GOUTAM K. JANA[1], RAM N. MAHALING[1], TANMOY RATH[1],
ANNA KOZLOWSKA[2], MAREK KOZLOWSKI[2], CHAPAL K. DAS[1][*]

Mechano-chemical recycling of sulfur cured natural rubber

Summary — The disposal of cured rubber has become a major environmental problem. Discarded rubber was devulcanized by an open two-roll cracker-cum mixing mill both in the presence or absence of diphenyl disulfide at 120 °C (Mechano-Chemical Process, MCP), and then the obtained devulcanized mass was revulcanized again by the addition of sulfur and *N*-cyclohexyl-2-benzothiazyl sulfonamide (CBS). A new look at the devulcanization mechanism and the influence of the devulcanizing agent on the mechanical properties of the ultimate revulcanized rubber are presented in this paper. Rheometric characteristics show that both the scorch time and curing rate were low for revulcanized rubber. One of the most interesting observations is that the mechanical properties of revulcanized rubber obtained by devulcanizing in the presence of disulfide were better than of the revulcanized rubber obtained by devulcanizing in absence of disulfide. The formation of extra crosslinking in disulfide containing revulcanized rubber was confirmed by crosslinking density data. By adopting this devulcanization technique mechanical properties of vulcanized natural rubber were retained in more than 87 %.

Key words: mechano-chemical process, devulcanization, revulcanization, devulcanization mechanism, mechanical properties, crosslinking density.

MECHANOCHEMICZNY RECYKLING KAUCZUKU NATURALNEGO WULKANIZOWANEGO ZA POMOCĄ SIARKI

Streszczenie — Opisano metodę recyklingu odpadów gumowych polegającą na ich dewulkanizacji w walcarce mieszankowej (rys. 1) w temp. 120 °C z dodatkiem lub bez disiarczku difenylu, a następnie rewulkanizacji otrzymanej masy za pomocą siarki i *N*-cykloheksylo-2-benzotioazol-sulfonamidu (CBS) jako przyspieszacza (tabele 1—3). Pomiary reometryczne wykazywały, że czas podwulkanizacji i szybkość wulkanizacji próbek rewulkanizowanych są mniejsze w porównaniu z tymi wielkościami dotyczącymi odpowiadającym im próbkom oryginalnych wulkanizatów (rys. 2—4). Stwierdzono, że użycie w procesie dewulkanizacji disiarczku difenylu daje lepsze właściwości mechaniczne i wyższą gęstość sieciowania rewulkanizowanych kauczuków w porównaniu z analogicznymi próbkami otrzymanymi bez tego dodatku (tabela 4, rys. 5—7).

Słowa kluczowe: proces mechanochemiczny, dewulkanizacja, rewulkanizacja, mechanizm dewulkanizacji, właściwości mechaniczne, gęstość sieciowania.

Cured rubbers have been a major disposal problem in the past and they continue to accumulate throughout the world today. Almost the entire amount of cured rubber from a worn out tyres is discarded. Very long time is needed for natural degradation due to the three-dimensional crosslinked network structure [1, 2]. It causes two serious problems, environmental pollution and wastage of a valuable rubber. The main approach to solve this problem is devulcanization and reuse of used and waste rubber [3—7]. Physically and chemically many attempts have been made to reuse the vulcanized rubber. The paths of physical processes were mechanical [8], thermomechanical [9], cryomechanical [10], microwaves or ultrasound ones [11]. In chemical process, disulfide [12], thiol and catalyst were used.

Recent technology [13—17] concerning the use of the reclaimed and devulcanized rubber as virgin rubber has affected many rubber industries but research works in this area are still limited. We have developed a new devulcanization process called the mechano-chemical process (MCP) [12, 18] to produce devulcanized rubber sheet at 120 °C with the help of open two-roll cracker-cum mixing mill. This mill has both the cracking zone and mixing zone on the same roll. The main function of this mill is to reduce the lump size. Its flight length, angle and ratio of up and down section are so adjusted that the bigger lumps are automatically transferred, after being cracked, to the mixing zone where disulfide is placed. The main advantage of this process is that it gives fine elastic powder, unlike cryoground rubber. It is very difficult to disperse the curatives well into the cryoground

---

[1] Materials Science Centre, IIT Kharagpur-721302, India.
[2] Materials Recycling Centre of Excellence, Wrocław University of Technology, Pl. Grunwaldzki 9, 50-377 Wrocław, Poland.
[*] Correspondence author; e-mail: ckd@matsc.iitkgp.ernet.in

rubber [19], but the elastic rubber, which was produced following our method, can accept the curatives throughout the mass and effectively dispersed it.

