Feasibility of oxidized soybean oil for rubber devulcanization

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Abstract. This study investigates the feasibility of using oxidized soybean oil (Ox-SO) for mechano-chemical devulcanization of sulfur-cured natural rubber. A 2$^2$ full factorial design of experiment was used to determine the effect of devulcanization time (20, 40 min) and amount of Ox-SO (6, 10 phr) in the crosslink density and sol-gel content of devulcanized VR (DVR). After conductive heating and stirring of soybean oil for 60 h, a peroxide value of 316.3 meq O$_2$ kg$^{-1}$ oil was achieved which corresponds to approximately 2500 ppm of lipid hydroperoxides. Decreasing the devulcanization time (from 40 to 20 min) and amount of Ox-SO (from 10 to 6 phr) decreased the crosslink density by 71.1% and increased the sol content by 228.2%. The optimum conditions are 20 min of devulcanization time and 6 phr of Ox-SO where the crosslink density of VR is reduced to $6.2 \times 10^{-5}$ mol cm$^{-3}$ and the sol content is 10.2% (control VR crosslink density: $2.1 \times 10^{-4}$ mol cm$^{-3}$, sol content: 3.1%). In summary, Ox-SO was found to be a feasible agent for rubber devulcanization. DVR blends with virgin rubber are required to assess Ox-SO’s commercial readiness.

1. Introduction
The inherent physical and chemical stability of waste vulcanized rubber (VR) makes it a significant contributor to solid waste in the Philippines. According to the status report of the National Solid Waste Management Commission of the Philippines status report, rubber waste comprises at most 0.37% which is currently equivalent to 58.7 thousand tons and 62.6 thousand tons in 2020. To mitigate this problem, waste VR finds use in energy recovery and filler applications. However, with the continued rise in rubber production, rubber recycling through devulcanization remains the most sustainable method to decrease the accumulation of waste rubber [1].

Mechanical devulcanization uses mechanical shear along with chemical modifiers for devulcanization. The mechanical shear is to be supplied during the milling of the waste rubber in which the crosslinks are subject to thermal and mechanical stresses which result to breakage of bonds. This type of devulcanization is the most common owing to its direct applicability to existing equipment of rubber processing facilities. This would mean higher ease of introducing the technology to the current process with less capital and operating costs. Some of the chemical agents that have been used in combination with mechanical shearing are disulfides, mixtures of rubber accelerators and activators collectively known as De Link reactant, a mixture of quinone group and benzoic acid which acts as a counter cure reagent, the modifying composition used in the Lev Gum process, benzoyl peroxide and various organic compounds such as dienophiles and acids incorporated with high pressure high temperature sintering [1,2].

Soybean oil (SO) is characterized by its high degree of unsaturation, with it having one of the highest amounts of polyunsaturated fatty acids (PUFAs) among edible oils [3]. Because of this, SO is prone to lipid peroxidation upon subjection to various conditions. Lipid peroxidation is the transformation of
PUFAs into lipid hydroperoxides in a degradation process initiated by either light, heat or oxygen [4]. Compared with other vegetable oils such as from corn, rapeseed and sunflower, SO appeared to have the highest oxidation rate when heated in a microwave oven reaching a peroxide value of ~30 meq O₂ kg⁻¹ after only 12 min of microwave exposure [5,6].

This work explores the possibility of the use of oxidized soybean oil (Ox-SO) as a devulcanizing agent for mechanochemical devulcanization of sulfur - cured VR compounds. The effect of devulcanization time and amount of Ox-SO were determined by analyzing the crosslink density and sol content of the devulcanized VR (DVR). Ox-SO has the potential to be an abundant and low-cost waste resource for recycling rubber, eliminating 2 sources of waste in one process that can benefit the community environmentally and economically.

2. Experimental

2.1. Materials

Pure and refined SO made from American soybeans were purchased from a local supermarket. PUFAs, monounsaturated fatty acids, and saturated fatty acids content are approximately 50, 14, and 19 g per 100 ml, respectively as stated in the product label (Simply Pure Soybean Oil). Glacial acetic acid (ACS grade, RCI Labscan), chloroform (ACS grade, RCI Labscan), potassium iodide KI (AR grade, Ajax Finechem), sodium thiosulfate pentahydrate (ACS grade, Duksan Reagents) and pure potato starch (Jandy Goods Corp.) were used for the peroxide value (PV) determination of Ox-SO. All rubber compounding ingredients – natural rubber SPR10, sulfur, N-cyclohexyl-2- benzothiazole sulfenamide (CBS), zinc oxide, and stearic acid are industrial grade and purchased from Philippine Belt Manufacturing Corporation (Quezon City, Philippines). Lastly, Acetone (AR grade, RTC), benzene (ACS grade, Merck) and isopropanol (ACS grade, Scharlau) were used for the characterization of DVR.

