

A Novel Devulcanization Technology for Vulcanized Natural Rubber

G. K. Jana, R. N. Mahaling, C. K. Das

Materials Science Centre, IIT, Kharagpur 721302, India

Received 6 December 2004; accepted 12 May 2005

DOI 10.1002/app.22984

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Devulcanization of waste rubber poses a challenging environmental, economical, and disposal problem in the world because of their cross-linked three-dimensional network structure. Devulcanization of gum natural rubber vulcanizate containing three different sulfur/accelerator ratios was carried out in 90°C for 10 min with the help of open two-roll cracker cum mixing mill in presence and absence of thiol acid as a devulcanizing agent. The vulcanizate properties markedly depended on devulcanizing agent and also devulcanization techniques. Revulcanized rubber obtained by devulcanizing with thiol acid offered better mechanical properties. Decrease in scorch time and increase in rheometric torque were observed for revulcanized rubber containing devulcanizing agent. The onset degradation tem-

perature largely depended on presence of thiol acid. IR spectroscopic results revealed that the main polymeric chain did not oxidize at the time of milling above the room temperature. Increase in storage modulus and decrease in loss modulus were observed for revulcanized rubber from DMA study. The SEM was considered to study the failure mechanism and homogeneity of the vulcanizate. By adopting this devulcanization technique, more than 85% mechanical property of vulcanized natural rubber was retained. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2831–2840, 2006

Key words: mechanical properties; cross-linking; infrared spectroscopy; thermogravimetric analysis (TGA)

INTRODUCTION

The disposal of worn tires and their economic devulcanization poses a great challenge now a days, since these materials do not decompose easily. Devulcanization of vulcanized rubber not only solve the disposal problem but also maintains the limited resource on the earth. Devulcanization converts the vulcanized materials into new rubber compounds that can be decomposed into virgin rubber and then revulcanized. Devulcanization produces the fracture of the cross-link bonds in the vulcanized rubber.¹

Recent technology to use the reclaimed rubber and devulcanized rubber as virgin rubbers has attracted many rubber industries, and research in this issue is still limited in the literature. Many attempts have been undertaken to reuse the vulcanized elastomer such as reclaiming,^{2–6} devulcanization,^{7,8} high-pressure high temperature sintering,^{9,10} fuel recovery,¹¹ and others. Unfortunately, no techniques recover more than 40% of the original rubber properties. Sulfur-vulcanized natural rubbers contain cyclic, mono, di, and poly sulfidic linkages. According to Tobolsky et al.,¹² the cross-linked sulfur–sulfur bond in all diene rubbers are the weakest chemical bonds.¹³ The carbon–carbon

single bond energy in peroxide-cross-linked vulcanized rubber is 93 kcal/mol, the bond energy of carbon–sulfur–carbon bond in monosulfide cross-linked rubber is 50–60 kcal/mol, whereas the bond energy of carbon–sulfur–sulfur–carbon bond in disulfide cross-linked rubber is 35 kcal/mol and the bond energy of carbon–(sulfur)_n–carbon in polysulfide cross-linked rubber is 27 kcal/mol. Hence, these sulfidic bonds can easily be cleaved by thiol acid¹⁴ as a devulcanizing agent at comparatively lower temperature by mechanical milling. The thiol side of devulcanizing agent reacts with sulfur–sulfur cross-linked bonds of vulcanized rubber at high temperature and breaks the sulfur cross-linked bond and converts the vulcanized rubber into usable rubber products. This technique is typically done at 90°C temperature with the help of open two-roll cracker cum mixing mill. In the present investigation, we have devulcanized the vulcanized natural rubber containing three different amounts of sulfur/accelerator ratios in the presence and absence of thiol acid as a devulcanizing agent, revulcanized them, and compared their properties with original natural rubber vulcanizate.

EXPERIMENTAL

Materials

Natural rubber NR (RMA 1X) was supplied by Birla Tires (India), and *N*-Cyclohexyl-2-benzothiazyl sulfe-

Correspondence to: C. K. Das (ckd@matsc.iitkgp.ernet.in).

TABLE I
Compound Formulation for Devulcanization Study

Ingredients (phr)	High sulfur (A)	Medium sulfur (B)	Low sulfur(C)
Natural rubber (RMA 1X)	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
Sulfur	2.2	1.4	0.6
CBS	0.6	1.2	2

namide (CBS) was supplied by Bayer (India) Ltd. Thiol Acid was prepared in our laboratory and used along with process oil.

Preparation of vulcanized natural rubber

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

Mechanochemical devulcanization process

The vulcanized rubber compound was ground with the help of open cracker cum two-roll mixing mill (developed at Materials Science Centre) at 90°C for 10 min with simultaneous addition of thiol acid and process oil at the same temperature. The cracker cum mixing mill is the newer type of mixing mill having both cracking zone and the mixing zone on a same roll. The main function of this mill is to get the bigger lumps into a smaller size lump (dust). Its flight length, angle, and land and sea ratio are so adjusted that the bigger lumps after being cracked are automatically transferred to the mixing zone where we put the devulcanizing agent. The advantage of this technique is that it gives fine elastic rubber powder, unlike cryoground rubber. Cryoground rubber powder is stiff and curatives do not easily disperse in it. In the fine elastic rubber powder developed by us, the curatives are easily dispersed.¹⁵ This devulcanized rubber was vulcanized again with the addition of proportionate amount of sulfur, CBS, and retarder (*N*-cyclohexane thiophthalimide) at 150°C up to the optimum cure.

Cure characteristics of rubber compound

Cure characteristics of rubber compound were studied with the help of Monsanto Rheometer, R-100 at 150°C. From these graphs the optimum cure time, scorch

TABLE II
Composition of Devulcanizing Agent Per 100 phr Natural Rubber Vulcanizate

Ingredients (phr)	D1	D2	D3	D4	D5	D6
Vulcanizate (A)	100	100	—	—	—	—
Vulcanizate (B)	—	—	100	100	—	—
Vulcanizate (C)	—	—	—	—	100	100
Process oil	6	6	6	6	6	6
Thiol acid	—	1	—	1	—	1

time, and rate of cure $\{t_{\max} - t_{\min} (dN\ m)\}$ were determined.

