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Life cycle assessment applied to a self-healing elastomer filled with ground tire rubber

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ABSTRACT

In this study, we present the first life cycle assessment (LCA) of a self-healing styrene-butadiene rubber (SBR) used in the production of marine fenders. Results show that a rubber with healing capabilities is not environmentally attractive if it cannot last for the same lifetime as a conventional product due to its lower mechanical performance and higher energy consumption. To overcome these constraints, we added a sustainable filler, ground tire rubber, which improved the mechanical properties of the self-healing SBR (x6 increase in tensile strength). Although this addition involved additional sub-processes, the additional environmental impacts were outweighed by the benefits achieved through improved material performance (28% decrease in global warming potential - GWP and 26% in primary energy demand - PED). This study used primary data on experimental healing efficiencies and healing cycles rather than conservative assumptions, which provides a more representative and trustworthy LCA of self-healing rubbers. Our findings have significant implications for the rubber industry, as self-healing rubbers offer a promising avenue for reducing the environmental impact of synthetic materials.

1. Introduction

The circular economy (CE) is a globally adopted social and economic system concept aimed at establishing more sustainable production and consumption (Gaustad et al., 2018; Vermeulen et al., 2018; Suchek et al., 2021). It encompasses various strategies known as the 7Rs (Reike et al., 2018; Velenturf and Purnell, 2021), and among them, the "Repair" strategy draws inspiration from nature's ability to heal wounds and regenerate tissues (White et al., 2001; Song et al., 2021). Within this concept, self-healing materials have emerged as an innovative technology that holds great significance. These materials possess the unique ability to autonomously repair themselves or respond to stimuli (Sattar et al., 2019; Sattar and Patnaik, 2020). The use of such innovative materials can extend the lifespan of products and contribute to waste prevention, thereby reducing both ecological and economic costs associated with future materials (Geitner et al., 2018; Sani et al., 2022).

Self-healing elastomers, a special class of materials, are regarded as a promising avenue for the development of sustainable products (Sani et al., 2022). While research in this field is expanding, self-healing rubbers still face significant challenges, particularly in terms of their mechanical strength compared to conventional rubbers in their pristine and fully cured states (Chen et al., 2019; Liu et al., 2019; Cao et al., 2021; Boden et al., 2022; Mohd Sani et al., 2022a, 2022b). To overcome this limitation in self-healing matrices, one pioneering approach has involved the incorporation of ground tire rubber (GTR) as a sustainable alternative to traditional reinforcing fillers (Hernández Santana et al.,

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2018; Araujo-Morera et al., 2019, 2021; 2022b; Utrera-Barrios et al., 2020; Alonso Pastor et al., 2022; Nuñez Carrero et al., 2022). GTR is a finely granulated recycled rubber derived from discarded tires (Karger-Kocsis et al., 2013; Forrest, 2014; Formela, 2021). Several studies have investigated the addition of GTR to different self-healing rubber matrices, reporting improvements in mechanical performance along with enhanced healing efficiency. (Hernández Santana et al., 2018; Utrera-Barrios et al., 2020; Saeb et al., 2022). Successful mechano-chemical modification of GTR has also been achieved (Araujo-Morera et al., 2021), striking a positive balance between healing efficiency and mechanical performance when combined with carbon black (Araujo-Morera et al., 2022b). Additionally, the utilization of devulcanized GTR in self-healing rubber composites has demonstrated a healing efficiency of 80% based on the recovery of mechanical properties (Alonso Pastor et al., 2022).

Another crucial aspect to consider is the environmental impact of self-healing materials, as it provides valuable insights for cleaner production and technical innovation. Life cycle assessment (LCA) stands out as a robust tool for evaluating new innovative materials that align with the CE model (Baumann and Tillman, 2004; Hellweg and Milà i Canals, 2014; Sandin et al., 2015; Bjørn et al., 2018, 2020;Tyre and Manufacturers Association - ETRMA, 2019; Muazu et al., 2021; Sala et al., 2021). Implementing LCA for this category of materials can offer researchers new perspectives to customize and optimize self-healing strategies. It is worth noting that self-healing concrete has achieved a higher level of maturity compared to other materials, which explains why most of the available literature on LCA of self-healing materials focuses on concrete. As an example, Cseke et al. (Cseke et al., 2020, 2022a) developed a new framework for assessing self-healing, scaling from the regular quantification of healing at a material level to a product level. Garces et al. (Garces et al., 2021, 2022) performed cradle-to-gate LCA studies of self-healing geopolymer concrete. In another investigation, Van den Heede et al. (van den Heede et al., 2018) developed a cradle-to-gate LCA of self-healing engineered cementitious composites with in-house developed superabsorbent polymers.

To the best of the authors' knowledge, only one recent study has been published on the LCA of self-healing elastomers. Cseke et al. (2022b) used a cradle-to-grave approach to study a self-healing product manufactured from polylactic acid and self-healing polyurethane by 3D printing. When comparing regular versus self-healing products, it was clear that the impacts were dominated by the electricity consumption of the manufacturing process. The objective of this investigation is to quantify and provide, for the first time, a comprehensive LCA of self-healing elastomers filled with GTR. A case study of self-healing rubber marine fenders will be assessed, and a comparative analysis will be performed, considering five different scenarios for the obtention of raw materials: i) conventional styrene-butadiene rubber (SBR); ii) self-healing SBR; iii) self-healing SBR filled with GTR; iv) self-healing SBR filled with devulcanized GTR (d-GTR) and v) self-healing SBR filled with chemically modified GTR (Ch-GTR). The results will provide a baseline upon which future studies on self-healing elastomers can be compared and unveil the environmental benefits of using a recyclable filler in search of sustainable self-healing rubbers.

2. Materials and methods

LCA was implemented according to ISO 14040 (ISO 14040:2006. Environmental management. Life cycle assessment. Principles and framework) and ISO 14044 (ISO 14044:2006. Environmental management. Life cycle assessment. Requirements and guidelines) using the GaBi LCA software (v10.6.2.9, Sphera Solutions Inc). The method used to calculate the environmental impacts was the ILCD/PEF v1.09. (EPLCA) The LCA framework followed the conventional steps: i) Definition of goal and scope; ii) Life cycle inventory analysis; iii) Impact assessment; and iv) Interpretation. Except for the new primary data for the foreground system, all relevant data sets were taken from the Gabi Professional life cycle inventory database. To ensure that the results in the LCA are comparable, we used energy, transport, and auxiliary materials database. Data relating to SBR, vulcanizing agents and consumption are European averages, while all data concerning the GTR are from Spain.

