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Recycling NR/SBR waste using probe sonication as a new devulcanizing method; study on influencing parameters

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In this work, a vulcanized blend of natural rubber (NR) and styrene butadiene rubber (SBR) (*i.e.* at weight ratio of 50 : 50) as a model for tire rubber was devulcanized using probe sonication. The effect of processing parameters such as sonication media, power, temperature and time on sol/gel contents and devulcanization percent of rubbery samples was investigated. Moreover, the influence of pre-immersion of vulcanized NR/SBR samples in different liquids (*i.e.* water, oil and toluene) was assessed for different sonication times (*i.e.* 10 to 60 min) and powers (*i.e.* 30 to 60 W). It was found that pre-immersion of rubber particles in oil significantly increased the devulcanization percent. The optimum conditions for devulcanization of the NR/SBR blend *via* probe sonication were found to be 60 Watts, 20 min, oil and 24 h for sonication power, sonication time, pre-immersion/sonication media and pre-immersion time, respectively. The highest obtained devulcanization percent in this step was about 40%. The effects of two devulcanizing chemical agents (*i.e.* diphenyl disulfide and VitaX) on devulcanization performances of the samples were also studied. Results showed that higher devulcanization percent (*i.e.* about 52%) was obtained by using VitaX. It was also observed that VitaX significantly improved re-vulcanization speed (*i.e.* cure rate index) and decreased scorch time. It was also found that lower content of VitaX (*i.e.* 0.6 phr) caused better curing properties but lower mechanical properties compared to the higher content (*i.e.* 1.2 phr).

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1. Introduction

Elastomers are a specific category of polymeric materials whose applications have been progressive in the modern-day world.^{1–3} There are various applications for elastomers ranging from medical to the tire industry. Cross-linking through vulcanization induces suitable physical/mechanical properties in elastomers^{4–6}

Nowadays, automobiles have become an undeniable human need. On this basis, the need for tire rubber has increased significantly in past decades. Millions of tires are produced annually in the world and they are turned into waste after usage. The tire waste, due to their huge content and negative effects on ecosystems, have become a major environmental problem. On this basis, recycling of waste tire rubber has been essential from environmental and economical points of view.^{7,8}

Some methods were used for elimination of waste tire rubbers that include burning as a heat source,⁹ landfilling,^{10,11} reclaiming^{12–14} *etc.* It has been known that burning and landfilling of tire rubbers impact environment by releasing

greenhouse gases (*i.e.* SO_x and CO_x) in the air and immigration of the toxic low molecular weight organic matters in to the soil, respectively.

Rubber reclaiming attracted attention of researchers in the beginning. However, reclaimed ground tire rubbers (GTRs), due to the very low mechanical properties, disappointed producers. In fact, during reclaiming a rubber, thermal/mechanical stresses are encountered to ground waste rubber particles that cause fracture in the polymer backbone and so significant decrement in the mechanical properties of the recycled product.^{15–17}

On this basis, an effective method is needed for recycling waste rubbers. Literature review among published articles in this field shows that devulcanization (*i.e.* reverse process of vulcanization) is a promising method for this purpose.^{18–20} Different methods has been introduced for devulcanization of rubbers especially for ground tire rubbers (GTRs). For instance, mechanical,²¹ thermal,²² thermo-mechanical,²³ chemo-thermo-mechanical,²⁴ ultrasonic²⁵ and microwave^{26,27} processes has been used for devulcanization of waste rubbers.

The aim of devulcanization is breaking in C–S and S–S bonds (*i.e.* cross-links) instead of C–C bonds (*i.e.* backbone) in the vulcanized rubber network. In theory, fracture in C–C bonds needs to higher energy than C–S and S–S bonds, but in real condition both chain scission and cross-link breakage occur

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during devulcanization.²⁸ On this basis, the best devulcanization method is a process with higher cross-link breakage to chain scission ratio.

Using ultrasonic waves is one of the most considerate methods for waste rubber recycling. Two sonication based methods have been conventionally used for rubber recycling: extrusion-sonication of waste rubber and sonication of rubber particles in an ultrasonic bath. Liang and Isayev *et al.*²⁹ used ultrasonic waves for devulcanization of rubbers by combination of sonication and extrusion methods. They assessed the effect of rubber compound and ultrasonic amplitude on devulcanization of unfilled and silica-filled natural rubber. Based on the results, ultrasonic amplitude had a direct relationship with power. However, the die pressure illustrated an inverse trend which is a consequence of rubber thixotropic properties and declining in the chain breakage. Also, sonication caused breaking in the NR chains that caused declining in the rubber-silica connections. The devulcanization of SBR contained carbon black (CB) was also investigated.^{30–32} It was performed by an extruder equipped to an ultrasonic die. It was claimed that the devulcanized samples prepared from devulcanized SBRs had close properties to the virgin rubber. The devulcanization of BR and SBR/BR blend *via* sonication-extrusion process was also investigated by Liang *et al.*^{33,34} They evaluated effects of different fillers (*i.e.* carbon black, silica and silanized silica) by a single screw extruder and various ultrasonic amplitudes. It was found that carbon black promoted the mechanical properties of SBR/BR blend compared to silica filler. It was proposed that CB made some bridges in rubber structure which caused improved properties. Based on the experiments, silica containing BR that contained long side branches, showed strong rubber-filler interactions that caused better distribution of silica in rubber matrix but declined rolling resistance of the rubber.

