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Recycling Natural Rubber Vulcanizates through Mechanochemical Devulcanization

G. K. Jana and C. K. Das*

Materials Science Centre, IIT kharagpur-721302, India

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Abstract: Sulfur-cured gum natural rubber vulcanizates were devulcanized using two different concentrations of diallyl disulfide. The devulcanization process was performed at 110 °C for 10 min in an open two-roll cracker-cum-mixing mill. Natural rubber vulcanizates having various sulfur/accelerator ratios were used to study the cleavage of monosulfide, disulfide, and polysulfide bonds. The properties of devulcanized natural rubber increased upon increasing the disulfide concentration and the mechanical properties of the revulcanized natural rubber increased upon decreasing the sulfur content in the original rubber vulcanizates. The scorch time and the maximum state of cure both increased when the ground vulcanizates were treated with higher amounts of disulfide. TGA and DMA were conducted to study the effects of the devulcanization on the thermal stability and the T_g behavior of the vulcanizates. SEM analysis was conducted to study how the failure mechanism was affected by the devulcanization process. It was possible to recover 70-80% of the original gum rubber properties by using this process. From IR spectroscopic analysis, we observed that the oxidation of the main chains did not occur during high-temperature milling.

Keywords: cracker-cum-mixing mill, cross-link density, cure characteristics, devulcanization, gum rubber vulcanizate, mechanical properties.

Introduction

The devulcanization and reutilization of cross-linked elastomers are difficult problem because of three-dimensional cross-linked network. This network makes the elastomer insoluble and infusible.

Discarded tires are one of the most serious sources of pollution in world. It is reported that approximately two billion tires in America was used as a landfill and the volume is increasing at a rate of 275 million tires per year.[1,2] Most of the tires are used as bumpers for ships or building reefs for marine life. The rubber powders are incorporated into roads, concrete and other materials.[2-5] Approximately 30% of scrap tires are burned as fuel, which produces many toxic gases, large amount of char and requires additional waste disposal. Landfills tires also creates serious health problem. They help for breeding of mosquitoes and rodents and create West Nile Virus. Another important problem which creates by tires are fire hazards because tire fire is lasted very long time. So, devulcanization of this cross-linked elastomer not only solves the waste disposal problem and maintains environmental quality but also saves the valuable and limited resource elastomer.

In every year numerous papers are published on the recycling of rubber where the waste rubber is used as filler or it is blended with virgin rubber. However, there are only few papers discussing the use of hundred percent waste rubbers to new rubber products.

Vulcanized natural rubber contains cyclic and mono, di and polysulfidic linkage at the cross-linked network structure.[6] According to Tobolsky *et al.*[7,8] these chemically cross-linked sulfur-sulfur bonds in diene rubber are the most weakest bonds[9] and it is responsible for oxidative degradation through interchange chemical mechanism. Hence, these sulfidic bonds can easily be cleaved by chemical (like diallyl disulfide) at high temperature. Many attempts were made to reuse the vulcanized natural rubber but no techniques reverts more than 50% mechanical properties of the vulcanized rubber. In the present investigation we have devulcanized the vulcanized natural rubber containing three different sulfur-accelerator ratios, by mechanical milling at high temperature in presence of diallyl disulfide as devulcanizing agent and compared the properties of vulcanized natural

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*e-mail: ckd@matsc.iitkgp.ernet.in

rubber and revulcanized natural rubber.

Experimental

Materials. Natural rubber NR (RMA 1X) was supplied by Birla Tyres (India), *N*-cyclohexyl-2-benzothiazyl sulfenamide (CBS) was supplied by Bayer (India) Ltd. Diallyl disulfide was supplied by Aldrich Chemcals (USA) 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. The rubber compound was cured at 150 °C for 15 min by compression moulding.

Mechanochemical Devulcanization Process. The vulcanized rubber compound was ground with the help of open cracker cum two roll mixing mill (own developed) at 110 °C for 10 min and was milled in open two roll mixing mill with simultaneous addition of diallyl disulfide and process oil at the same temperature. The advantage of this technique is that it gives fine elastic rubber powder, unlike cryoground rubber. Cryoground rubber is stiff and curatives do not easily dispersed in it. Fine elastic rubber powder developed by us, the curatives are easily dispersed[10] into it. This devulcanized rubber was vulcanized again with the addition of proportionate amount of sulfur, CBS and retarder 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 this graphs the optimum cure time, scorch 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 moulding 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. Five 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 5%. Hardness was measured in terms of Shore A.

Table I. Compound Formulation for Devulcanization Study

Ingredients (Phr)	High Sulfur (H)	Medium Sulfur (M)	Low Sulfur (L)
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

Determination of Cross-link Density. The cross-link density was determined by immersing the small amount of sample in 100 mL benzene for 72 hrs 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 up to constant weight. Then the chemical cross-link density was calculated by Flory Rehner equation.[11]

Fourier Transformed Infrared Spectroscopy (FTIR). Fourier Transformed Infrared spectroscopy were done using a NEXUS 870 FTIR (Thermo Nicolet) in dry air atmosphere in room temperature on original rubber sample and revulcanized sample directly. Spectra were taken from 4500-0 wave number (cm^{-1}) in the transmission mode.