Determination of tensile properties

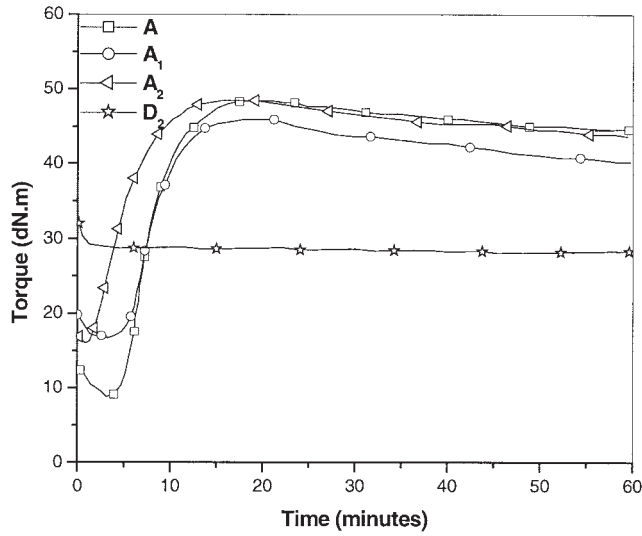
Slabs were prepared with the help of compression molding and the dumbbell shaped specimen was punched out. The tests were done by universal tensile testing machine, Hounsfield H10KS. Moduli at 100%, 200% elongation, tensile strength, tear strength, and percentage of elongation at break were measured at room temperature. The initial length of the specimen was 25 mm and the speed of separation was 500 mm/min. Four samples were tested for each condition at same elongation rate. The value of tensile strength, modulus 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.

Determination of cross-link density

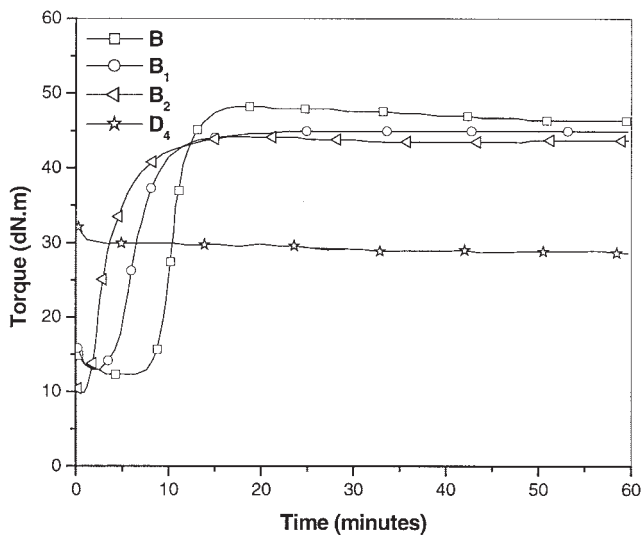
The cross-link density was determined by immersing the small amount of sample in 100 mL benzene for 72 h to attain equilibrium swelling. After swelling, the sample was taken out from benzene and the solvent was blotted from the surface of the sample and weighed immediately. This sample was then dried out at 80°C until constant weight was reached. Then the chemical cross-link density was calculated by Flory Rehner equation.¹⁶

TABLE III
Compound Formulation for Revulcanization Study

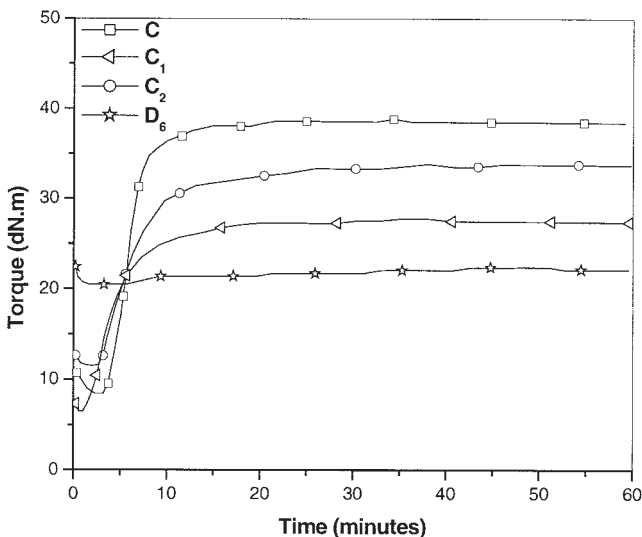
Ingredients (phr)	A1	A2	B1	B2	C1	C2
D1	100	—	—	—	—	—
D2	—	100	—	—	—	—
D3	—	—	100	—	—	—
D4	—	—	—	100	—	—
D5	—	—	—	—	100	—
D6	—	—	—	—	—	100
Sulfur	2.2	2.2	1.4	1.4	0.6	0.6
CBS	0.6	0.6	1.2	1.2	2.0	2.0
Retarder	1	1	1	1	1	1



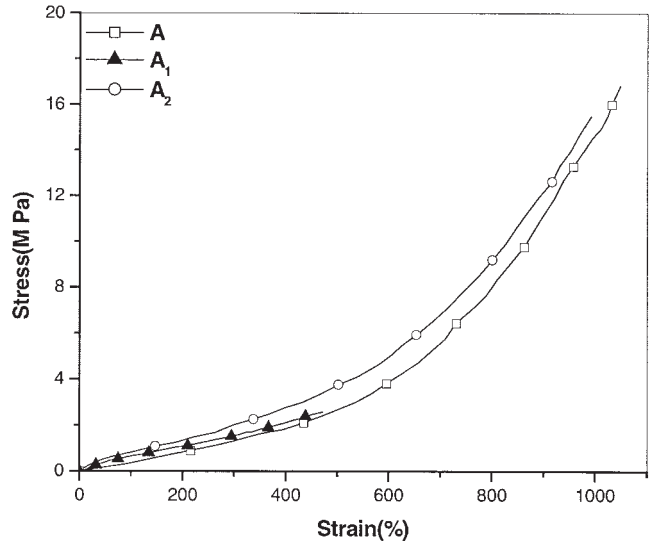
(a)