Saputra *et al.*³⁵ investigated effect of deep eutectic solvents and their content at different heating times on devulcanization of GTR in an ultrasonic bath. They assessed the relationship between devulcanization performances and solvents viscosity. It was found that low viscosity solvent led to success in de-cross-linking process. They realized that increase in the heating time caused decline in the cross-link density and enhancement of devulcanization percentage. The Horikx theory was also used to determine chain scission to cross-links breakage ratio. It was found that the most broken bonds belonged to cross-links which exposed to a selective devulcanization.

Kim *et al.*³⁶ investigated devulcanization of waste tire rubber through probe sonication. They studied devulcanization of rubber through determination of prepared free sulfur content that formed by cross-links breakage. The rubber fragments were prepared by cryogenic processing of tire scrap (*i.e.* both the tread wear and sidewall). The fragmented samples were immersed in acetone for 24 h to extract plasticizers, paraffin's and antioxidants. The samples showed increased volume that confirmed suitable swelling. Thereafter, the samples were sonicated by a probe ultrasonic device and then refluxed and filtered to remove carbon black. The samples then dried and analyzed for sulfur content. It was found that sonication in

presence of H₂O₂ effectively increased fracture in the sulfur bonding and cross-links.

Based on the literature review, it was found that sonication-based devulcanization of waste rubbers have been studied in few researches. Besides, in most cases ultrasonic devulcanization performed by altering mechanical stresses (*i.e.* in an extruder) along with sonication by a horn or ultrasonic bath.³⁷ In one investigation, probe sonication was used for devulcanization of waste tire rubber but the devulcanization properties (gel/sol fractions and devulcanization percentage) and process parameters (sonication power, time and *etc.*) were not assessed. Due to the fact that probe sonication is a simple method and involve higher energies to the rubber particles (*e.g.* GTRs) compared to sonication bath, investigating the method and the influencing parameters would be a challenging subject.

In this study, probe sonication was used for devulcanization of a cured NR/SBR blend as a model tire rubber. For this purpose, NR/SBR blend (*i.e.* at NR : SBR ratio of 50 : 50) was prepared and vulcanized. The sample were ground to particles with mesh size of 16. The crumbed particles were devulcanized by probe sonication and also sonication in presence of chemical agent (DPDS and VitaX). Effect of sonication media, swelling media, sonication power-time and chemical agent content on devulcanization percent, cross-link density, sol/gel fractions, curing and mechanical properties of the devulcanized samples was evaluated. The samples characterized with oscillating disc rheometer (ODR), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric (TGA) analysis. Finally the mechanical properties of the recycled rubbers in blend with pristine rubber was evaluated.

2. Experimental

2.1. Material

Masterbatches of styrene-butadiene rubber (SBR) and natural rubber (NR) were supplied from Mouj Andishe Novin Baspar Company (Tehran, Iran) that their components are listed in Table 1.

2.2. Preparation of vulcanized NR/SBR

SBR and NR compounds were blended at NR : SBR ratio of 50 : 50. The master batches were mixed by a two-roll mill at room temperature for 15 min. At this stage, 1.5 phr of sulfur and 1.5 phr of *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS) were added to the rubber as vulcanizing agent and curing accelerator, respectively. After homogenization and 24 hours conditioning,

Table 1 The composition of the used NR and SBR master batches

Sample	NR Masterbatch (phr)	SBR Masterbatch (phr)
Raw elastomeric gum	100	100
Carbon black (N550)	60	60
Process oil	20	20
ZnO	5	5
Stearic acid	1	1



Finally, the samples were dried in an oven at 70 °C for 12 h to evaporate the rest of solvent and then weighted again. The cross-link density (eqn (1)) was calculated using Flory–Rehner equation⁴¹ as following:

$$\text{CLD} = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{V_1 \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right)} \quad (1)$$

Where V_r , χ and V_1 depict the volume fraction of the polymer in the swollen sample, the Flory–Huggins polymer–solvent interaction parameter and the molar volume of the solvent (106.3 mL mol⁻¹), respectively. The Flory–Huggins polymer–solvent interaction parameter (χ) for NR/SBR blend was considered as 0.393.²⁴

The volume fraction of polymer in swollen specimen (V_r) was measured as following:

$$V_r = \frac{\frac{\text{weight of rubber}}{\text{density of rubber}}}{\frac{\text{weight of dry rubber}}{\text{density of rubber}} + \frac{\text{weight of solvent absorbed}}{\text{density of solvent}}} \quad (2)$$

The density of dry samples was measured according to ASTM D6814 (ref. 42) using the eqn (3) as following:

$$\text{Density at } 23 \pm 2 \text{ °C g cm}^{-3} = 0.793 \times \frac{A}{A - B} \quad (3)$$

In which, A and B are weight of the specimen in air (g) and methanol (g), respectively. On this basis, the density of pristine NR/SBR sample was obtained 1.129 g cm⁻³.

