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# Efficient thermo-oxidative reclamation of green tire rubber and silanized-silica/rubber interface characterization

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## Abstract

A stepwise separation of reclaimed silanized silica (r-SS) from waste green tire rubbers was achieved using a thermo-oxidative reclamation process, and the interfacial interaction between silanized silica and rubber was quantified. The exfoliation of the residual and bound rubber from the r-SS surfaces under different temperatures ranging from 150 °C to 230 °C was investigated, with or without the addition of vegetable oil. The particle size of r-SS decreased from hundreds of micron-meters to nanometers with the increase of reclamation degree, i.e., the degree of devulcanization of vulcanized rubber, as quantified by the sol content and crosslinking density, and the thickness of the bound rubber layer decreased to 4-6 nm at 230 °C. This work provides a feasible solution for recycling of waste green tires, and also promote the understanding of the interfacial interactions between silanized silica and rubber by thermo-oxidative reclamation

## Introduction

Traditional rubber tires contain carbon black as the reinforcement filler, exhibiting high mechanical robustness and wear resistance while facing ‘magic triangle’ trade-offs, i.e.,

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the rolling resistance, wet-skid resistance and abrasion resistance of the tire tread rubbers cannot be satisfied simultaneously. Partial replacement of carbon black with silica particles has shown promise in balancing the three properties, so that reduces the fuel consumption and carbon emission as compared to conventional tires, and makes the tire 'green'. The market size of green tire was about 27.24 billion dollars in 2019, and is expected to reach 38.35 billion dollars by 2027.<sup>1</sup> The rapid development of the green tire market has been driven by the wide awareness of its enhanced performance including low rolling resistance, high skid resistance and high abrasion resistance. With the expansion of the green tire market, the waste management of the end-of-life green tires has always been an issue yet to be solved.

To achieve better dispersion and reinforcement of silica in rubbers, the abundant active silanol groups on the silica surface need to be modified with surfactant, such as silane, to break the hydrogen bonding among the silica particles, reduce the agglomerates and improve the interfacial adhesion between silica and rubber matrices. As compared to the physical entanglement between carbon black and rubber molecular chains, the chemical interaction between silanized silica and rubber is much stronger. For reclamation of waste green tires, understanding the interfacial bonding between silanized silica and rubber is important for effectively separation of silica fillers from waste rubber matrices and increase the reclamation efficiency. Sarkawi et al.<sup>2</sup> presented an insight into the morphology of silanized silica-reinforced natural rubber interface and explored its interaction from the direction of the positive reaction. Nevertheless, the recycling of silanized silica from green tire rubber is a reverse reaction of the reinforcement, the investigation of the reclamation process will help to understand the interfacial interaction mechanism between silanized silica and the rubber matrix.

Pyrolysis<sup>3,4</sup> and reclaiming<sup>5,6</sup>, are the most efficient recycling methods of waste tire

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rubber in industry, where temperature plays a key role in the pyrolysates especially on the chemical composition and structure of the resultant solid products<sup>7,8</sup>. Ivanov et al.<sup>9</sup> reported a method to obtain reclaimed silanized silica via subjecting the tread rubber of green tire to pyrolysis-cum-water vapor between 300 and 1000 °C, and obtained a product containing 65% of silica. The same method was used by Omar et al.<sup>10,11</sup> and also found that temperature (500~700 °C) affects the structure of the reclaimed silanized silica to a large extent. The obtained products were used to compound with natural rubber and replace conventional fillers. However, both processes require high temperature and are energy-intensive.

Moving forward, a more efficient, energy-saving and environmental-friendly method is needed for recycling of fillers from waste green tire rubber. According to our previous studies on the thermo-oxidative reclamation of waste tire rubbers<sup>12,13</sup>, with the assistance of a small amount of vegetable oil, a high reclamation process of waste tire rubber under low temperature (150 °C) was achieved within xx (how long?). The vegetable oil can effectively swell the rubber matrices thus facilitates the penetration of oxygen and thermo-oxidative degradation.