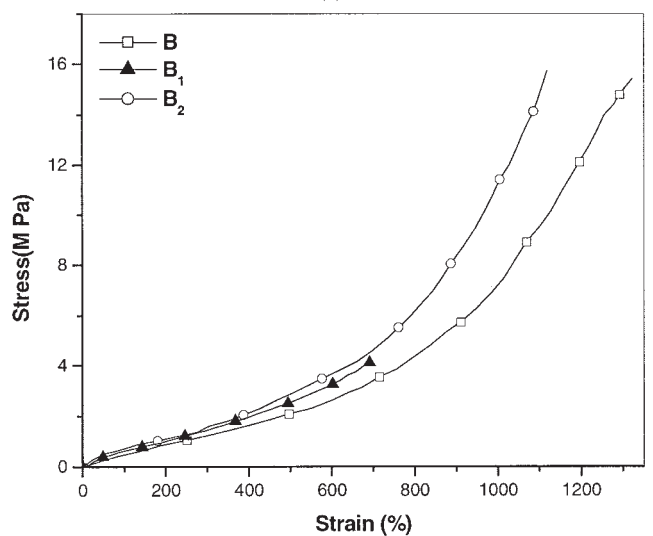
(b)



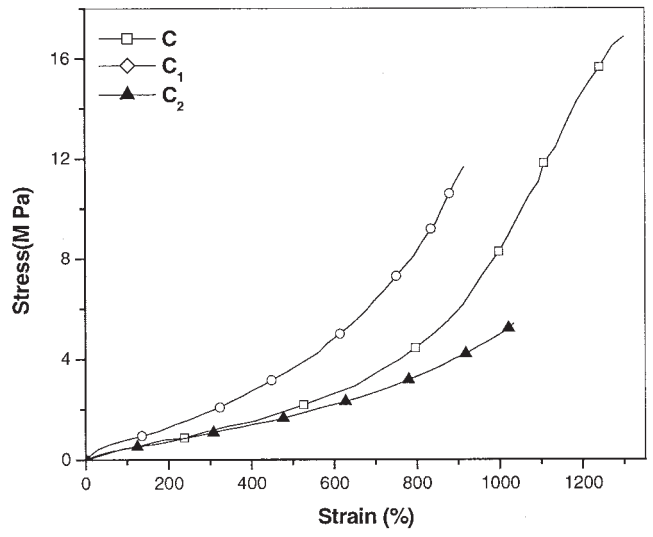
(c)



(a)



(b)



(c)

Figure 1 Rheometric plot of the (a) high sulfur, (b) medium sulfur, and (c) low sulfur vulcanizate.

Figure 2 Stress-Strain curves of the (a) high sulfur, (b) medium sulfur, and (c) low sulfur vulcanizate.

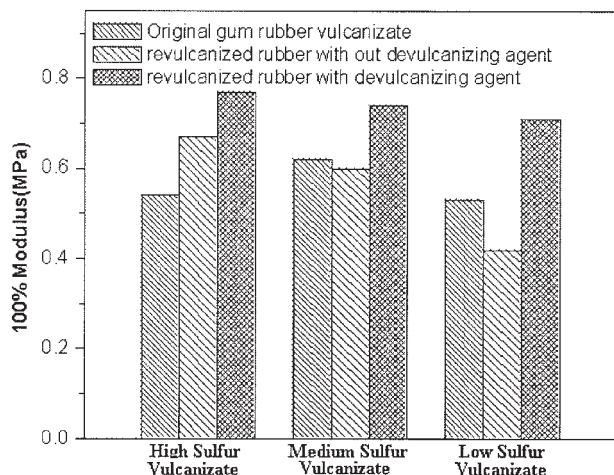


Figure 3 Variation of 100% modulus as a function of devulcanizing agent.

Sol-gel determination

The sol fraction was taken as the indication of degree of revulcanization and it was calculated as

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

where, W_0 is the dry sample mass before swelling, and W_1 is the dry sample mass after swelling.

The gel fraction can be calculated as

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction}$$

Fourier transform infrared spectroscopy (FTIR)

FTIR was done using a NEXUS 870 FTIR (Thermo Nicolet, Japan) in dry air atmosphere in room temperature using original rubber sample and revulcanized

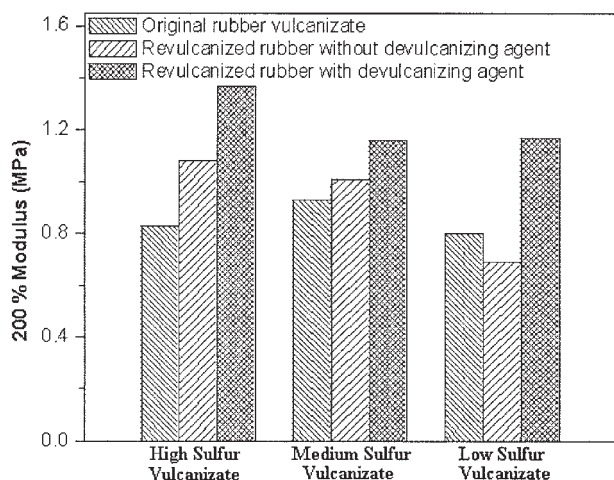


Figure 4 Variation of 200% modulus as a function of devulcanizing agent.

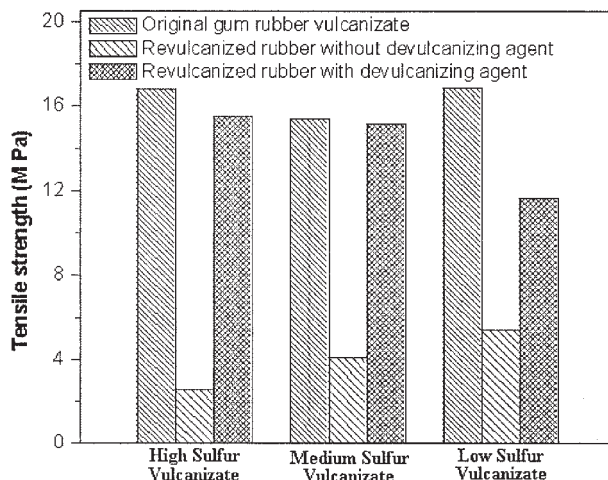


Figure 5 Variation of tensile strength as a function of devulcanizing agent.

sample directly. Spectra were taken from 4500 to 650 (cm^{-1}) wave numbers in the transmission mode.

Thermal characterization

Thermo gravimetric analysis (TGA) was carried out using Universal V1.12E TA instrument in the temperature range 50–700°C at a heating rate 20°C/min in nitrogen atmosphere.

Scanning electron microscopy

The tensile fracture of the samples were studied in scanning electron microscope (JSM-5800 of JEOL Co.) after coating of the failed surface with gold at a zero degree felt angle.

