

Article

Mechanochemical Recycling of Tire-Derived Styrene–Butadiene Rubber Using a Regeneration Agent

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Abstract

Mechanochemical regeneration aims to selectively cleave the crosslinked network of vulcanized rubber. In this study, a tire-grade styrene–butadiene rubber (SBR) compound was vulcanized and then subjected to mechanochemical regeneration using a zinc (II) dithiocarbamate complex (ZNIBU) at 6, 8, and 10 phr. The regenerated materials were subsequently revulcanized, and their properties were assessed before and after both processing steps. The regenerated (non-revulcanized) samples exhibited reduced crosslink density and increased swelling, indicating effective network cleavage by the regenerator. After revulcanization, the compounds presented higher hardness (23%) but lower tensile strength (75%) and tear strength (25%) compared to the virgin vulcanizate. Overall, ZNIBU proved highly effective for the mechanochemical regeneration of SBR, with optimum performance observed at 8 phr.

Keywords: mechanochemical regeneration; recycling; SBR rubber; ZNIBU; end-of-life tires

1. Introduction

The disposal of end-of-life tires poses a major environmental challenge [1,2]. Globally, about 17 million tonnes of scrap tires are generated each year [3], and this volume may reach 1.2 billion units annually by 2030 [1,4].

Tires contain 40–60% rubber, which is vulcanized to produce a durable, crosslinked molecular structure with enhanced strength and elastic recovery [5–7].

This highly stable network resists biological degradation, contributing to the long-term accumulation of improperly discarded tires in the environment. Their hollow geometry also creates ideal habitats for mosquito breeding, facilitating the spread of vector-borne diseases such as dengue, chikungunya, and Zika. In addition, open burning releases toxic compounds, contaminates groundwater, and pollutes the atmosphere, and is therefore prohibited by law [1,5].

Several tire recycling techniques have been developed to identify sustainable disposal routes. Currently, the most widespread industrial practice is coprocessing, where scrap tires serve as supplementary fuel in cement kilns [8,9]. This method recovers energy by combusting rubber at high temperatures to supply the substantial thermal demand of clinker production. Replacing 40% of conventional coke with tire-derived fuel reduces fuel costs by about 25% during clinker production [10]. However, tire combustion generates pollutants from rubber additives, including sulfur oxides (SO_x), carbon monoxide (CO),



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and carbon dioxide (CO₂), contributing to acidification, air pollution, and greenhouse gas emissions [8,11].

Regeneration of post-consumer rubber has emerged as an alternative disposal route [6,12–15]. This process selectively cleaves a portion of the crosslinks in vulcanized rubber using thermal, mechanical, chemical, or biological energy, producing a moldable material that can be revulcanized [12,16,17]. Chemical regeneration, in particular, offers high selectivity in breaking crosslinks via regenerating agents and may be enhanced by additional thermal or mechanical input [6,12,17–19].

Certain vulcanization accelerators also function as regenerating agents. Accelerators increase the rate and efficiency of vulcanization [20,21], but their effect depends on processing conditions. High temperatures and pressures favor vulcanization, while milder temperatures promote regeneration [22,23]. Sulfonamides and dithiocarbamates are among the most relevant agents in this dual-function category [22].

However, some dithiocarbamate-based regenerators pose toxicity concerns due to secondary amines in their structure, which may form carcinogenic nitrosamines upon reaction with nitrites or nitrogen oxides [22–24].

To address this issue, less hazardous regenerating agents have been explored, including organic solvents [6,12], supercritical CO₂ [6], and bio-based alternatives [3,25]. Among these, dithiocarbamate derivatives such as bis(4-methylphenylsulfonyl)dithiocarbamate zincate (II) tetrabutylammonium (ZNIBU) have been investigated as effective SBR regenerators. ZNIBU has been studied at the Center of Excellence in Recycling and Sustainable Development (NERDES) at the Federal University of Rio de Janeiro (UFRJ) [22] and has demonstrated additional utility as a vulcanization accelerator for natural rubber (NR) [26], nitrile rubber (NBR) [23], and polybutadiene rubber (BR) [24].