In this study we have devulcanized the vulcanized natural rubbers containing sulfur/accelerator at three different ratios, in absence or presence of devulcanizing agent. The properties of vulcanized and revulcanized rubber were compared.

EXPERIMENTAL

Materials

Natural rubber (NR, type RMA 1X) was supplied by Birla Tyres (India).

N-cyclohexyl-2-benzothiazyl sulfonamide (CBS) was delivered by Bayer (India) Ltd. Retarder RE (thiophthalimide type) was purchased from Aldrich Chemicals (USA). Diphenyl disulfide (devulcanizating agent) was prepared in our laboratory and used along with process oil (aromatic oil) supplied by Bayer Ltd. (India).

Preparation of vulcanized natural rubber

The compounding formulation of natural rubber with various ingredients (high, medium or low sulfur content) are shown in Table 1. The mixing was done in open two roll mixing mill at a friction ratio of 1:2. These rubber compounds were cured at 150 °C for 15 min by compression molding.

Table 1. Compound formulations for devulcanization study of three types of rubber with different content of sulfur

Type of vulcanizate	Ingredients content, phr				
	natural rubber	zinc oxide	stearic acid	sulfur	CBS
A	100	5	2	2.2	0.6
B	100	5	2	1.4	1.2
C	100	5	2	1.2	2.0

Vulcanized rubber sheets were aged for 96 h at 60 °C in order to maintain the analogy with aged scrapped rubber product.

Mechano-chemical devulcanization process

The vulcanized rubber compound was ground with the use of open cracker-cum two-roll mixing mill (own developed, shown in Figure 1) at 120 °C for 10 min with simultaneous addition of diphenyl disulfide and process oil at the same temperature. This devulcanized rubber was vulcanized again with the addition of proportional amounts of sulfur. CBS and retarder at 150 °C up to the optimum curing.

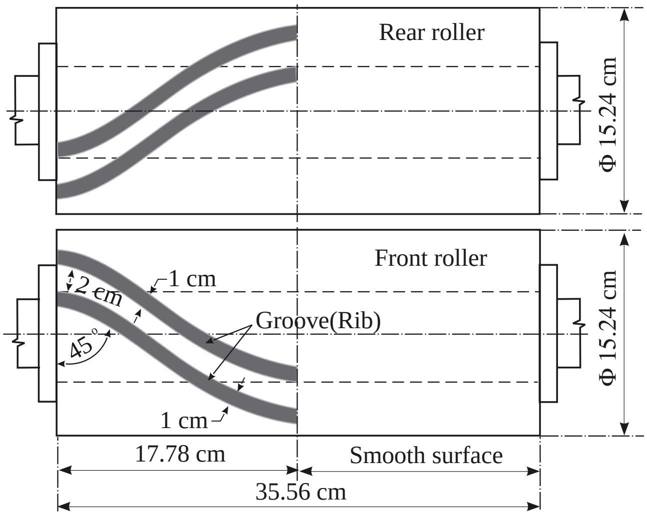


Fig. 1. Scheme of open cracker-cum two-roll mixing mill

Method of testing

Characteristics of curing

Curing characteristics of the rubber vulcanizate was studied using Monsanto Rheometer, R-100 at 150 °C. From the graph obtained, the minimum torque (M_L), the maximum torque (M_H), the scorch time (t_2) *i.e.* the time to two units of torque above the minimum, optimum curing time (t_{90}) *i.e.* the time to 90 % of maximum torque developed and state of curing ($t_{max} - t_{min}$) were determined.

Tensile properties

Slabs were prepared by compression molding and the dumbbell shaped specimens were cut out. The tests were done using the universal tensile testing machine, Hounsfield H10KS. Moduli at 100 % and 200 % elongation, tensile strength, tear strength and elongation at break were measured at room temperature. The initial gauge length of the specimen was 25 mm and tensile speed was 500 mm/min. Four samples were tested for each condition at the same elongation rate. The values of tensile strength, moduli at 100 % elongation, 200 % elongation and elongation at break were averaged. The relative error was below 4 %. Hardness was measured in terms of Shore A.

