problem that many governments face, and the recycling of end-of-life tires is a great concern for academia and tire industries.

The recycling processes described in the literature and on granted patents (evidenced in Appendix A) are: cryogenic, microwave, pyrolysis, and microbiological. These are the main tire recycling processes recognized by the scientific community. The aim of this paper was to propose the reuse of rubber waste from end-of-life tires. To achieve this purpose, we analyzed the mix of end-of-life rubber tire particles, together with isophthalic thermosetting resin, providing some practical applications of this material. The search on granted patents, as well as the literature review, showed that there are no similar studies on the market, and the method for reusing ELTs presented in this paper is original.

To prove the usefulness of the material, some mechanical tests were done, in order to verify the chemical absorption methods, having chemical interaction between matrix and ELTs. The tests applied were: Izod impact resistance, hardness shore D, scanning electron microscopy (SEM), and flexural strength.

The greater the amount of tire rubbers in the composition with the thermosetting resin, the greater is its Izod impact resistance. Izod impact resistance tests show that the best results are those with 60% ELTs in their mixture with isophthalic thermoset resin (0.97 KJ/m^2), while also having the best energy absorption level (0.062 J) for 60% load samples of tire rubbers.

As for the Shore hardness test, it can be concluded that the lower the amount of ELT in the mixture, the higher the hardness of the material. The determination of the immersion specimen density test shows that the higher the concentration in the ELT mixture (at 60%), the lower the density due to the presence of the waste tire rubber particles. This is also due to the adsorption of the matrix rubber tire particles, promoting an interaction between the different materials.

Scanning electron microscopy (SEM) tests show aspects of interphase interaction, where it can be concluded that there is adsorption between ELTs and isophthalic thermoset resin, to the point of bringing new results to the mechanical tests performed in this article. Adsorption is more intense the higher the concentration of methyl ethyl peroxide.

The flexural strength results of this study with ELTs confirm what Blessen's studies (8) say, where the flexural strength may change slightly according to the amount of ELTs in the mixture with the isophthalic resin. This justifies the slight change in results with ELT concentrations. The best test result came from 60% tire rubble residue (15.63 MPa).

The overall results of the mechanical tests indicated that the 60% concentration of ELTs in the mixture provides better mechanical test results than the 20% and 40% concentrations. In other words, applications with 60% of rubber waste concentrations had the best performance in the tests. This means that this 60% rate favors a higher level of ELT reuse, which has been promoting the recycling of end-of-life tire rubber.

Observing only the results of the mechanical tests, it is noted that there is a greater impact resistance with 60% ELTs in the composition, reaching 0.062 J; while there is an intermediate Shore D hardness of 73.4 to 60% ELTs. In the mechanical test of density determination, it was found that the material with 60% ELTs is the maximum (1163 g/cm3). Already the flexural strength test indicates that with 60% has the best result (15.63 MPa). Thus, it is concluded that the 60% ELT-added material is the most suitable, for example, for the manufacture of decorative tiles and building tiles.

Other studies, from the literature, indicate that it is possible to have adsorption of ELT particles with the matrix, which is in agreement with the authors cited earlier in this article, so that it can be concluded that there is potentiation of chemical reactions, and that the adsorption between the ELT particles and the thermosetting polymer matrix enables technical applications for civil construction. This is proven by the results of the mechanical tests.

It should be noted that tires used as fuel for burning in industrial furnaces is not a recommended practice; the use of ELTS in recycling processes to obtain oils is not economically viable due to the high costs involved. In both cases, there is environmental pollution, which occurs by emitting large amounts of carbon dioxide [8].

The traditional recycling process ends up being harmful to the environment, having to remove clay, and marble from nature to make decorative pieces. This research infers that the use of the material proposed in this paper could help diminish these negative impacts, because the tires are removed from nature, generating products with commercially added value, in substitution to those traditional products from clay and marble. Our research presents a process that favors the recycling of end-of-life tire rubbers, not using burning in the process, thus avoiding the emission of air, soil or water pollution. We also indicate possible practical applications for the market. Thus, with this process, the level of environmental impact reduction can be achieved due to the management of ELTs, bringing sustainability to generate a deferred destination for ELTs.

Another feature of the prototype materials is the characteristic of the surfaces. The prototypes have a smooth surface, due to the mold plates used, which does not demand extra finishing process on them. Also, different molds can provide diverse category of designs, which is another originality of research in the field of ELTs recycling.

The limitations of this study are related to the technical comparisons of this work with other similar research, since similar studies were not found in the literature or in granted patents.

For future work, research with other resins is recommended, as well as analysis of sound insulation and thermal properties.