The devulcanization percentages of the samples was also calculated using eqn (4):⁴¹

$$\text{DP (\%)} = \left[1 - \left(\frac{\text{Cross-link density of devulcanized rubber}}{\text{Cross-link density of control crumb rubber}} \right) \right] \times 100 \quad (4)$$

2.8. Characterization methods

Pyrolysis Fourier transform infrared spectroscopy (Pyrolysis-FTIR) analysis was performed by a PerkinElmer TGA 8000 instrument. Thermogravimetric analysis (TGA) was performed on the samples by NETZSCH STA 449 F3 Jupiter device (Germany) at heating rate of 10 °C min⁻¹ to provide information about thermo-oxidative degradation of the samples.⁴¹ Differential scanning calorimetry was carried out in N₂ environment at heating rate of 10 °C min⁻¹ in the range of -100 to 300 °C by NETZSCH DSC 200F3 instrument to depict curing behavior and glass transition temperature of the samples before and after devulcanization. The curing behavior of samples were evaluated at 160 °C in an oscillating disk rheometer (ODR) (Monsanto, R-100 Oscillatory Disk rheometer) according to ASTM D 2084.⁴³

The tensile tests were carried out on dumbbell-shaped specimens (type C) using a SANTAM STM150 Universal Machine at room temperature (25 ± 2 °C) to evaluate tensile strength and elongation at break of the pristine and re-vulcanized samples based on the ASTM D 412.⁴⁴ The uniform crosshead speed of 500 mm min⁻¹ was applied in tension and the test was repeated 10 times for each sample.

3. Results and discussions

3.1. Effects of pre-immersion and sonication media

Three kinds of liquids (*i.e.* oil, water and toluene) and their mixture were used as sonication media in this study. To compare effect of different liquids, the ultrasonic power and time were kept constant (*i.e.* 45 Watt and 20 min), at the first step. Results are shown in Fig. 1.

Fig (1a) shows the effect of sonication media on devulcanization percentage. It is clearly seen that type of sonication media affects the devulcanization percent (*i.e.* in the samples processes without pre-immersion). It is well known that breakage of these bubbles induce sonication energy to the ground rubber particles. However, due to the hydrophobic nature of rubber particles, they had not intimate contact to water (in contrary to toluene) that this decreased induced

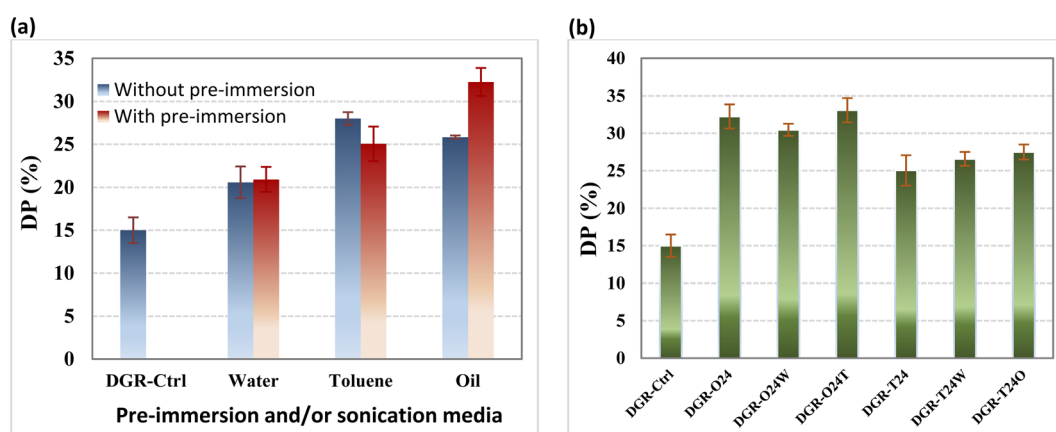


Fig. 1 The devulcanization percentage of the samples in different liquids (*i.e.* sonicated at 45 W for 20 min): (a) effect of pre-immersion and (b) effect of using different liquids for pre-immersion and sonication.