In this work, thermo-oxidative reclamation is used for separation of silanized silica from waste green tire in a tubular furnace. The stepwise exfoliation of r-SS from the rubber vulcanizates was achieved with the increase of the reclamation temperature from 150 °C to 230 °C. The structural and chemical composition evolution of r-SS was characterized by evaluating the residual rubber hydrocarbon content, thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffractometer, stereomicroscopy and transmission electron microscopy. An effective thermo-oxidative reclamation process is provided for energy-saving recycling of waste green tires, and the interfacial interaction between silanized silica and the rubber matrix was discussed from the perspective of reverse reactions.

## **Experiment**

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## Materials

Natural rubber (NR) (SVR 3L), silica (1165MP), bis[3-(triethoxysilyl) propyl] tetra sulfide (TESPT), softener (TDAE oil), rubber ingredients including stearic acid (SA), zinc oxide (ZnO), sulfur (S), N-cyclohexyl benzothiazole-2-sulphenamide (Accelerator CZ), diphenyl guanidine (Accelerator DPG) and sunflower oil were all commercial grades.

## Preparation of Green Tire Rubber

Simulated green tire rubber was prepared as the following formula and vulcanized according to the optimum curing time under 150 °C: NR 100 phr, silica 60 phr, TESPT 4.8 phr, ZnO 2.5 phr, SA 1.0 phr, softener 10 phr, accelerator CZ 2.0 phr, accelerator DPG 1.5 phr and sulfur 1.7 phr.

## Reclamation of Green Tire Rubber

The vulcanized NR was masticated and sifted by a 10-mesh sieve first, and then blended with 10 phr of sunflower oil before fed into tubular furnace under different temperatures varying from 150 °C to 230 °C, at an interval of 20 °C for 30min.

## Characterization

The sol fractions of reclaimed rubber were measured with a Soxhlet extraction method using toluene as the solvent. The samples were refluxed in toluene for 72 h under 145 °C, and then dried in vacuum at 60 °C till constant weight. The sol fraction ( $S_f$ ) was calculated according to Equation 1.

$$S_f = \frac{m_0 - (m_l + m_s)}{m_0 \times \omega} \times 100 \% \quad (1)$$

where  $m_0$  is the mass before extraction,  $m_l$  is the mass of dried sample,  $m_s$  is the mass of soluble materials and  $\omega$  is the rubber content.

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Residual rubber hydrocarbon content is one of the important indicators to characterize rubber composite materials. The compounds were first mixed with acetone to remove the sunflower oil and then mixed with toluene at room temperature for 7 days, after that, dried at 50°C in the vacuum oven till constant weight. The calculation formula of the residual rubber hydrocarbon content is shown in Equation 2 where  $R_b$  is the content of bound rubber;  $W_A$  is the mass of the sample after extraction of toluene;  $W_B$  is the mass of the sample before toluene extraction;  $W_{silica}$  is the mass of silica in the sample:

$$R_b (\%) = (W_A - W_{silica}) \div (W_B - W_{silica}) \times 100 \% \quad (2)$$

The thermal degradation behavior of the r-SS was investigated by Thermogravimetric Analyzer (TGA, Q5000IR, TA Instruments, USA). 5-10 mg of samples were heated from 50 °C to 800 °C in a nitrogen atmosphere, the heating rate was 20 °C min<sup>-1</sup>.

The chemical composition of the r-SSs was characterized using FTIR (Fourier Transform Infrared Spectroscopy) (Spectrum 100, Perkin Elmer, Inc., USA), in the wavenumber range from 4000 to 650 cm<sup>-1</sup>.

X-ray diffraction (XRD) pattern was measured on a BRUKER D8 ADVANCE using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ).

The r-SS samples obtained under different temperatures were ultrasonically dispersed into toluene (0.025 g/ml) and was applied to the slide and dried before being subjected to the stereomicroscopy.

The samples dispersed in toluene were also placed onto a carbon grid by a micropipette and dried in a vacuum oven at 50 °C for 24 h, the microstructure of r-SS was observed by transmission electron microscopy (TEM, JEM-2100, JEOL Ltd., Japan).