Author Contributions: Conceptualization, A.H.B., V.L.d.S. and J.d.M.S.; Methodology, A.H.B. and R.N.P.; Validation, A.H.B.; Formal analysis, A.H.B. and R.N.P.; Writing, review and editing, A.H.B., R.N.P. and V.L.d.S.; Visualization, A.H.B., J.L.K. and R.N.P.; Supervision, J.L.K. and R.N.P.; Project administration, J.L.K.; Funding acquisition, J.L.K.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Results of the main patent analyzed.

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
1	CN206913515U	23/01/2018	Low temperature crushing equipment to junked tire recycle	Wan Zhitao	Cryogenic	The tire is moistened and then suffers the cryogenic process. It is fragmented into small particles through the process of roller pressing	Tire particles in various granulometry
2	CN207013116U	16/02/2018	Ultra-fine powder production apparatus	Li Shaotong	Cryogenic	Equipment that generates ultra-fine particle through cryogenics, using a very rigorous and controlled process, and for particles filtration presents/displays centrifuge.	Produces ultra fine particles of waste rubber tires
3	CN206887031U	16/01/2018	Continuous cracking system of low temperature for rubber	Canção Dingquan	Cryogenic	Continuous low temperature fractionation system	Produces tire rubber fractionation

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
4	CN207072657U	06/03/2018	Cinders, a split cooling air feed means	Zhao Ran et al.	Cryogenic	Producing tire rubber screening by cooling caused by cold air promoted by similar means to the cryogen	Production of rubber tire particles
5	CN206653561U	21/11/2017	Rubber powder apparatus for producing based on low temperature is broken	Niu Dongyu Indus Yu Yitong	Cryogenic	Double freezing of the rubber and its breaking into smaller particles. In the filtration process, the equipment removes metals by magnetic means	Generates rubber tire particles
6	CN206913515U	23/01/2018	Low temperature crushing equipment to junked tire recycle	Wan Zhitao	Cryogenic	Equipment that grinds unwanted tire rubbers by cryogenic process	Produces tire particles in various granulometry
7	CN206198950U	31/05/2017	An exhaust gas cryogenic adsorption and product utilization spraying apparatus	Liu Jingwei Duan Xiaoyu Shi Yan	Cryogenic	Describes a machine with cryogenic process, whose function is the breaking of tires into particles. The machine has three chambers, a tank for liquid, and a tank for disposal of process impurities.	-
8	CN205980525U	22/02/2017	Pin-connected panel refrigerator and this refrigerator box inner tube of a tire foaming mold utensil	Tao Xiaoyan	Cryogenic	Chlorogen gas (nitrogen) cooler, with area that will be in contact with the tire rubber, and the freezing provoked will promote breaking of the particulate rubber.	
9	CN207013116U	16/02/2018	Ultra-fine powder production apparatus	Li Shaotong	Cryogenic	Apparatus with a stirring pre-processor, cryogenic liquid mixers, among other components and functionalities.	-

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
10	CN206387181U	08/08/2017	Energy-saving high purity nitrogen plant of precooling	Xu Hao et al.	Cryogenic	Particle purification unit containing high purity nitrogen.	-
11	CN207227348U	13/04/2018	System cracking waste rubber	Ma Tibing et al.	Cryogenic + Pyrolisis + Microwave	Microwave pyrolysis chamber and other processes and functionalities.	-
12	CN206887031U	16/01/2018	A continuous cracking system of low temperature for rubber	Canção Dingquan	Cryogenic	Continuous cryogenic system for breaking tire rubber. Includes a cleavage unit, oil and gas processing unit, thermal unit and treatment unit by exhaustion gas.	-
13	CN207072926U	06/03/2018	A tire pyrolysis gas recycling equipment	Zhang Bin et al.	Pyrolisis	Equipment for tire gas recycling.	Generates oil by pyrolysis process
14	CN205974398U	22/02/2017	Junked tire pyrolysis and catalytic cracking system	Camada camada, Chen Shuiying, Xiao Lei	Pyrolisis	Pyrolysis process to generate gas for fuel.	Fuel oil
15	CN206143129U	05/03/2017	From junked tire pyrolysis of dust removal type and cracking system	Camada camada, Chen Shuiying, Xiao Lei	Pyrolisis	By tire pyrolysis, there is a breakdown of the tire structure generating gas for fuel.	Gas for fuel
16	CN207121575U	20/03/2018	One kind of waste tires regenerative moving bed pyrolysis system	Camada camada et al.	Pyrolisis	Process by pyrolysis that regenerates waste tires.	Generates gas and oils
17	CN206986099U	20/02/2018	One kind of recycling waste tire recycling apparatus	Meng Qiaoli Zhang Yan Zhao Ran	Pyrolisis	Side-filling device for the recycling of tires by pyrolysis.	-
18	CN205974393U	22/02/2017	Junked tire pyrolysis and pyrolysis tube cracking system	Camada camada, Chen Shuiying, Xiao Lei	Pyrolisis	Tire recycling machine using pyrolysis.	-