However, ZNIBU's efficacy as a regenerating agent has been investigated exclusively within a styrene–butadiene rubber (SBR) formulation. This composition comprised sulfur, stearic acid, zinc oxide, Irganox, tetramethylthiuram disulfide (TMTD), and 2-mercaptobenzothiazole (MBT), a blend not intended for tire manufacturing [22]. Consequently, the evaluated rubber matrix did not account for the typical complexity of tire formulations, which include reinforcing fillers such as carbon black, among other components. Therefore, the application of ZNIBU in the devulcanization of end-of-life tires (ELTs) represents a novel approach in the literature. Furthermore, ZNIBU exhibits a dual functional character, acting simultaneously as a vulcanization accelerator and a regenerating agent [22]. This multifunctionality allows for a reduction in the number of chemical additives required, thereby simplifying the reaction system and aligning the process with the principles of Green Chemistry.

Thus, ZNIBU (Figure 1) is characterized as a nontoxic material because its anionic structure lacks nitrogen atoms linked to alkyl or anilino groups, and its tetrabutylammonium cation does not promote nitrosation. Consequently, it does not generate nitrosamines [24,26], unlike its structural analogs, the dithiocarbamates.

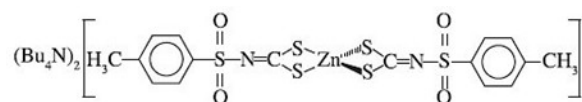


Figure 1. Chemical structure of ZNIBU.

The aim of the present study was to evaluate the performance of ZNIBU, at varying concentrations, as a regenerator for an SBR formulation used in tire manufacturing.

2. Results

The results for the vulcanized, regenerated, and revulcanized SBR samples are presented together to facilitate comparison.

2.1. Rheometric Properties

The study began with the vulcanization of the SBR formulation. As reported in the literature [27,28], rheometric parameters are useful indicators of curing behavior in rubber compounds. Figure 2 shows the curing curves for the original vulcanizable material and for the regenerated samples prepared with different ZNIBU concentrations, while Table 1 summarizes the corresponding rheometric values.

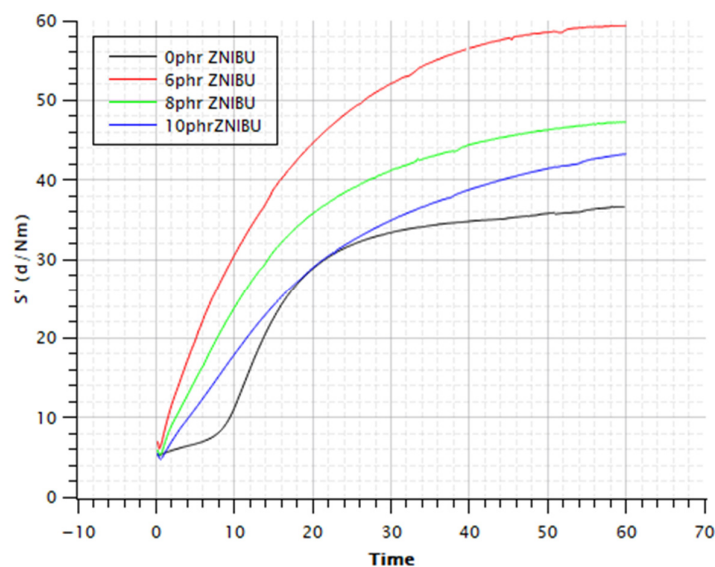


Figure 2. Curing curves of the TBBS-vulcanized material (original) and of the regenerated and revulcanized materials containing different ZNIBU concentrations (6 phr, 8 phr and 10 phr).

Table 1. Rheometric properties obtained using a rubber processing analyzer for the original TBBS-vulcanized composition and for the regenerated and revulcanized SBR compositions prepared with ZNIBU.

ZNIBU Concentration (phr)	Optimal Curing Time— t_{90} (min)	Scorch Time— t_{s1} (min)	Maximum Torque— M_H (dN·m)	Minimum Torque— M_L (dN·m)	Torque Variation— ΔM (dN·m)
0.0 *	26.2	3.2	35.1	5.2	29.9
6.0	33.6	1.2	59.4	6.0	53.4
8.0	36.2	1.4	47.9	5.2	42.7
10.0	42.2	1.2	43.3	4.7	38.6

* Non-regenerated TBBS-vulcanized SBR composition.