A simplified attributional LCA (ALCA) study was set as a comparative cradle-to-grave study, quantifying the environmental impacts of self-healing rubbers versus a traditional rubber. The methodology involved the use of two environmental indicators: Global Warming Potential (GWP) and Primary Energy Demand (PED) to assess categories of environment protection and resources depletion, respectively. Since the purpose of this work is to develop an approach for assessing the environmental impact of self-healing materials, rather than specific impact values, the discussion has been conducted only with these two indicators, for purposes of clarity. Data of other indicators are reported in Supporting information S1. Furthermore, an uncertainty analysis on the parameters related to the chemical modification process of the GTR and the healing ability of the composites was carried out.

2.1. *Goal and scope definition*

2.1.1. *Goal definition*

The goal of this LCA is to contribute to the field of self-healing rubbers with scientific knowledge regarding the determination of their environmental benefits and suggest priorities for future materials development research on how to optimize the environmental impact of self-healing rubber products. To meet this goal, this study quantifies and analyzes the potential environmental impacts of sustainable self-healing rubber composites and compare them with those from conventional rubber. It examines the environmental impact of novel self-healing SBR composites reinforced with GTR (Hernández Santana et al., 2018; Alonso Pastor et al., 2022; Nuñez Carrero et al., 2022), considering various material scenarios, as discussed in Section 2.1.4.

2.1.2. *Functional unit*

This LCA focuses on the production and use of a 25 kg cylinder-shaped marine fender with a tensile strength of 16 MPa and a lifespan of 10 years. (Shibata Fender Team, 2021) Marine fenders are protective elements widely used in seaports to protect vessels from collisions when they approach or are placed next to a port structure. They are produced only from rubber, without any metal component or any other additional material, and the manufacturing process is simple. Photographs of the marine fender are shown In Supporting information S2.

2.1.3. *System boundaries*

The LCA, established as a cradle-to-grave system, is divided in four stages. Stage A includes the raw material extraction, mixing and compounding of the rubber composites. The transformation of the rubber composite into a marine fender by extrusion molding and vulcanization of the final product is compressed in Stage B. The use phase, including the repair process for those fenders made of self-healing rubbers, is considered in Stage C. Finally, the end-of-life treatment of the marine fenders is included in Stage D. Fig. 1 shows the system boundaries and the complete LCA flow chart considered in this study. All the studied materials (represented with circled numbers in Stage A) follow the same process flow. The life cycle inventories of each stage are described in section 2.3.

2.1.3.1. Stage A: Compounding. This stage involves the procurement of the rubber matrix (SBR), the vulcanizing agents (ZnO, SA, CBS and S) and reinforcing fillers (CB, GTR, d-GTR and Ch-GTR), as well as the compounding process. With respect to the rubber matrix and vulcanizing agents, conventional industrial processes contained in the GaBi database were considered; data used were from European average values. On the other hand, tire rubber was mechanically grinded to

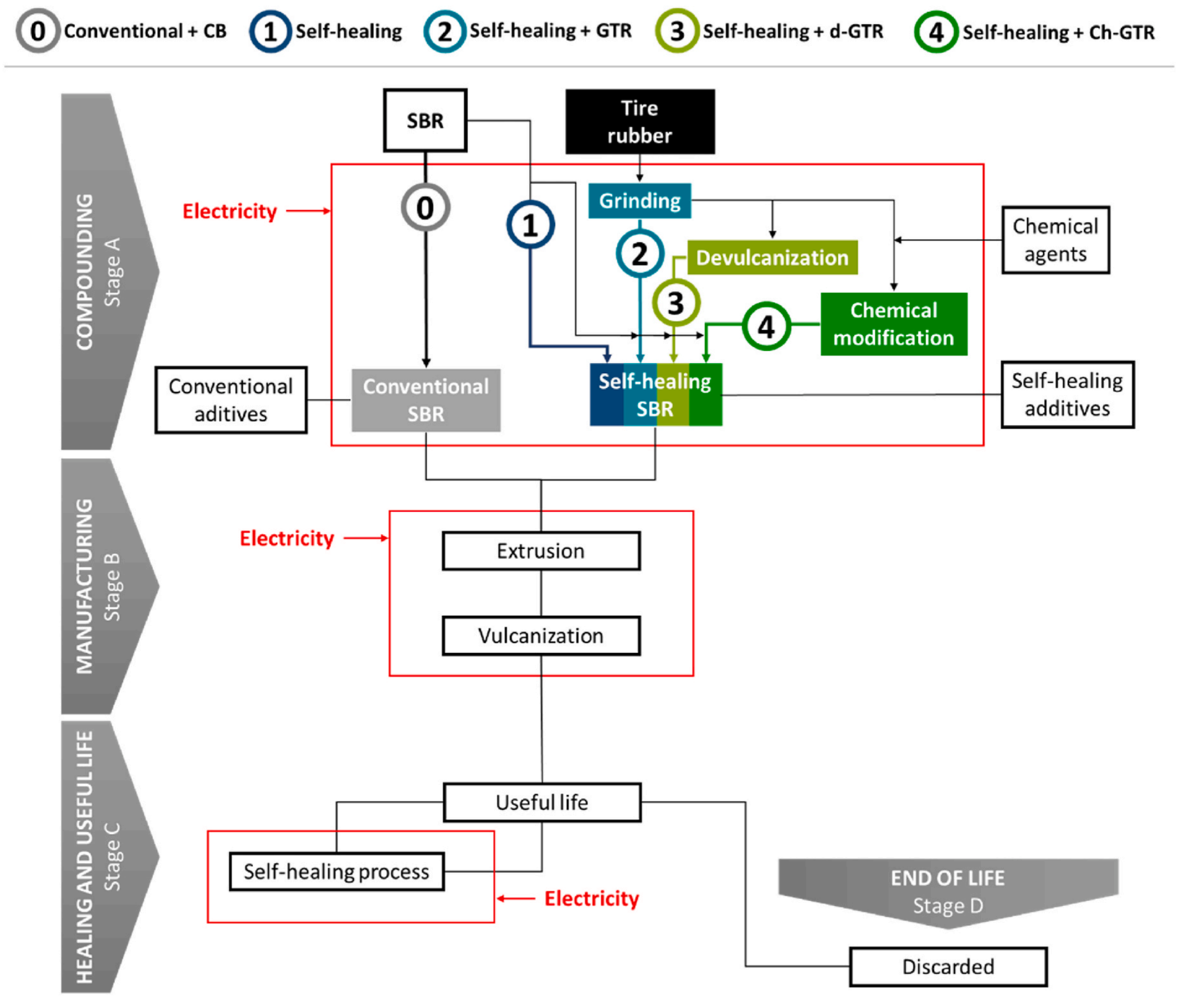

Fig. 1. LCA flow chart with boundaries. In summary, Stage A includes the series of processes involved in obtaining conventional and self-healing rubber compounds, where numbers represent the alternative scenarios (see section 2.1.4). Stage B includes the manufacture of marine fenders, which is equal for all the scenarios. Stage C comprises the useful life and, if applicable, the self-healing process. Finally, Stage D corresponds to the disposal of the products.