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
19	RU169883U1	04/05/2017	Apparatus for the pyrolysis of recyclable rubber materials	Vladimir Sergeevich Malkin	Pyrolisis	The reactor is cylindrical with a flat bottom that transforms particles of tire rubbers of size between 10 and 15 mm into smaller particles.	-
20	CN205838923U	28/12/2006	Tire rapid pyrolysis system	Zhao Yanbing, Chen Shuiying, Schonson	Pyrolisis	Pyrolysis system.	-
21	CN206204225U	31/05/2017	Continuous pyrolysis treatment scrap tire fixed bed reactor of low temperature	Wu Xiaofei et al.	Pyrolisis	Reactor of continuous pyrolysis for the treatment of tire waste and magnetic separator of metal impurities.	-
22	CN206089570U	12/04/2017	System for pyrolysis junked tire	Zhang Hongwei Zhao Yanbing, Chen Shuiying	Pyrolisis	Equipment for the reuse of tire residue by means of particle breaking by pyrolysis.	
23	CN206051560U	29/03/2017	System by junked tire preparation active carbon with built-in dust collector	Zhao Yanbing, Chen Shuiying, Jiang Chaoxing	Pyrolisis	System for pyrolysis process with impurities remover.	Generates gas and produces quality active carbon
24	CN205664385U	26/10/2018	Organic matter self-power is dry to divide resource system with pyrolysis, complete set	Li Aimin Zhang Lei	Pyrolisis	Drying of waste to promote pyrolysis.	-
25	RU172538U1	11/07/2017	Apparatus discharging dry pyrolysis products	Vyacheslav Anatolievich Filippenkov	Pyrolisis	Device for solid urban waste processing, including tires.	-
26	CN207227348U	13/04/2018	System cracking waste rubber	Ma Tibing et al.	Pyrolisis	Fractioning system for rubbish waste from processed tires.	-
27	CN206089578U	12/04/2017	Comprehensive utilization equipment of rubber waste	Gao Qiong Ma Jin Li Weibo	Pyrolisis	Equipment for waste recycling.	Extraction of oil and gas

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
28	CN207224368U	13/04/2018	Magnetic waste tire recovery	Li Guoyou	Pyrolisis	Tire recycling equipment with metal particle separator.	-
29	CN206916075U	23/01/2018	Waste tire cracking furnace	Ele Xiaofeng, Yu Hualong, Zhang Zhentang	Pyrolisis	Tire recycling oven.	Oil
30	CN206109318U	19/04/2017	Concise system of pyrolysis oil	Mingguo Ying et al.	Pyrolisis	Tire oil extraction system.	-
31	CN206278916U	27/06/2017	System for innocent treatment discarded object	Wu Xiaofei et al.	Pyrolisis	System with oven for extraction of oil by pyrolysis.	Oil
32	US9884804B2	06/02/2018	Surface treated carbon catalysts produced from waste tires for fatty acids to biofuel conversion	Zachary D. Hood et al.	Pyrolisis	The tire particles are pyrolyzed to produce carbon composite parts. These parts are milled for later production of acid catalysts and biofuel.	Biofuel
33	US9920262B1	20/03/2018	Methods of separation of pyrolysis oils	Jonathan Lyle Wistrom et al.	Pyrolisis	Separation of a lighter fraction and a denser fraction of oil generated by pyrolysis, allowing the extraction of chemical compounds.	Extraction of sulfur and nitrogen from tire oil
34	US9920712B1	20/03/2018	Method for forming a plurality of plugs of carbonaceous material	Ravi Chandran et al.	Pyrolisis	System that uses tire material for gas generation by thermochemical reaction.	Gas via thermochemical reaction
35	CN206405159U	15/08/2017	System for handle solid wastes material	Zhao Yuejing et al.	Pyrolisis	Method for handling particles of recycled products, such as tires.	-
36	CN206799535U	26/12/2017	A equip for suspending catalytic cracking glowing plastics or rubber discarded object	Yin Xiaolin	Pyrolisis	Catalytic method that aims at the breaking of rubbers, generating particles.	Rubber particles