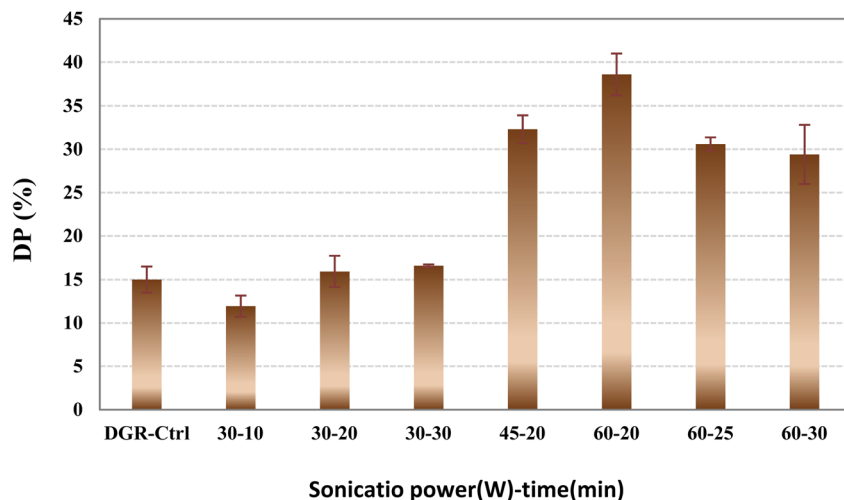


Fig. 2 Devulcanization percent of the DGR-O24 samples sonicated at different powers and times in oil (after 24 h pre-immersion in oil).

highest DP was obtained at sonication power and time of 60 W and 20 min (38%), respectively. Similar to the CLD and sol fraction results, herein the DP increased with increment in the induced energy. The reverse results was obtained at sonication times of 25 and 30 min at amplitude of 60 W. It was postulated that due to the very high energies encountered to the particles, their surface scorched and formed an insulated layer which decreased wave intrusion toward the particles core. Fig. 3 shows a schematic for partial devulcanization of the rubber particles that happened under probe sonication.

In these schematic, the mechanism of partial devulcanization of ground rubber particle due to sonication was illustrated. The degree of cross-links breakage incredibly depends on ultrasonic amplitude, time and kind of liquid. The more sonication amplitude causes decrement in the area of intact cross-linked core and improvement in the DP and crosslinks breakage. In contrast, at low sonication powers, devulcanization just occurs at a thin surface layer of the particles.

3.3. Effect of chemicals agents

On the basis of the obtained results, DGR-O24(60-20) and DGR-O24(30-10) samples were selected as the best and worst

devulcanized samples by probe sonication. The effect of chemical agents (*i.e.* DPDS and VitaX) on devulcanization performances was evaluated in these samples. Table 3 shows the CLD and sol/gel fraction results. It was found that using VitaX caused better devulcanization of the samples compared to DPDS at both low and high sonication energies. The CLD and sol fraction of the samples decreased using VitaX. In fact, it decreased chain scission and increased cross-links breakage. In contrary, DPDS caused significant decrease in the sol fraction while considerable increase in the CLD. It means that DPDS caused some new cross-linking in the rubber structure. It was occurred due to accelerating effect of DPDS during revulcanization process. It also enhanced the chain scission at the same time. The negative effect of DPDS was not observed at lower sonication energy and time (*i.e.* 30 W for 10 min).

Fig. 4 shows that both chemical agents significantly increased devulcanization percent of the sonicated samples (DGR-O24), however, higher DPs were obtained using VitaX. Devulcanization percent was improved considerably at higher VitaX loading content (*i.e.* 1.2 phr). The VitaX content had negligible effect on devulcanization percent at lower sonication energies. Furthermore, DPDS had lower impact on

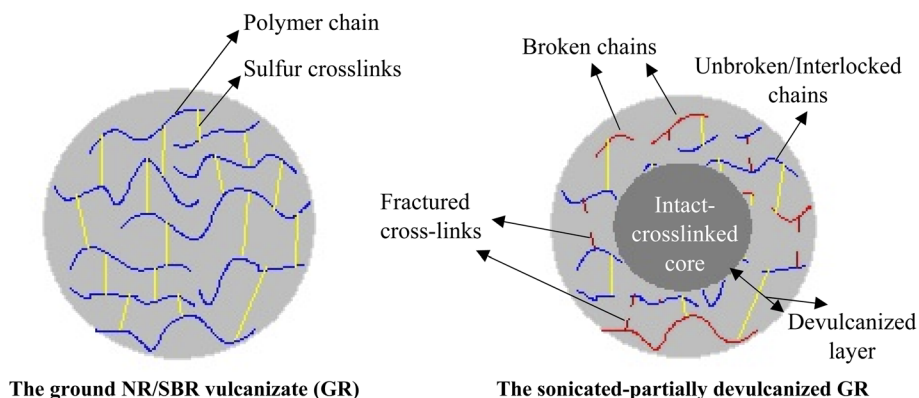


Fig. 3 Schematic of devulcanization of rubber particles under probe sonication.