transform it into ground tire rubber (GTR). The GTR was, on the one hand, thermo-mechanically devulcanized in an extruder at ambient temperature to obtain d-GTR, and, on the other hand, it was treated with H_2SO_4 at 100 °C and then washed with water to obtain Ch-GTR. Detailed information about devulcanization and chemical modification process can be found in (Alonso Pastor et al., 2022; Araujo-Morera et al., 2021) respectively. Regarding the compounding process, rubber compounds are prepared in an open two-roll mill at room temperature. The different additives are sequentially added keeping the mixing time constant for all compounds (≈20 min).

2.1.3.2. Stage B: Manufacturing. In this stage, the rubber compound is extrusion moulded and then vulcanized to produce the marine fender. According to information reported by manufactures, cylindrical-shaped marine fenders are industrially manufactured in two stages. (Shibata Fender Team, 2021) First, the rubber compound is shaped by extrusion molding. Then, the cylindrical part is placed in an autoclave, where pressure and temperature are applied to vulcanize the rubber. This process was the same in all four scenarios, with a consumption of 1.5 kWh per kg of rubber compound.

2.1.3.3. Stage C: Healing and useful life. To assess the healing capability of a rubber, a macroscopic damage is introduced to rectangular rubber samples by manually making a straight cut along the width using a fresh scalpel blade. Then, the two damaged surfaces are carefully repositioned together by hand applying light pressure. In this case study healing requires the application of heat. Thus, the cut samples are then healed in an oven under a controlled temperature for a fixed time (see Supporting information S2). The healing protocol applied was 130 °C for 5 h. Finally, the healed samples are mechanically retested.

The healing efficiency (η), calculated as the ratio of the tensile strength (σ_b) in the pristine and healed states, is used to quantify the mechanical recovery, following equation (1) (see Supporting information S2):

$$\eta\ (\%) = \frac{\sigma_{b\,healed}}{\sigma_{b\,pristine}} \times 100 \quad (1)$$

Self-healing is described as a material property, and the metrics used to calculate η do not necessarily match those of a self-healing product (Cseke et al., 2020). In this LCA, we assume that the healing capability of the rubber compound is equivalent to that of the marine fender manufactured thereof. It is also assumed that marine fenders made from self-healing rubbers (Scenarios 1–4) can be repaired a limited number of times after their useful life, before being discarded (Wool, 2008; Hernández et al., 2016).

2.1.3.4. Stage D: End of life. Marine fenders will be discarded when they cannot be subjected to any more healing cycles (Scenarios 1–4) and/or their useful life has elapsed (Scenario 0). This stage will not be considered in this LCA for simplification purposes and for focusing on the useful life of the materials.

2.1.4. Scenarios

Five material-based scenarios were examined. We considered a conventional SBR (Scenario 0), with no healing properties as reference material, and compared to the following:

- self-healing SBR (Scenario 1)
- self-healing SBR reinforced with GTR (Scenario 2)
- self-healing SBR reinforced with d-GTR (Scenario 3)
- self-healing SBR reinforced with Ch-GTR (Scenario 4).

The effect of adding a sustainable filler like GTR on the production of self-healing composites is also assessed, emphasizing on the differences in structure and morphology between all GTRs and comparing them to a conventional filler like carbon black (CB).

For all the scenarios, the elastomeric matrix was a commercial cold emulsion SBR (Buna® SE 1502, Arlanxeo). The vulcanizing additives were zinc oxide (ZnO), stearic acid (SA), N-cyclohexylbenzothiazole-2-sulphenamide (CBS) sulfur (S), CB, GTR, d-GTR and Ch-GTR. ZnO and SA act as activating complex of the vulcanization, S and CBS form the curing system, and CB, GTR, d-GTR and Ch-GTR are the reinforcing additives. Table 1 describes the composition of the rubber composites expressed in weight (w/w) and the properties used in the analysis for each scenario.

2.2. Assumptions

Certain assumptions are necessary for this study, especially if one considers that self-healing is still an emerging technology. As experimental data on self-healing rubber products becomes available in the future, more realistic environmental estimates will be set. In this study, it was considered that in all scenarios the product designs were identical. What differed were the materials' properties and their consequent frequency of repair or replacement. The material properties observed in test specimens were extrapolated to an assumed product (marine fender). Thus, the behavior of the self-healing material was translated to the software, which was done by means of a series of calculations, as detailed below.

From previous knowledge of the authors, we can state that self-healing rubbers partially recover their original properties a limited number of times (Wool, 2008; Hernández et al., 2016). Considering such premises, both the performance of the healed products and the number of healing cycles had to be defined. This is an important condition that gives trustworthiness to this study; many of the studies reported up to date using self-healing materials only consider ideal situations in which: i) the material fully recovers the original properties, i.e. a 100% healing efficiency; ii) healing takes place unlimited times; iii) healing is fully autonomous with no energy requirements (van den Heede et al., 2018; Garces et al., 2021; Cseke et al., 2022b). Thus, the properties of the materials were expressed in terms of lifetime, for which Scenario 0 (conventional SBR) was taken as reference (equation (2)):

$$\textit{Lifetime}\ (\text{year}) = \frac{\sigma_b(\text{MPa}) \times 10\ \text{year}}{16\ \text{MPa}} \tag{2}$$

From the calculated lifetime, one can determine the number of products needed to cover the functional unit. Table 2 (a) shows the lifetime of one marine fender and the number of products needed to cover the functional unit calculated using tensile strength (16 MPa) as reference property.

