

Butyl rubber reclamation by combined microwave radiation and chemical reagents

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ABSTRACT: Rubber recycling is growing worldwide because of increasing raw material costs. In addition, extensive use of rubber articles and their eventual disposal is a major concern for the environment. Butyl rubber (IIR) was devulcanized by microwave radiation with the aid of devulcanizing reagents and oil. The effect of several devulcanizing reagents, hexadecylamine (HAD), diphenyl disulfide (DPDS), *N*-cyclohexyl-2-benzothiozyl sulfenamide (CBS), and tetramethylthiuram disulfide (TMTD) on devulcanization process, was studied. The investigation was carried out in various microwave radiation temperatures and different amounts of aromatic and paraffinic oils. The results showed that waste rubber powder with a median particle size of 279 μm was devulcanized efficiently. It was confirmed when devulcanization % of the devulcanizates were measured by swelling tests. Among of the devulcanizing reagents and based on Horix analysis, HDA with the sol fraction, crosslink density (CLD), and devulcanization percent of 14%, 25 mol/m³ and 64%, respectively, was the most suitable devulcanizing reagent. In addition, compound with 30 and 6 phr paraffinic oil and HDA in formulation, respectively, had maximum devulcanization % (83%). The devulcanizing temperature of this compound was 180°C. For the most of all compounds, during microwave radiation, a part of disulfides crosslinks were broken and released sulfurs giving new mono and polysulfides bridges. This resulted in the higher CLDs for some compounds when they compared with CLD of the initial waste rubber. In the morphological study of the devulcanized compounds, vulcanized rubbers clearly showed in the SEM micrographs surrounded by a matrix of devulcanized rubber. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43363.

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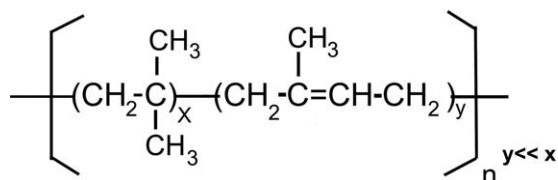
INTRODUCTION

Rubber recycling is growing in importance worldwide because of increasing raw material costs, diminishing resources, and the growing awareness of environmental issues and sustainability.¹ In rubber devulcanization, three-dimensional rubber networks which are the outcome of vulcanization reactions, are broken. In sulfur vulcanization, the formation of both C—S and S—S bonds takes place, and it is therefore expected that during devulcanization, only C—S and S—S bond cleavage should occur. In fact, in an ideal devulcanization process, crosslinks should be broken without main-chain scission.² Several techniques were used for rubber devulcanization.³ They are chemical, thermochemical, mechanical, radiation, and biological processes. Radiation process may include microwave radiation. The three-dimensional rubber network can be broken down by microwave.^{4–8} The energies required to break monosulfidic C—S, polysulfidic S—S, and peroxide C—C bonds are 270, 240, and 345 kJ/mol, respectively.⁹ Hence, enough caution should be considered during microwave radiation to break, only C—S and S—S bonds during devulcanization.

RECYCLING OF BUTYL RUBBER (IIR)

Butyl rubber (Scheme 1¹⁰) is the common name for the copolymer of isobutylene and 1 to 3% isoprene produced by cold (−100°C) cationic solution polymerization.¹⁰ It was developed in 1937, by researchers William J. Sparks and Robert M. Thomas, at Standard Oil of New Jersey's Linden, N.J., laboratory.¹¹ Isoprene provides unsaturation required for vulcanization. The most distinguished characteristics of butyl rubber refer to high level of its saturation, i.e., high resistance to the diffusion or solution of gas molecules.¹⁰ Butyl rubber, the same of other rubbers reaches to its end of the service and life and subsequently, its recycling is a must. Few research works were done on butyl rubber recycling and devulcanization.^{12–15}

Kuan *et al.*¹² used supercritical CO₂ along with devulcanizing reagent, diphenyl disulfide (DD) to completely devulcanize butyl rubber. They found reclaimed rubber could not be cured by sulfur due to numerous decreases in the active crosslinking sites and the remaining DD. In another attempt,¹³ microwave without any chemical devulcanizing reagent, was used to



Scheme 1. Butyl rubber (IIR).¹⁰

devulcanize bromobutyl rubber (BIIR). The effects of various microwave powers and heating times on devulcanizing efficiencies were examined. The best operating conditions were obtained in 780 s as radiation time and 2000 W. Feng and Isayev¹⁴ investigated the devulcanization of unfilled butyl rubber with a grooved-barrel ultrasonic reactor under various processing conditions. They concluded that devulcanized butyl rubber was more elastic than the virgin gum. In addition, the vulcanizates of the devulcanized butyl rubber had comparable mechanical properties to those of the virgin vulcanizates. In another work¹⁵ an attempt to understand the structural changes during ultrasonic treatment of unfilled cured butyl rubber was studied.

Authors¹⁶ already studied the effect of various operative parameters including several devulcanizing reagents on microwave devulcanization of ethylene-propylene-diene monomer (EPDM) rubber. In this study, the same parameters along with several more complementary aspects on butyl rubber microwave devulcanization will be considered and discussed.

EXPERIMENTAL

Materials: Waste Rubber, Filler, and Rubber Chemicals

Bicycle and motorcycle butyl rubber waste tubes were obtained from local city sites and subsequently ground to particles with a median size of 279 μm . Thermogravimetric analysis (TGA; STA 1500, Scinco Co., Ltd.) was subsequently used to determine the composition of the waste powder. TGA was performed in a nitrogen atmosphere below 550°C and in the air above 550°C, respectively. The TGA curves and corresponding compositions are shown in Figure 2 and Table I. The other ingredients were Diphenyl disulfide (DPDS, Sigma-Aldrich), *N*-cyclohexyl-2-benzothiozyl sulfenamide (SANTACURE-CBS, Flexsys), hexadecylamine (HDA, Cayman Chemical Co.), tetramethylthiuram disulfide (Perkacit TMTD, Flexsys), zinc oxide (activator; Harcros Durham Chemicals, UK), stearic acid (activator; Anchor Chemicals Ltd., UK), elemental sulfur (curing reagent; Solvay Barium Strontium, Hannover, Germany), and aromatic and paraffinic oils with boiling points, 270 and 280°C, respectively, as processing aids (Mehran Tyre 290 and Fariman), 2-Propanethiol, hexylamine, and cyclohexanethiol for mono, di, and polysulfidic crosslink measurement (Sigma Aldrich).