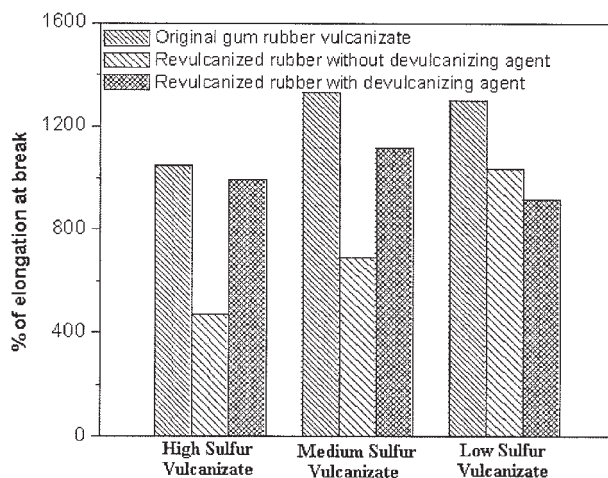


Figure 6 Variation of percentage of elongation at break as a function of devulcanizing agent.

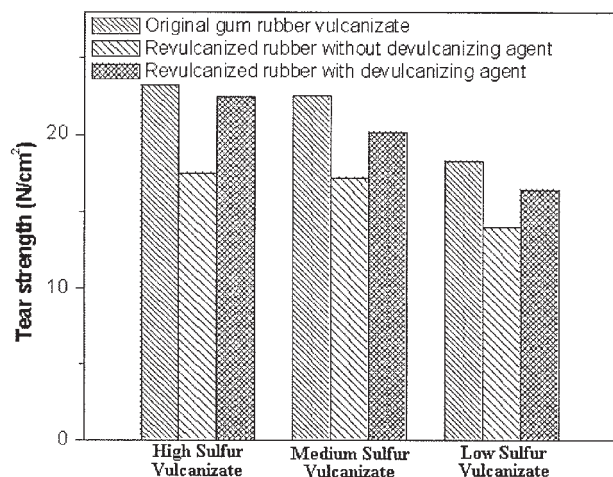


Figure 7 Variation of cross-link density as a function of devulcanizing agent.

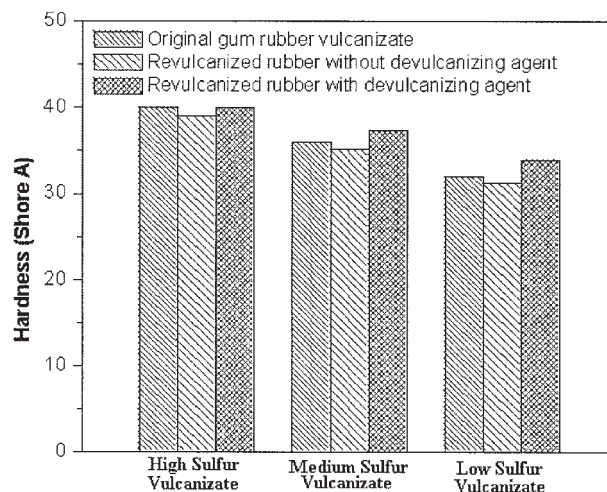


Figure 8 Variation of gel fraction as a function of devulcanizing agent.

Dynamic mechanical analysis

Dynamic mechanical properties of the vulcanizate were analyzed using a TA Instrument (DMA 2980) dynamic mechanical analyzer under tension mode. The samples were subjected to a sinusoidal displacement of 15 μm at a frequency of 1 Hz from room temperature to 170°C and at a temperature rate of 5°C/min.

RESULTS AND DISCUSSION

Compounding formulation for high sulfur (conventional system), medium sulfur (semi EV system), and low sulfur (EV system) containing vulcanizate are given in Table I and the compounding formulation for devulcanization study of all vulcanizates are shown in Table II. For revulcanization, the amounts of additives such as sulfur and CBS were used based on 100 g of rubber (Table III), irrespective of the amount of sulfur and CBS that comes from devulcanized rubber in mixing, because according to De et al.,¹ the amount of additives of natural rubber devulcanizate that were originated from parent compound were inactive and the same feature were observed in rheometric study [Fig. 1(a), graph D_2 , Fig. 1(b), graph D_4 , and Fig. 1(c), graph D_6] after the devulcanization the rheometric plots were almost straight.

Cure characteristics of the vulcanizates

The rheometer curves for high sulfur, medium sulfur, and low sulfur containing original gum rubber vulcanizates with their corresponding revulcanized rubber are shown in Figures 1(a,c). For revulcanized rubber, there is a decrease in maximum rheometric torque and scorch time. The revulcanized rubber vulcanizates contain less gel fraction¹⁷ (Fig. 8) compared with orig-

inal rubber vulcanizates, which reduces the maximum rheometric torque. The reason for decrease in scorch time is less evident, however, Phadke et al.¹⁸ and Yehia et al.¹⁷ observed a similar effect for filled natural rubber vulcanizate with ground scrap rubber. According to De et al.,¹ the devulcanized rubber contains active cross-linking gel, which reduces the scorch time. Scheele and Helberg¹⁹ reported that the CBS first decomposes to amine and dibenzothiazole disulfide. The dibenzothiazole disulfides then dissociate to form MBT, which is only responsible for cross-linking. For this reason, sulfenamide is a delayed action accelerator. Thus, MBT diffusion into the matrix would reduce the scorch time. Again according to Gibala et al.,²⁰ the accelerator migrated from ground rubber to the matrix when the ground rubber was accelerator/sulfur cured and that species reduces the scorch time. Figure 1(a)–1(c) also showed that the rate of cure of revulcanized

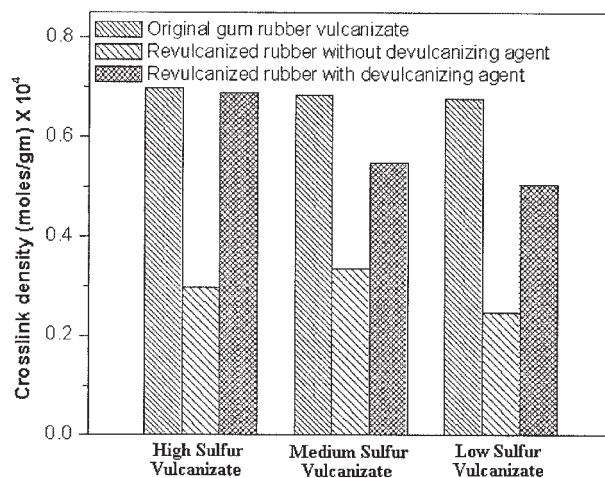


Figure 9 Variation of tear strength as a function of devulcanizing agent.