And the analysis of element content on r-SS surface was characterized by X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Shimadzu, Japan) using a monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ).

## Results and discussion

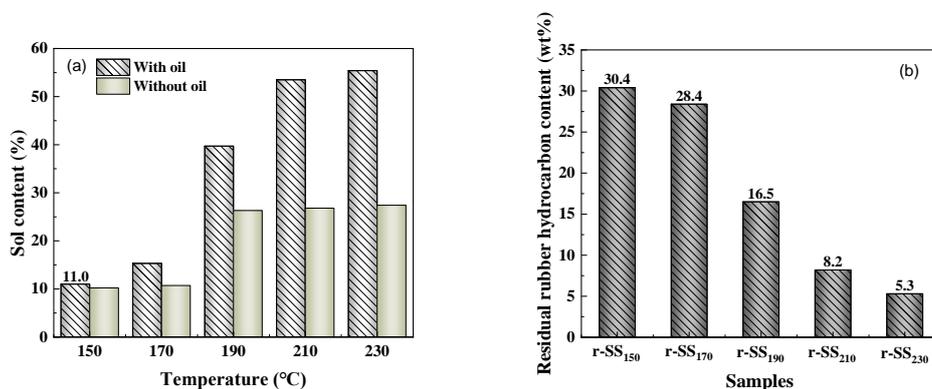


Figure 1. (a) Effect of sunflower oil (10phr) on the sol contents of waste tire rubber under different temperatures (b) residual rubber hydrocarbon content of r-SSs

Reclamation degree refers to the degree of devulcanization of vulcanized rubber, which is often characterized by sol content. Figure 1 (a) shows the effect of sunflower oil (10 phr) on the sol content of reclaimed waste tire rubber under different temperatures. The reclamation degree increased with the increase of the temperature, especially the ones with sunflower oil. This is accordant with our previous study<sup>6</sup> while in this case, we reduced the addition of sunflower oil from 150 phr to 10 phr. It shows that only 10 phr sunflower oil can still effectively swell the cross-linked rubber network and weaken the polymer chain entanglement. This has facilitated oxygen to transport through the swollen cross-linked network and oxidative breakage of molecular chains at high temperature, especially when the temperature is over 170 °C. The sol content of the sample with 10 phr oil increased from 15.3% to 53.5% rapidly and is twice of the sample without oil. And the growth of the sol content is gradually slow down after 210 °C, the differentiation between r-SS<sub>210</sub> and r-SS<sub>230</sub> is only 1.9%, indicating the committed step occurred between 170 °C and 190 °C.

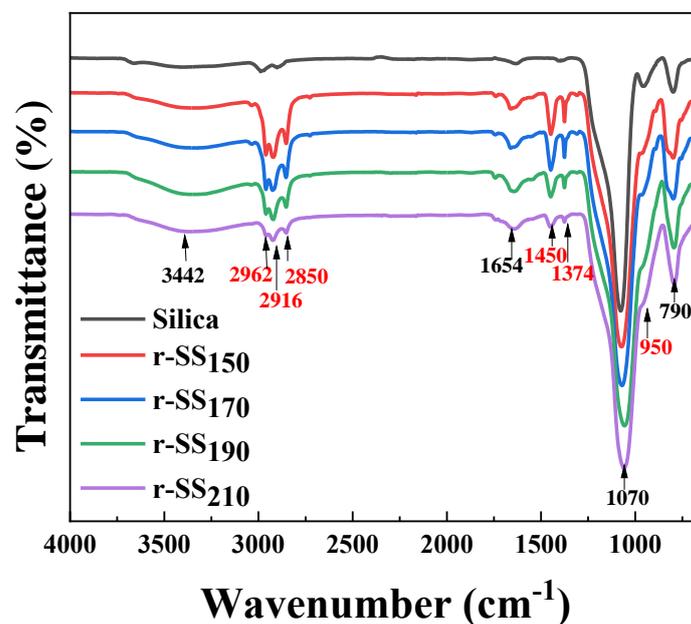


Figure 2. FTIR spectra of r-SSs obtained under different temperatures as compared to pure silica.