DEVULCANIZATION OF THE WASTE POWDER AND PREPARATION OF THE RUBBER COMPOUNDS

Waste powder samples were extracted with acetone to remove low molecular substances, i.e., oils, residue of curing chemicals and uncrosslinked rubbers using a Soxhlet apparatus and 300 mL of acetone and 100 g of the rubber for 24 h at 70°C, as described in ASTM D297-93. After extraction, the samples were dried in an oven with circulating air for 12 h. Four grams of

CBS, DPDS, TMTD, and or HDA which were used as devulcanizing reagents, were mixed with 30 g oil and then added to 100 g waste powder in a 500 mL glass beaker. The waste powder was soaked in the oil for 12 h at 80°C in an oven to allow it to penetrate into the rubber fully. This produced four compounds (compounds A–D; Table II). There was also a reference compound (RC), which was mixed with the aromatic oil and no chemical (Table II). The beaker was placed in a microwave oven (GMO-530, Gosonic) with an output power of 900 Watt, frequency of 2000 MHz, and internal capacity of 30 L. The devulcanized rubber compounds were bulky in size after they were recovered from the microwave oven. They were subsequently processed in a laboratory, two roll mill with cylinders 14 cm in diameter and 32 cm long for 2 min to produce sheets which were easier to work with.

To investigate the effect of different amounts of the devulcanizing reagent (HDA) and aromatic and paraffinic oils on the devulcanization of the waste rubber, six more compounds were prepared (compounds E, F, G, H, I, and J; Table II). Compounds in Table II were devulcanized at 180°C with the exception of compounds M and N which devulcanized at 140°C.

MEASUREMENT OF THE CROSSLINK DENSITY (CLD), SOL FRACTION, MONO, DI, AND POLYSULFIDIC CROSSLINKS AND DEVULCANIZATION % OF THE RUBBER COMPOUNDS

In the first stage, the low molecular polar substances of the devulcanized rubber, i.e., polar oils, residues of accelerators, and curing chemicals was extracted with acetone and subsequently nonpolar components, nonpolar oils, and noncrosslinked rubber residues were extracted with toluene for 48 h at 110°C using a Soxhlet apparatus. The extraction was performed using 300 mL of acetone and or toluene with 100 g of the rubber. After the extractions, the samples were dried in an oven with circulating air for 12 h. The sol fraction was defined as the sum of the soluble fractions in both, acetone and toluene and after correction for added oils to samples before devulcanization.

The solvent used for the crosslink density (CLD) determination was toluene. For the determination, 5 g of extracted rubber was placed in 300 mL of the solvent in labeled bottles and allowed to swell for 16 h at 21°C. The swollen gel was weighed and the solvent was then removed. The samples were dried in air for

Table I. Physical Properties and Composition of the used IIR Waste Powder

Property	Amount
Sol content (%)	3
Density (g/cm^3)	1.15
Crosslink Density (CLD) ^a (mol/m^3)	69
TGA	
Unburned mineral and metal (%)	13 + 2
Carbon black (%)	9
Rubber (%)	69
Oil (%)	7

^aCLD was calculated using the Flory-Rehner equation.¹⁷

Table II. Devulcanizing formulation for the Waste Rubber Powders (Devulcanization Temperature, 180°C)

Compound	Waste rubber (phr)	HDA ^a	DPDS ^a	CBS ^a	TMTD ^a	Aromatic oil (phr)	Paraffinic oil (phr)
Reference (RC)	100					30	
A	100	4				30	
B	100		4			30	
C	100			4		30	
D	100				4	30	
E	100	2				30	
F	100	6				30	
G	100	8				30	
H	100	6					15
I	100	6					30
J	100	6					45
M ^b	100	6				30	
N ^b	100	8				30	

^aDevulcanizing reagent (phr).^bDevulcanization temperature, 140°C.

9 h and then in an oven at 85°C for 24 h, and allowed to stand for an extra 24 h at 23°C before reweighing. The CLD was then calculated using the Flory–Rehner equation¹⁷:

$$V = -\frac{1}{V_s} \frac{\ln(1-v_r^0) + v_r^0 + x(v_r^0)^2}{(v_r^0)^{1/3} - v_r^0/2} \quad (1)$$

where V is the CLD (mol/m³), V_s is the molar volume of toluene (1.069×10^{-4} m³/mol at 25°C), v_r^0 is the volume fraction of

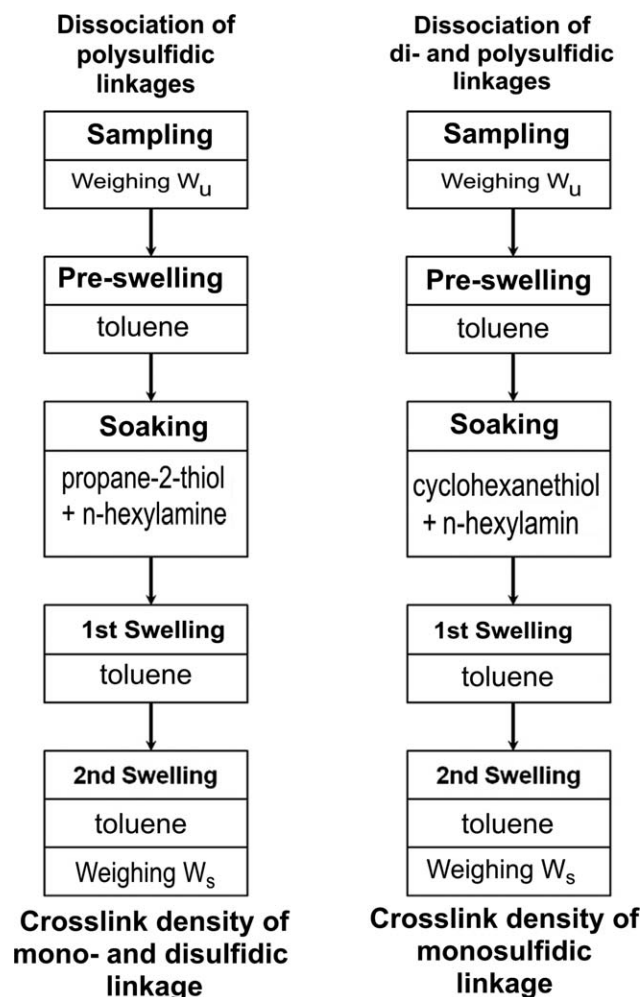
rubber (polymer) in the swollen gel, and χ is the interaction parameter ($\chi = 0.557^{18}$), which was calculated using the following equation^{5,18}:

$$v_r^0 = \frac{1}{1 + \frac{d_r}{d_s} \left(\frac{1}{1-f_{fil}} \right) \left(\frac{w_s}{w_0} - 1 \right)} \quad (2)$$

where d_r (1.15 g/cm³) and d_s (0.867 g/cm³) are the densities of the rubber and solvent, respectively; f_{fil} is the initial weight

