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Recycling of scrap automobile tube

Mechano-chemical process (MCP) is an improved method for devulcanization of the scrap rubber through the application of mechanical shearing and a devulcanizing agent, at lower temperature of about 100°C. One of the most interesting observations is that the retention of tensile strength of devulcanized rubber, with respect to original rubber vulcanizate is higher when devulcanized in presence of devulcanizing agents. The formation of extra crosslink bonds for devulcanized rubber containing devulcanizing agent was confirmed by crosslink density data. The thermal stability and storage modulus are enhanced for devulcanized scrap tubes, accompanied by the loss of $\tan \delta$ values. SEM was studied to elucidate the fracture mechanism and the homogeneity of the vulcanizate after devulcanization. Three types of chemicals, namely aryl disulfide, benzyl disulfide, phenyl disulfide were taken into consideration as devulcanizing agents. It was observed that the type and dose of devulcanizing agents have tremendous effect on the recovery of the mechanical properties of the scrap automobile tubes after devulcanization. This process facilitates only the breakage of crosslinking sites, not the main chain, thus retaining the main chain properties. After devulcanization the crosslinking sites are produced, depending on the type and dose of the devulcanizing agent, which are responsible for the new crosslinking, when it is again devulcanized in presence of usual vulcanizing agents.

Key words: devulcanization, mechano-chemical process, devulcanizing agent

Recykling zużytych dętek samochodowych

Proces mechanochemiczny (MCP) to metoda dewulkanizacji odpadów gumowych udoskonalona przez zastosowanie obróbki mechanicznej w obecności substancji dewulkanizującej w temperaturze ok. 100°C. Spośród bardziej interesujących spostrzeżeń można wymienić fakt, że rewulkanizaty materiału uzyskanego z zastosowaniem środka dewulkanizującego w większym stopniu zachowują pierwotną wytrzymałość. Badania gęstości usieciowania potwierdziły obecność dodatkowych wiązań poprzecznych w próbkach zawierających związki przyspieszające dewulkanizację. Stabilność termiczna i składowa rzeczywista (elastyczna) modułu zespolonego gumy dętek wykonanych z rewulkanizatu ulegają poprawie, natomiast pogarszają się wartości tangens delta.

W celu wyjaśnienia mechanizmu degradacji badanego materiału oraz jego jednorodności po procesie dewulkanizacji dokonano analizy obrazów SEM. Substancjami dewulkanizującymi były: disiarczki aryłowy, disiarczki benzyłowy i disiarczki fenylowy. Zaobserwowano, że rodzaj i ilość użytej substancji ma ogromny wpływ na odzyskanie pierwotnych właściwości mechanicznych dewulkanizowanego materiału. Omawiany proces ułatwia jedynie destrukcję wiązań poprzecznych, łańcuchy główne polimeru nie ulegają degradacji, dlatego też właściwości materiału po dewulkanizacji, a następnie rewulkanizacji, pozostają niezmienione. Podczas dewulkanizacji tworzą się nowe miejsca umożliwiające powstawanie wiązań poprzecznych w procesie powtórnej wulkanizacji z udziałem powszechnie stosowanych zespołów sieciujących.

Słowa kluczowe: dewulkanizacja, proces mechanochemiczny, środek dewulkanizujący

1. Introduction

Elastomers have major class of applications, ranging from footwear to automobile tires. This is because

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of their unique mechanical properties such as very good elastic behavior even at large deformation, good energy absorbing capacity etc. To get the final shape of rubber product, vulcanization is an absolute must.

Development of a suitable process to devulcanize the rubber waste, especially worn out automobile tubes and tires is a worldwide problem and is becoming very much complicated due to their three-dimensional network structure, non-biodegradability and they can not be remelted or dissolved in organic solvents. Recent technology [1-4] to use the reclaimed and devulcanized rubber as virgin rubbers has attracted many rubber industries and researchers in this issue, are still limited in the literature. Many attempts have been undertaken to reuse the vulcanized elastomer, such as reclaiming [5-9], devulcanization [10-13], high-pressure high-temperature sintering [14,15], fuel recovery [16] and others.