After being subjected to acetone and toluene extraction, r-SS was separated from the sol content. The chemical structure of the r-SSs obtained by thermo-oxidative reclamation under different temperatures were characterized and compared with pure silica, as shown in Figure 2. All the r-SSs exhibits C–H stretching vibration of  $-\text{CH}_2-$  groups in the rubber backbone at 2916 and 2850  $\text{cm}^{-1}$ ,  $\text{CH}_2-$  bending vibration at 1450  $\text{cm}^{-1}$ ,  $-\text{CH}_3$  bending vibration at 1374  $\text{cm}^{-1}$ , and Si–O stretching of Si–alkoxy compound at 1070 and 950  $\text{cm}^{-1}$  which is defined as TESPT characteristic peaks by Chorai et al.<sup>14</sup> The broad peak at 3442  $\text{cm}^{-1}$  corresponds to  $-\text{OH}$  stretching of Si–OH in silica.

The characteristic peaks of rubber hydrocarbon at 2916, 2850, 1450 and 1374  $\text{cm}^{-1}$  appeared on all the r-SS samples, indicating the existence of a bound rubber coated on the surface of the reclaimed silica. The peak intensity of the abovementioned peaks was decreased with the increased temperature proved the stepwise exfoliation of the bound

rubber. r-SSs obtained under higher temperatures especially at 190, 210 and 230 °C exhibits stronger characteristic peaks of Si–alkoxy compound at 3442, 1070 and 950  $\text{cm}^{-1}$  which implies that the structural destruction during reclamation was proceeded both on the three-dimensional crosslinked polymer network and the modified filler-matrix interface. According to Luginsland’s study, the tetra-sulfur bonds in TESPT mainly break around the temperature of 170 °C which may explain the sharp increase in sol content and strong characteristic peak intensity of Si–alkoxy compound.<sup>15</sup> Since oxidative reaction also happened during the reclamation process, characteristic peaks of carbonyl groups (C=O) at 1733  $\text{cm}^{-1}$  also exists in all r-SSs comparing to pure silica.

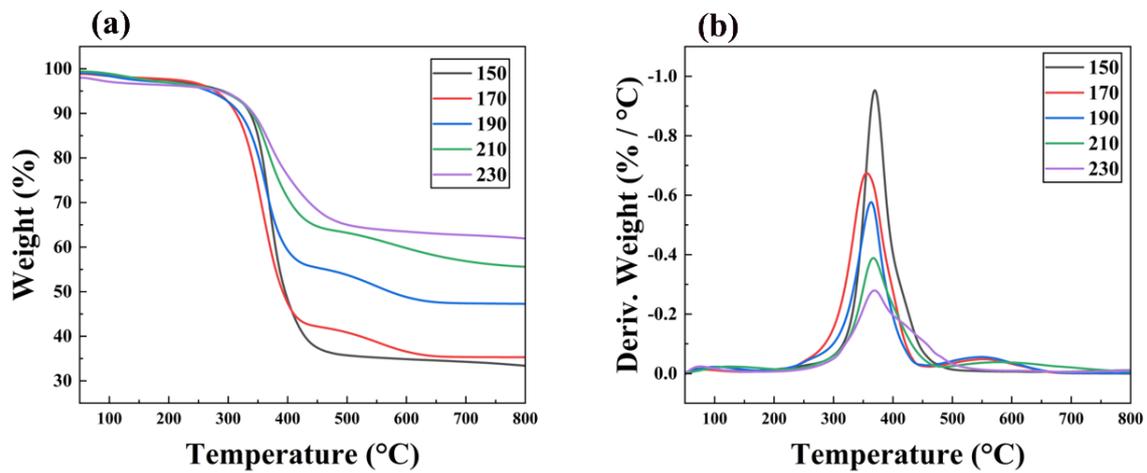


Figure 3. (a) Thermogravimetric curves of r-SSs. (b) Differential thermogravimetric curves of r-SSs.