Crosslinking density

The crosslinking density was determined by immersing a small amount of a sample in 100 ml of benzene to attain equilibrium swelling. After swelling the sample was taken out from benzene and the surface was blotted from the solvent, then the sample was weighed immediately. This sample was then dried at 80 °C to the constant weight. Then the chemical crosslinking density was calculated by Flory-Rehner equation [20]. The value of Huggin's parameter (μ) used in Flory-Rhener equation for natural rubber (NR) is 0.44.

Determination of sol-gel fraction

The small pieces of rubber samples were placed in benzene for five days at room temperature for sol-gel fraction determination. Gel was filtered, washed with benzene and dried to the constant weight. Sol fraction (in %) was calculated according to equation:

$$\text{Sol fraction} = (W_0 - W_1)\ 100\ \%/W_0 \qquad (1)$$

where: W_0 — *dry sample mass before swelling*, W_1 — *dry sample mass after swelling*.

The gel fraction (in %) can be calculated as:

$$\text{Gel fraction} = 100\ \% - \text{sol fraction} \qquad (2)$$

RESULTS AND DISCUSSION

For devulcanization study everyone of three types of vulcanized rubbers were used with addition of process oil and with or without disulfide in amounts listed in Table 2. For revulcanization sulfur and CBS are used based on virgin rubber because according to De *et al.* [21] and Gibala *et al.* [22] the devulcanized rubber does not undergo vulcanization itself. The formulations of revulcanized mixtures are given in Table 3.

Table 2. Composition of devulcanizing agent for vulcanizate (in phr, in relation to vulcanizate)

Symbol of devulcanized rubber	Type of vulcanizate	Ingredient content, phr	
		process oil	diphenyl disulfide
D_1	A	6	—
D_2	A	6	1
D_3	B	6	—
D_4	B	6	1
D_5	C	6	—
D_6	C	6	1

Curing characteristics of the rubber vulcanizate

The curing characteristics of the original rubber blend's vulcanizates (conventional system, semi EV system and EV system) compared with their corresponding revulcanized rubber blends are shown in Figures 2—4.

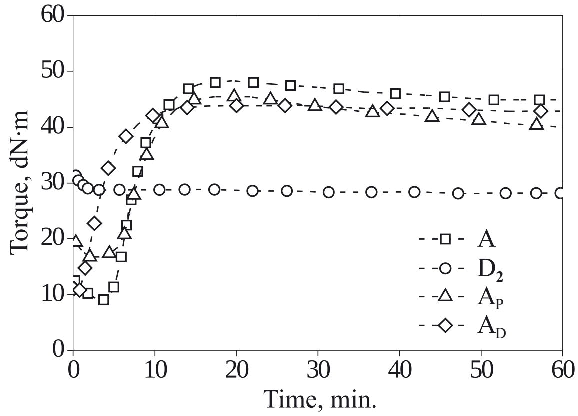


Fig. 2. Rheometric plot of the rubber blends (high sulfur content): A — original blend, D_2 — devulcanized rubber blend (from A) without curatives, A_P — recycled rubber blend (from A) without disulfide, A_D — recycled rubber blend (from A) with disulfide

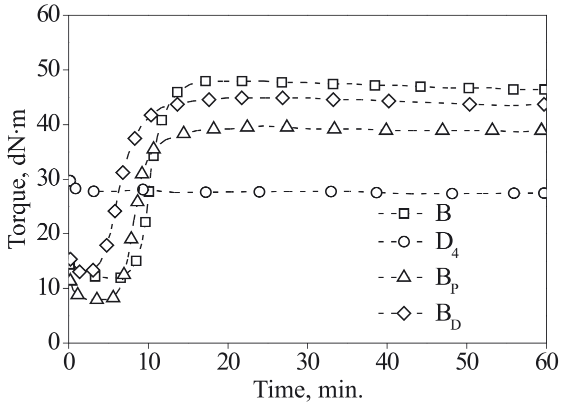


Fig. 3. Rheometric plot of the rubber blends (medium sulfur content): B — original blend, D_4 — devulcanized rubber blend (from B) without curatives, B_P — recycled rubber blend (from B) without disulfide, B_D — recycled rubber blend (from B) with disulfide