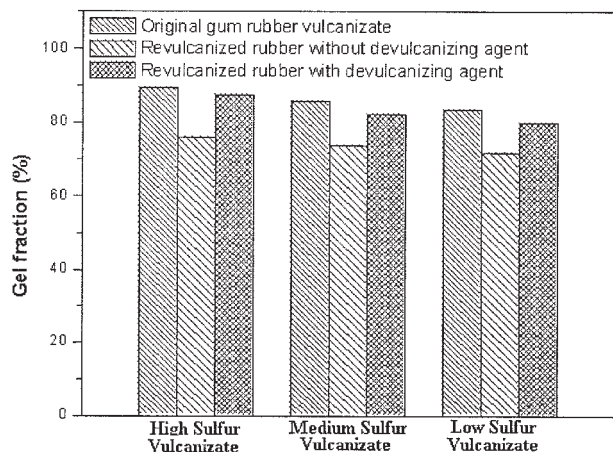


Figure 10 Variation of hardness as a function of devulcanizing agent.

rubber obtained by devulcanizing with thiol acid was higher than the revulcanized rubber obtained without devulcanizing agent. This may be due to the fact that devulcanizing agent breaks the cross-link bond more of original gum rubber vulcanizate at the time of mechanical milling (90°C) and creates higher active cross-link sites in devulcanized rubber, and these active sites will form new cross-link bonds in the time of revulcanization at 150°C with sulfur and CBS.

Mechanical properties of the vulcanizates

The stress-strain curves for high sulfur, medium sulfur, and low sulfur containing vulcanizates of original rubber and their corresponding revulcanized rubber are given in Figures 2(a,c) and the corresponding parameters like 100% modulus, 200% modulus, tensile strength, and percentage of elongation at break are shown in Figures 3–6. From the Figures 3 and 4 it was

clear that the 100% modulus and 200% modulus of revulcanized rubbers A₂, B₂, and C₂ are higher than the original rubber vulcanizate. This was due to restriction of molecular chain flexibility. From these figures it is also clear that 100% modulus and 200% modulus of revulcanized rubber obtained by devulcanizing with thiol acid were higher than the revulcanized rubber obtained without thiol acid. This may be due to increase in cross-link density.

Figures 5 and 6 show the comparison of tensile failure properties, i.e., the elongation at break and tensile strength of revulcanized rubber in the absence of and in the presence of devulcanizing agent with original rubber vulcanizate. The tensile properties of revulcanized rubber were enhanced in the presence of devulcanizing agent. This enhancement of tensile properties manifests itself in Figures 7 and 8 by a sharp increase in cross-link density and gel fraction. On the other hand, the tensile strength and elongation at break of revulcanized rubber were lowered compared with original rubber vulcanizates. During devulcanization by mechanical shearing at 90°C, some main polymeric chain of vulcanized rubber was broken. In the case of original rubber vulcanizate at the time of elongation the rubber chain orient themselves in the direction of stretching and it creates crystallites, these crystallites tie together number of network chain and contribute high tensile strength and elongation. But for revulcanized rubber, the main polymeric chain breaks before the formation of crystallites as it contains certain amount of main chain degradation and lowers the percentage of elongation at break and tensile strength. Another factor, which may be responsible to decrease the tensile strength, is the presence of greater amount of cross-linked gel in revulcanized rubber compared with original rubber vulcanizate, which are not dispersed in the continuous matrix of

TABLE IV
Vulcanizate Properties of Fresh Natural Rubber and Revulcanized Rubber (High Sulfur)

Nature of the vulcanizate	100% modulus (MPa)	200% modulus (MPa)	Tensile strength (MPa)	% of elongation at break	Tear strength (N/mm)	Hardness (Shore A)	Cross-link density (mol/g) ($\times 10^4$)	Gel fraction (%)
Original rubber vulcanizate	0.54	0.83	16.82	1047	23.23	40	0.69811	89.44
Revulcanized NR (devulcanized in absence of thiol acid)	0.67	1.081	2.58	471	17.5	39	0.29844/0.2029 ^a	76.14
% Retention	124	130	15.3	44.9	75.3	97.5	42.7	85.1
Revulcanized NR (devulcanized in presence of thiol acid)	0.77	1.37	15.49	992	22.43	40	0.68756/0.0317 ^a	87.47
% Retention	142.6	165	92.7	94.7	96.6	100	98.5	97.8

^a Crosslink density of corresponding de-vulcanized rubber.

devulcanized rubber. Such type of gel remains as weak sites for stress-transmission, resulting in lower tensile strength.

Figure 9 illustrates the tear strength of rubber vulcanizate having various amount of sulfur/accelerator ratio. Here again, tear strength of revulcanized rubber vulcanizates, devulcanized by thiol acid as devulcanizing agent was higher compared with revulcanized rubber without thiol acid. The hardness of revulcanized rubber obtained using devulcanizing agent was also higher than revulcanized rubber without devulcanizing agent, and those results are shown in Figure 10. The increase in hardness of revulcanized rubber probably increases the cross-link density as observed from Figure 7. The cross-link density of devulcanized rubber obtained in the presence of thiol acid is very low in comparison with devulcanized rubber obtained in absence of thiol acid (Table IV). This phenomenon again confirmed that the devulcanizing agent thiol acid tremendously breaks the sulfur cross-links and creates more active cross-link side. As a result, on revulcanization with sulfur and CBS, the cross-link density and gel fraction increases in thiol acid containing revulcanized rubber.

Effect of devulcanizing agent on mechanical properties

Table IV represents the mechanical properties, cross-link density, and gel fraction values of original vulcanizate and revulcanized rubber vulcanizate obtained by devulcanizing in the absence and presence of thiol acid. From this Table, it is clear that the cross-link density of revulcanized rubber is low. Since mechanical properties of the vulcanizate mainly depend upon cross-link density, mechanical properties of revulcanized rubber are low. The percent retention of tensile strength of revulcanized natural rubber vulcanizate with respect to original vulcanizate is 15.2% and 92.7%, when devulcanized in the absence of thiol acid and in the presence of thiol acid, respectively. Similarly, the percent retention of elongation at break of revulcanized rubber is 44.7% and 94.7%, when devulcanized in the absence of thiol acid and in the presence of thiol acid, respectively. From these observations, it is clear that the thiol acid plays an important role to devulcanize the rubber vulcanizate in the time of milling.