The cure curves show a gradual increase in rigidity over time, characteristic of vulcanization [29]. Key parameters, including the optimal curing time (t_{90})—the time required to reach 90% of maximum crosslinking—are derived from these curves [27]. The original composition exhibited a shorter t_{90} than the regenerated materials (33.6–42.2 min), indicating faster curing. This difference stems from the different accelerator systems: the initial vulcanizate used tert-butyl benzothiazolyl sulfenamide (TBBS), a fast accelerator [22,23], whereas the regenerated samples were revulcanized using only ZNIBU, a slow accelerator [22–24,26]. It is emphasized that, in the revulcanization process, ZNIBU is used exclusively due to its dual functionality, acting simultaneously as a regenerating agent and a vulcanization accelerator. During the vulcanization stage in the press, the increase in

temperature facilitates the activation of ZNIBU, which predominantly assumes the role of the accelerator, promoting the formation of new crosslinks and thereby enabling the revulcanization of the regenerated material. Consequently, the use of TBBS is unnecessary, since ZNIBU alone is capable of driving the revulcanization process.

Scorch time (t_{s1}), defined as the onset of crosslink formation [27], was markedly shortened for the regenerated materials (1.2–1.4 min) when compared to the original vulcanizate (3.2 min). This rapid onset is attributed to the reactive Zn–S–C complexes formed by ZNIBU with ZnO and sulfur, which promote early formation of active sulfur species and accelerate initial crosslinking [30]. The approximately 65% reduction in scorch time is consistent with the trends shown in Table 1 and Figure 2.

Maximum torque (M_H), which correlates with crosslink density postvulcanization, was significantly higher in the regenerated and revulcanized compounds (59.4–43.3 dN·m) when compared to the original material (35.1 dN·m) (Figure 2 and Table 1). The literature [22] notes that only about 70% of all original crosslinks are cleaved during regeneration [31,32]. The remaining network, combined with new crosslinks formed during revulcanization, increases the final crosslink density.

Minimum torque (M_L), an indicator of viscosity and processability [27], decreased with increasing ZNIBU concentration. Lower M_L values indicate more effective chain scission and higher plasticity.

ZNIBU may function predominantly as a vulcanization accelerator or regenerating agent depending on reaction conditions [22]. Among the regenerated formulations, the 6 phr composition showed the highest ΔM , indicating that the accelerator behavior of ZNIBU was more pronounced. As the ZNIBU concentration increased, ΔM progressively declined, suggesting a stronger regeneration effect at 8 and 10 phr.

2.2. Swelling and Crosslink Density

Figure 3 shows the crosslink density and degree of regeneration for the initial vulcanized material and the regenerated, non-revulcanized samples, calculated using the swelling method [33,34].

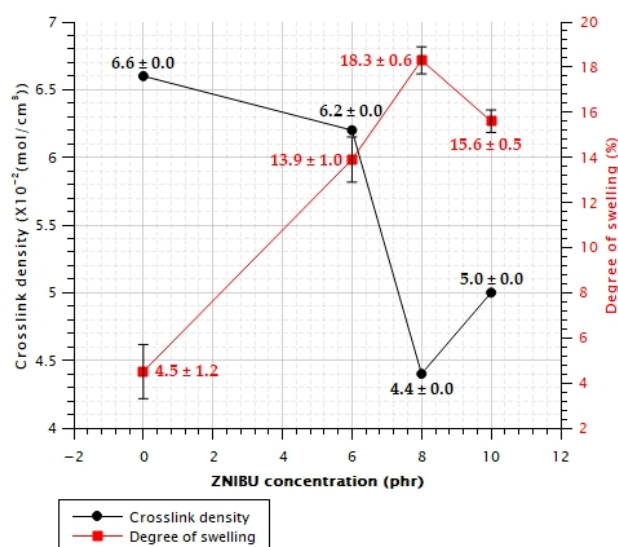


Figure 3. Swelling degree of the original non-regenerated vulcanized SBR and the regenerated, non-revulcanized SBR samples containing different ZNIBU concentrations, measured in toluene.

As expected, the original vulcanized rubber exhibited the highest crosslink density. All regenerated materials showed lower crosslink densities than the non-regenerated

vulcanizate, confirming that ZNIBU effectively cleaves part of the network and enables subsequent revulcanization and reprocessing.