The rheometric plots for devulcanized rubber (Fig. 2, plot D_2; Fig. 3, plot D_4 and Fig. 4, plot D_6) were almost straight. Though retarder has been added to revulcanized rubber but maximum rheometric torque, rate of curing and scorch time were lower than that of the original rubber blends. The revulcanized rubber contains more

Table 3. Compound formulations for revulcanization study (in phr, in relation to devulcanized rubber)

Symbol of sample	Type of devulcanized rubber	Ingredients content, phr					
		devulcanized rubber	sulfur	CBS	process oil	diphenyl disulfide	retarder
A_P	D_1	100	2.2	0.6	6	0	1
A_D	D_2					1	
B_P	D_3		1.4	1.2		0	
B_D	D_4					1	
C_P	D_5		0.6	2.0		0	
C_D	D_6					1	

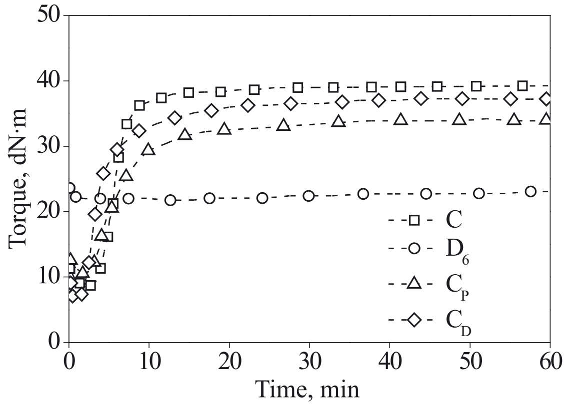


Fig. 4. Rheometric plot of the rubber blends (low sulfur content): C — original blend, D_6 — devulcanized rubber blend (from C) without curatives, C_P — recycled rubber blend (from C) without disulfide, C_D — recycled rubber blend (from C) with disulfide

sol fraction than the original rubber blends, which may reduce the maximum rheometric torque. The curatives from devulcanized rubber can migrates during revulcanization; this is expected to result in higher crosslinking degree of the revulcanized rubber and hence diminished curing rate. The reasons for scorch time decrease is less evident although. Phadke *et al.* [8] observed the same results for revulcanized rubber. According to De *et al.* [21] the revulcanized rubber contains active crosslinking sites, which reduce the scorch time. Scheele and Helberg [23] explained that the sulfonamide first decomposes to an amine and dibenzothiazole disulfide, which than dissociates and forms 2-mercaptobenzothiazole (MBT). After MBT generation only crosslinking occurs. For this reason sulfonamide is a delayed action accelerator. Thus MBT diffusion into the rubber matrix may reduce the scorch time. The amine, which also migrated from the sulfonamide, may hasten the crosslinking [24]. Again Gibala and Hamed [22] reported that the accelerator migrated from ground rubber to revulcanized rubber matrix at the time of revulcanization and that species reduced the scorch time. The rate of curing of revulcanized rubber obtained by devulcanization in the presence of disulfide was greater than in absence of disulfide. This may be due to the fact that at the time of revulcanization diphenyl disulfide breaks the sulfur crosslinking of the original rubber vulcanizate and creates new more active crosslinking sites in devulcanized rubber. Those active sites will form new crosslinking during revulcanization with sulfur and CBS at 150 °C.

Mechanical properties of the rubber vulcanizates

The tensile strength, moduli (at 100 % and 200 % of elongation) and elongation at break were used to estimate the effect of devulcanizing agent diphenyl disulfide on the mechanical properties of the revulcanized rubber vulcanizates (Figs. 5—7).