However, self-healing rubbers can extend their lifetime with each healing cycle, and the number of cycles that a self-healing rubber can support is limited and conditioned by the healing efficiency (η) (Araujo-Morera et al., 2022a). Thus, a single self-healing product can cover various lifetimes, and these are determined by its healing efficiency. It should be noted that, since an ideal full healing is not assumed, the mechanical properties of the material decrease after each healing cycle (Supporting information S3). Also, we can see a decay on tensile strength with healing cycles for the considered self-healing materials (Supporting Information S4). Since the mechanical properties decrease with each healing cycle, the environmental assessment was conducted assuming different healing cycles for each of the self-healing scenarios. For each of them, the number of cycles leading to the lowest impact was selected. The environmental impact as a function of healing cycles is shown in the Supporting information S5. Table 2 (b) shows the number of healing cycles for the considered self-healing products.

Table 1
Composition and properties of SBR composites for each scenario.

	Scenario				
	0 *Conventional SBR*[a]	1 *Self-healing SBR*	2 *Self-healing SBR + GTR*	3 *Self-healing SBR + d-GTR*	4 *Self-healing SBR + Ch-GTR*
Component	w/w				
SBR	7.12×10^{-1}	9.26×10^{-1}	7.81×10^{-1}	7.81×10^{-1}	7.81×10^{-1}
ZnO	3.60×10^{-2}	4.60×10^{-2}	3.90×10^{-2}	3.90×10^{-2}	3.90×10^{-2}
SA	1.40×10^{-2}	9.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}
CBS	1.10×10^{-2}	9.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}
S	1.40×10^{-2}	9.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}
CB	2.14×10^{-1}	-	-	-	-
GTR	-	-	1.56×10^{-1}	-	-
d-GTR	-	-	-	1.56×10^{-1}	-
Ch-GTR	-	-	-	-	1.56×10^{-1}
Tensile strength, σ_b (MPa)	16[a]	0.97 ± 0.06	1.86 ± 0.13	2.70 ± 0.16	6.50 ± 0.10
Healing efficiency, η (%)	-	67 ± 1	30 ± 2	23 ± 1	85 ± 12

[a] Data from (Shibata Fender Team, 2021).

Table 2
(a) Lifetime calculated from the tensile strength of the different material-based scenarios, and (b) Healing cycles of each self-healing scenario, indicating the total number of products needed to cover the functional unit.

(a)

Scenario	Type of rubber	Type of reinforcement	Lifetime (years)	No. of products needed to cover the functional unit
0 (Ref)	Conventional	CB	10	1
1	Self-healing	-	0.6	17
2		GTR	1.2	9
3		d-GTR	1.7	6
4		Ch-GTR	4.1	3

(b)

Scenario	Healing cycles	No. of products needed to cover the functional unit
1	3	7
2	1	7
3	1	4
4	2	1

2.3. Life cycle inventory (LCI)

The LCI is divided into three sections in accordance with the useful life stages of the flow chart (Fig. 1) and taking into consideration the relevant materials involved in each scenario. The inputs and outputs of the different sub-processes in each stage were found. Data were taken from the database of GaBi version 2022.2 whenever available. However, it was also necessary to take information from other sources (bibliography, previous projects), in these cases the source of information is indicated; if it is not indicated, it means that it was taken from GaBi database.

2.3.1. Stage A: Compounding

This stage includes the procurement of the matrix (SBR), the vulcanizing agents (ZnO, SA, CBS, S) and reinforcements (CB, GTR, d-GTR, Ch-GTR) and the formulation process to obtain the SBR composites. More specifically, it includes: i) raw rubber (SBR) acquisition; ii) grinding of tire rubber; iii) subsequent devulcanization or chemical modification of GTR and iv) formulation and mixing process of rubber composites.

Regarding the raw materials, the same SBR was used for both conventional and self-healing composites, as well as the rest of additives, being the only difference the amount of each of them. Conventional SBR was reinforced with CB, with the amount specified in the literature used for marine fenders, 30%. w/w, (Shibata Fender Team, 2021) whereas the reinforcing fillers used in self-healing SBR were GTR, d-GTR or Ch-GTR, using 20%. w/w as the optimum amount determined in previous work (Hernández Santana et al., 2018; Alonso Pastor et al., 2022; Nuñez Carrero et al., 2022). Detailed information about GTR modification can be found elsewhere (Araujo-Morera et al., 2021). These data were complemented with the energy consumption from the grinding, devulcanization and chemical modification sub-processes. Table 3 (a) compiles the data considering the total number of marine fenders required in each of the scenarios (Table 2 (b)).

2.3.2. Stage B: Manufacturing

The process definition is necessary to figure out the energy consumption for the marine fender manufacturing. In the framework of this LCA model, and according to the literature,(Shibata Fender Team, 2021) it has been established that the energy consumption for the manufacturing of a marine fender is equivalent to that of a tire (1.5 kWh per kg of rubber processed) (Continental, 1999; Ortíz-Rodríguez et al., 2017; Dong et al., 2021). Table 3 (b) shows input and output data corresponding to this stage.

2.3.3. Stage C: Healing and useful life

Self-healing is conceived as a thermally triggered mechanism; temperature is needed to induce motion in rubber chains and promote the reformation of broken bonds at the molecular level. The healing mechanism in unfilled SBR compound is a result of the combination of two distinct processes. The initial process involves the interdiffusion of polymer chains and the formation of physical entanglements, leading to a partial restoration of the interface/interphase. Subsequently, long-range interactions and disulfide exchange reactions occur, facilitating the nearly complete recovery of mechanical performance (Araujo-Morera et al., 2022a). Regarding the SBR composites filled with GTR and devulcanized GTR (d-GTR) the interdiffusion of rubber chains and the rearrangement of broken and reversible S–S bonds at the healed interface are favored (Alonso Pastor et al., 2022). In the case of SBR filled with chemically modified GTR (Ch-GTR), in addition to the disulfide exchange reaction healing mechanism, the chemical modification induces the presence of hydroxyl groups (-OH) on the surface of GTR. These groups enable the formation of reversible ionic associations, with the ZnO contained within the rubber composites. These ionic associations act as healing moieties due to the re-association of the ionic groups at the interphase damaged sample (Araujo-Morera et al., 2022b). A schematic representation of the healing mechanisms that govern each scenario are shown in Fig. 2.

Table 3
Inputs and outputs for (a) the SBR compounding stage; (b) for the marine fender manufacturing stage, and (c) for the healing and useful life stage. Data correspond to the total number of marine fenders needed.