In every year large number of papers are published on recycling of vulcanized rubber products where the rubber powder is used as a filler or blended with virgin rubber [17,18] or the modified rubber powder is incorporated in different composite materials [19-23]. However, there are few papers [14,15] discussing about the total use of waste rubber to new rubber products. Unfortunately no techniques recover more than 40% of the original rubber properties.

We have developed a newer type of process, where we used the mechanical shearing, thermal energy and delinking chemicals simultaneously for devulcanization termed as mechano-chemical process (MCP). The main advantage of this technique is that, it gives fine elastic rubber powder, unlike cryoground rubber. It is very difficult to disperse the curatives well into the cryoground rubber [24], but the elastic rubber which has been produced following our method, can accept the curatives uniformly throughout the mass and effectively dispersed it.

In the present work we have devulcanized the vulcanized rubber containing different concentrations of devulcanizing agents (aryldisulfide, benzyldisulfide, and phenyldisulfide) by mechanical milling.

2. Experimentation and measurements

2.1. Mechano-chemical devulcanization process

Vulcanized rubber compound was grounded with the help of an open cracker-gum-two roll mixing mill at 110°C for 10 minutes, and then milled in an open two roll mixing mill with simultaneous addition of the devulcanizing agents and the 1 phr of process oil at the same temperature. (The two-roll open cracker-gum-mixing-mill consists of both cracking zone and mixing zone on the same roll. The main function of this mill is

to reduce lump size. Its flight length, angle and land and sea ratio are so adjusted that the bigger lumps are automatically transferred, after being cracked, to the mixing zone, where we place the devulcanizing agent). The devulcanization formulation is given in Table-1A. This devulcanized rubber was revulcanized with sulfur, CBS and cure retarder (thiophthalimide type) at 145°C, up to the optimum cure time. Revulcanization formulation is given in Table-1B

Table 1A. Devulcanization formulation
Tabela 1A. Receptury dewulkanizatów

Sample	Aryldisulfide (phr)	Benzyl-disulfide (phr)	Phenyl-disulfide (phr)	Aged tube rubber (phr)	New tube rubber (phr)
OR	–	–	–	–	100
A	1.5	–	–	–	100
B ₁	–	1	–	–	100
B ₂	–	1.5	–	–	100
C ₁	–	–	1	–	100
C ₂	–	–	1.5	–	100
C ₃	–	–	1	100	–

Table 1B. Revulcanization formulation
Tabela 1B. Receptura rewulkanizatu

Ingredients	phr
Vulcanizate	100
MBTS	1.2
TMT	1
Sulphur	3.2
Retarder	1

2.2. Cure characteristics of rubber compound

Cure characteristics of the rubber vulcanizate have been studied using Monsanto Rheometer, R-100 at 145°C. Minimum torque, ML (dN·m); the maximum torque, MH (dN·m); the scorch time, t₂ (min) i.e. the time to two units of torque increases above the minimum; optimum cure time, t₉₀ (min) i.e. the time to 90% of maximum torque developed; state of cure {t_{max} - t_{min} (dN·m)} and cure rate index (CRI), i.e. the rate of rubber vulcanization were determined, where CRI = 100/(t₉₀ - t₂) min⁻¹.

2.3. Mechanical characterization

Vulcanized slabs were prepared by compression molding, and the dumbbell shaped specimens were

punched out. The tests were done by means of a universal tensile testing machine, Hounsfield H10KS. The modulus at 100% and 200% elongation, tensile strength, tear strength and elongation at break were measured at room temperature. The initial length of each specimen was 25 mm and the speed of the jaw separation was 500 mm/minute.

Three samples were tested for each set of conditions, at the same elongation rate. The values of the tensile strength, modulus at 100% and 200% elongation, elongation at break were averaged. Shore A hardness was measured.