2.2. Preparation and characterization of Ox-SO

SO underwent induced lipid peroxidation through direct conduction heating using a hotplate stirrer (IKA C-MAG HS 10 digital) at 80°C. Samples were taken every 2 h and stored in a freezer at -20°C to halt peroxidation. The open-air oxidation of PUFAs below 100°C yields conjugated hydroperoxides which produces free radicals [7]. Storage of Ox-SO at low temperatures and without the presence of metals stabilize the primary oxidation products [4].

Iodometric titration was performed for each sample to measure PV. A small amount of oil is mixed with 50 ml of a 3:2 glacial acetic acid:chloroform solvent. 0.5 ml of saturated KI solution was then added and left for 2 min with gentle swirling every 30 s. 30 ml H₂O was added immediately followed by titration with 0.01 N sodium thiosulfate solution until equivalence point indicated by addition of starch indicator. SO and Ox-SO samples also underwent Fourier transform infrared spectroscopy - attenuated total reflection (FTIR-ATR) analysis (Thermo Scientific Nicolet TM 7000). The samples were scanned at a resolution of 4 cm⁻¹ in the mid-infrared range of 1000-1700 cm⁻¹ and the band intensities were expressed in absorbance.

2.3. Mechanochemical devulcanization of VR

Compounded rubber with the formulation – NR SPR10(100 phr) , zinc oxide(5 phr), stearic acid(2 phr), sulfur(1.4 phr) and CBS(1.2 phr) was processed in the laboratory using a twin roll mill (Bharaj BM-06) and then Vulcanized at 160°C for 15 min using a hydraulic lab press model (Chemplast). The resulting rubber sheets were then ground using an industrial cracker mill (Rhodeco Rubber Processing Services, Inc.) at ambient conditions. Ground Vulcanized rubber (GVR) (<2 mm) were then stored in air-tight plastic bags and in cool dark cabinets before devulcanization.

DVR was produced by loading GVR into an open twin roll mill with 0.5-mm gap at ambient temperature (see figure 1). After 2 min of passing the GVR between the rolls, Ox-SO was added, and the process was continued to reach desired devulcanization. A 2² full factorial design of experiment (DOE) was employed with the factors and levels – sulfur ratio (high, medium, low), devulcanization time
(20, 40 min) and amount of Ox-SO (6,10 phr). The operational matrix is shown in table 1. Main effects and interaction effects factorial plots were generated using Minitab® 17.1.0.

Table 1. Operational DOE matrix used in the study.

| Devulcanization Conditions | Control | DVR6-20 | DVR10-40 | DVR6-40 | DVR10-20 |
|---------------------------|---------|---------|----------|---------|----------|
| Amount of SO (phr)        | 6       | -       | -        | -       | -        |
| Amount of Ox-SO (phr)     | -       | 6       | 10       | 6       | 10       |
| Devulcanization time (min)| 20      | 20      | 40       | 40      | 20       |

Figure 1. Mechanochemical devulcanization of VR.

2.4. Sol-gel analysis and crosslink density determination of DVR
To determine the crosslink density, DVR samples were swollen in 50 ml of benzene for 72 h at ambient temperature. The swollen samples were dried in a forced convection oven (Binder FED 56) for 24 h at 70°C. The dried samples were then weighed. Density of the dried rubber $\rho_{dr}$ was measured using a 10 ml pycnometer (Blaubrand®) and isopropanol at 25°C. The mass of the pycnometer with sample and alcohol A and the mass of pycnometer with alcohol only B were also measured. Equation (1) was used to calculate $\rho_{dr}$.

$$\rho_{dr} = \frac{0.9971 \times m_{dr}}{m_{dr} - (A - B) \times \rho_{isop}}$$  \hspace{1cm} (1)

Where $m_{dr}$ is the weight of the dried rubber and $\rho_{isop}$ is the density of isopropanol at 25°C. The Flory-Rehner equations (2) and (3) is used for calculation of crosslink density $\nu_e$.

$$V_r = \frac{m_{dr}}{\rho_{dr} + (m_a - m_{dr})/\rho_{benzene}}$$  \hspace{1cm} (2)

$$\nu_e = -\frac{\ln(1 - V_r) + V_r + \chi_1 V_r^2}{[V_1(V_r^{1/3} - V_r)/2]}$$  \hspace{1cm} (3)
Where $m_s$ is the weight of the rubber at the end of swelling and before drying, $\chi_1$ is the polymer-solvent interaction parameter at 25 °C and $V_2$ is the molecular volume of benzene [8]. For sol-gel analysis, the samples first underwent Soxhlet extraction with hot acetone for 8 h to eliminate acetone-solubles. After drying, weighed samples were each subjected to Soxhlet extraction with benzene at 80 °C for 6 h. The DVR samples were then dried in a forced convection oven before being weighed. Sol content was calculated using equation (4) [9].

\[
\text{Sol content} = \frac{D - E}{D} \times 100
\]  

Where D is the mass of the sample after acetone extraction and drying and E is the mass of the sample after benzene extraction and drying.