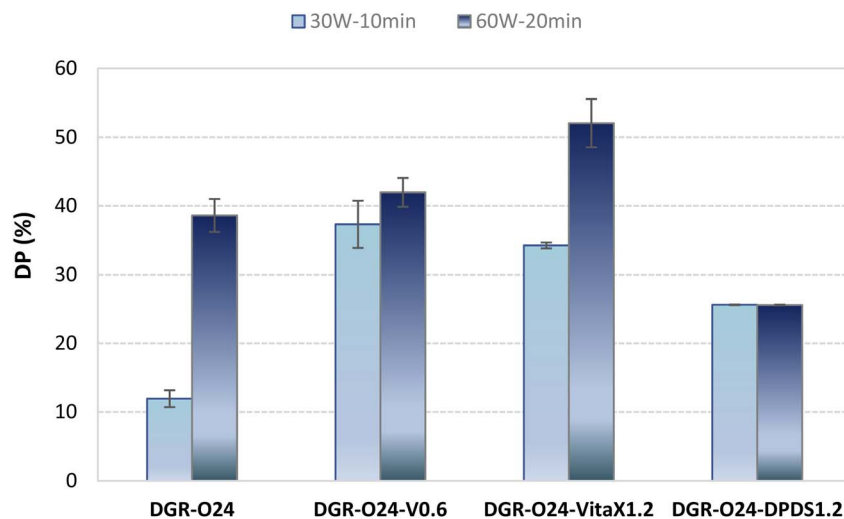


Fig. 4 Devulcanization percent of the samples devulcanized in presence of different chemical agents.

devulcanization percent compared to VitaX at low and high sonication energies. The better results obtained by VitaX were related to its complex chemistry and its different application process.²⁷ In fact, using processing oil along with VitaX caused more intrusion of the VitaX into the particles core. On the other hand, using VitaX increased the thickness of the devulcanized layer in the partially devulcanized particles. In the case of using DPDS, it just acted on the surface of the rubber particles this limited its devulcanizing performance. The results were in good correlation with CLD and sol fraction results.

3.4. Effect of sonication method

In previous researches, ultrasonic bath mostly used to devulcanize the crumbed rubber particles. In this study, the performance of probe sonication was compared to sonication bath. Results are given in Fig. 5. It is obvious that probe sonication illustrated higher devulcanization performances than ultrasonic bath. It was attributed to the higher energies induced

to the particles in probe sonication and also direct contact between rubber particles and the sonication source (*i.e.* probe).

3.5. Characterization

3.5.1 FTIR analysis. Fig. 6 shows results of FTIR analysis of the virgin rubber (uncured NR/SBR compound), control sample (crumbed DGR-Ctrl) and the sample with highest devulcanization percentage (DGR-O24(60-20)-VitaX1.2). Table 4 depicts the characterized peaks in the curves.

Comparing the spectrums of the virgin NR/SBR and DGR-Ctrl samples showed that rubber grinding and then mechanical devulcanization affected the rubber network structure according to the peaks appeared at wavelength of 2800 to 3200 cm^{-1} . It is apparent that the intensity of the peaks related to CH and CH_2 groups are reduced and CH_3 has been added after grinding. This change simply confirmed chain scission and creation of new CH_3 groups at the end of the broken chains. The peak at 3500 cm^{-1} is related to tension vibration of hydroxyl

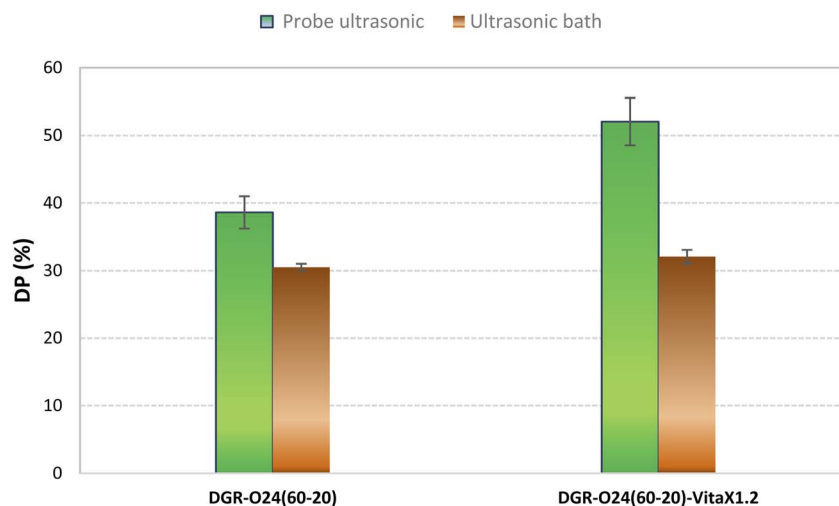


Fig. 5 Devulcanization percent of the samples devulcanized by probe and bath sonication.