In order to further analyze the composition of the r-SSs, they were subjected to TGA and the results were shown in Figure 3. The sharp weight loss in the range of 300-410 °C observed in the five samples is mainly due to the degradation of NR since the maximum decomposition temperatures of NR is about 360 °C, while which of silica is relatively high (over 1000 °C) due to its amorphous structure<sup>16,17</sup>. The residual rubber hydrocarbon content in the r-SSs gradually decreased with the increase of temperature (Fig. 3(a)). In addition, with the increase of reclamation degree, the decomposition efficiency of the residual rubber hydrocarbon on the r-SS surface is slower and much

more difficult (Figure 3(b)), which implies that the interaction between the silanized silica and the rubber molecular chain is stronger. According to the curves of TG and DTG, the residue rubber content in r-SS has been calculated and shown in Figure 1 (b), which is obviously reduced with the increase of reclamation degree. The participation of oxygen under high temperature realized the efficient destruction of the polymer network and captured the generated active free radicals timely by oxidative reaction. And the mechanism of oxidative reclamation has already been reported by our previous reaserch.<sup>13</sup> The r-SS<sub>210</sub> and r-SS<sub>230</sub> contained relatively low ratio of residual rubber which indicates the high reclamation degree of the waste green tire rubber and high silica proportion in r-SS.

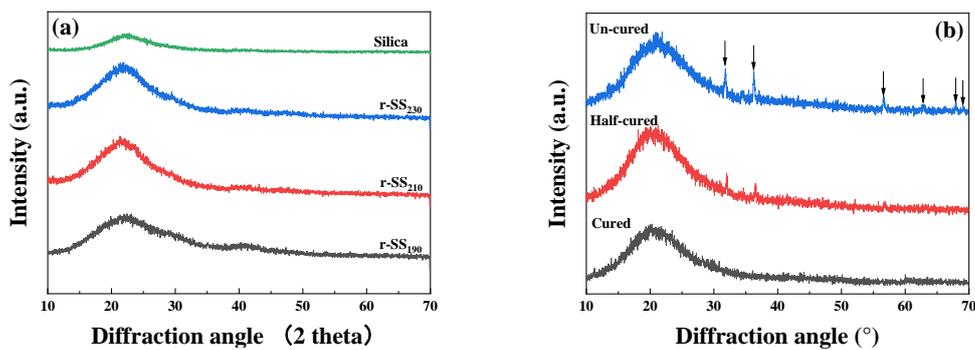


Figure 4. X-ray diffraction patterns of (a) r-SSs (b) rubber with different curing extents

To further analyze the effects of temperature on the composition of the r-SS, XRD tests were performed on the samples, and the results were shown in Figure 4(a). Comparing to silica, the exist of bound rubber formed a week peak at 40° and which is weakened with the increase of reclamation degree. Different from the reclaimed carbon black from waste tire rubber, the characterized peaks of ZnO didn't appeared on the surface of the r-SS as concluded by our previous research.<sup>18</sup> Therefore, rubber compound was cured to different extents, un-cured, half-cured and cured, and subjected to XRD. As shown in Figure 4(b), with the proceeding of vulcanization, the intensity of ZnO characteristic

peaks decreased to disappear, which indicates the complexation reaction of ZnO and silica proceeds with the progress of the vulcanization. Unlike carbon black, the strong surface activity of silica easily leads to the gathering of ZnO on the near surface before subjected to silanization, as shown in Figure 5. The acidic nature silanol groups on the surface of silica will react with alkali like ZnO which may lead to the formation of strong chemical bonds. Reuvekamp et al.<sup>19</sup> confirmed that ZnO primarily interferes with the reaction between the coupling agent and the silica surface. This may explain the absence of ZnO on the surface of r-SS and the order of the silanization reaction between silica, TESPT, and rubber ingredients.