Thermal Characterization. Thermo gravimetric analysis (TGA) was carried out using Universal V1.12E TA instrument in the temperature range 30-700 °C at a heating rate 20 °C/min.

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

Dynamic Mechanical Analysis (DMA). Dynamic mechanical properties of the vulcanizate were analyzed using a TA Instrument DMA 2980 dynamic mechanical analyzer under tension clamp. The samples were subjected to a sinusoidal displacement of 15 μm at a frequency of 1 Hz from -80 to 170 °C and a temperature rate of 5 °C/min.

Results and Discussion

Compounding formulations for high sulfur (conventional system), medium sulfur (semi EV system) and low sulfur (EV system) containing vulcanizate are represented in Table I. The amounts of additives such as sulfur and CBS were

Table II. Composition of Devulcanizing Agent per 100 phr Natural Rubber Vulcanizate

Ingredients (Phr)	H_a	H_b	M_a	M_b	L_a	L_b
Vulcanizate (H)	100	100	-	-	-	-
Vulcanizate (M)	-	-	100	100	-	-
Vulcanizate (L)	-	-	-	-	100	100
Process oil	6	6	6	6	6	6
Diallyl disulfide	0.70	1.00	0.70	1.00	0.70	1.00
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

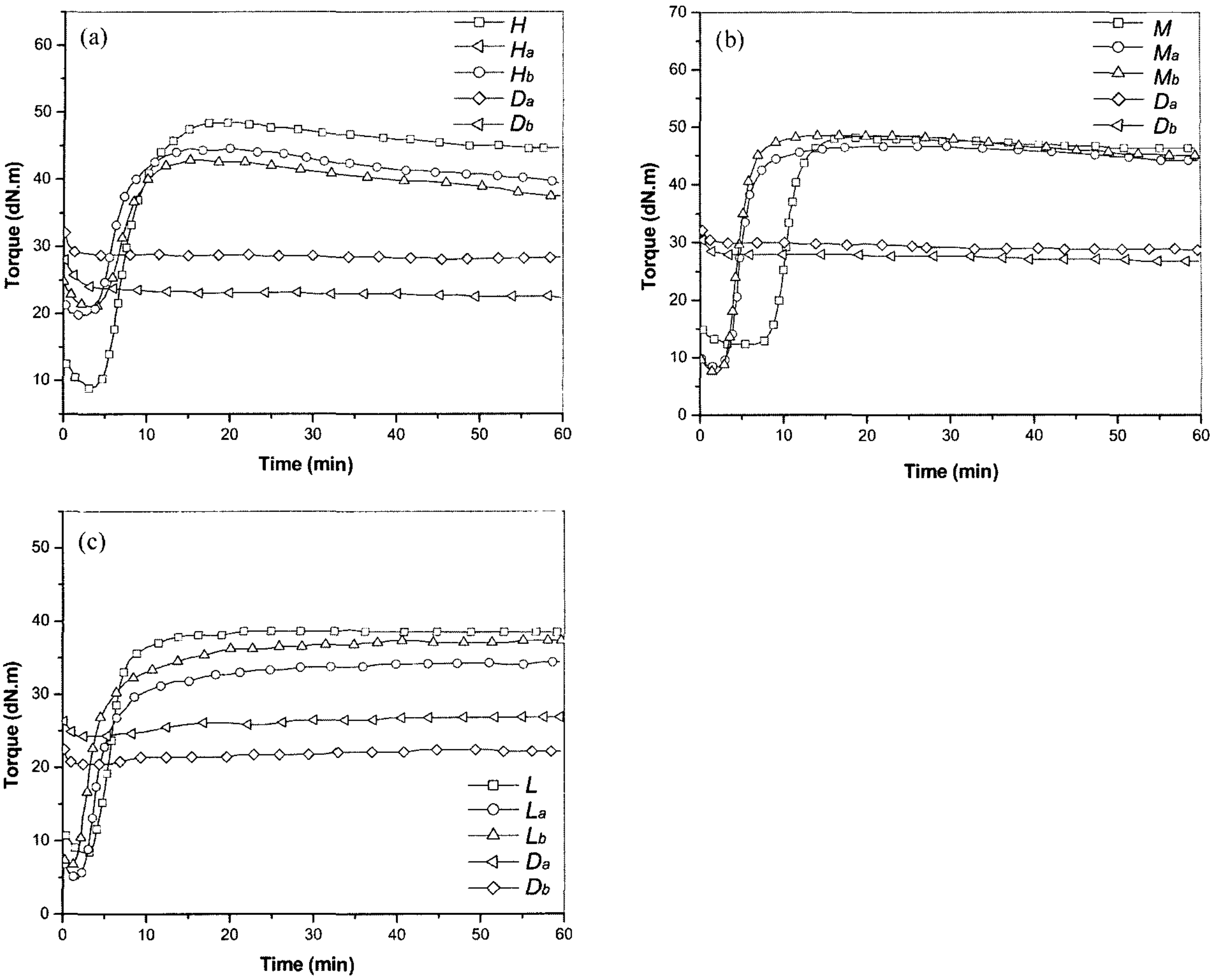

Figure 1. Rheometric plots of the vulcanizate. (a) high sulfur, (b) medium sulfur, and (c) low sulfur.

used based on 100 gm rubber irrespective of the amount of sulfur and CBS comes from devulcanized rubber in mixing, because it was observed in rheometric study that after devulcanization the rheometric curve was almost straight (Figure 1(a), 1(b) & 1(c), graph D_a & D_b), which indicates additives of NR devulcanizate, which was originated from parent compound were inactive.