(a) Stage A: Compounding

Input	Output	Amount				
		Scenario				
		0	1	2	3	4
SBR (kg)		17.8	162	137	97.6	19.5
ZnO (kg)		0.890	8.17	6.82	4.87	0.975
SA (kg)		0.356	1.593	1.4	1	0.2
CBS (kg)		0.267	1.593	1.4	1	0.2
S (kg)		0.356	1.593	1.4	1	0.2
CB (kg)		5.3	–	–	–	–
Tire rubber (kg)		–	–	27.6	19.7	3.94
Grinding process (MJ)[a]		–	–	35.1	25.1	5
Devulcanization process (MJ)[b]		–	–	–	89.9	–
Chemical process (MJ)		–	–	–	–	5.85
H_2SO_4 (kg)		–	–	–	–	29.25
Water (kg)		–	–	–	0.195	890
	Conventional SBR (kg)	25	–	–	–	–
	Self-healing SBR (kg)	–	175	175	125	25

(b) Stage B: Manufacturing

Input	Output	Amount				
		Scenario				
		0	1	2	3	4
Conventional rubber (kg)		25	–	–	–	–
Self-healing rubber (kg)		–	175	175	125	25
Electricity (MJ)		135	945	945	675	135
	Marine fender (u)	1	7	7	4	1

(c) Stage C: Healing and useful life

Input	Output	Amount				
		Scenario				
		0	1	2	3	4
Marine fender (units)		1	7	7	4	1
Self-healing process (MJ)		–	1890	630	450	180
	Marine fender (units)	1	7	7	4	1

[a] Data from ("Life Cycle Assessment – C1", LIFE SOUNDLESS project - new generation of eco-friendly asphalts with recycled materials and high durability and acoustic performance, LIFE14 ENV/ES/000708).
[b] (Li et al., 2014).

Since we are considering that healing is not fully autonomous, it was necessary to define the energy consumption of the healing process. It was assumed that each healing process required a proportional part of the energy needed for the manufacture of a marine fender: 2/3 of 1.5 kWh/kg (= 1.0 kWh/kg), since the process requires heating but no pressure. Thus, total energy consumption was calculated based on the service life and number of marine fenders, as detailed in Table 3 (c).

3. Results and discussion

The information provided by the LCA was evaluated to determine: i) the environmental impact of self-healing rubbers; ii) the effect of the addition of GTR on the production of self-healing rubbers and iii) the potential of these self-healing materials for reducing the environmental

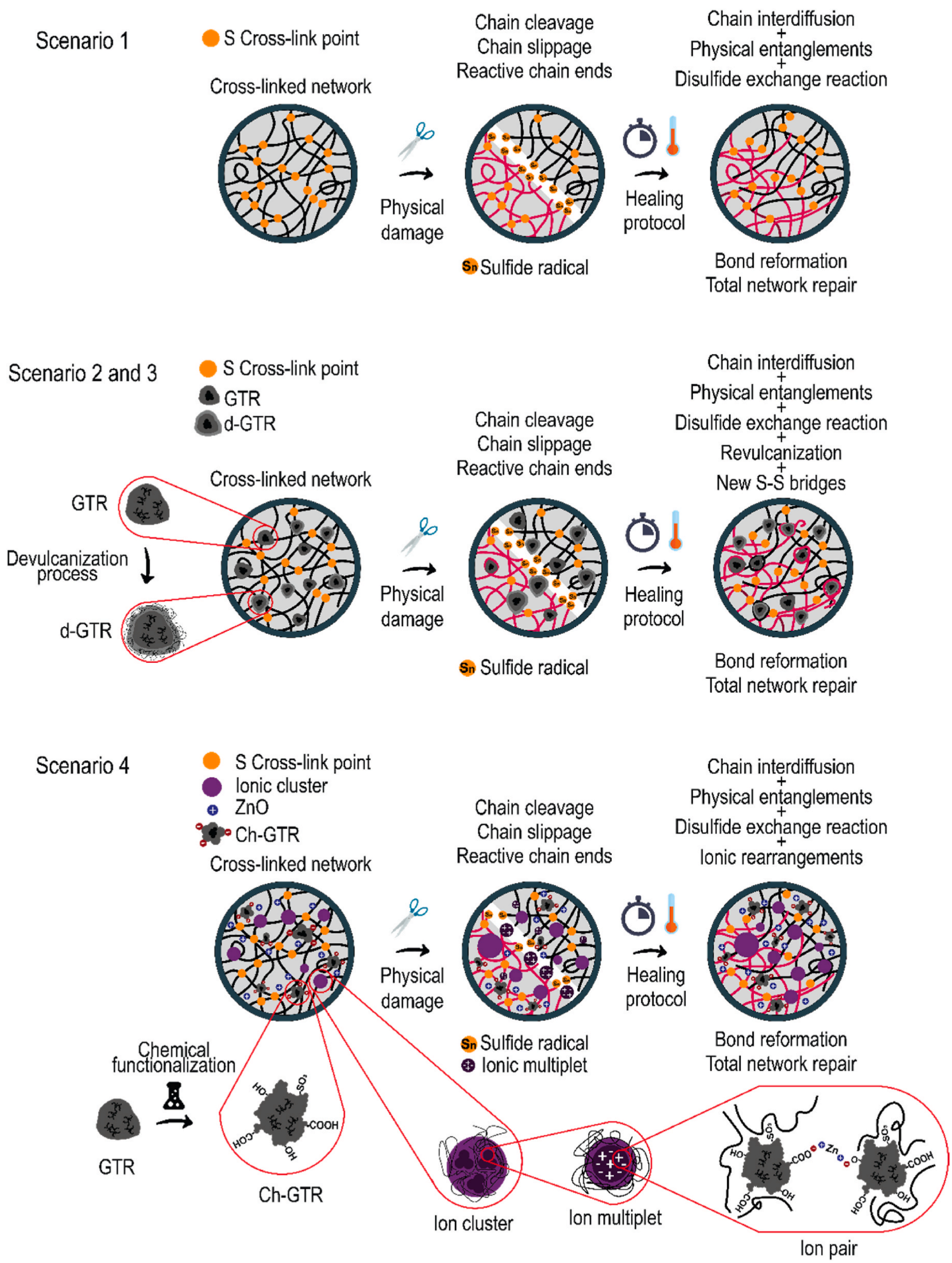

Fig. 2. Schematic representation of the healing mechanisms for the different scenarios.

impact of a conventional rubber. Firstly, the different self-healing scenarios are discussed (Scenarios 1–4) based on the sub-processes involved in Stage A and the final properties of the material/product. Then, the most favorable scenario is compared with the reference material (Scenario 0).