3. Results and discussion

3.1 Synthesis of Ox-SO through lipid peroxidation

Figure 2 shows the increase in PV value in the SO as it is being oxidized through direct conductive heating with stirring. The oil sample starts to become rancid after the first 24 h where it reaches a value of 50 meq O$_2$ kg$^{-1}$ oil. After 60 h of heating, the PV value reached 316.3 meq O$_2$ kg$^{-1}$ oil which corresponds to about 2500 ppm of hydroperoxides. Heating was stopped after such time because it was observed that further heating results to the polymerization of the oil. The polymerized oil is solidified and is unsuitable for use in rubber processing.

![Figure 2. PV of Ox-SO as a function of heating time.](image)

Figure 3 shows the FTIR-ATR spectra of Ox-SO and SO. The major changes that are observed are the increase in band intensity of peak “a” and the disappearance of peak “b”, which are results of the oxidative deterioration that SO was subjected to during heating. The increase of peak “a” at 1160 cm$^{-1}$ (C-O ester groups) is caused by the hydrolysis of triglycerides which produces fatty acids and glycerols. Moreover, the disappearance of peak “b” at 1637 cm$^{-1}$(C=C stretching vibration) is caused by the loss of double bonds upon oxidative degradation [10].
3.2 Extent of devulcanization by Ox-SO

Figure 4 shows the effect of lipid peroxidation process of SO on sol content and crosslink density of DVR. Devulcanization is achieved when the crosslink density is decreased, and the sol content is increased due to the cleaving of sulfur-sulfur and carbon-sulfur bonds in the rubber matrix. Upon devulcanization of VR with SO, the sol content increased by 35.7% and the crosslink density decreased by 18.1% only. This can be attributed to the mechanical and thermal stresses present during devulcanization wherein SO acted as a plasticizer to make the process more efficient [11]. On the other hand, devulcanization of VR with Ox-SO increased the sol content by 94.2% and the decreased the crosslink density by 71.1%. This shows the clear potential of Ox-SO in the devulcanization of VR.

3.3 Main factor and interaction effects on extent of devulcanization

In this section, the main factor effects - figure 5 (a) and (b), and interaction effects – figure 5 (c) and (d), are determined from factorial plots generated from the $2^2$ full factorial DOE that was used. In figure 5 (a) and (b), a higher extent of devulcanization (lower crosslink density and higher sol content) is consistently observed at 40 min of devulcanization time and 6 phr of added Ox-SO. A longer processing time allows for a better dispersion of the Ox-SO into the rubber matrix, making the process more...
efficient. This also allows for more interaction with mechanical and thermal stresses from the milling equipment, which helps with the devulcanization. The preference for a lower amount of Ox-SO is counter-intuitive, knowing that this also means there is a lower amount of lipid hydroperoxides present to devulcanize the rubber. This is probably due to the excessive plasticizing effect of the Ox-SO at the higher levels (10 phr) wherein the rubber matrix flows easily during milling, decreasing the friction felt, and subsequently lowering the efficiency of devulcanization.

This explanation is further supported by figure 5 (c) and (d) where the factor interactions are shown. The optimal conditions for a higher extent of devulcanization are 40 min of devulcanization time and 6 ml of Ox-SO added. This combination resulted in the 71.1% decrease in crosslink density and 228.2% increase in sol content (control VR crosslink density: $2.1 \times 10^{-4}$ mol cm$^{-3}$, sol content: 3.1%).

![Figure 5](image)

**Figure 5.** Main factor effects factorial plots for (a) crosslink density, (b) sol content and interaction effects factorial plots for (c) crosslink density and (d) sol content from $2^2$ full factorial DOE.

4. Conclusions

Ox-SO was successfully prepared from SO using direct conductive heating via a hotplate stirrer at 80°C. The PV of the resulting Ox-SO is 316.3 meq O$_2$ kg$^{-1}$ oil which is approximately 2500 ppm of lipid hydroperoxides. The Ox-SO was used as a chemical agent for mechanochemical devulcanization of VR. At 10 min devulcanization time and 6 ml, Ox-SO was found to be a feasible devulcanization agent for VR, as it lowers the crosslink density and increases the sol content of VR by 71.1% and 228.2%,
respectively. Revulcanization experiments using blends of DVR with virgin rubber are currently in progress to assess applicability for commercial use

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