IR spectral analysis

The FTIR spectra of original rubber vulcanizate (high sulfur) and corresponding revulcanized rubber (high sulfur) were shown in Figures 11(a,c). From all the vulcanizates (vulcanized and revulcanized), a typical polyisoprene peak were clearly detected. The peak at 1660 cm^{-1} for $\gamma_{\text{C}=\text{C}}$ stretching,

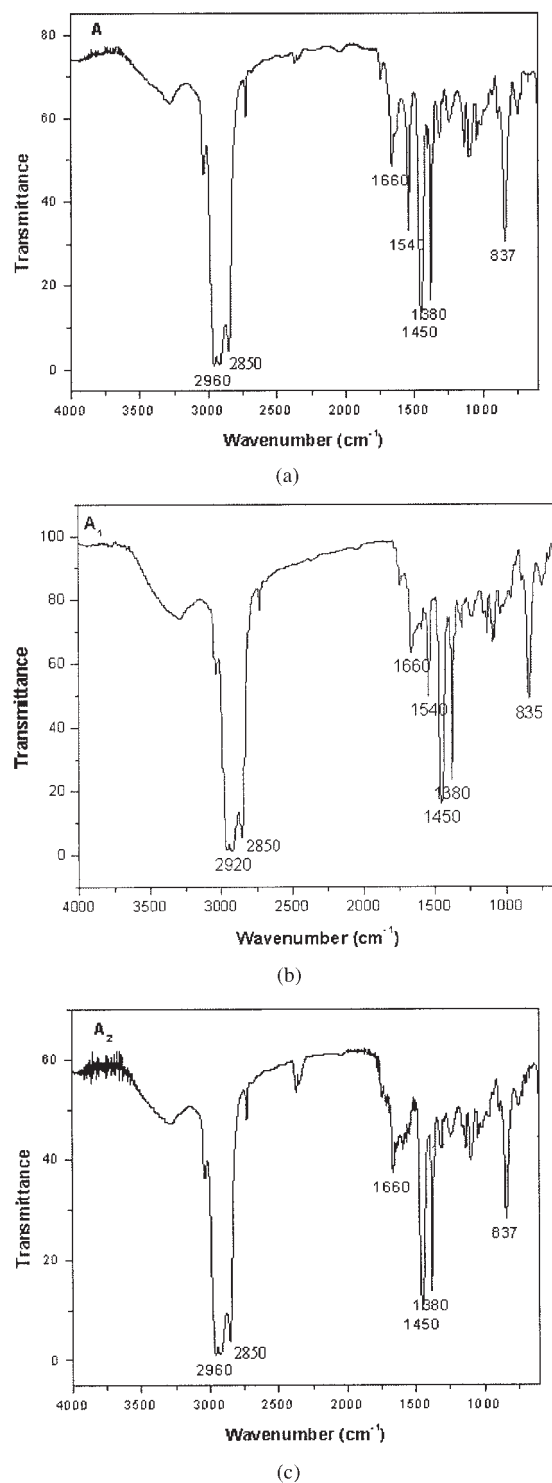


Figure 11 FTIR of (a) original rubber vulcanizate (high sulfur), (b) revulcanized rubber vulcanizate (without devulcanizing agent), and (c) revulcanized rubber vulcanizate (with devulcanizing agent).

and 1450 and 1380 cm^{-1} for δCH_2 deformation, 837 cm^{-1} for $\delta\text{C}-\text{H}$ bending, and the peak from 2960 to 2850 cm^{-1} for $\gamma\text{C}-\text{H}$ saturated stretching were observed from all the figures. The additional peak at 1540

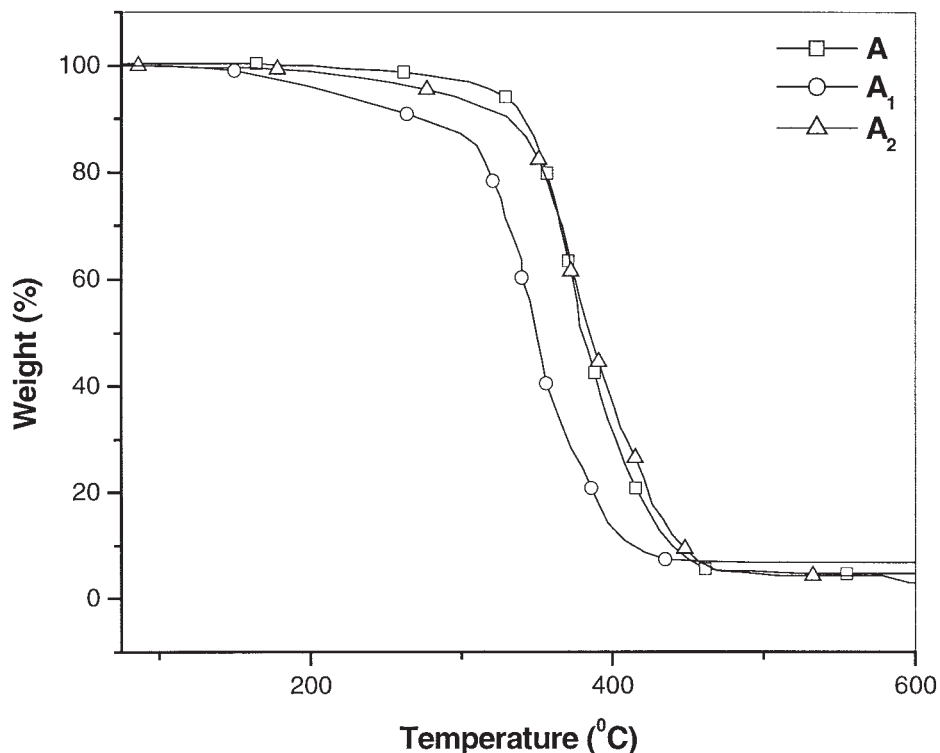


Figure 12 TGA plots (high sulfur) of (A) fresh rubber vulcanizate, (A₁) revulcanized rubber vulcanizate (without devulcanizing agent), and (A₂) revulcanized rubber vulcanizate (with devulcanizing agent).

cm^{-1} for stretching frequency of methyl assisted conjugate double bond [$\gamma\text{-(CH=CH)}_n\text{—}$, where $n > 6$ ^{21,22}] was also observed from these figures. The mechanical property of rubber vulcanizates markedly depended on the number of conjugate double bonds. From these figures, it was clear that the peak at 1540 cm^{-1} was diminished in revulcanized rubber vulcanizate without devulcanizing agent and it totally vanished for revulcanized rubber with devulcanizing agent. These observations suggested that for the first case, the retarder may react with carbon-carbon double bond^{9,23} and lowers the reversion reaction. For the second case, both the retarder and the devulcanizing agent (thiol acid) may react together with carbon-carbon double bond, so that it completely vanishes and increases the mechanical properties of revulcanized rubber. It may also be possible that after revulcanization, certain amount of the pending —C=C— moiety was being used up. Another important observation was that unlike

Padella et al.²⁴ for revulcanized rubber, there was no peak at 1730 cm^{-1} (carbonyl stretching frequency), which indicates that the main polymeric chain did not oxidize at the time of milling with the help of open two-roll cracker cum mixing mill at 90°C , which also increase the mechanical properties of revulcanized rubber.