Figure 3 shows that all regenerated materials displayed higher swelling degrees than the original material, demonstrating the regenerator's efficiency in breaking some crosslink bonds.

According to the literature [33,34], the equilibrium swelling ratio is inversely proportional to crosslink density: lower crosslink density results in higher swelling, whereas more densely crosslinked networks swell less.

Thus, the regenerated materials consistently showed reduced crosslink density and increased swelling compared with the non-regenerated samples (0.0*), which had the highest crosslink density and lowest swelling degree.

Table 2 summarizes the crosslink density results and the calculated degree of regeneration for the initial vulcanized rubber and the regenerated, non-revulcanized samples.

Table 2. Crosslink density and degree of regeneration for the original vulcanized material and the regenerated, non-revulcanized SBR compositions.

ZNIBU Concentration (phr)	Degree of Regeneration (%)
0.0 *	0.0
6.0	5.9
8.0	33.6
10.0	23.9

* Non-regenerated SBR composition.

The regeneration degree varied among the compositions. The formulation containing 8 phr ZNIBU achieved the highest regeneration degree (33.6%), while the 10 phr ZNIBU sample showed an intermediate value. At higher ZNIBU loadings, the compound increasingly acted as an accelerator, forming new crosslinks and competing with regeneration reactions.

These results change significantly after revulcanization.

As shown in Figure 4, all regenerated and revulcanized samples exhibited higher crosslink density than the original non-regenerated vulcanizate, consistent with the trends observed in the M_H values.

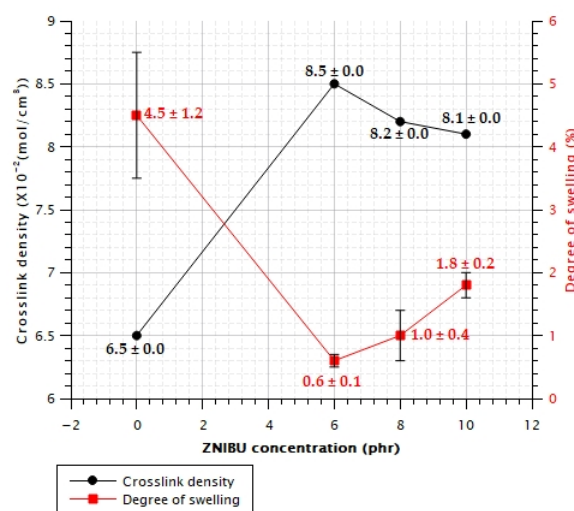


Figure 4. Crosslink density and regeneration degree for the original vulcanized material and the regenerated and revulcanized SBR compositions.

Among the regenerated and revulcanized samples, the 6 phr ZNIBU formulation showed the greatest increase in crosslink density and the highest M_H value.

The revulcanized materials also demonstrated reduced swelling relative to the original vulcanizate, reflecting the formation of additional crosslinks that limit solvent uptake.

2.3. Thermal Properties

The thermal behavior of the vulcanized rubber and regenerated, non-revulcanized samples was evaluated by thermogravimetric (TGA) and derivative thermogravimetric analysis (DTG), as presented in Figure 5.