2.4. Determination of cross-link density

The cross-link density was determined by immersing a small amount of sample in 100 ml benzene to attain equilibrium swelling. After this the sample was taken out from the benzene and the solvent was blotted

2.7. Scanning electron microscopy (SEM)

The tensile fracture surfaces of the samples were studied in a scanning electron microscope (JSM-5800 of JEOL Co.), after coating their surfaces with gold.

3. Results and discussion

3.1. Cure characteristics of revulcanized rubber

From the curing study, it is clear that the rate of cure of revulcanized rubber obtained by devulcanizing agent, benzyldisulfide, is higher than the revulcanized rubber obtained with devulcanizing agent, aryldisulfide, in original tube rubber at the temperature of 110°C. The devulcanizing agent phenyldisulfide was

Table 2. Curing characteristics
Tabela 2. Parametry wulkanizacji

Sample	Minimum torque (dN·m)	Maximum torque (dN·m)	Difference in torque (dN·m)	Scorch time (minute)	Cure time (minute)	Cure rate index
A	11	18	7	5	35	3.3
B ₁	11	30	19	5	30	4.0
B ₂	11	27	16	5	18	7.7
C ₁	17	30	13	4	27	4.3
C ₂	18	25	7	5	22	5.9
C ₃	10	27	17	6	23	5.9

from the surface of the sample and weighed immediately. This sample was then dried out at 80°C to constant weight. Then the chemical cross-link density was calculated by the Flory-Rehner equation [25].

2.5. Thermal characterization

Thermo-gravimetric analysis (TGA) was carried out using a Universal V1.12E TA instrument in the range 30°C–900°C at a heating rate of 20°C/min in a nitrogen atmosphere.

2.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of the vulcanizate were analyzed using a TA Instrument DMA 2980 dynamic mechanical analyzer in 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, with a heating rate of 5°C/min.

studied separately in original tube and aged tube. Phenyldisulfide shows the better curing properties in case of revulcanized aged tube in comparison to revulcanized original tube. This is probably due to the extent of breaking the cross-link bonds aided by benzyldisulfide is more in case of the original rubber vulcanizate (and phenyldisulfide in aged tube) at the time of mechanical milling and creates higher active cross-link sites in devulcanized rubber, which makes more new cross-link bonds at the time of revulcanization.

3.2. Mechanical properties of the revulcanized rubber

From the Table 3, it is evident that the modulus at 100% elongation and that in 200% elongation of revulcanized rubber is lower compared to original tube. This may be due to the degradation of main polymeric chain at the time of mechanical milling. From the Table 3, it is also clear that benzyldisulfide is more efficient in the original tube rubber. In aged tube phenyldisulfide is

Table 3. Mechanical properties
Tabela 3. Właściwości mechaniczne

Sample	100% modulus (MPa)	200% modulus (MPa)	Tensile strength (MPa)	% of elongation at break	Tear strength (N/mm)	Hardness (Shore A)	Crosslink density (moles/ml) $\times 10^4$
OR	1.85	3.22	11.2	1256	28.26	53	3.097
A	0.32	0.68	6.98	2007	19.26	35	1.539
B ₁	0.54	1.01	7.45	1576	18.30	44	1.106
B ₂	0.56	1.10	8.05	1680	21.26	46	2.636
C ₁	0.44	0.82	7.87	1384	20.00	49	3.935
C ₂	0.48	0.85	7.70	1427	18.87	46	2.885
C ₃	0.88	1.24	8.96	1224	27.75	50	5.382

more efficient than in original tube. Same trends have been observed during estimation of tear strength and hardness. The increase in hardness of revulcanized rubber is probably due to increase in crosslink density.

3.3. Thermo-gravimetric analysis (TGA)

Table 4 shows the thermo gravimetric analysis of the original tube and revulcanized rubbers. It can be seen from the table 4 that, with the addition of devulcanizing agents, onset degradation temperature of revulcanized rubber increases in comparison to original rubber tube. However, onset degradation temperature has found to decrease in the revulcanized rubber aided by benzyldisulfide. The delayed degradation in case of revulcanized rubber aided by phenyldisulfide, suggests more thermal stability of revulcanized rubber.