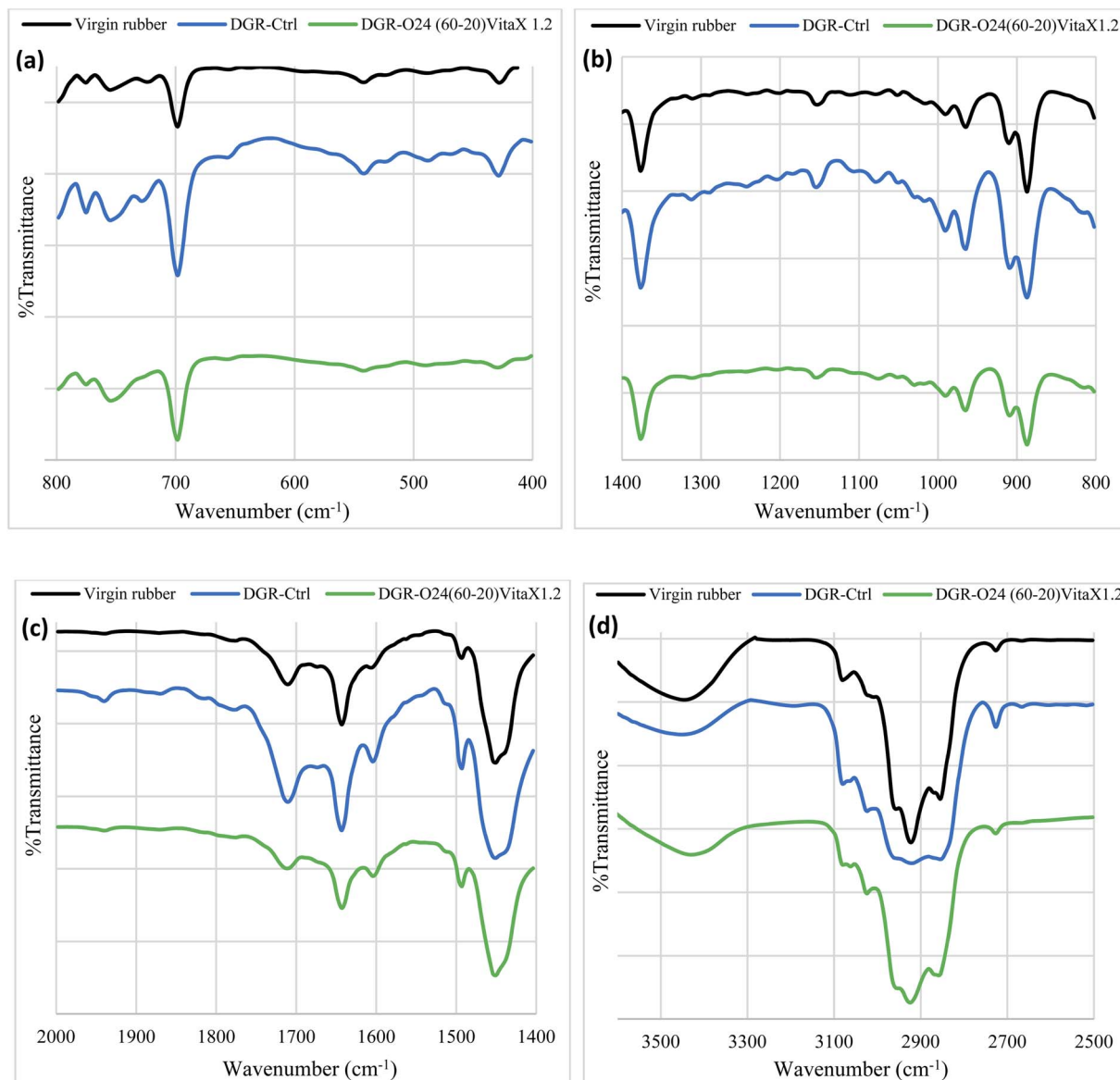


Fig. 6 Pyrolysis-FTIR spectra of different samples; (a) from 400 to 600 cm^{-1} , (b) from 600 to 1200 cm^{-1} , (c) from 1200 to 1550 cm^{-1} and (d) from 1550 to 1800 cm^{-1} .

Table 4 Characterized bonds by Pyrolysis-FTIR analysis of the selected samples

Characterized peak	Wavenumber (cm^{-1})	Components	Ref.
S-S stretching	540	Crosslinks	7,12,15
C-S stretching	603	Crosslinks	7,26
C=C bending	870	NR	15
C-C bending	900–1000	NR & SBR	15
C-C stretching	1018	Carbon black	5,7,15
C=C stretching	1645	NR/SBR	12,15,26
C=O	1720	CBS-stearic acid	5,9,12
C=C-H	3070	—	15,21,26

groups of carbon black. Moreover, the presence of a sharp peak at 1650 cm^{-1} (bending vibration of OH groups) could also confirm the presence of moisture in the sample. The observed peak at 1690 cm^{-1} was related to $-\text{CH}=\text{CH}-$ groups in the virgin and control rubbers. The twin peaks at 1450 and 1550 cm^{-1} should be attributed to the benzene rings in the SBR. Peaks in the range of 750 to 1200 cm^{-1} was corresponded to the flexural vibration of alkane compounds ($-\text{CH}_2-\text{CH}_2-$) which increased by grinding of vulcanized rubber. This confirmed occurrence of chain scission and formation of smaller chains in the mechanically devulcanized sample (DGR-Ctrl). The increase in the intensity of the peaks in DGR-O24(60-20)-VitaX1.2 sample confirmed more failure of the rubber network after sono-chemical devulcanization.