Cure Characteristics of Rubber Vulcanizate. The torque verses time curves for high sulfur, medium sulfur and low sulfur containing vulcanizate with their corresponding revulcanized rubber were shown in Figure 1(a), 1(b), and 1(c). From these curves it was noted that the optimum cure time of three NR vulcanizate did not change with increasing the concentration of disulfide but the cure rate (t_{max} - t_{min}) increased with increasing the concentration of disulfide. This increase in cure rate may be due to the fact that with increasing concentration of disulfide, the devulcanization reaction increased and creates higher active cross-link sites in devulcanized rubber, accelerates the cross-linking reaction more when the devulcanized rubber heated at 150°C with sulfur and CBS. For all the cases the scorch time of revulcanized rubber decreases. This decrease in scorch time was due to presence of active cross-linking sites in the devulcanized rubber.[12] The compounds with longer scorch time had to accelerate the rate of cure in order to achieve same cure time (because cure time did not change with increase in disulfide concentration). This was why the revulcanized rubber containing higher concentration of disulfide had higher cure rate than the revulcanized rubber having lower amount of disulfide.

Mechanical Properties. Tensile strength, modulus, percentage of elongation at break, tear strength and hardness are shown in Table III and the stress strain curves of original natural rubber vulcanizate containing three different amount of sulfur and CBS with their corresponding revulcanized natural rubber are shown in Figure 2(a), 2(b) and 2(c). It was found from the table that modulus of all natural rubber vulcanizates increased with increasing concentration of disulfide in devulcanization step. This was due to two possible reason, one being restriction of molecular chain mobility

Table III. Vulcanizate Properties of Fresh Natural Rubber and Revulcanized Rubber

Sample Code	100% Modulus (MPa)	200% Modulus (MPa)	Tensile Strength (MPa)	% of Elongation at Break	Tear Strength (N/cm^2)	Hardness (Shore A)	Cross-link Density (moles/gm) $\times 10^4$	Gel Fraction (%)
H	0.51	0.81	16.82	1048	23.23	40	0.69811	
H_a	0.74	1.21	10.45	970	18.33	38	0.48756	
H_b	0.78	1.28	12.35	1007	19.21	40	0.62556	
M	0.62	0.93	15.4	1330	22.5	36	0.68361	
M_a	0.60	1.04	12.56	845	16.82	39	0.53401	
M_b	0.63	1.15	15.5	910	21.15	44	0.63026	
L	0.53	0.85	16.87	1300	18.26	32	0.67711	
L_a	0.53	0.82	14.1	1030	15.54	36	0.39024	
L_b	0.70	0.97	15	1010	17.01	37	0.41153	