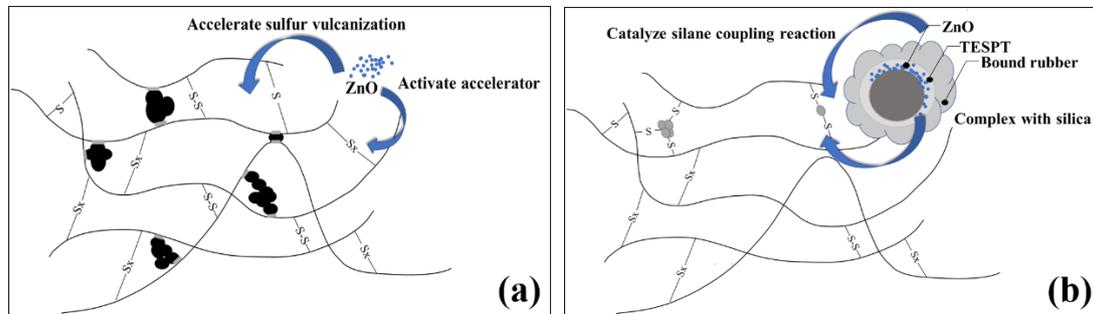


Figure 5. (a) Reinforcement mechanism of carbon black, (b) reinforcement mechanism of silica

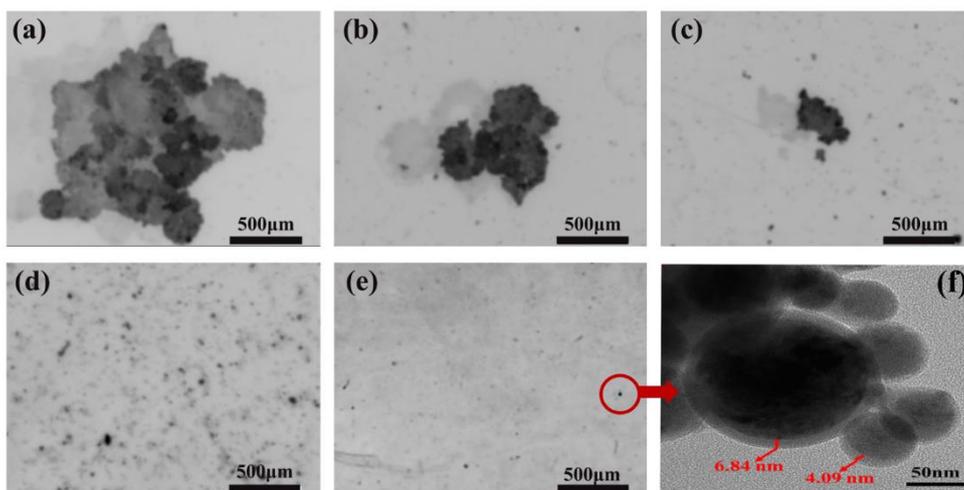


Figure 6. Morphology of r-SSs (a) r-SS<sub>150</sub> (b) r-SS<sub>170</sub> (c) r-SS<sub>190</sub> (d) r-SS<sub>210</sub> (e) r-SS<sub>230</sub>  
 (d) TEM micrograph of r-SS<sub>230</sub>

According to the morphology of r-SS in Figure 6, it can be connoted that the size of the r-SS is reduced with higher temperature. Since the vulcanized rubber was crushed and sifted out through a 10-mesh sieve originally, the particle size of r-SS<sub>150</sub> is around 1 mm, which proves its low reclamation degree. With the increase of the temperature, the particle size of r-SS gradually decreased from 1 mm to almost imperceptible and the thick bonded rubber layer on the surface of r-SS is gradually peeled away.

In order to further explore the microstructure of highly reclaimed r-SS, TEM test was also carried out on r-SS<sub>230</sub> and the results were shown in Figure 7. The spherical structure of silica is convenient for observation as dark parts. The silica particles in r-SS existed both as agglomerates with the size about several hundred nanometers and primary particles with the size of 20-40 nm. A distinct layer of low-contrast substance with thickness of 4-6 nm can be observed coated on the surface of the silica. According to Sarkawi et al<sup>2</sup>, this layer is caused by the gradual stripping of the loosely bound rubber shell from the tightly bound rubber skin which implies the effective exfoliation of r-SS from the rubber matrix during the process of thermal oxygen reclamation.