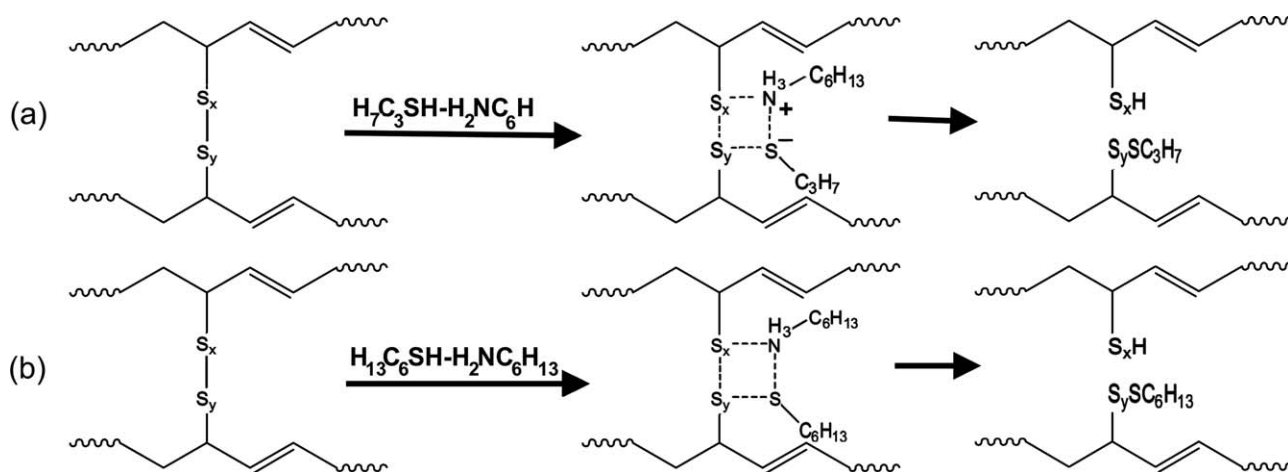
Table III. Devulcanization Temperature, Sol Fraction, Crosslink Density, and Devulcanization % of the Compounds

Compound	Devulcanization chemical	Devulcanization temperature (°C) ^a	Sol fraction (%)	CLD (mol/m ³)	Devulcanization %
RC	—	180	19	40	42
A	HDA	180	14	25	64
B	DPDS	180	25	139	—
C	CBS	180	17	35	50
D	TMTD	180	11	151	—
E	HDA	180	20	54	22
F	HDA	180	15	19	72
G	HDA	180	21	19	73
H	HDA	180	13	12	83
I	HDA	180	24	12	82
J	HDA	180	24	25	64
A-1	HDA	140	5	35	49
A-2	HDA	160	13	31	55
A-3	HDA	200	23	20	71
A-4	HDA	220	31	17	75
A-5	HDA	240	28	20	72
A-6	HDA	260	31	203	—
M	HDA	140	14	19	73
N	HDA	140	8	20	71



Scheme 2. Experimental procedure for the measurement of types and densities of sulfur crosslinks.²³ Note, in this study and to increase the efficiency of S—S di bonds breakage, hexanethiol replaced with cyclohexanethiol.

fraction of filler in the sample after double extractions by acetone and toluene; w_s is the weight of the swollen gel; and w_0 is the weight of the dried sample.



Scheme 3. Mechanism of sulfur crosslinks breakage by (a) propane-2-thiol + *n*-hexylamine (b) cyclohexanethiol + *n*-hexylamine.

The devulcanization % were calculated as follows:

$$\text{Devulcanization (\%)} = 100 \times \frac{(\text{initial waste rubber CLD} - \text{final rubber CLD})}{\text{initial waste rubber CLD}} \quad (3)$$

The initial waste rubber CLD was calculated as 69 mol/m^3 (Table I). Note that the Krause correction was not made because the results were used primarily to compare the CLD of the compounds tested. The devulcanization temperature, devulcanization %, sol content, and CLD of the devulcanized rubbers were summarized in Table III.

For analyzing the relationship between sol content and CLD, Horix analysis¹⁹ was used. When only main chain scission takes place during devulcanization, the relative decrease in CLD is given by²⁰:

$$1 - \frac{\vartheta_f}{\vartheta_i} = 1 - \left[\frac{(1 - s_f^{0.5})^2}{(1 - s_i^{0.5})^2} \right] \quad (4)$$

and when pure crosslink scission takes place during devulcanization, the relative decrease in CLD is given by:

$$1 - \frac{\vartheta_f}{\vartheta_i} = 1 - \left[\frac{\gamma_f (1 - s_f^{0.5})^2}{\gamma_i (1 - s_i^{0.5})^2} \right] \quad (5)$$

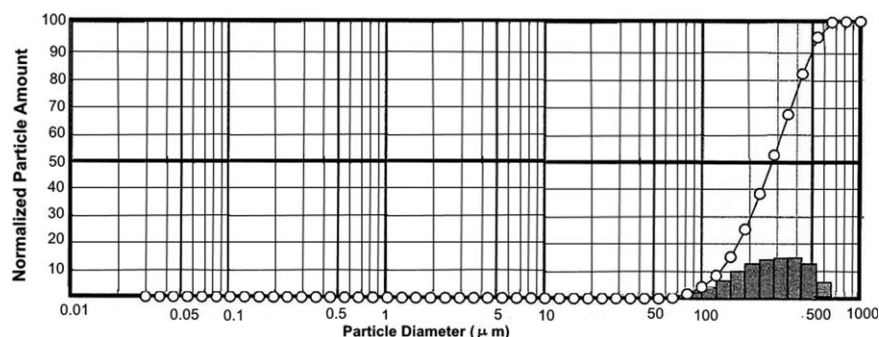
where s_i , ϑ_i , and s_f , ϑ_f are sol contents/100 and CLDs before and after devulcanization, respectively. In these experiments, s_i and ϑ_i are 0.03 and 69 mol/m^3 (Table I), respectively. γ_i and γ_f are the average number of crosslinks per chain in the remaining insoluble network before and after devulcanization, respectively. The relationship between γ and s is as follows²¹:

$$\text{Mechanism of } s = \frac{[(2 + \gamma) - (\gamma^2 + 4\gamma)^{0.5}]}{2\gamma} \quad (6)$$