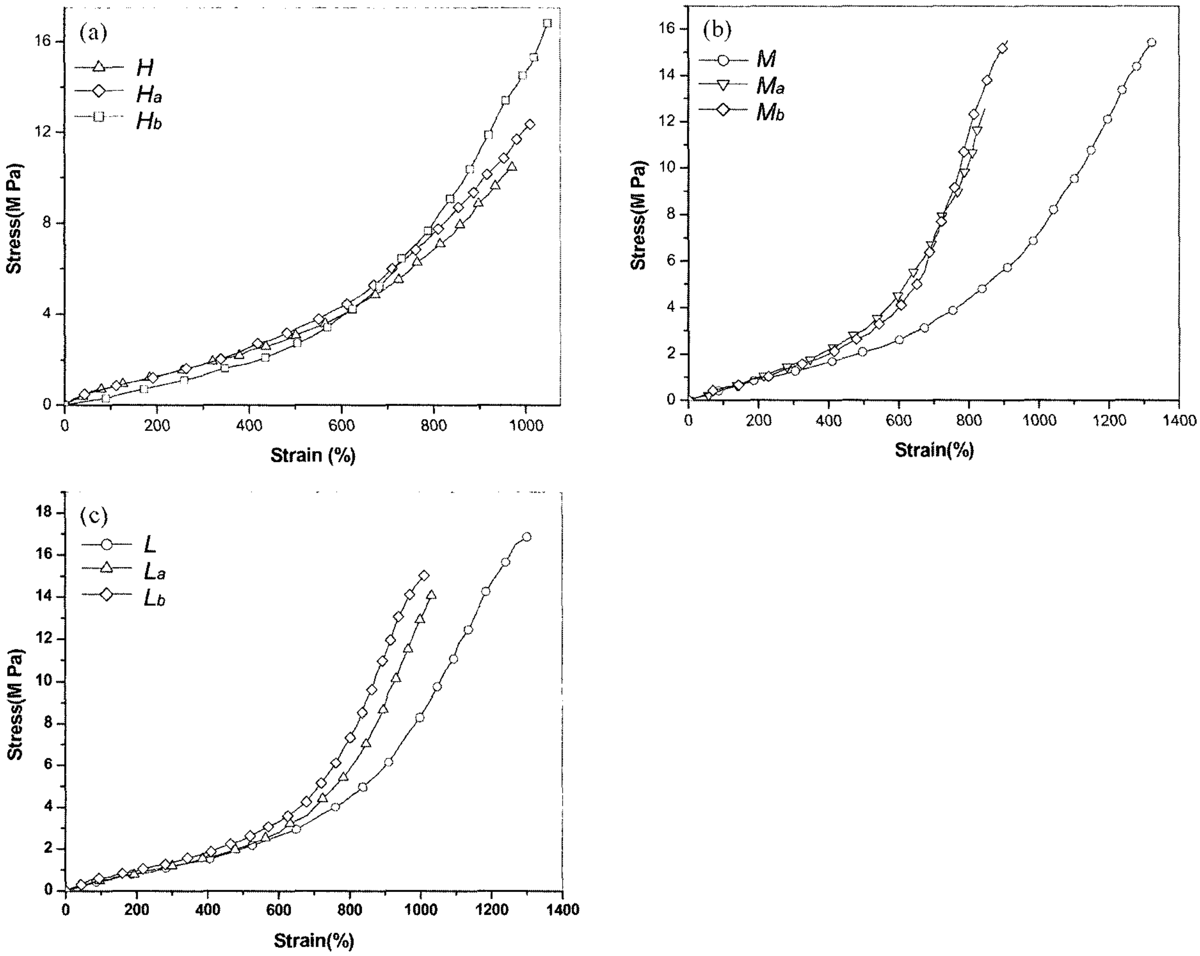

Figure 2. Stress-strain curves of the vulcanizate. (a) high sulfur, (b) medium sulfur, and (c) low sulfur.

and other being an increase in cross-link density. The latter can be explained by cross-link density data, which was shown in Table III. It was clear that addition of higher amount of disulfide increased the devulcanization reaction and increased the cross-link density in the next revulcanization steps. For former, revulcanized rubber contains certain amount of main chain degradation, which restricted the molecular chain mobility under tension force, and hence increased modulus. From all figures it was found that revulcanized natural rubber vulcanizate have lower tensile strength and percentage of elongation at break compared to original one. This can be explained as for revulcanized rubber contains certain amount of main chain degradation, which lowers the percentage of elongation and hence 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 to original vulcanizate, these are not dispersed in the continuous matrix of devulcanized rubber. Such types of gel remain as weak sites for stress transmission resulting lower tensile strength.[12]

From Table III it was clear that tear strength of revulcanized rubber were lowered than the original one, but it increased on increasing the concentration of diallyl disulfide, as on increasing disulfide concentration the devulcanization reaction increased and on revulcanization the cross-linking reaction increases. The hardness also increased with increasing the concentration of disulfide, whose results were shown in Table III. The increase in hardness of the vulcanizates was possibly caused by the increase in cross-link density as observed from theTable III.

Table IV. TGA Parameters

Sample Code	T_1	T_{10}	T_{50}	T_{90}
H	330	355	395	455
H_a	315	345	403	462
H_b	326	352	404	460

From the Table IV it was observed that the cross-link density of revulcanized rubber is increased with increasing the concentration of disulfide on devulcanization step. The cross-link density is increased with increasing the concentration of disulfide as the active cross-linking sites on devulcanized rubber are increased that create the new cross-link bond on revulcanization.

IR Spectral Analysis. FTIR spectra of original vulcanized natural rubber and corresponding revulcanized natural rubber were shown in Figure 3(a), 3(b) and 3(c). Typical polyisoprene peak were clearly detected in both the vulcanized natural rubber and revulcanized natural rubber. 1660 cm^{-1}