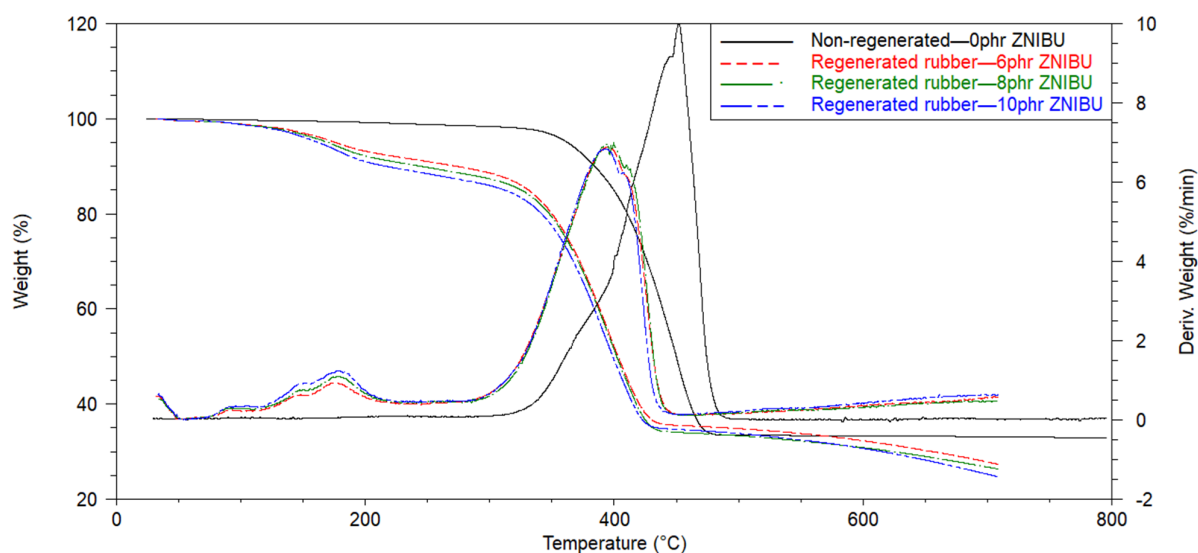


Figure 5. Thermogravimetric curves and derivative thermogravimetric analysis of the original vulcanized rubber and the regenerated SBR samples containing different ZNIBU concentrations (non-revulcanized).

The TGA curves represent mass loss as a function of temperature, while the DTG curves indicate the rate of mass loss, highlighting the main thermal degradation events.

Crosslinks in vulcanized rubber improve thermal stability by restricting chain mobility as temperature increases, thereby limiting flow and softening. Consequently, vulcanized rubber resists melting upon heating and better maintains its shape and mechanical integrity at elevated temperatures [2]. In addition, the three-dimensional network formed by these crosslinks also distributes thermal energy more evenly throughout the material, reducing localized stress concentrations that could initiate thermal degradation [2].

During regeneration, partial cleavage of the network allows thermal energy to disrupt covalent bonds in the polymer backbone more readily, causing degradation at lower temperatures. Thus, regeneration generally reduces the thermal stability of rubber [2,35]. This behavior is reflected in the DTG results presented in Table 3.

Table 3. Thermogravimetric analysis results for the original vulcanized SBR and non-revulcanized SBR compositions regenerated with ZNIBU.

ZNIBU Concentration (phr)	Maximum Degradation Temperature (°C)
0.0 *	451.91
6.0	395.1
8.0	399.6
10.0	394.0

* Non-regenerated SBR composition.

The maximum degradation temperature, obtained from the peak of the DTG curve, provides a reliable indicator of thermal stability [2,35]. All regenerated materials exhibited lower DTG peak temperatures than the original vulcanizate, confirming that the regeneration process decreased network integrity and reduced thermal stability.

Additionally, it is possible to observe that all regenerated materials exhibited a peak around 180 °C. This event is attributed to the volatilization and decomposition of species with lower thermal stability generated during the regeneration process, such as chain fragments, oligomers, and weakly bound sulfur species [35].

2.4. Mechanical Properties

Table 4 presents the mechanical properties of the original vulcanized SBR formulation and the regenerated SBR formulations containing ZNIBU and subjected to revulcanization.

Table 4. Mechanical properties of the original vulcanized SBR and the regenerated SBR formulations.

ZNIBU Concentration (phr)	Hardness (Shore A)	Tear Strength (N/mm)	Rupture Stress (MPa)	Elongation at Break (%)
0.0 *	68.0 ± 1.7	67.6 ± 6.9	22.9 ± 1.7	324.3 ± 17.8
6.0	85.0 ± 1.3	18.1 ± 1.5	10.6 ± 1.0	47.9 ± 2.3
8.0	83.0 ± 0.5	16.8 ± 1.7	11.15 ± 0.4	55.1 ± 2.0
10.0	81.0 ± 1.2	19.0 ± 4.6	6.44 ± 0.3	54.8 ± 1.8

* Non-regenerated SBR composition.

Hardness, which is directly influenced by crosslink density [36,37], was higher for all regenerated and revulcanized materials compared to the original vulcanizate, with a slight decrease observed as the ZNIBU concentration increased.

When hardness was compared among the regenerated materials, the concentration of the regenerating agent directly affected crosslink density. The lowest ZNIBU concentrations produced the highest crosslink densities, resulting in the highest hardness values.