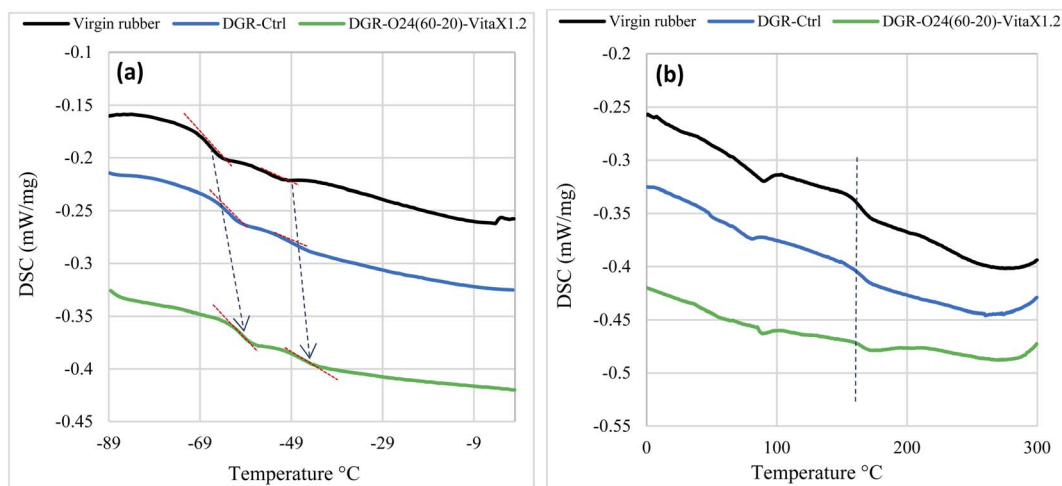


Fig. 7 Results of DSC analysis at temperature between (a) -90 – 0 $^{\circ}\text{C}$, and (b) between 0 – 300 $^{\circ}\text{C}$.

Table 5 The glass transition temperature (T_g) of the samples (determined from DSC curve)

Samples	T_{g1} ($^{\circ}\text{C}$)	T_{g2} ($^{\circ}\text{C}$)	ΔC_p at curing temperature ($\text{J g}^{-1} \text{K}^{-1}$)
Vulcanized NR/SBR	-66.75	-54.25	0.095
R-DGR-Ctrl ^a	-62.44	-51.94	0.02
R-DGR-O24 (60-20)VitaX1.2 ^a	-60.08	-50.08	0.077

^a Revulcanized samples.

The peak appeared at 720 cm^{-1} was related to the $-\text{C}-\text{SH}$ bonds which increased in devulcanized samples. This confirmed that more breakage happened in the cross-links (*i.e.* $-\text{S}-\text{S}-$ bonds) in presence of sonication.

3.5.2 DSC analysis. Fig. 7 shows the DSC results for virgin rubber, DGR-Ctrl and DGR-O24(60-20)-VitaX1.2 samples. The detected T_g of the samples is given in Table 5.

As it is seen, the T_g values for both NR (*i.e.* T_{g1}) and SBR (*i.e.* T_{g2}) parts were increased in the mechanically and sono-chemically devulcanized samples compared to the uncured virgin rubber. This was attributed to the networked structure that created due to the primary and secondary vulcanization steps that was performed on the devulcanized samples. The exothermic peak observed at about 160 $^{\circ}\text{C}$ in all samples was corresponded to the curing temperature of the rubbers. It is obviously seen that this peak weakened in the mechanically and sono-mechanically samples due to lower cross-links occurred in these samples compared to the virgin rubber.

According to the results, the glass transition temperature increased in the DGR-O24(60-20)-VitaX1.2 compared to the DGR-Ctrl sample. This was attributed to presence of higher amounts of low molecular weight chains (*i.e.* broken chains) in the mechanically devulcanized sample. This confirms more crosslinks breakage instead of chain scission in the sono-chemically devulcanized sample.

3.5.3 TGA analysis. Fig. 8 shows the TGA curves of the revulcanized VitaX containing samples compared to the cured NR/SBR. The results were listed in Table 6. The weight loss in temperature range of 35 – 320 $^{\circ}\text{C}$ was corresponded to the degradation of low molecular weight organic matters and humidity (see Fig. (8a)). It is clearly seen that the weight loss in this region increased in the samples contained VitaX. This confirmed more fractures occurred in the rubber network and creation of low molecular weight chains in presence of VitaX.