The value of γ_i was calculated by replacing s_i in eq. (6) by the value of 0.03 ($\gamma_i = 5$). By fixing the values of γ_i and s_i in eqs. (4) and (5) and with the cooperation of eq. (6), Horix curves can be drawn (Figs. 3–7). Mono, di, and polysulfidic fractions in sulfur crosslinks of the rubber compounds were measured

Table IV. Mono, Di, and Polysulfides Fractions in Sulfur Bridges for Selected Rubber Compounds

Compound no.	Total CLD (mol/m ³)	Monosulfide %	Disulfide %	Polysulfide %
Initial waste rubber powder	69	0	72	28
H	12	19	54	27
N	20	5	56	39
B	139	19	5	76
D	152	16	49	35
A-6	203	20	17	63

**Figure 1.** Waste rubber particle size distribution.

and calculated using propane-2-thiol, hexylamine, and cyclohexanethiol as described in literature (Scheme 2).²² Note, in this study and to increase the efficiency of S—S di bonds breakage, hexanethiol is replaced with cyclohexanethiol. Sulfur crosslinks breakage by propane-2-thiol + *n*-hexylamine and cyclohexanethiol + *n*-hexylamine are depicted in Scheme 3a and 3b, respectively. Mono, di, and polysulfide % in sulfur bridges for selected rubber compounds were presented in Table IV.

EXAMINATION OF THE DEVULCANIZED RUBBER SURFACES BY SCANNING ELECTRON MICROSCOPY

The surfaces of the devulcanized rubber compounds were examined by a LEO 1530 VP field emission gun scanning electron microscope (SEM). Small pieces of the rubber samples approximately 5 mm × 5 mm in dimensions were coated with gold and then examined and photographed in the SEM. The rubber surfaces were then studied from the SEM micrographs.

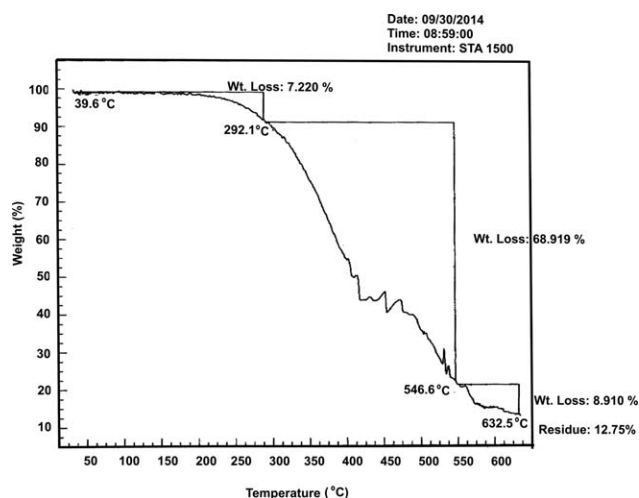
RESULTS AND DISCUSSION

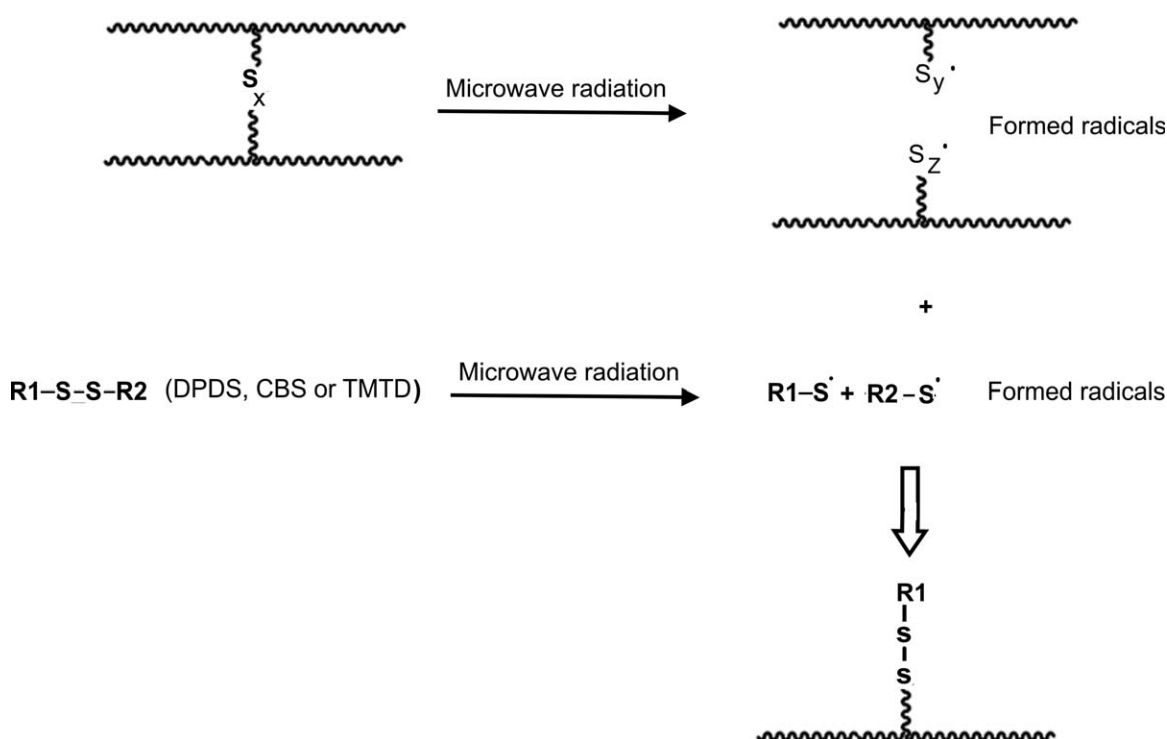
Devulcanization of the Waste Powder

Authors¹⁶ already found that the particle size of the waste powder is an important factor in controlling devulcanization temperature. For larger particles, i.e., 0.5 cm in diameter, hot spots appeared in the sample during microwave radiation and when a part of the sample degrades, the other party may still remain cold and practically, rubber remained unchanged and vulcanized. The same difficulties were observed in this study for waste rubber powder with the median particle size, greater than 279 μm. Figure 1 shows used waste rubber powder particle size distribution. The median particle size of this powder was 279 μm. The change of the particle shapes and states during microwave radiation showed the availability of an efficient devulcanization.

This fact subsequently confirmed when devulcanization % of the devulcanizates were measured by swelling test (Table III). Figure 1 also shows that 10, 50, and 90% of the waste rubber particles have diameters less than 130, 279, and 500 μm, respectively.