In the remaining properties (tear strength, tensile strength, and elongation at break), the revulcanized materials exhibited lower values than those of the non-regenerated vulcanized material. This may be attributed to two factors. The first relates to the reduction in polymer molar mass, which occurs from backbone degradation during regeneration with varying concentrations of ZNIBU, directly influencing polymer properties [38]. The second factor may be associated with the formation of additional crosslinks during revulcanization, which increases the rigidity of the polymeric network, rendering the material harder but more brittle [37]. Consequently, despite a higher crosslink density than that of the virgin material, an increase in hardness was observed simultaneously with a decrease in the other mechanical properties. This combination highlights the trade-off in regenerated elastomers, wherein gains in rigidity come at the expense of mechanical fragility, resulting from both backbone degradation and excess crosslinking.

Tear strength and tensile strength showed no statistically significant differences among the regenerated samples when standard deviations were considered, although all values remained lower than those of the virgin (non-regenerated) rubber. Consequently, the regenerated and revulcanized materials are unsuitable for high-performance applications such as tire production but may be viable for less demanding technical uses.

3. Materials and Methods

Figure 6 provides a schematic overview of the experimental procedure. An original SBR compound commonly used in tire manufacturing was first prepared and then subjected

to regeneration with ZNIBU concentrations, followed by revulcanization. The original compound, regenerated rubber, and revulcanized products were subsequently characterized.