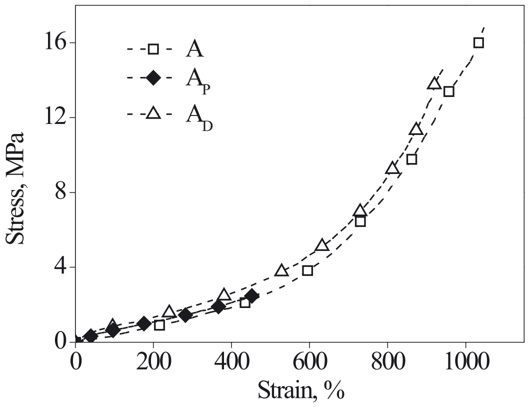


Fig. 5. Stress-strain curves of the vulcanizates (high sulfur content): A — original rubber vulcanizate, A_P — revulcanizated rubber vulcanizate (from A) without disulfide, A_D — revulcanized rubber vulcanizate (from A) with disulfide

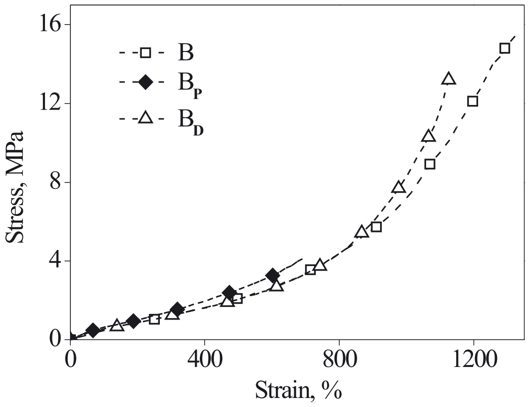


Fig. 6. Stress-strain curves of the vulcanizates (high sulfur content): B — original rubber vulcanizate, B_P — revulcanizated rubber vulcanizate (from B) without disulfide, B_D — revulcanized rubber vulcanizate (from B) with disulfide

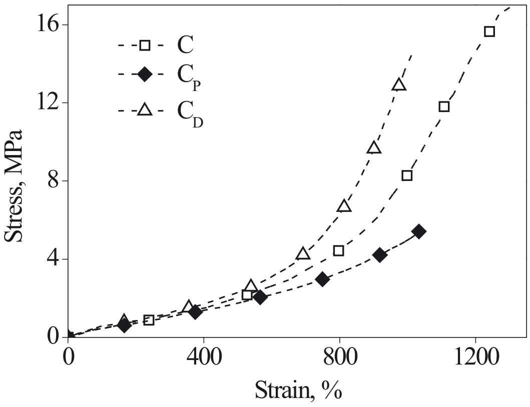


Fig. 7. Stress-strain curves of the vulcanizates (high sulfur content): C — original rubber vulcanizate, C_P — revulcanizated rubber vulcanizate (from C) without disulfide, C_D — revulcanized rubber vulcanizate (from C) with disulfide

The tensile properties of the revulcanized rubber are lower than that of the original vulcanized rubber. The reduction in the tensile properties of the revulcanized rubber may be due to the chain scission during the time of mechanical shearing. This will result in devulcanized rubber showing lower molecular weight than the original rubber. Also during revulcanization some part of crosslinking can be broken further due to heat and pressure from another vulcanization cycle. Furthermore, during revulcanization the crosslinking broken by diphenyl do not recombine again. And there is a possibility of desulfurization, decomposition and side reactions that may produce cyclic sulfides, sulfide pendant groups and other non-active groups. Another factor, which may be responsible for decrease in tensile strength, is the presence of greater amount of crosslinked gel in revulcanized rubber in comparison to original rubber vulcanize. The crosslinked gel is not well enough dispersed in the continuous matrix of revulcanized rubber. Such type of gel forms the weak sites for stress transmission and results in low tensile strength.

trend. The increase in hardness of revulcanized rubber is probably due to increase in crosslinking density.

Effect of diphenyl disulfide on mechanical properties of revulcanized rubber

Table 4 compares the tensile strength, elongation at break, moduli, tear strength, Shore hardness, crosslinking density and gel fraction values of the original rubber vulcanizate (high sulfur content) and the corresponding revulcanized rubber both in absence and presence of disulfide. The retention of tensile strength of the revulcanized rubber in relation to the original rubber vulcanizate was 15.3 % when devulcanized in absence of disulfide and 86.6 % in the presence of disulfide. Similarly, the retention of crosslinking density of the revulcanized rubber was 42.7 % and 97.8 %, when devulcanized in absence and in the presence of disulfide, respectively. Many of these mechanical properties of revulcanized rubber were comparable with those of industrially manufactured rubber and one can believe that the revulcanized rubber produced by the mechano-chemical process (MCP) may be able to replace virgin natural rubber in numerous applications.