Table 1. Element compositions on the surface of r-SS<sub>230</sub> and vulcanized rubber

Sample	Element composition (wt%)				
	C	O	S	Si	Zn
r-SS <sub>230</sub>	58.57	20.89	1.34	18.25	0.95
<b>Vulcanized rubber</b>	76.45	12.17	1.76	8.55	1.07

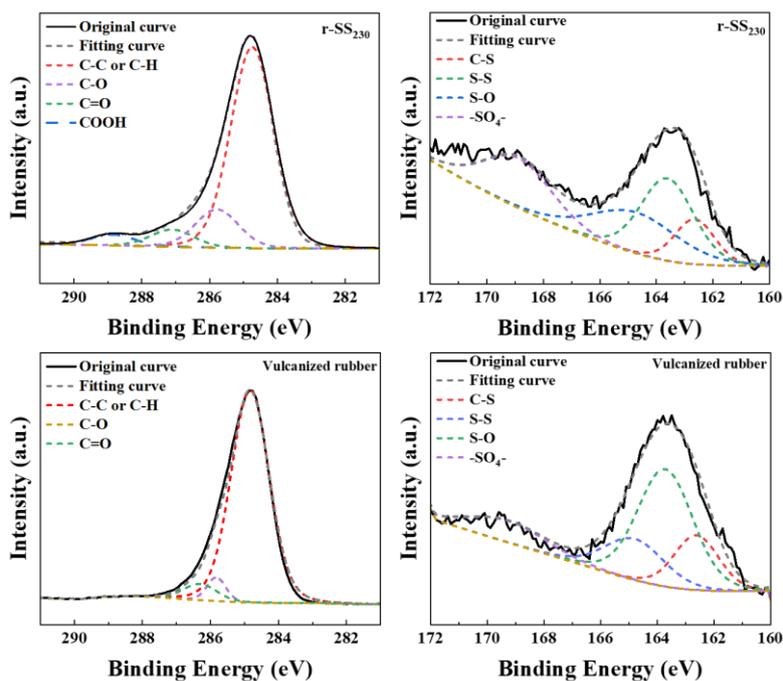


Figure 7. Deconvoluted XPS spectra of r-SS<sub>230</sub> and vulcanized rubber

The chemical composition of r-SS<sub>230</sub> was compared with vulcanized rubber by XPS, which is beneficial to the study of interaction mechanism between silanized silica and rubber matrix from the reverse process. The results were shown in Figure 7 and the element compositions were displayed in Table 1. It can be concluded that carbon (C) dominated the element composition of r-SS<sub>230</sub> and vulcanized rubber followed by oxygen (O) and silicon (Si). After being subjected to reclamation, the amount carbon related bonds (C-C, C-H, C-S) decreased due to the exfoliation of crosslinked rubber from silanized silica. In the meantime, the amount of oxygen-containing groups (C-O, C=O, -COOH, S-O, -SO<sub>4</sub>-) increased because of the participation of oxygen during the breakage of the crosslink bonds and mainchain weak bonds while thermo-oxidative reclamation proceeded. A small portion of sulfur (S) and zinc (Zn) elements were also detected. The exist of the thinner bound rubber layer on the silanized silica core may attributed to the less portion of C and higher amount of Si in r-SS<sub>230</sub>. Due to the effective thermal oxidation reclamation, sulfide bonds were broken and the oxidation scission reaction occurs leading to the presence of S and O.<sup>20,21</sup> The detection of Zn which is not present in the XRD results can ascribe to the reaction of activator ZnO and silica. Reuvekamp<sup>19</sup> and Susanna<sup>22</sup> studied the catalytic effect on the reaction between

silanized silica and rubber matrix and stated that ZnO particles are anchored on the surface of silica before its reaction to rubber matrix which limits its migration from inside of the bound rubber to the surface of r-SS. Since XPS can only detect a depth of 4nm, the ZnO near the surface of silanized silica core in r-SS<sub>230</sub> cannot be detected in large quantities compared to the vulcanized rubber.