Table 4. TGA parameters of the vulcanizates
Tabela 4. Parametry TGA wulkanizatów

Sample	Onset degradation temperature (°C), T ₁	Completion temperature (°C), T ₂	% weight loss
OR	199.32	575.20	96.78
A	201.90	566.41	95.56
B ₁	195.22	549.12	94.97
B ₂	174.14	557.16	96.51
C ₁	365.10	550.30	97.00
C ₂	382.90	551.10	96.90
C ₃	381.20	548.90	97.10

3.4. Dynamic mechanical analysis (DMA)

Figure 1 shows the temperature dependence of the storage modulus (E') for the original tube and different

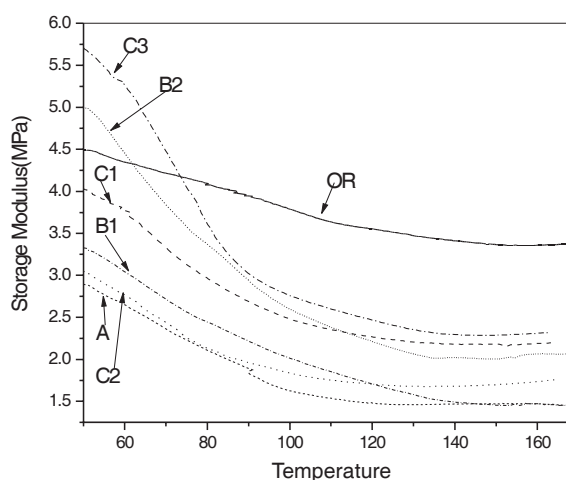


Figure 1. Variation of storage modulus as a function of temperature

Rysunek 1. Zmiany składowej rzeczywistej modułu zespolonego w funkcji temperatury

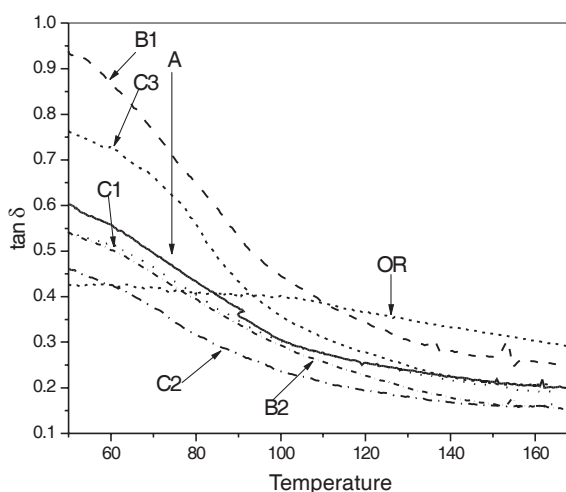


Figure 2. Variation of tan delta as a function of temperature

Rysunek 2. Zmiany tangens delta w funkcji temperatury

Table 5A. Variation of storage modulus as a function of temperature

Tabela 5A. Zmiana składowej rzeczywistej modułu zespolonego w funkcji temperatury

Sample	Storage modulus (MPa) at 60°C	Storage modulus (MPa) at 100°C	Storage modulus (MPa) at 140°C	Storage modulus (MPa) at 170°C
OR	4.345	3.788	3.414	3.380
A	2.640	1.630	1.483	1.449
B ₁	3.074	2.006	1.505	1.449
B ₂	4.573	2.585	2.028	2.050
C ₁	4.260	2.890	2.260	2.160
C ₂	3.210	2.090	1.690	1.680
C ₃	6.000	3.440	2.470	2.270

revulcanized rubbers. With increase in temperature the storage modulus of the revulcanizates sharply decrease.