3.1. Impact analysis of self-healing scenarios

Fig. 3 (a) shows a comparison of the environmental impacts corresponding to each of the sub-processes involved in Stage A (Rubber compounding). As can be seen, acquisition of the rubber matrix (SBR) reflects the highest impact for all scenarios in both environmental categories. SBR production is more complex than the tire rubber grinding

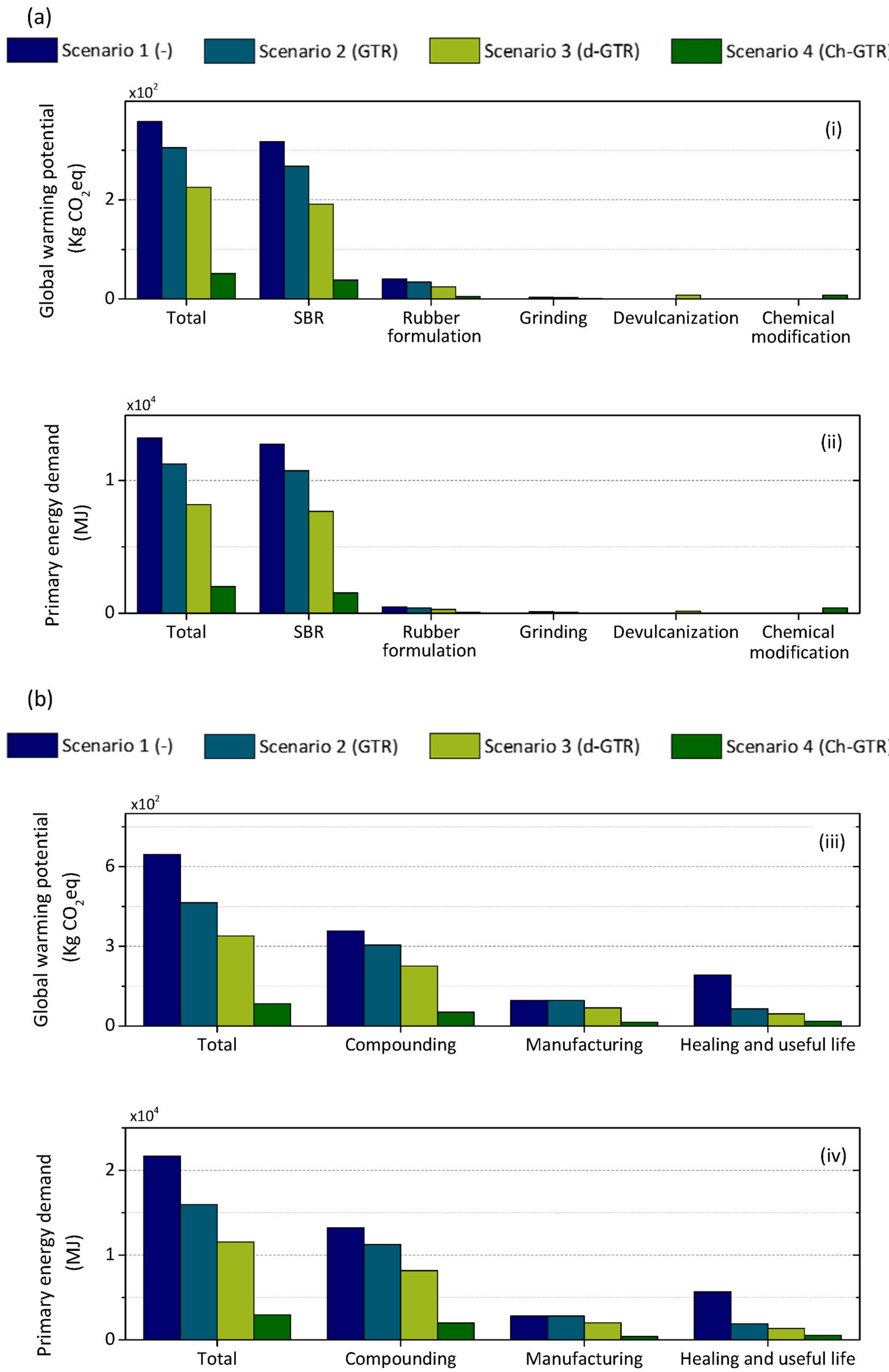

Fig. 3. (a) Comparative graphs of the environmental impact associated with the sub-processes involved in the compounding stage of SBR compounds. Graph (i) refers to GWP and (ii) to PED. (b) Graphs of: (iii) GWP and (iv) PED, of the self-healing scenarios. Graphs show the total impact value and the partial contribution of each stage.

and the considered GTR modification processes. In addition, SBR accounts for 80% of the weight of marine fenders, and as several marine fenders are needed to cover the functional unit, its contribution is multiplied. The formulation of the rubber comes next, with a decreasing trend due to: i) the addition of recycled reinforcements, whose environmental impact proves to be lower (difference between Scenarios 1 and 2, where the same number of marine fenders are needed to cover the functional unit, see Table 2 (b)) and ii) the reduction in the number of products needed to cover the functional unit (Scenario 1 vs. Scenarios 3 and 4, a reduction from 7 marine defenses to 4 and 1 respectively, Table 2 (b)). Meanwhile, the impact of those sub-processes associated with the reinforcing filler and its specific modification routes (grinding, devulcanization and chemical modification) are significantly lower for both categories. This is consistent since grinding and devulcanization processes only requires one step and the chemical modification process two, which are comparatively simpler processes, and reinforcement accounts for only 20% of the total weight of the product.

From the point of view of the material properties, the comparative results for the different self-healing scenarios are presented in Fig. 3 (b). The non-reinforced self-healing rubber (Scenario 1) shows the highest environmental impact in terms of GWP and PED. The main drawback of this material is its poor base mechanical properties, which in the LCA translates into numerous marine fenders (7) being necessary to cover the functional unit; thus, increasing the global warming and the energy requirements. The healing ability of this rubber lies in the possibility of the polymeric chains to both reorganize and form new bonds after a damage event and in presence of a thermal trigger. This is achieved by reducing the degree of crosslinking and lengthening the crosslinks, which goes in the opposite direction of obtaining the cross-linked network necessary for the good mechanical performance of the rubber (Hernández et al., 2016). Thus, although the self-healing SBR compound of Scenario 1 can recover a noteworthy percentage of its tensile strength ($\eta = 67\%$), its mechanical performance ($\sigma_b = 1$ MPa) is very poor if compared to the conventional rubber used for the manufacturing of a marine fender ($\sigma_b = 16$ MPa). Therefore, without adequate base properties, the ability to recover the departing mechanical properties fully or partially does not stand out as advantageous.