Table I and Figure 2 show the TGA results for the used waste rubber powder. The results show that IIR degradation began at 292°C and finished at 549°C. Mass loss was also observed in the range 40 to 292°C, because of the presence of oil in the sample. In addition to the mass loss related to the oil and rubber, a transition in the range 549 to 633°C was observed. This was attributed to the combustion of carbon black (after changing

**Figure 2.** Thermogravimetric analysis test results for waste butyl rubber powder.



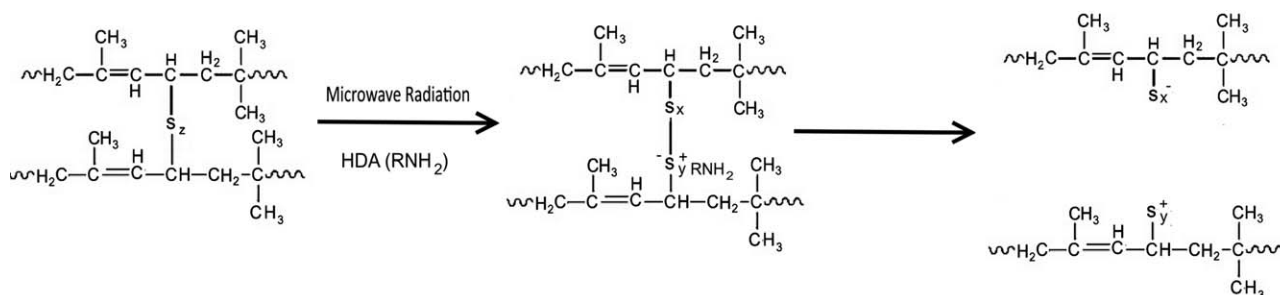
Scheme 4. Proposed radical devulcanization mechanism by DPDS, CBS, and TMTD.

the atmosphere to air at 550°C). The unburned residue was attributed to the minerals and metals in the sample.

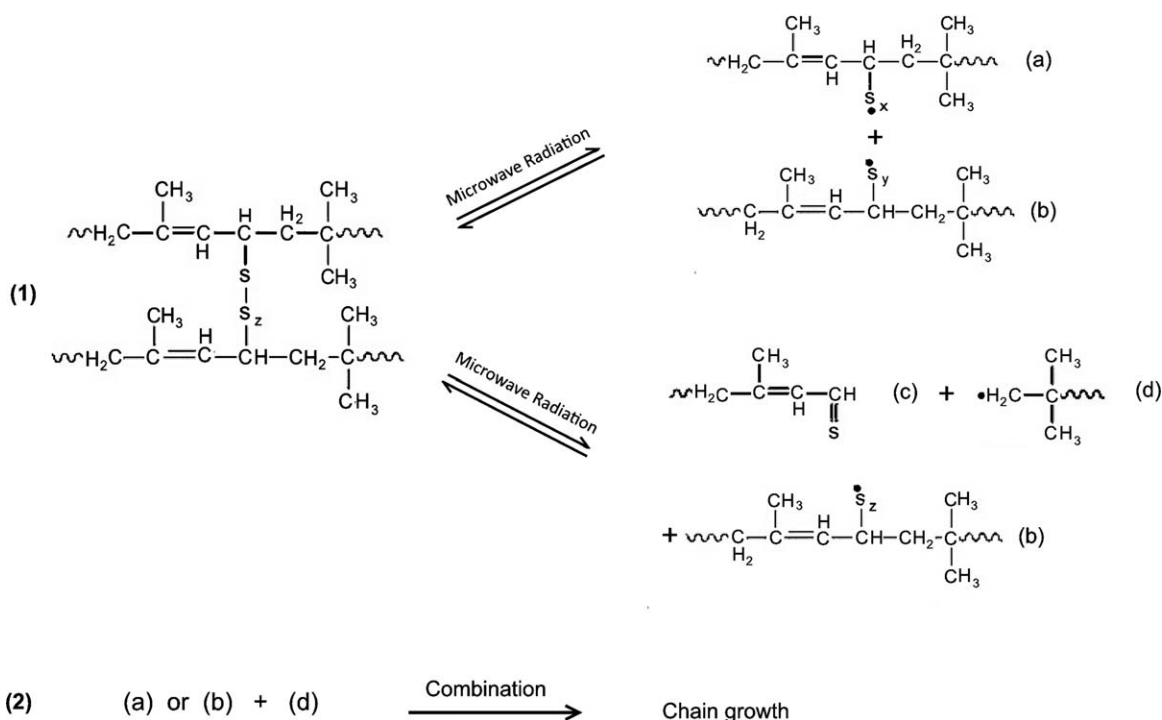
Proposed radical and ionic devulcanization mechanism of butyl rubber by DPDS, CBS, TMTD, and HDA shown in Schemes 4 and 5, respectively. For the case of DPDS, CBS, and TMTD, first, polymer chains divide into two radicals through sulfur bridges by microwave radiation. Subsequently, formed radicals combine with the radicals of the reagents (these radicals simultaneously produce by microwave radiation) and make stable molecules. The devulcanization mechanism for HDA is ionic (Scheme 5). Here, the polymer chains with the aid of HDA and microwave radiation divide into two ions through their sulfur crosslinks.

The sol fractions versus relative reduction in CLDs ($1 - \frac{v_f}{v_i}$) for irradiated compounds prepared with different devulcanizing reagents, HDA, DPDS, CBS, TMTD and reference compound (Compounds A,B,C,D and RC, without devulcanizing reagent, Table II) at 180°C are depicted in Figure 3 (CLDs of B and D

were more than CLDs of the initial rubber waste and consequently, their data were not indicated in Figure 3). As it observes, among of the devulcanizing reagents, HDA with the sol fraction and CLD of 14% and 25 mol/m³, respectively, has the highest devulcanization percent, 64% (Table III, compound A) and the closest point to the sulfur crosslink scission curve [eq. (5), the dotted curve in Figure 3]. If only sulfur crosslinks break during devulcanization, data points should lie on the dotted curve and in case of complete main chain scission, they should lie in the solid curve. Note, dotted and solid curves were constructed by using eqs. (4) and (5) as described in Ref. 21, respectively. Lying data between these two curves mean a mixing of sulfur crosslink and main chain scission occurred during devulcanization. The closer data points to the dotted curve show more sulfur crosslinks break down when compared with main chain scission. The sol fraction and CLD values for RC, CBS, DPDS, and TMTD (Compounds RC,C,B and D, Table III) were 19% and 40 mol/m³, 17% and 35 mol/m³, 25% and 139 mol/m³, and 11% and 151 mol/m³, respectively. Interestingly,



Scheme 5. Proposed ionic devulcanization mechanism of IIR by HDA.