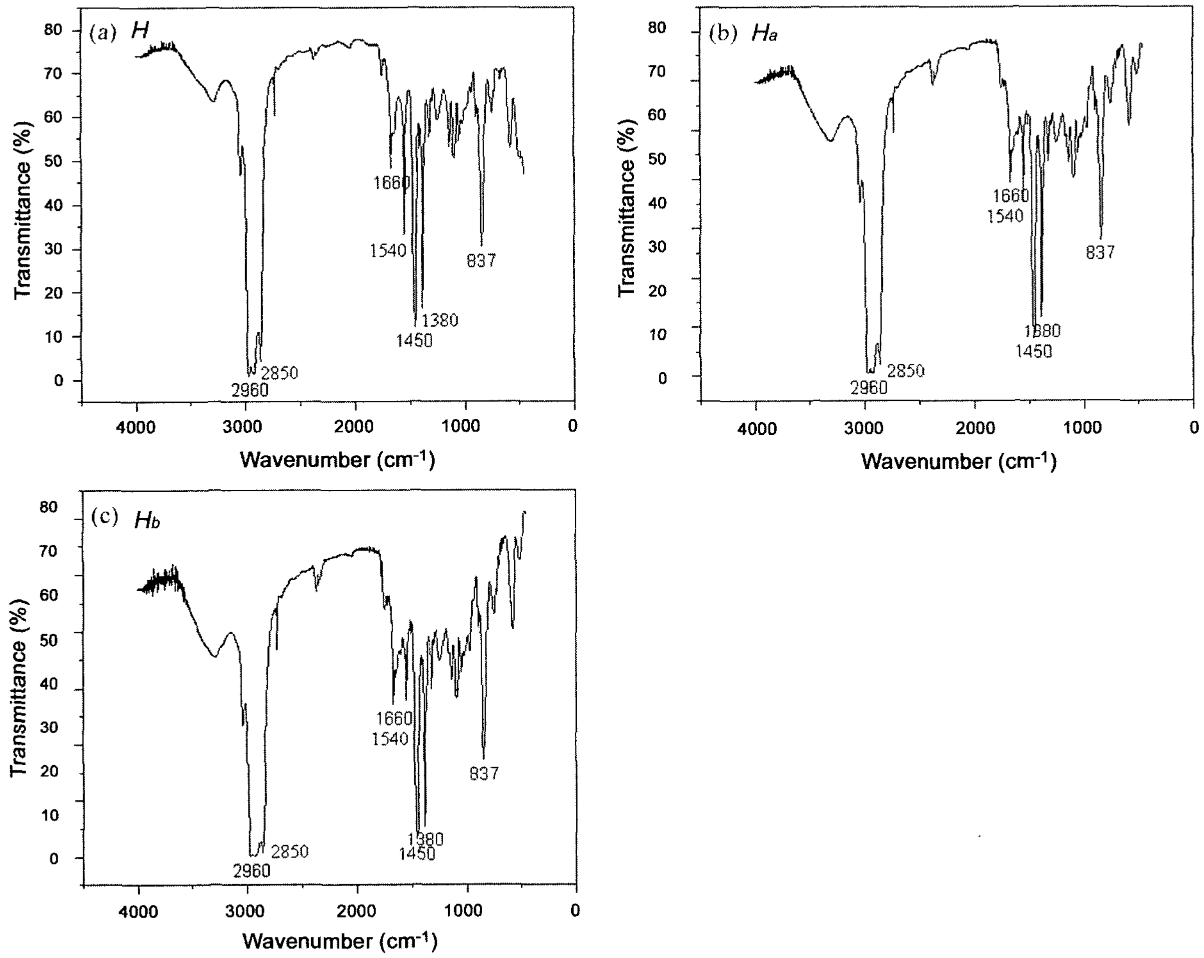

Figure 3. (a) FTIR of original rubber vulcanizate (high sulfur), (b) FTIR of revulcanized (high sulfur) rubber vulcanizate, and (c) FTIR of revulcanized (high sulfur) rubber vulcanizate.

for vCH$_2$, 1450 and 1380 cm^{-1} for δCH$_2$ deformation, 837 cm^{-1} for δC-H bending and peak from 2960 to 2 8 50cm^{-1} for vC-H saturated stretching were observed in the figure. There was an additional peak that appears for vulcanized natural rubber at 1540 cm^{-1} due to stretching frequency of methyl assisted conjugate double bond [ν-(CH=CH)$_n$-, Where $n > 6$].[13,14] It is well known that with increasing conjugated double bond (due to reversion), the mechanical properties of rubber compound decreases. With addition of retarder followed by revulcanization the transmittance intensity of the peak at 1540 cm^{-1} was diminished substantially (Figure 3(b), 3(c)). These observations suggest that retarder reacts with the carbon-carbon double bonds and slower the reversion reaction rate and hence increases the mechanical properties of the vulcanizates. Another important observation was that unlike Padella *et al.*[15] there was no peak in the range of 1730 cm^{-1} (> C=O stretching peak), which indicated that the oxidation of main polymeric chain did not occur at the time of rubber milling with the help of cracker cum mixing mill at high temperature.

Thermal Analysis. High temperature TGA (30-700 °C) curves of the vulcanizates were showed in Figure 4. The TGA curve for all vulcanizates shows one-step degradation. The onset degradation temperature (T_i), the temperature at which 10% degradation occurred (T_{10}), the temperature at which 50% degradation occurred (T_{50}) and the temperature at which 90% degradation occurred (T_{90}) were calculated from TGA plots and given in Table IV. It was observed that the onset degradation temperature was higher for vulcanized natural rubber than the revulcanized rubber and for revulcanized rubber it increased with increasing the concentration of disulfide on devulcanization step. The onset degradation temperature decreased in the case of revulcanized rubber due to decrease in cross-link density. Cross-linking increased the rigidity of the system, which in terns increased the thermal stability. The rate of degradation was almost same up to 90% degradation for all vulcanizate.