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
37	CN206765151U	19/12/2017	Rubbing crusher that old and useless rubber recycling production used	Luo Weichuan et al.	Pyrolisis	Tire rubber crusher.	Tire Rubber Particles
38	CN207224369U	13/04/2018	Pulverizing waste tires desulfurization apparatus	Li Guoyou	Pyrolisis	Equipment with ammonia tank, which aims to grind the tires, producing smaller particles.	Particles with lower oxidation rates
39	RU2624202C1	03/04/2017	Method of producing synthetic fuel from worn tires and installation for its implementation	Dmitry Isaakovich et al.	Pyrolisis	Describes the process of extraction of synthetic fuel derived from tires.	Synthetic fuel
40	KR101798355B1	15/11/2017	Pyrolysis gasifier including automated ash treating apparatus	Lim Duk-joon Lim Young Taek	Pyrolisis	Describes the process of pyrolysis and waste treatment.	To produce gas by breaking the molecules of tires
41	RU2632293C1	03/10/2017	Device for processing rubber waste	Alexey Sergeevich et al.	Pyrolisis	Reactor with cylindrical furnace with evaporator and other systems for waste management.	-
42	CN205999124U	08/03/2017	Rubber mud bed anaerobic fluent disposal system	Xu Xia	Microbiological	Equipment that uses tire particles to filter water in an anaerobic effluent treatment process.	Water filtration process
43	CN206867976U	12/01/2018	Ozone oxidation sprays tire waste gas treatment device who uses together with alkali lye	Jin Yongping, Gu Yuhui	Microbiological	Describes an equipment for waste gas treatment, such as from tires.	-
44	CN206613569U	17/11/2017	Present invention is practical	Qu Xiugang	Microbiological	Describes tire recycling apparatus.	-
45	RU168093U1	18/01/2017	Bio-electrochemical cell	Nikolai Dmitrievich et al.	Microbiological	Chambers with microbiological process and bioeletrochemical element for waste management.	-

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
46	JP6276489B1	07/02/2018	Modified cellulose nanofibers and a rubber composition containing the same	Kotaro Ito Ito Shinichi Onogi Masahiro Masuda	Microbiological	Nanoparticles fibers from cellulose and modified rubber.	-
47	CN206562405U	17/10/2017	Junked tire recovery processing	Qu Xiugang	Microbiological + pyrolisis	Model for tire recovery.	-
48	CN206799535U	26/12/2017	Suspension for flameless combustion catalytic cracking waste rubber or plastics equipment	Yin Xiaolin	Microwave + chemical	Equipment for the breakdown of rubber molecules.	Fuel
49	CN206646052U	17/11/2017	Continuous microwave radiation macromolecular material modification device	Hao Xiaoli, Bao Weiwei, Deng Zhifeng, Jiang Peng.	Microwave	Tire rubber macromolecule breaker.	-
50	CN207130588U	23/03/2018	A microwave thermal regeneration in situ complete unit	Zhang Jiangyong et al.	Microwave	Complete equipment with zone of tire heating and rubbers.	Renewed asphalt emulsion
51	CN207044468U	27/02/2018	Reproducing one kind of waste rubber mix production system	Jiang Shuijin et al.	Microwave	Microwave equipment for the recycling of rubber tires.	-
52	CN206799498U	26/12/2017	Improve useless rubber cracking transmission power's waveguide device	Li Zhihua Guo Nan	Microwave	Description of the process for recovering cracks in tire rubbers, extending the time of use.	Tires recovered with extended service life
53	CN105949557B	10/04/2018	A method of use of waste rubber foam insulation material is prepared	Chen Sichi et al.	Microwave	Equipment that aims to recover tire failures.	
54	CN205904223U	25/01/2017	Oil solid waste resource recovery device	Bao Minglan et al.	Microwave	Oil solid waste resource recovery device, using microwaves to promote the pyrolysis process.	-

Table A1. *Cont.*

N	Patent	Date of Grant	Patent Name	Author(s)	Recycling Process Used	Main Characteristics	Subproduct Generated
55	US2017096537	06/04/2016	Benzoxazine cyanate ester resin for pyrolisis densification of carbon-carbon composites	Fowler Gray E.	Pyrolisis	Method for carbon composite, includes carbon fibers with a benzoxazine resin compound and cyanide ester blend.	-
56	RU2015122814	10/01/2017	Method for synthesis of benzocyclobutene by pyrolisis of quaternary ammonium salts of 2-methylbenzyl-(trialkyl) ammonium chlorides	Levchenko Konstantin Sergeevich et al.	Pyrolisis	A high conversion product can be obtained with a minimum yield of corrosive by-products (harmful to the metal surfaces of the vacuum equipment).	
57	CN105419827	23/03/2016	Oil sediment pyrolisis system of plasma double-pipe heat exchanger	Liu Fei Geng Jian	Pyrolisis	Oil sedimented by pyrolysis and with the aid of plasma to accelerate production.	
58	CN206768087	19/12/2017	Inspection microbiological incubator	Wang Suijia	Microbiological	Equipment for the microbiological inspection of rubber by a microbiological control mechanism.	
59	CN105462612	06/04/2016	Novel environmental-protection biological rubber tire filling oil production process	Han Junchang	Biological	Rubber recovery by biological means of tires with the combination of mineral and synthetic oil.	

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