The inclusion of GTR and d-GTR (Scenarios 2 and 3, respectively) was set as a strategy to increase the tensile strength of the rubber, acting as reinforcing fillers; however, the dichotomy between mechanical performance and healing ability remained (see Supporting information S6). From the environmental point of view, the incorporation of untreated GTR to the self-healing rubber (Scenario 2) involves an additional sub-process related to the grinding of GTR, as discussed above. However, the overall impact is reduced with respect to Scenario 1 (28% in GWP and 26% in PED), and consequently, the cost-benefit balance of using GTR as a reinforcing filler is favorable. In a similar context, the use of GTR in bituminous mixtures is reported to give benefits with respect to energy saving (GER) and greenhouse emission gain (GWP), derived from the recycling and recovery of co-products such as GTR (Farina et al., 2017).

The same trend was observed with d-GTR (Scenario 3). Despite the inclusion of a second sub-process (i.e., the devulcanization process) and more energy consumption, the impact is notably reduced with respect to Scenarios 1 and 2 (47 and 27% in GWP and 47 and 28% in PED). The improvement lies in the fact that the devulcanization process partially breaks the cross-linked structure of the GTR, generating a plastic interface on the surface, which improves its interaction with the SBR matrix, resulting in a composite with improved mechanical performance (Alonso Pastor et al., 2022). However, it was the chemically modified filler (Scenario 4) that showed a noteworthy difference with two-fold advantages. On one side, the incorporation of Ch-GTR improves not only the mechanical performance but also the healing ability of the self-healing SBR (see Supporting information S6). On the other hand, it appears as the scenario with the lowest overall impact. Although the sub-process related to the chemical modification of the filler is to be considered and signifies additional environmental costs, the extraordinary material properties ($\eta = 85\%$ and $\sigma_b = 6.5$ MPa) mitigate these costs and increase the environmental benefits. The reduced impact contribution of this scenario results from the requirement of only one marine fender and two repair cycles to cover the functional unit, unlike previous scenarios where various products (between 4 and 7) were mandatory with their corresponding repair cycles. These improvements are attributed to the presence of -OH groups on the surface of the chemically modified GTR (Araujo-Morera et al., 2021). The interaction of these polar functional groups with the SBR matrix favors interphase adhesion, thus improving the mechanical performance of the composite. In addition, the -OH groups generate reversible ionic pairs that, when the temperature increases, behave as dynamic bonds, thus also promoting healing (Araujo-Morera et al., 2022b).

In view of these results, it is clear that the compromise between mechanical properties and healing ability, i.e. a higher mechanical performance, a lower healing efficiency, and vice versa, is a limitation also from the environmental point of view; and that the number of marine fenders required to cover the functional unit supposes a greater impact versus the energy consumed when increasing the healing cycles or when including additional sub-processes. Likewise, the environmental cost of incorporating a recyclable filler like GTR in a self-healing SBR matrix seems to be outweighed by the savings achieved through the improved material properties.

3.2. Impact analysis of self-healing vs. conventional scenarios

Fig. 4 (a) shows the comparison between the most favorable self-healing scenario (Scenario 4, Ch-GTR) and the conventional one (Scenario 0). In both situations, one marine fender covers the functional unit; even though the self-healing fender needs to be repaired twice, because of its inferior mechanical performance (40% of Scenario 0). It is obvious that the energy consumed during the healing stage carries most of the impact for both categories and is responsible for the lower environmental benefit (-12% in GWP and −25% in PED) of the self-healing material in terms of useful life stages (Stages A, B and C). This result clearly reflects that if the self-healing product is not able to withstand the same lifetime of a conventional product (due to lower mechanical strength), its healing capability does not make it environmentally attractive. This confirms that the healing/mechanical performance trade-off also governs the environmental benefits of these materials.

It can also be seen that during the compounding stage, the self-healing product shows an improvement in the GWP category but a deterioration in PED, as shown in Fig. 4 (a) and (b). This difference is related to the chemical modification process of GTR, which requires energy, sulfuric acid (H_2SO_4) and water. The impact of this chemical process regarding PED is slightly higher than in GWP, meaning that the chemical modification has a higher benefit in terms of environmental protection (measured by means of GWP) than in terms of resource depletion (measured by PED).

Fig. 4 (b) shows the breakdown of the contributions of the compounding stage. The procurement of the raw rubber is the sub-process with the highest impact for both categories. The contribution of Scenario 4 is slightly higher because a major amount of SBR is needed as the reinforcement content is lower, 20 vs 30%. w/w for CB (Scenario 0) and Ch-GTR (Scenario 4), respectively. The opposite trend is seen for the rubber formulation sub-process, where the impacts of the reference material are clearly higher than those of the self-healing equivalent. The reason is the following. Considering the current formulations, the weight of the vulcanization additives (ZnO, SA, CBS and S) with respect to the reinforcing fillers is lower (see Table 3 (a)); hence, it is mainly the contribution of the reinforcement what is reflected in Fig. 3 (b). Under these premises, the environmental benefit of the self-healing rubber reinforced with Ch-GTR (Scenario 4), is significantly higher over the reference material reinforced with CB (Scenario 0). Thus, if equivalent properties are achieved, total or partial substitution of CB by GTR can