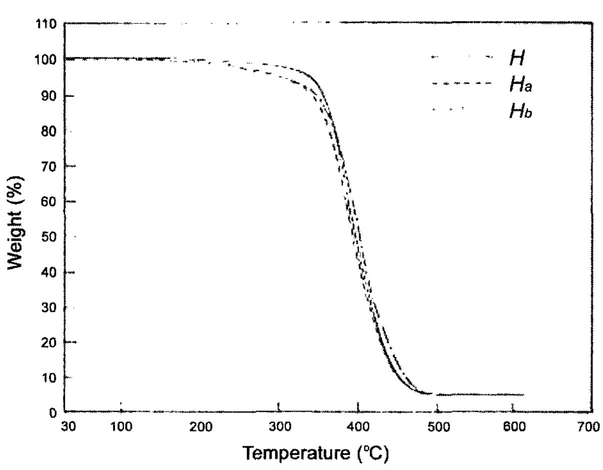

Figure 4. TGA plots of, (*H*) fresh rubber vulcanizate, (*H$_a$*) revulcanized rubber with lower amount of disulfide on devulcanization step, and (*H$_b$*) revulcanized rubber with higher amount of disulfide on devulcanization step.

DMA Analysis. The storage modulus, loss modulus and tanδ verses temperature plots were shown in Figures 5(a), 5(b), 6, and 7. Below the glass transition temperature (Figure 5(a)) of the vulcanizate, the storage modulus of revulcanized rubber was higher than the original vulcanizate and it increased with increasing the concentration of disulfide in devulcanization step. At above ambient temperature (Figure 5(b)) the storage modulus of the revulcanized rubber also higher than the original rubber vulcanizates as shown in Table VI. This may be due to increase in modulus of revulcanized rubber (Table III).

Figure 6 showed the loss modulus (E'') verses temperature of the vulcanizates. The T_g of the vulcanizates were taken at the maximum of E'' and shown in Table V. The increase in T_g of the vulcanizate is due to increase in molecular chain

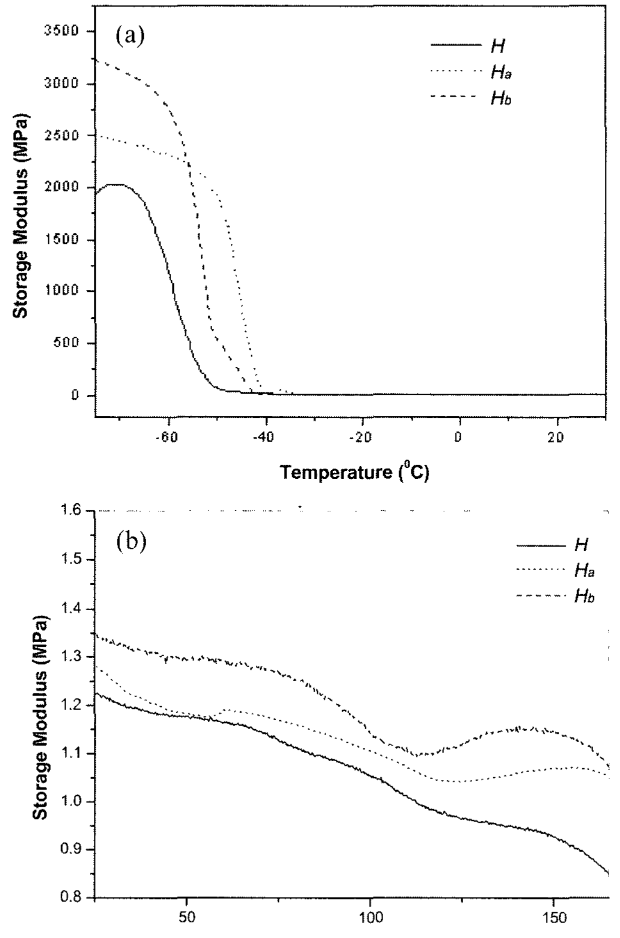

Figure 5. (a) Storage modulus of the vulcanizate (high sulfur) as a function of temperature (below room temperature) and (b) storage modulus of the vulcanizate (high sulfur) as a function of temperature (above room temperature).

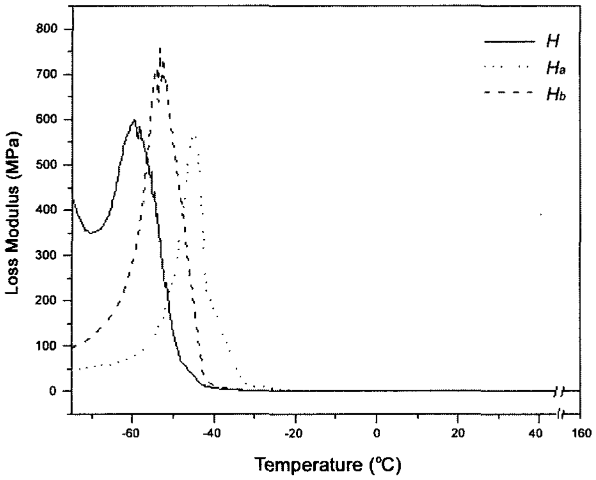

Figure 6. Loss modulus of the vulcanizate (high sulfur) as a function of temperature.