Table 5B. Variation of tan delta as a function of temperature

Tabela 5B. Zmiana tangens delta w funkcji temperatury

Sample	tan δ at 60°C	tan δ at 100°C	tan δ at 140°C	tan δ at 170°C
OR	0.097	0.105	0.097	0.084
A	0.211	0.188	0.152	0.137
B ₁	0.165	0.145	0.119	0.105
B ₂	0.195	0.171	0.139	0.120
C ₁	0.130	0.130	0.110	0.090
C ₂	0.150	0.140	0.110	0.090
C ₃	0.130	0.150	0.110	0.090

It is due to the decrease in stiffness of the revulcanizates. The increase in storage modulus suggests improvement in degree of cross linking. Table 5A shows that the storage modulus of original tube, A, B₁, B₂, C₁, C₂ and C₃.

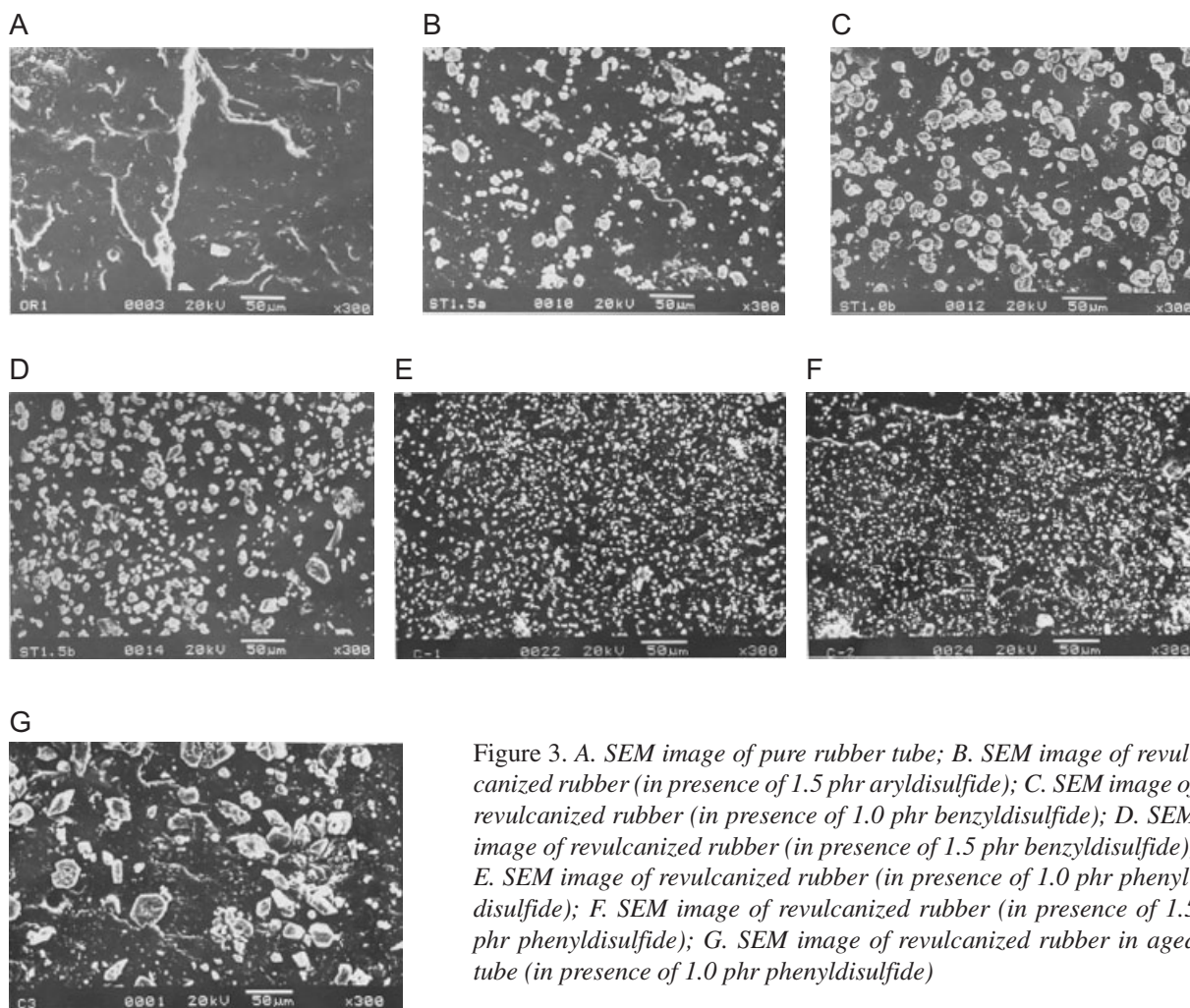


Figure 3. A. SEM image of pure rubber tube; B. SEM image of revulcanized rubber (in presence of 1.5 phr aryl disulfide); C. SEM image of revulcanized rubber (in presence of 1.0 phr benzyl disulfide); D. SEM image of revulcanized rubber (in presence of 1.5 phr benzyl disulfide); E. SEM image of revulcanized rubber (in presence of 1.0 phr phenyl disulfide); F. SEM image of revulcanized rubber (in presence of 1.5 phr phenyl disulfide); G. SEM image of revulcanized rubber in aged tube (in presence of 1.0 phr phenyl disulfide)

Rysunek 3. A. Obraz SEM wyjściowej gumy dętkowej; B. Obraz SEM rewulkanizatu (dewulkanizacja w obecności 1,5 phr disiarczku arylowego); C. Obraz SEM rewulkanizatu (dewulkanizacja w obecności 1,0 phr disiarczku benzylowego); D. Obraz SEM rewulkanizatu (dewulkanizacja w obecności 1,5 phr disiarczku benzylowego); E. Obraz SEM rewulkanizatu (dewulkanizacja w obecności 1,0 phr disiarczku fenylowego); F. Obraz SEM rewulkanizatu (dewulkanizacja w obecności 1,5 phr disiarczku fenylowego); G. Obraz SEM rewulkanizatu w dętce poddanej starzeniu (dewulkanizacja w obecności 1,0 phr disiarczku fenylowego)

Variation in $\tan \delta$ with temperature is being displayed in Figure 2. Only one relaxation peak was observed over the whole temperature range. The maximum loss tangent is higher for revulcanized rubber A than B or C. It is accepted that the higher the $\tan \delta_{\max}$ the greater is the mechanical loss. This is due to the improved cross-linking of the devulcanizing agent arylsulfide, benzyldisulfide and phenyldisulfide respectively.