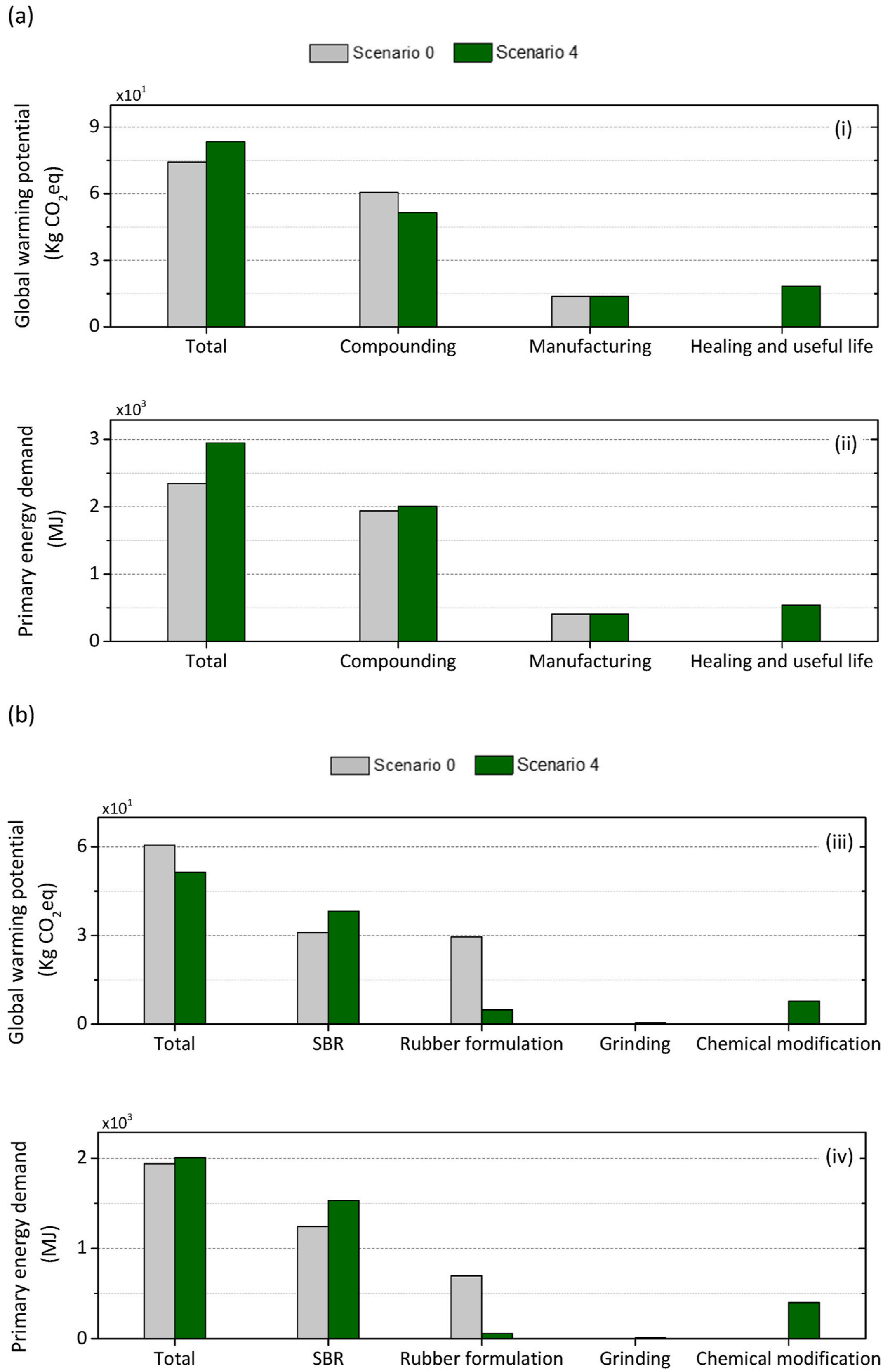

Fig. 4. (a) Comparative graphs of (i) GWP and (ii) PED; between the most favorable self-healing material (Scenario 4) and the reference material (Scenario 0). Graphs show the contribution of each stage and total. (b) Comparative graphs of (iii) GWP and (iv) PED; between the most favorable self-healing material (Scenario 4) and the reference material (Scenario 0). Graphs show the contribution for each sub-process of the compounding stage.

reduce the environmental impact of the rubber composite, outweighing the impact of the self-healing process.

3.3. Uncertainty analysis

To corroborate the main conclusions in this article, an uncertainty analysis was performed. The analysis concerned the study's target and most significant processes. In particular, the Ch-GTR content and healing efficiency were analyzed as the target parameters of the study, and the processes of manufacturing marine fender and healing were considered as the processes with the greatest significance. It should be mentioned that the compounding stage was not analyzed due to its low degree of uncertainty. For the compounding process, the greatest contribution to the environmental impact comes from SBR synthesis that is a process described in the data base. The main results of the uncertainty analysis are discussed below. However, data from the analysis can be found in Supporting information S7.

Regarding the target parameters, Ch-GTR content was changed from 20%. w/w to 0 and 40%. w/w, and healing efficiency decreased from 85% to 60%. From the comparative analysis of both parameters, the decrease in healing efficiency has a much greater effect on the environmental impact than the variation of Ch-GTR content. The former increases in 82% the PED and in 80% the GWP; while for the latter, the change of the total environmental impact was minimal, ±4% for PED and ±1% for GWP. On the other hand, energy consumption of marine fender manufacturing and healing processes were varied by ± 10%. For the marine fender manufacturing process, the deviation in the total environmental impact was of ±1.4% for PED and ±1.5% for GWP. With respect to the healing process, it was of ±1.9% for PED and ±2.1% for GWP. Therefore, variations in the healing process seem to play a more representative role. These results are promising as they show the potential of healing to address the environmental impact.

4. Conclusions

Our study presents, for the first time, the LCA of a self-healing SBR to produce a marine fender. The results, in terms of GWP and PED, clearly demonstrate that the use of a SBR with a healing capability of 67% does not necessarily translate into environmental benefits if it cannot last for the same lifetime as conventional products due to its lower mechanical performance (↓ 94% respect to conventional) and higher energy consumption (↑ 730% in PED and ↑ 670% in GWP respect to conventional). However, we also showed that the incorporation of 20%. w/w of a sustainable filler such as GTR can overcome these limitations and improve the material properties in 550%, thus leading to a more favorable environmental performance (28% decrease in GWP and 26% in PED), even though this incorporation involves additional subprocesses such as grinding, devulcanization and chemical modification. Moreover, a variation in GTR content (between 0 and 40%. w/w) supposes minimal additional environmental impact (±4% for PED and ±1% for GWP).

Our research also highlights the importance of using experimental healing efficiencies and cycles instead of conservative assumptions in assessing the environmental impact of self-healing rubbers. However, it is crucial to address the limitations of this study concerning the extension of material properties to the ultimate product. We recommend that future efforts should focus on optimizing mechanical properties and achieving autonomous healing, which can translate into lower energy requirements and extended lifetime, leading to a more sustainable material. In conclusion, this study provides a valuable contribution to the understanding of the environmental performance of self-healing rubbers and the potential benefits of incorporating sustainable fillers. Further research is needed to refine and improve the use of these materials in various applications, and we hope our findings can guide future efforts in this direction.

Credit authorship statement

L.E.A.P.: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing—original draft, Writing—review and editing; K.C.N.C.: Conceptualization, Formal analysis, Resources, Writing—review and editing, Visualization, Supervision, Funding acquisition; M.G.: Conceptualization, Formal analysis, Resources, Writing—review and editing, Visualization; J.A.-M.: Investigation, Formal analysis, Data curation; G.P.: Formal analysis, Writing-review and editing; J.M.P.: Supervision, Project administration, Funding acquisition; M.H.S.: Conceptualization, Formal analysis, Writing—review and editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2023.138207.

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