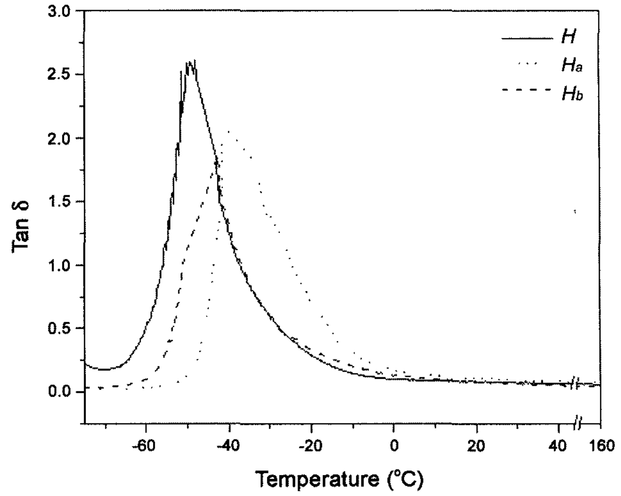

Figure 7. Tan δ of the vulcanizate (high sulfur) as a function of temperature.

mobility, decrease in cross-link density, as in revulcanized rubber. But the T_g value increased further with increasing the concentration of disulfide. This may be due to with increasing the concentration of disulfide the cross-link density on revulcanized natural rubber increased and chain mobility decreased. The E'' was slightly decreased for revulcanized rubber vulcanizate H_a, however for H_b, significant improvement in E''_{max} was observed.

The temperature variations of tanδ were shown in Figure 7. Only one relaxation was observed with in the temperature study. The α-relaxation peak of the vulcanizate was shifted to higher temperature side for vulcanizate H_a but it shifted again towards low temperature sides for vulcanizate H_b and the peak maxima decreased for vulcanizate H_b than the H_a. It seems that revulcanized rubber contain certain amount of main chain degradation (evidence from decrease in cross-link density, Table III), which restricted the molecular chain mobility, hence, the α-relaxation peak temperature shifted towards higher side.[16]

Table V. T_g of the Vulcanizates at its E''_{max} Value

Sample Code	T_g (°C)	E''_{max} (MPa)
H	-59.45	601.1
H_a	-45.13	567.6
H_b	-53.28	757

Table VI. Storage Modulus of the Vulcanizates at Different Temperatures

	Storage Modulus (MPa)					
Sample Code	25 °C	50 °C	75 °C	100 °C	125 °C	150 °C
H	1.122	1.177	1.127	1.055	0.9667	0.8375
H_a	1.286	1.183	1.171	1.105	1.043	1.068
H_b	1.353	1.293	1.267	1.14	1.122	1.146

SEM Study. The tensile fractured samples were scanned after gold coating and were represented in Figures 8(a), 8(b), 8(c) (conventional system) and 9(a), 9(b), 9(c) (semi EV system). The fractogram of the original gum rubber vulcanizate was represented in Figure 8(a) and 9(a). The smooth fractured surface observed here for all vulcanizates, which were the characteristic of gum-vulcanized elastomer. The micrograph of original vulcanizate showed the unidirectional tear path oriented along the direction of flow, which is smooth rubbery in nature. In Figure 8(b) and 9(b) (low disulfide containing revulcanized rubber) is again characterized by a unidirectional crack path without any folding making the vulcanizate high tensile and high elongation at break. With high disulfide containing vulcanizate (conventional system) (Figure 8(c)) the fracture mode is almost same, two unidirectional crack paths was observed. The presence of such types of crack path may be responsible for highest modulus vulcanizate because of higher cross-link density. Lower elongation at break for medium sulfur containing vulcanizate is probably responsible for brittle type of failure as evident from the Figure 9(b) and 9(c). Similar observations were observed in the case of EV system (not shown in the figure).

Conclusions

The vulcanized rubber caused problem on devulcanization. Therefore, we tried to solve this problem with mechanochemical devulcanization for effective reuse. This article describes the devulcanization process by diallyl disulfide, as devulcanizing agent, at high temperature with the help of open two roll cracker cum mixing mill. The cross-link density of the devulcanized rubber was decreased with increasing