Table 2. Areas of C1s and S2p peaks

Samples	Peak area of C1s and S2p			
	C <sub>1</sub> (C-H or C-C)	C <sub>2</sub> (C-O)	C <sub>3</sub> (C=O)	C <sub>4</sub> (COOH)
r-SS <sub>230</sub>	69.8	19.4	6.4	4.38
Vulcanized rubber	87.1	4.9	5.9	0
S2p	S <sub>1</sub> (C-S)	S <sub>2</sub> (S-S)	S <sub>3</sub> (S-O)	S <sub>4</sub> (-SO <sub>4</sub> -)
	r-SS <sub>230</sub>	15.8	26.0	31.0
Vulcanized rubber	19.2	53.0	19.4	8.4

In order to further analyze the chemical composition of r-SS and the interfacial interaction mechanism of silanized silica, the C1s and S2p peaks were fitted into specific peaks as shown in Figure 7 and the relative content was summarized in Table 2. As for C1s peak, there were four peaks which is C-H or C-C bond at  $284.6 \pm 0.2$  eV, C-O bond at  $285.4 \pm 0.2$  eV, C=O bond at  $286.8 \pm 0.2$  eV and HO-C=O bond at  $289.4 \pm 0.2$  eV, respectively.<sup>23,24</sup> The carbon-carbon skeleton of bound rubber caused the highest content of C<sub>1</sub> (C-C or C-H). The oxidation of the allyl group of NR molecular chains and the breakage of chemical bonds resulting to the formation of oxygen-containing groups including C<sub>2</sub> (C-O), C<sub>3</sub> (C=O) and C<sub>4</sub> (COOH). To analyze the types of cross-linking bond, such as monosulfide bond (C-S-C), disulfide bond (S-S) or polysulfide bond (-S<sub>x</sub>-), the S2p peaks were fitted into four peaks, which are C-S bond at 161.9–162.9 eV, S-S bond at 163.3–164.8 eV, S-O bond at 165.3–165.9 eV and -SO<sub>4</sub>- group at 169.2–169.5 eV.<sup>25-27</sup> It can be seen that S element of r-SS is mainly present in the form of S-S, S-O bonds or -SO<sub>4</sub>- group. During the oxidation scission process, the cross-linking bonds formed between rubber-rubber molecular chains and silanized silica-rubber molecular chains caused by tetrasulfane bonds of TESPT can be broken

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randomly and further oxidized into S-O bond or -SO<sub>4</sub>- group in the form of sulfone or sulfate ion that exists in the bound rubber.<sup>28</sup>

## **Conclusions**

An efficient and controllable reclamation of silica-reinforced rubber was realized by a thermo-oxidative reclamation process assisted with 10 phr sunflower oil, which proves to be a feasible solution for recycling of waste green tire rubbers.

More sol content was derived with temperature increasing from 150 °C to 230 °C, and obtained 55.4 wt% at 230 °C with the assistance of 10 phr oil, twice of those without oil. The bound rubber was gradually exfoliated from the surface of r-SSs with the increase of the reclamation degree. The bound rubber content decreased along with degradation as the reclamation temperature increased, and finer r-SS particles were resulted. The chemical bonds between silanized silica and rubber matrix were broken under thermal oxygen synergy which also induced new functional groups (-S=O and -C=O) on the surface of r-SSs.

Moreover, the reinforcement mechanism of silica is further demonstrated through the thermo-oxidative reclamation process. With the catalytic effect of ZnO, the silanol groups on the silica surface reacted with the alkoxy groups of the silane and formed strong chemical bonds between silanized silica and the rubber matrix during vulcanization.

In summary, thermo-oxidative reclamation assisted with up to 10 phr sunflower oil successfully degraded and reclaimed the silanized silica-reinforced rubber with controllable reclamation degree. The r-SSs were separated from the vulcanizates and restored its surface activity, which helps illustrate the interface interaction between silanized silica and the rubber matrix.

## **Acknowledgements**

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