Scheme 6. Polymer sulfur crosslink and chain growth mechanism for butyl rubber.

for compounds, B and D the CLDs were more than CLD of the initial waste rubber powder before devulcanization (69 mol/m^3 , Table I). Here, for these two compounds, with increasing sol fractions, CLDs, were also increased. Generally, increasing the rubber sol fraction is accompanied with CLD reduction and it indicates the extent to which the rubber main chains and crosslinks are broken.²⁰ It can be concluded that unexpectedly, for the Compounds B and D after radiation, new crosslinks were

made. The reason refers to a group of new main chain reactions named “main chain un saturation volatile formation crosslinking”²³ and also formation of new mono and polysulfide sulfur bridges as it is shown in Table IV. Scheme 6 clearly describes the formed radicals after microwave radiation and subsequent chain and sulfur crosslinks growth. Our findings are in conformity with the other’s report.²⁴ Here, unlike of the other chemicals, DPDS and TMTD acted as vulcanizing reagents

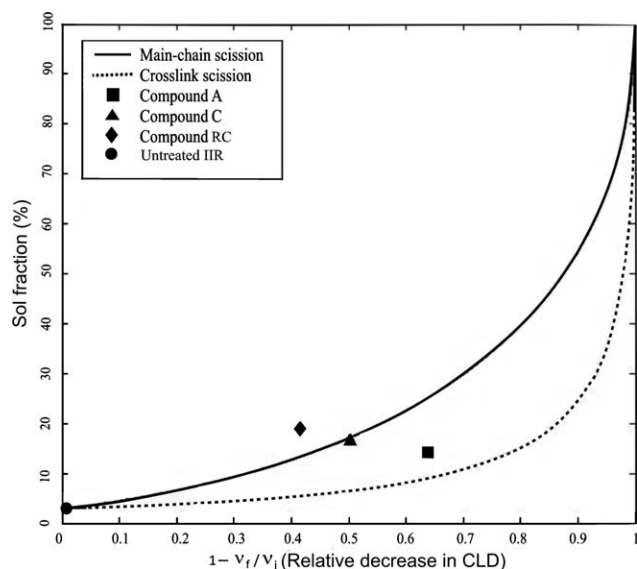


Figure 3. The relative decrease in CLD versus the sol fraction of Compounds A to D and reference Compound (devulcanization temperature, 180°C).

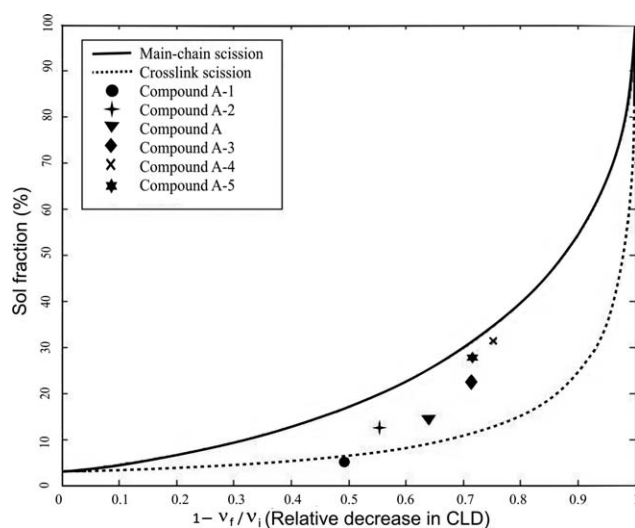


Figure 4. The relative decrease in CLD versus the sol fraction of Compounds A and A-1 to A-6 at various devulcanization temperatures.

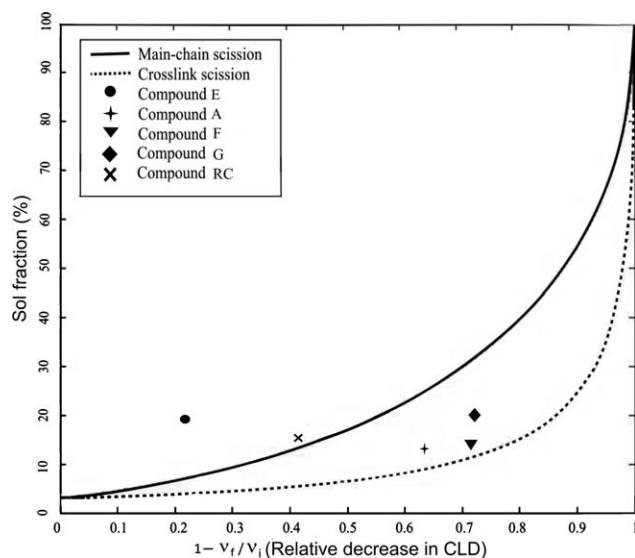


Figure 5. The relative decrease in CLD versus the sol fraction of Compounds E, A, F, and G (devulcanization temperature, 180°C).

rather than devulcanizing reagents. A similar conclusion was made by Dijkhuis for recycling of EPDM using DPDS as chemical reagent.²¹ The data for compounds RC and C in Figure 3 show unpleasant main chain scission for these compounds during devulcanization. They lie absolutely close to the main chain scission curve (solid curve). In addition, the devulcanization percent of Compound A (64%, Table III) is the highest when compared with Compounds C and RC. It can be concluded that HDA is the most suitable devulcanizing reagent in this study. Figure 4 shows sol fractions versus relative reduction in CLDs for HDA devulcanized compounds (Compound's A and A-1 to A-6, Table III) at various temperatures, 140, 160, 180, 200, 220, 240, and 260°C. Generally, devulcanization percent of

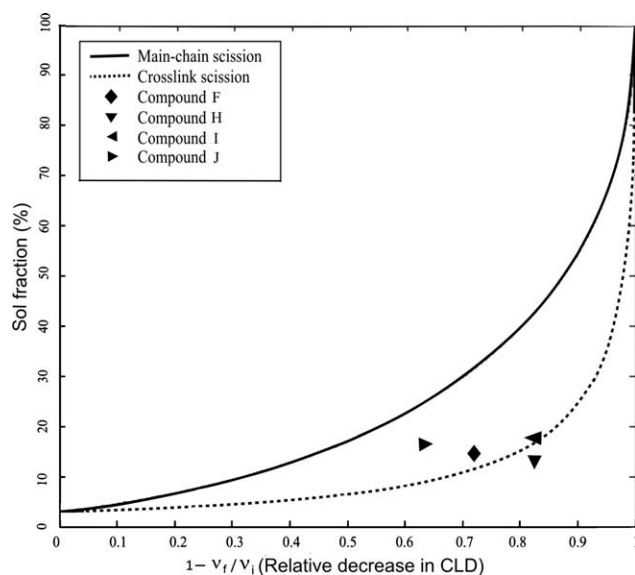


Figure 6. The relative decrease in CLD versus the sol fraction of Compounds H, I, J, and F (devulcanization temperature, 180°C).