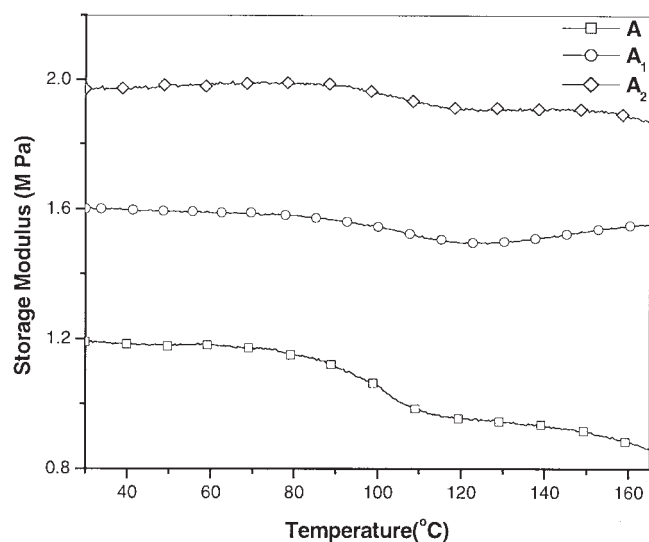


Figure 13 Storage modulus of the vulcanizate (high sulfur) as a function of temperature.

TABLE V
TGA Parameters

Sample code	T_1	T_{10}	T_{50}	T_{90}
A	330	355	395	455
A1	230	306	380	436
A2	327.8	350	400	459.5

TABLE VI
Storage Modulus (MPa) of the Vulcanizates at Different Temperatures

Sample code	30°C	50°C	75°C	100°C	125°C	165°C
A	1.192	1.182	1.168	1.059	0.9496	0.8583
A1	1.601	1.592	1.583	1.546	1.496	1.33
A2	1.972	1.985	1.990	1.961	1.906	1.871

Thermal analysis

High temperature TGA (50–700°C) plots of all vulcanizates (high sulfur) were shown in Figure 12. All the TGA curves show one-step degradation. The different degradation temperatures calculated from Figure 12 were given in Table V. The onset of degradation (T_1) of the revulcanized rubber A_1 started at 230°C. Ten percent degradation (T_{10}), 50% degradation (T_{50}), and 90% degradation (T_{90}) of the same vulcanizate started at 306, 380, and 436°C, respectively. For the revulcanized rubber A_2 , the onset degradation (T_1) occurred at higher temperature (327.8°C). The T_{10} , T_{50} , and T_{90} of the vulcanizate A_2 occurred at 350, 400, and 459.5°C, respectively. The delayed degradation of the revulcanized rubber A_2 suggested that the vulcanizate A_2 was more stable towards thermal degradation because of extra cross-linking introduced in revulcanized rubber A_2 due to devulcanizing agent. Cross-linking increased the rigidity of the system, which in turn increased the thermal stability. Similar results were observed in case of semi EV and EV system (not shown in figure).

Dynamic mechanical analysis

The storage modulus (E') vs. temperature curve (high sulfur) was shown in Figure 13. The storage modulus of the revulcanized rubber A_2 was higher than the revulcanized rubber A_1 as shown in Table VI. This may be due to the vulcanizate A_2 that has higher cross-link density than the vulcanizate A_1 . This observation was in line with the change in tensile modulus with the addition of devulcanizing agent (Figs. 3 and 4).

Figure 14 showed the loss modulus (E'') vs. temperature of the vulcanizates. From this figure, it was observed that the loss modulus of the revulcanized rubber was lower compared with original rubber vul-

TABLE VII
Loss Modulus (MPa) of the Vulcanizates at Different Temperatures

Sample code	30°C	50°C	75°C	100°C	125°C	165°C
A	0.0779	0.0655	0.0587	0.0475	0.0314	0.0218
A1	0.0803	0.0639	0.0501	0.0412	0.0277	0.0221
A2	0.0598	0.0484	0.0429	0.0348	0.0272	0.0246

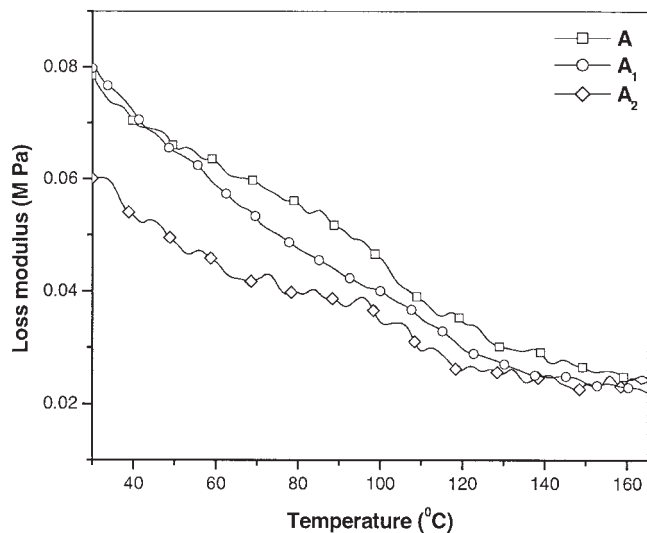
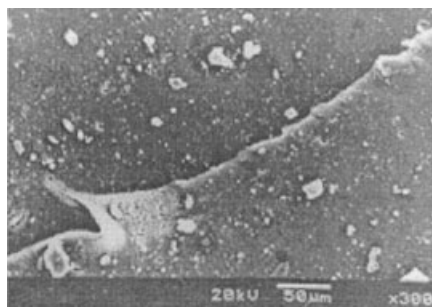


Figure 14 Loss modulus of the vulcanizate (high sulfur) as a function of temperature.