Table 4. Properties of vulcanizate of fresh natural rubber and revulcanized one (vulcanizate A — high sulfur content)

Nature of the vulcanizate	100 % Modulus MPa	200 % Modulus MPa	Tensile strength MPa	Elongation at break, %	Tear strength N/mm	Hardness Shore A	Crosslinking density · 10^4 moles/g	Gel fraction %
vulcanizate A	0.54	0.83	16.82	1047	23.23	40	0.6981	89.44
AP (devulcanized absence of disulfide)	0.67	1.08	2.58	471	17.5	37	0.2984	76.14
% of retention	124	130	15.3	44.9	75.3	92.5	42.7	85.1
AD (devulcanized in the presence of disulfide)	0.74	1.31	14.58	942	23.14	40	0.6825	86.34
% of retention	137	159	86.6	89.9	99.6	100	97.76	96.5

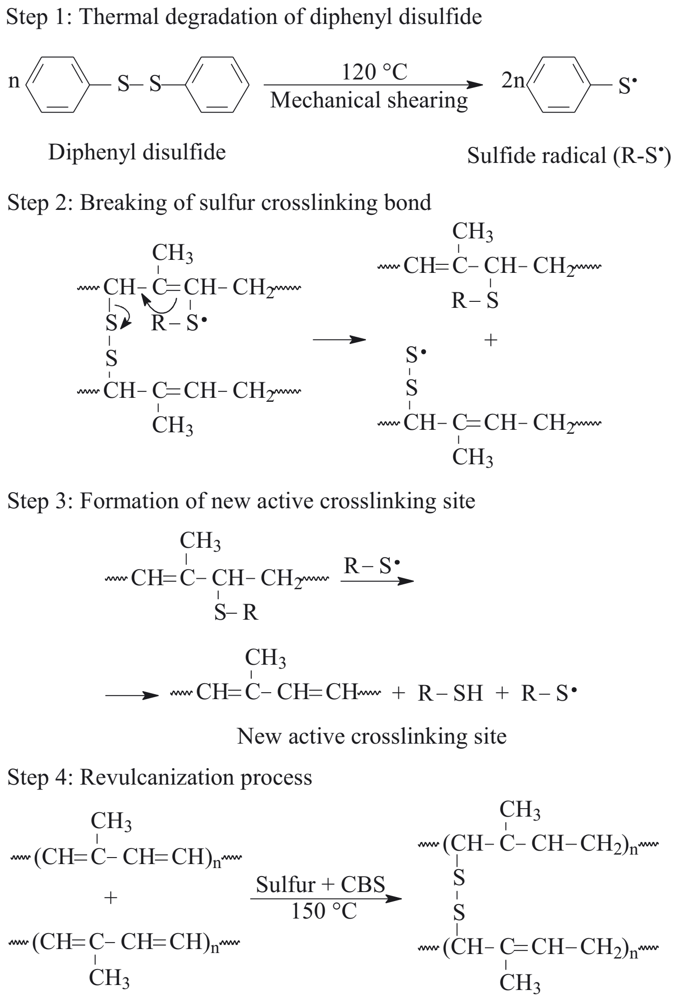
As shown in Figs. 4—6, tensile strength and elongation at break of revulcanized rubber obtained by devulcanization in presence of disulfide was higher than in absence of disulfide. Enhancement of these mechanical properties manifests itself in Table 4, by a sharp increase in crosslinking density and gel fraction. This was due to the fact that diphenyl disulfide breaks the sulfur crosslinking of the vulcanized rubber, which forms more new crosslinking during the revulcanization with sulfur and CBS.

It can be seen in Table 4, the moduli of revulcanized rubber A_D were higher than of the revulcanized rubber A_P. The increase in moduli of revulcanized rubber A_P can be caused by higher crosslinking density. Higher crosslinking density of the revulcanized rubber can restrict the molecular chain mobility under a tension force, and hence increases the modulus.