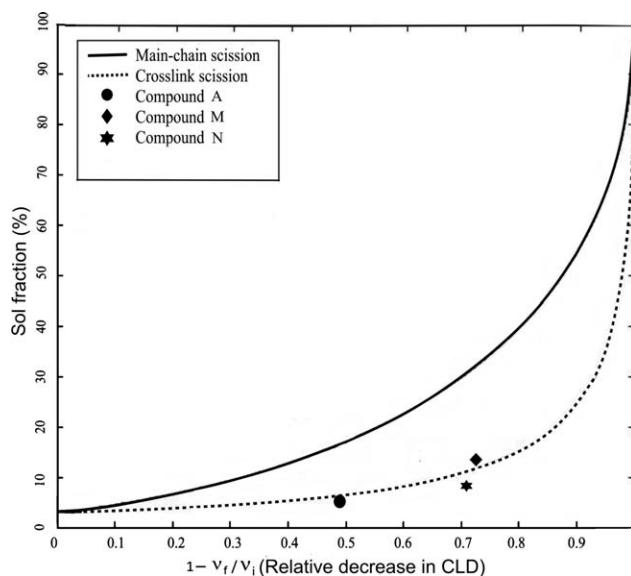


Figure 7. The relative decrease in CLD versus the sol fraction of Compounds A, M, and N (devulcanization temperature, 140°C).

the compounds increased with temperature up to 220°C with the value of 75%. For 240°C, the devulcanization percent, reduced to 72%, but for 260°C the situation completely changed and the same of Compounds B and D, sudden increase in CLD was observed (203 mol/m³, Table III). The data for three Compounds, A, A-1 and A-2 are completely close to the sulfur crosslink breakage curve (dotted curve). However, at 140°C, the point lies a little under the curve. Among the above-mentioned compounds, Compound A has the highest devulcanization percent and it can be selected as optimum compound. Figure 5 compares sol fractions versus relative reduction in CLDs for Compounds A, E, F, G, and RC with different HDA contents of 4, 2, 6, and 8 phr and without HDA, respectively. It was shown that increasing HDA has beneficial effect in the devulcanization process. The data of two Compounds, E and

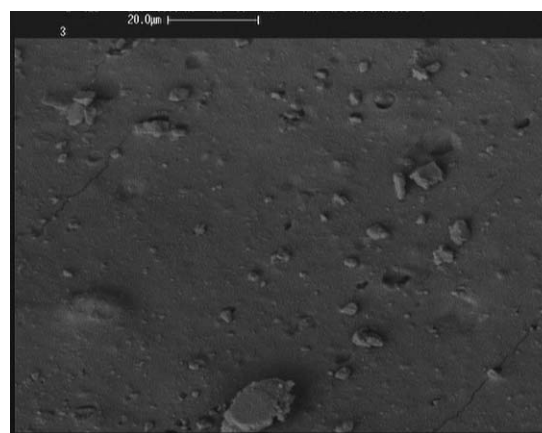


Figure 8. SEM micrograph showing the interior of the waste rubber after freeze-fracture.

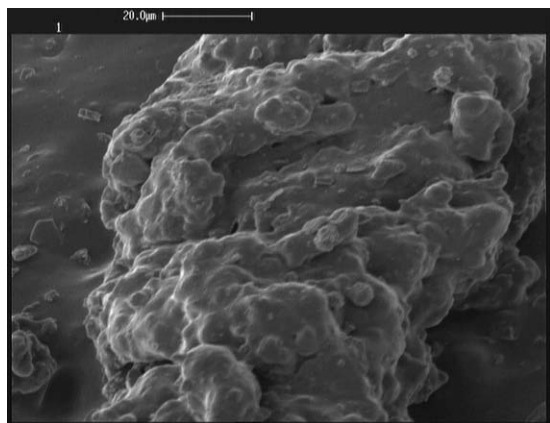


Figure 9. SEM micrograph showing the interior of the Compound E after freeze-fracture.

RC are beyond of the main chain scission curve and unacceptable. Among the rest of compounds, data of the Compound F with 6 phr HDA were closer to sulfur crosslink breakage curve than those of the Compounds A and G with the HDA values of 4 and 8 phr, respectively. Figure 6 investigates the effect of oils content and type on devulcanization process. The values of paraffinic oil content were 15, 30, and 45 phr for Compound's H, I, and J, respectively. Increasing paraffinic oil from 15 to 30 phr did not change the devulcanization percent effectively (compare Compound H with I in Table III) but it has a beneficial effect on devulcanization process through laying the data points on the sulfur crosslink breakage curve (Figure 6; dotted curve). Extra increasing of paraffinic oil had a detrimental effect on devulcanization process. Extra oil may cause devulcanization reagent to reach macromolecules with difficulty. Comparison between devulcanization percents of two Compounds F and I with the same amounts (30 phr) of aromatic and paraffinic oils, respectively, reveals adverse effects of aromatic oil on the devulcanization process (Table III and Figure 6). The reason may refer to the lower solubility of HDA in aromatic oil when compared with paraffinic oil. Table III and Figure 7 compare the devulcanization parameters of three Compounds A, M, and N with HDA values of 4, 6, and 8 phr, at 140°C, respectively. As it observes, increasing HDA from 4 to 6 and 8 phr was beneficial to devulcanization process through increasing devulcanization percents to 73 and 71% for Compounds M and N, respectively. However, Compound M with 6 phr HDA lies exactly between two curves and therefore, it is more acceptable than Compound N with 8 phr HDA. Feng and Isayev¹⁴ devulcanized gum (unfilled) butyl rubber in an ultrasonic reactor without using any chemical reagents. They found by changing the amplitude of the ultrasonic waves, the CLDs (devulcanization %) reduce between 36 and 73%. The devulcanization % for RC in this study was 42% without using any reagents and only with the help of microwave radiation. With consideration of this point that RC has filler (carbon black) in the formulation, it can be concluded that microwave radiation is quit comparable with the ultrasonic devulcanization method. In another attempt, Kuan *et al.*¹² used supercritical carbon dioxide to devulcanize unfilled butyl

rubber vulcanizates. With changing pressure and temperature of the reactor, they reached to sol percents with the values of 30 to near 100%. The maximum sol % in this study was 31% for Compound A-4 and A-6. Note, availability of filler in vulcanized rubbers may affect the devulcanization parameters. The raw rubber used in this study was waste butyl rubber while Kuan *et al.* used their formulated unfilled butyl rubber as initial rubber for devulcanization.