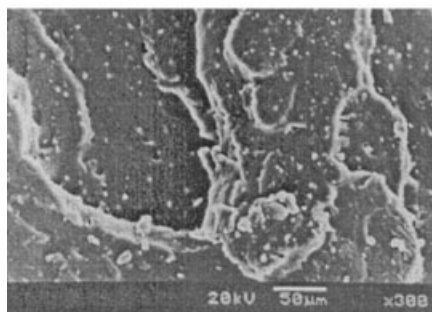
canizate. This indicates that the heat build up for revulcanized rubber will be to a lower extent. This is an added advantage for the devulcanized rubber vulcanizate.

SEM study

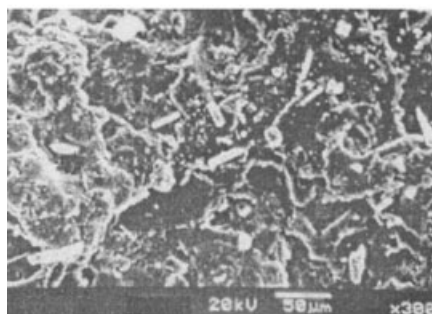
SEM photographs of the vulcanized and revulcanized rubber samples were taken to study the phase morphological structure and homogeneity of the vulcanizate. Figures 15(a,c) show SEM photographs of tensile fracture sample for original rubber vulcanizate A, revulcanized rubber A_1 , and A_2 , respectively. The smooth fractured surface observed for all vulcanizates exhibited the characteristic feature of vulcanized gum natural rubber. The micrograph of original rubber vulcanizate A [Fig. 15(a)] showed unidirectional tear path oriented along the direction of flow, showing weak rubbery failure with higher tensile strength. The revulcanized rubber A_1 [Fig. 15(b)] was having several number of crack paths in different directions with number of holes, making the vulcanizate vulnerable under mechanical stress. The micrograph also indicated that the fractured surface of the vulcanizate had less homogeneity than that of original rubber vulcanizate. This may be due to the absence of devulcanizing agent, the phase boundary of revulcanized rubber produced defects between the rubber molecular structure due to less amount of cross-linking, and this may have reduced the tensile strength and elongation at break. In the thiol acid containing revulcanized rubber vulcanizate A_2 [Fig. 15(c)], the fracture mode showed the failure mode that is less rubbery in nature without any hole, suggesting the occurrence of extra cross-link bond at the time of revulcanization. Similar results



(a)



(b)



(c)

Figure 15 SEM photographs of the (a) fresh rubber vulcanizate, (b) revulcanized rubber vulcanizate (without devulcanizing agent), and (c) revulcanized rubber vulcanizate (with devulcanizing agent).

were observed for both semi EV and EV systems (not shown in the figure).

CONCLUSIONS

Mechanochemical devulcanization by thiol acid, as devulcanizing agent, at comparatively lower temper-

ature with the help of open two-roll mixing mill represented an ideal method for making value added rubber products from waste rubber. The revulcanized rubbers obtained from this process have very good mechanical properties compared with original rubber vulcanizates. With incorporation of small amount of acid, it is possible to recover more than 85% original gum rubber properties. Therefore, the devulcanization of vulcanized elastomer is possible through mechanochemical process. The properties of revulcanized rubber markedly depend on the concentration of devulcanizing agent.

References

- De, D.; Maiti, S.; Adhikary, B. *J Appl Polym Sci* 1999, 73, 2951.
- Kawabata, N.; Okuyama, B.; Yamashita, S. *J Appl Polym Sci* 1981, 26, 1417.
- Yu Levin, V.; Kim, S. H.; Isayev, A. I.; Massey, J.; Von Meerwall, E. *Rubber Chem Technol* 1996, 69, 104.
- Takachinsky, A.; Schworm, D.; Isayev, A. I. *Rubber Chem Technol* 1996, 69, 92.
- De, D.; Maiti, S.; Adhikary, B. *J Appl Polym Sci* 2000, 75, 1493.
- Padke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, D. *Rubber Chem Technol* 1983, 56, 726.
- Roberson, P. R. U.S. Pat. 6,095,400 (2000).
- Mayers, R. D. U.S. Pat. 5,798,394 (1998).
- Tripathy, A. R.; Morin, J. E.; Williams, D. E.; Eyles, S. J.; Farris, R. J. *Macromolecules* 2002, 35, 4616.
- Morin, J. E.; Williams, D. E.; Farris, R. J. *Rubber Chem Technol* 2003, 75, 955.
- Lehmann, C. M. B.; Abadi, M. S.; Road, M. J.; Sun, J. *Energy Fuels* 1998, 12, 1095.
- Tobolsky, A. V. *Polymer Science and Materials*; Wiley-Interscience: New York, 1960.
- Dluzneski, P. *Rubber Chem Technol* 2001, 74, 3.
- Cotton, F. H.; Gibbons, P. A. U.S. Pat. 2,408,296 (1946).
- Mathew, G.; Singh, R. P.; Nair, N. R.; Thomas, S. *Polymer* 2001, 42, 2137.
- Manik, S. P.; Banerjee, S. *Die Angewandte Makromolekulare Chemie* 1969, 6, 171.
- Yehia, A. A.; Ismail, M. N.; Hefny, Y. A.; Abdel-Bary, E. M.; Mull, M. A. *J Elastomers Plast* 2004, 36, 109.
- Phadke, A.; Chakraborty, S.; De, S. K. *Rubber Chem Technol* 1984, 53, 19.
- Scheele, W.; Helberg, J. *Rubber Chem Technol* 1965, 38, 189.
- Gibala, D.; Hamed, G. R. *Rubber Chem Technol* 1994, 67, 636.
- Colleman, M. M.; Shelton, J. R.; Coneing, J. L. *Rubber Chem Technol* 1972, 45, 173.
- Koneing, J. L.; Coleman, M. M. *Rubber Chem Technol* 1971, 44, 904.
- Jana, G. K.; Das, C. K. *Prog Rubber Plast Recycl Technol* 2005, 21, 1.
- Padella, F.; Cavalieri, F.; D'Uva, G.; La Barbera, A.; Cataldo, F. *Polym Recycl* 2001, 6, 11.