Table 4 again illustrates the tear strength of rubber vulcanizate (high sulfur content) as a funcion of diphenyl disulfide concentration. The tear strength of revulcanized rubber obtained by devulcanization with disulfide was higher than without disulfide. The Shore hardness of revulcanized rubber also follows the same

Revulcanization mechanism

The proposed revulcanization mechanism [12] for vulcanized natural rubber is shown in Scheme A. Step 1 represents the hemolytic cleavage of the diphenyl disulfide at 120 °C in the presence of mechanical shearing to formation of sulfide radicals. These newly formed sulfide radicals react with sulfur crosslinking sites present in main polymeric chain of vulcanized rubber and break the crosslinking, which is shown in Step 2. Another sulfide radical captures one hydrogen atom from the main polymeric chain (shown in Step 3) and creates new active crosslinking site in the main polymeric chain of revulcanized rubber. These active crosslinking sites form new crosslinking during the revulcanization with sulfur and CBS (Step 4) at 150 °C.



Scheme A

CONCLUSIONS

The cured rubber can be devulcanized by mechanochemical process. The mechanical properties (moduli, tensile strength, tear strength, elongation at break) and crosslinking density of revulcanized rubber obtain in the presence of disulfide were higher than those of the revulcanized rubber obtained in absence of disulfide. The all results indicated that diphenyl disulfide played an important role in devulcanization of the waste rubber.

ACKNOWLEDGMENTS

Authors are very much thankful to Lady Davis Fellowship, that Prof. C. K. Das was awarded during the period of which the part of the work has been conducted in the Chemical Engineering Department IIT Technion Haifa, Israel.

REFERENCES

1. De D., Maiti S., Adhikary B.: *J. Appl. Polym. Sci.* 1999, **73**, 2951.
2. De S. K.: *Prog. Rubber Plast. Recycl. Technol.* 2001, **17**, 113.
3. Naskar A. K., Bhowmik A. K., De S. K.: *J. Appl. Polym. Sci.* 2002, **84**, 622.
4. Bilgili E., Dybek A., Arastoopour H., Bernstein B.: *J. Elastomers Plast.* 2003, **35**, 235.
5. Kim J. K., Lee S. H.: *J. Appl. Polym. Sci.* 2000, **78**, 1573.
6. Ishiaku U. S., Chong C. S., Ismail H.: *Polym. Test.* 1999, **8**, 621.
7. Yehia A. A., Ismail M. N., Hefny Y. A., Abdel-Bery E. M., Mull M. A.: *J. Elastomers Plast.* 2004, **36**, 109.
8. Phadke A. A., Bhattacharya A. K., Chakraborty S. K., De S. K.: *Rubber Chem. Technol.* 1983, **56**, 726.
9. Harshaft A. A.: *Environ. Sci. Technol.* 1972, **6**, 412.
10. Phadke A. A., De S. K.: *Conser. Recycl.* 1986, **9**, 271.
11. Tukachinsky A., Schoworm D., Isayev A. I.: *Rubber Chem. Technol.* 1996, **69**, 92.
12. Jana G. K., Das C. K.: *Prog. Rubber Plast. Recycl. Technol.* 2005, **21**, 183.
13. Kojima M., Ogawa K., Mizoshima H., Tosaka M., Kohjiya S., Ikeda Y.: *Rubber Chem. Technol.* 2003, **76**, 957.
14. Adhikari B., De D., Maiti S.: *Prog. Polym. Sci.* 2001, **25**, 909.
15. Jang J. W., Yoo T. S., Oh J. H., Iwasaki I.: *Resources Conservation and Recycling* 1998, **22**, 1.
16. Fang Y., Zhan M., Wang Y.: *Mater. Des.* 2001, **22**, 123.
17. Fukumori K., Matsushita M., Okamoto H., Sato N., Suzuki Y., Takeuchi K.: *Soc. Automotive Eng. Japan* 2002, **23**, 259.
18. Jana G. K., Das C. K.: *Macromol. Res.* 2005, **13**, 30.
19. Mathew G., Singh R. P., Nair N. R., Thomas S.: *Polymer* 2001, **42**, 2137.
20. Manik S. P., Banerjee S.: *Angew. Makromol. Chem.* 1969, **6**, 171.
21. De D., Maiti S., Adhikari B.: *J. Appl. Polym. Sci.* 2000, **75**, 1493.
22. Gibala D., Hamed G. R.: *Rubber Chem. Technol.* 1994, **67**, 636.
23. Sheele W., Helberg J.: *Rubber Chem. Technol.* 1965, **38**, 189.
24. Morita W.: *Rubber Chem. Technol.* 1980, **53**, 393.

Received 6 XII 2005.