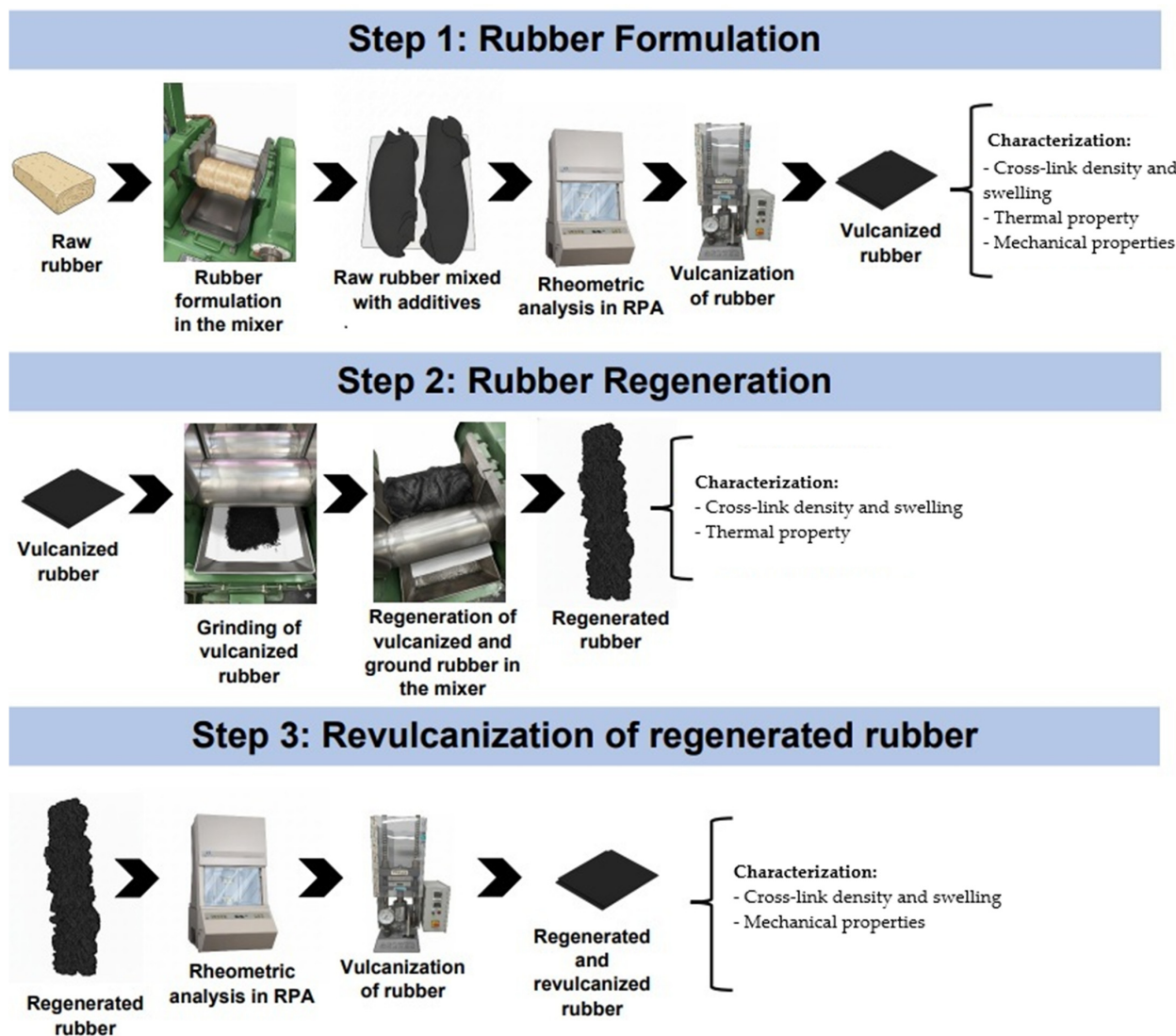


Figure 6. Schematic representation of the SBR regeneration study.

3.1. Formulation of the Original SBR Composition

The original SBR compound was prepared according to ASTM [39], a standard rubber formulation for tire compounds. SBR 1502 was used instead of SBR 1500 due to availability constraints; this grade differs mainly in its higher styrene content and larger proportion of trans-1,4 units. The formulation contained 100 phr SBR, 1.75 phr sulfur, 3 phr zinc oxide, 1 phr stearic acid, 1 phr TBBS, and 50 phr carbon black [39].

Mixing was performed in an open two-roll mill (30–90 W Berstorff) operating at 24 rpm (front roll) and 30 rpm (back roll), with roll temperatures between 50 °C and 70 °C. The rubber was first masticated for 7 min, followed by the sequential incorporation of sulfur for 3 min, zinc oxide and stearic acid for 5 min, TBBS for 2 min, and carbon black for 15 min [39].

Transverse cuts ($\frac{3}{4}$ cuts) were performed throughout mixing to promote uniform dispersion. The sheeted compound was passed through the mill for an additional 5 min, yielding a total mixing time of 34 min, then stored in the dark for 24 h [39].

3.2. Rheometric Analysis of the Material

Rheometric behavior was analyzed using a Rubber Process Analyzer (RPA 2000, Alpha Technologies, Hudson, OH, USA) following ASTM [40]. Tests were conducted at 150 °C with a 0.2° oscillation arc and a frequency of 1.7 Hz, and each run lasted 1 h.

3.3. Vulcanization in a Hydraulic Press

Using the optimum cure time (t_{90}) obtained from rheometry, the compounds were vulcanized and molded into 12 cm × 12 cm sheets with a thickness of 2.0 mm using a hydraulic press (Carver, MA 098, USA). Vulcanization was carried out at 150 °C under 8 tonnes of pressure, in accordance with ASTM [41], using the respective t_{90} of each formulation.

3.4. Regeneration of Vulcanized Rubber

The revulcanized rubber was regenerated using a mechanochemical approach in which ZNIBU served as the regenerating agent while mechanical shear from an open two-roll mill (30–90 W Berstorff) enhanced process efficiency. This method was developed through two studies [42,43].

ZNIBU was synthesized by the NERDES/UFRJ research group, and its characterization is reported in previous publications by the group [23,44–46].

The vulcanized rubber sheets were mechanically ground at room temperature to increase surface area in contact with the regeneration agent, producing particles of approximately ±0.8 mm [47,48].

Regeneration was performed using the base recipe: 100 phr vulcanized rubber, ZNIBU at 6, 8, and 10 phr, 10 phr sulfur, 0.7 phr zinc oxide, and 0.7 phr stearic acid [22]

ZNIBU was added for 6 min, followed by sulphur for 6 min, zinc oxide and stearic acid for another 6 min, and finally 5 min of cross-cutting (3/4 cuts) to ensure homogeneity.

The regenerated samples were stored in the dark for 24 h before rheometric analysis and revulcanization, the latter performed using the same conditions applied to the original compound, except that ZNIBU replaced TBBS as the sole accelerator.

3.5. Characterization of the Regenerated Rubber

3.5.1. Swelling Analysis

Regeneration efficiency was evaluated based on swelling behavior and crosslink density.