MONO, DI, AND POLYSULFIDES FRACTIONS IN SULFUR BRIDGES FOR SELECTED RUBBER COMPOUNDS

Table IV depicts mono, di, and polysulfide percents in sulfur bridges for selected rubber Compounds H, N, B, D, A-6, and waste rubber powder. As observed, the sulfur bridges in the initial waste rubber have 28% poly and 72% disulfides without monosulfide in structure. It can be concluded that the waste rubber was cured by a conventional cure system with relatively high concentration of the elemental sulfur. A quick look in Table IV reveals that for the Compounds, B, D, and A-6, after microwave radiation, a part of disulfides were broken and some new mono and polysulfides were made. This resulted in higher CLDs when compared with CLD of the initial waste rubber. The CLD of the waste rubber was 69 mol/m³ which increased to the values of 139, 151, and 203 mol/m³ for Compounds, B, D, and A-6, respectively. For Compounds B and D, 4 phr devulcanizing reagents, DPDS and TMTD, respectively, were used at devulcanization temperature, 180°C. For these compounds, first, a part of disulfides bridges were broken, and released sulfurs made new mono and polysulfides bridges. Comparison between sulfur crosslinks composition of two Compounds B and D showed that DPDS was more effective for disulfides crosslink breakage when compared with TMTD. As a result, DPDS and TMTD deteriorated devulcanization process and acted as vulcanization reagents. Compound A-6 is an exception when compared with Compounds A and A-1 to A-5 (Table III). Up to 240°C, the sulfur crosslinks were not broken and no new crosslinks were made. When temperature increased to 260°C, devulcanization was replaced with revulcanization by making new sulfur and nonsulfur crosslinks. The CLDs of the

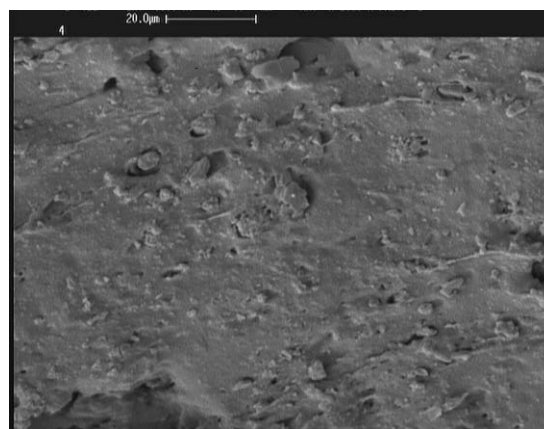


Figure 10. SEM micrograph showing the interior of the Compound H after freeze-fracture.

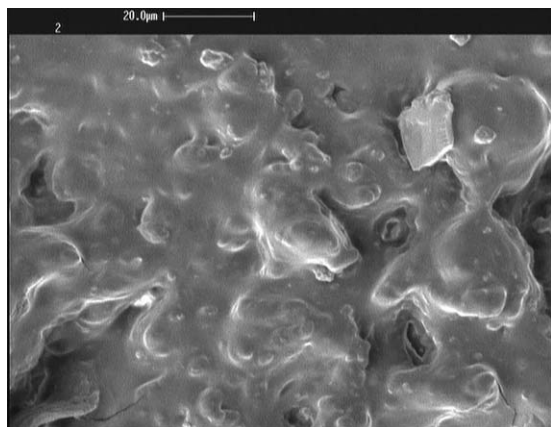


Figure 11. SEM micrograph showing the interior of the Compound J after freeze-fracture.

Compounds H and N (Table IV) were less than that of the waste rubber. Therefore, devulcanization was observed for these compounds. However, their sulfur crosslink compositions changed from di and polysulfides to mostly, monosulfide with the values of 5 and 19% for Compounds N and H, respectively.

THE MORPHOLOGY OF THE DEVULCANIZED WASTE RUBBER POWDER

Figures 8 to 11 show the filler dispersion and internal structure of the waste rubber and Compounds E, H, and J, (Table II) after freeze-fracture, respectively. The mechanical properties of the blends were affected by the resulting polymer morphology.¹⁶ Figure 8 shows weak filler (carbon black) dispersion in the waste rubber matrix with the average particle size of approximately less than 10 μm . No noticeable difference between the microstructures of the rubber was observed.

Figure 9 clearly shows the internal structure of the Compound E with the least devulcanization percent (22%, Table III). Devulcanized rubbers were clearly observed in the middle of micrograph surrounded by a matrix of vulcanized rubbers. The vulcanized rubbers appear like an agglomerate bulky part in a smooth (devulcanized rubbers) background. Filler particles will be seen in both, devulcanized and vulcanized zones. Figure 10 belongs to the Compound H with 83% devulcanization (Table III). The predominant microstructure matrix is devulcanized rubber and few percents vulcanized rubber and filler can be observed in the image. Due to the high level of devulcanized rubbers in this compound, the border between vulcanized and devulcanized rubbers is unclear and distinguishing them is difficult. The border of the matrix with vulcanized rubber in this compound is coarse and not smooth. This is attributed to low levels of the oil in the formulation of this compound (15 phr). Figure 11 represents microstructure of the Compound J. This compound has 45 phr oil in its composition and its devulcanization percent is 64%. Although, its devulcanization percent is less than that of the Compound H, but due to it has a high level of oil in its structure, distinguishing between two zones, devulcanized and vulcanized is not easy. Oil smoothed the border of these two zones.

CONCLUSIONS

From this study, it can be concluded:

- Butyl rubber can be devulcanized by combination of microwave radiation and chemical reagents effectively.
- Waste rubber particle size distribution is an important factor for successful devulcanization. The result showed that waste rubber powder with a median particle size of 279 μm was suitable.
- Among several devulcanizing reagents, HDA was the most useful one.
- The compounds with paraffinic oils and 6 phr HDA in their formulations and at 180°C as devulcanizing temperature, had the best devulcanizing efficiencies.
- For most compounds, during microwave radiation, a part of disulfides crosslinks were broken and released sulfurs made new mono and polysulfides bridges. This resulted higher CLDs for some compounds when compared with CLD of the initial waste rubber.
- In the morphological study of the most devulcanized compounds, vulcanized rubbers were clearly observed in the middle of micrograph surrounded by a matrix of devulcanized rubber. The effect of oil content was obvious.

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