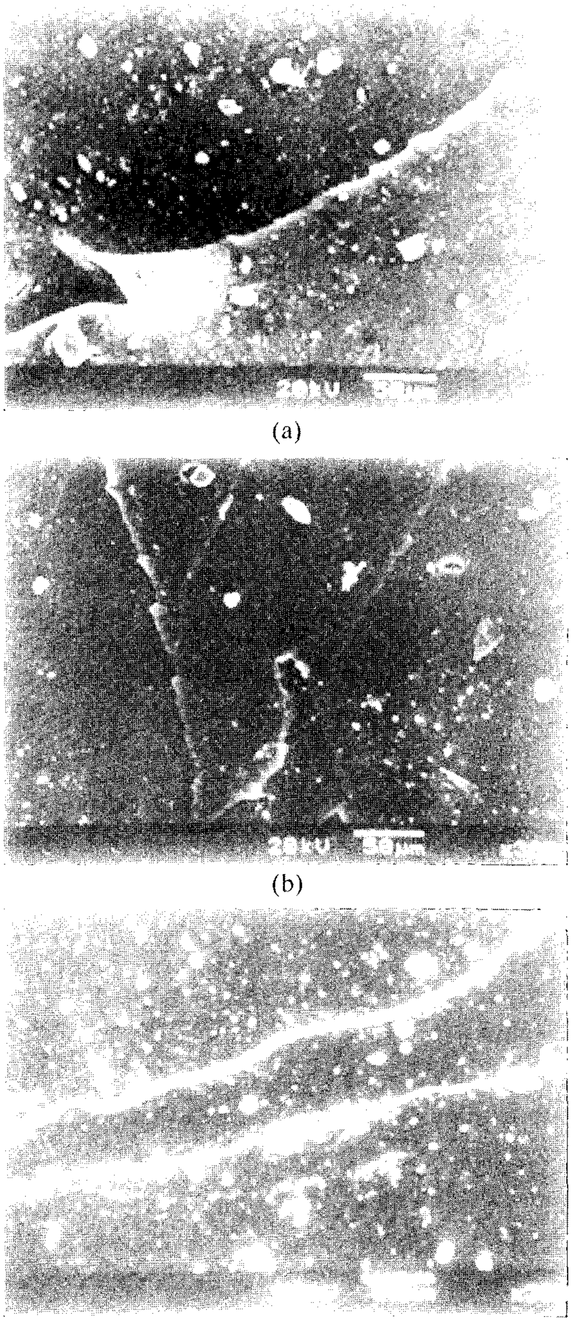

Figure 8. SEM photographs of, (a) fresh rubber vulcanizate, (b) revulcanized rubber with lower amount of disulfide on devulcanization step, and (c) revulcanized rubber with higher amount of disulfide on devulcanization step.

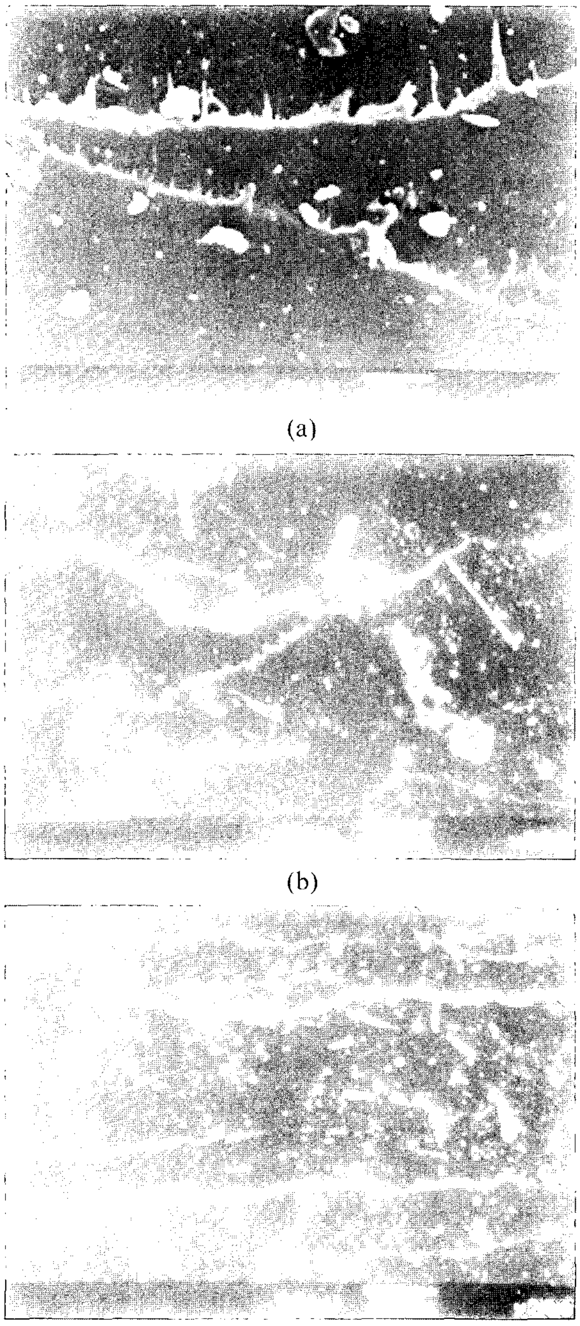

Figure 9. SEM photographs of, (a) fresh rubber vulcanizate, (b) revulcanized rubber with lower amount of disulfide on devulcanization step, and (c) revulcanized rubber with higher amount of disulfide on devulcanization step.

the concentration of disulfide. Next, we investigate the effect of diallyl disulfide on the revulcanized products. We used sulfur and CBS with devulcanized rubber, which was obtained from original rubber vulcanizate. The mechanical properties of the revulcanized rubber vulcanizate increased with increasing the concentration of disulfide on devulcanization steps. Optimum cure time of the revulcanized rubber vulcanizate was almost same to the original rubber vulcanizate. The rate of cure of revulcanized rubber increased with disulfide concentration, because with increasing the concentration of disulfide the active cross-link sides on the devulcanized rubber increases, which was well supported by cross-link density data and TGA analysis.

Therefore, we believe that devulcanization of vulcanized natural rubber is possible through mechanochemical process. The mechanical properties of the revulcanized natural rubber markedly depend on the concentration of disulfide.

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