3.5. SEM study

SEM micrographs of the original tube and revulcanized rubber are taken into study (Figure 3A-3G) to describe the phase morphological structure and homogeneity of the vulcanizates. Homogeneous distribution is exhibited throughout.

The tensile fractured samples were scanned after the gold coating and are shown in the figures 3A-3G. The micrograph of original vulcanizate showed the unidirectional tear path oriented from a flow, which is smooth rubbery in nature. For the revulcanizates the homogeneity of the distribution is better in case of 1.5 phr benzyldisulfide (fig. 3D) used as devulcanizing agent than that of 1.5 phr arylsulfide (fig. 3B) when used as devulcanizing agent, suggesting highest cross-linking density in the former case. The morphology becomes more homogeneous when phenyldisulfide is used as devulcanizing agent accompanied by smaller particle distribution when 1.5 phr is used (fig. 3E and 3F). However, when aged tube has been considered the particle size distribution is larger which may be due to the presence of certain unde vulcanized portions of highly crosslinked aged tube during the service life.

4. Conclusions

In this study, the mechano-chemical devulcanization process has been applied to the tube rubber waste generated from the scrap tube. It represents a novel method for making value-added rubber product from waste tube. The mechanical properties like modulus, tensile strength, tear strength, cross-linking density of revulcanized rubber obtained in presence of disulfides, were higher compared to revulcanized rubber obtained in absence of disulfide. These indicate that the disulfides play an important role in the devulcanization of the waste tube. Amongst the three disulphidic devulcanizing agents studied the phenyldisulphide serves the best possible purpose that arylsulfide and benzyldisulphide.

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