Samples ($2.0 \times 2.0 \times 0.2 \text{ cm}^3$) were immersed in toluene for 7 days in the dark and then weighed. They were subsequently dried at room temperature for 4 days to constant mass [49,50]. Crosslink density was calculated using the Flory–Rehner equation (Equations (1) and (2)).

$$\eta = - \left[\frac{\ln(1 - V_r) + V_r + X v_r^2}{V_0 \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right)} \right] \quad (1)$$

where η is the crosslink density, V_r the volume fraction of the swollen rubber, V_0 the molar volume of toluene (106.3 mL/mol), and X the polymer-solvent interaction parameter. The value of V_r was calculated using Equation (2).

$$V_r = \frac{M_1 \rho_r^{-1}}{M_1 \rho_r^{-1} + \rho_s^{-1} (M_2 - M_3)} \quad (2)$$

Here, M_1 , M_2 and M_3 denote the masses of the unswollen, swollen, and dried samples (after solvent removal), respectively.

The swelling degree (S%) was calculated using Equation (3).

$$S(\%) = \left(\frac{m_1 - m_3}{m_1} \right) \times 100 \quad (3)$$

3.5.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE, USA) to assess material regeneration. Non-revulcanized materials typically show reduced thermal stability relative to the original vulcanizate [2,35], making TGA a complementary method to swelling. Analyses were conducted under nitrogen flow (20 mL/min) from 30 °C to 700 °C, at a heating rate of 20 °C/min.

3.6. Characterization of Vulcanized Samples

3.6.1. Hardness

Hardness was measured according to ASTM [51] using a Shore A2 durometer (The Shore Instrument and MFG Co. Inc., New York, NY, USA). To meet the standard thickness requirement, three tear-test specimens were stacked. Five measurements were taken per stack, and the median value and standard deviation were reported.

3.6.2. Tear Strength

Tear strength was evaluated in accordance with ASTM [52], using Type C specimens. Five specimens were cut from each composition and tested on a universal testing machine (Emic DL2000, Denkei Corporation, Schaumburg, IL, USA), with elongation applied along the longitudinal axis. Results were expressed as the median of the five replicates for each formulation.

3.6.3. Tensile Strength

Tensile testing was performed on five specimens following DIN [53] using a universal testing machine (Emic DL2000) with a grip separation rate of 200 mm/min and a 100 kgf load cell. Specimens measured approximately 4.0 mm wide, 2.0 mm thick, and 20 mm long. Results were expressed as the median of five measurements for each composition.

4. Conclusions

Mechanochemical regeneration of vulcanized styrene–butadiene rubber (SBR) using the zinc (II) dithiocarbamate complex (ZNIBU) at 50–70 °C proved effective in recovering tire-grade rubber.

Regenerated nonvulcanized samples exhibited increased swelling and reduced crosslink density relative to the original vulcanizate, indicating successful network cleavage. Thermogravimetric analyses confirmed these findings.

Rheometric torque variation (ΔM) revealed that ZNIBU acts primarily as an accelerator at 150 °C and 6 phr during revulcanization. At concentrations ≥ 8 phr and temperatures of 50–70 °C during regeneration, ZNIBU functions mainly as a regenerating agent by reducing crosslink density.

Hardness increased with crosslink density, and revulcanized rubbers displayed higher hardness than the virgin rubber. However, tear strength, tensile strength, and elongation at break of regenerated rubbers remained inferior to those of the virgin vulcanizate. Thus, the regenerated and revulcanized materials are unsuitable for high-performance applications such as tires but remain viable for less technical uses. This improves resource efficiency, reduces the need for virgin raw materials, and contributes to more sustainable end-of-life tire management.

Future work will expand the scope of the regeneration study by investigating a broader range of ZNIBU concentrations (2, 4, 12, and 14 phr) to better establish its influence on regeneration and revulcanization. In addition, the process will be applied to formulations derived from waste tires. Finally, the resulting regenerated rubber will be blended with virgin rubber to decrease the primary elastomer content in new tire manufacturing, consistent with circular economy objectives.

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Abbreviations

The following abbreviations are used in this manuscript:

SBR	Styrene–butadiene rubber
ZNIBU	Zinc (II) dithiocarbamate complex
T ₉₀	Optimal curing time
T _{s1}	Scorch time
M _H	Maximum torque
M _L	Minimum torque

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