The temperature regions of 320 – 425 $^{\circ}\text{C}$ and 425 – 540 $^{\circ}\text{C}$ was attributed to degradation of NR and SBR parts of samples, respectively. It is obvious that both NR and SBR parts of sonicated samples showed lower weight losses compared to the cured NR/SBR sample due to the fractures occurred in polymers chains. It is also seen that the weight loss related to NR part was lower in the devulcanized samples in presence of VitaX compared to DGR-O24(60-20) sample. This shows that in presence of VitaX, fractures occurred mostly in the SBR network instead of NR structure.

Higher thermal stabilities were observed in revulcanized samples due to the presence of intact-crosslinked core of particles that acted as reinforcing filler in devulcanized matrices.

Fig. (9b) shows DTG curves for the samples. The results confirmed the higher thermal stabilities of the devulcanized samples compared to the cured NR/SBR sample due to the increment in the degradation temperatures of the NR and SBR parts.



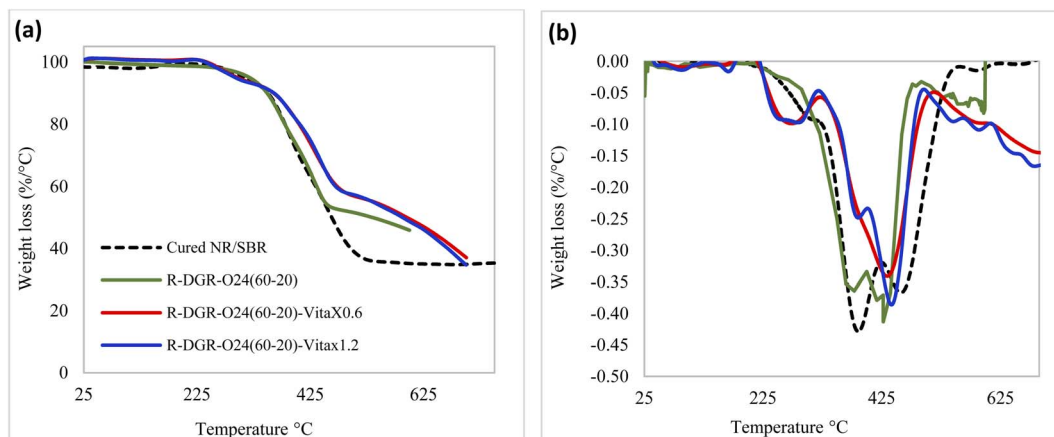


Fig. 8 The effect of VitaX on thermogravimetric properties of the samples; (a) TGA curve and (b) DTG curve.

Table 6 Results of TGA-DTG analysis for the vulcanized/re-vulcanized samples

Compounds	Data	Low molecular weight organic mater	NR part	SBR part	Inorganic residues
	ΔT [°C]	35 to 320	320 to 425	425 to 540	540 to 750
Cured NR/SBR	Δm [%]	5.90	34.21	27.24	35.8
	T_{max} [°C]	—	386	457	—
R-DGR-O24(60-20)	Δm [%]	5.75	29.64	14.85	49.69
	T_{max} [°C]	—	383.03	437.27	—
R-DGR-O24(60-20)-VitaX0.6	Δm [%]	7.56	19.64	18.95	54.7
	T_{max} [°C]	—	389.96	433.92	—
R-DGR-O24(60-20)-VitaX 1.2	Δm [%]	7.9	18.62	20.26	54.53
	T_{max} [°C]	—	384.46	439.98	—

3.6. Curing properties

The curing properties of the samples was evaluated by ODR. Results are shown in Fig. 9 and Table 7. The results showed that $M_H - M_L$ content which is a representative of cross-link density (CLD) increased for sonication assisted devulcanized samples compared to the mechanically devulcanized sample. It was attributed to the more breakages that happened in the cross-links in this sample that made more chances for revulcanization of the compound during ODR test. However, the curing rate

index (CRI) was higher in the sonicated samples in presence of VitaX. It was also found that by addition of 0.6 phr of VitaX to the sonicated sample, the CRI increased considerably and the scorch time deceased very much. This finding proved the positive effect of lower contents of VitaX on desired devulcanization of NR/SBR compounds.

3.7. Mechanical properties

Fig. 10 shows the comparative tensile properties of the rubber samples. It is clearly seen that the tensile strength of DGR-O24(60-20)-VitaX1.2 is so close to the virgin sample that illustrates effect of VitaX on suitable devulcanization of sonicated rubbers (*i.e.* it caused the least rubber chain scission). Moreover, this chemical agent increased cross-linking chance in the revulcanization process which caused increment in the tensile strength. On the other hand, in the samples which contained lower concentration of VitaX, the mechanical properties declined because of the high CLD and toughness and low flexibility.

Based on the results, modulus of the samples were obtained. For the effectively devulcanized sample, the modulus content confirmed the TS results. In comparison to the virgin sample, the modulus of VitaX containing samples was considerably increased because of their higher CLD and toughness. Therefore

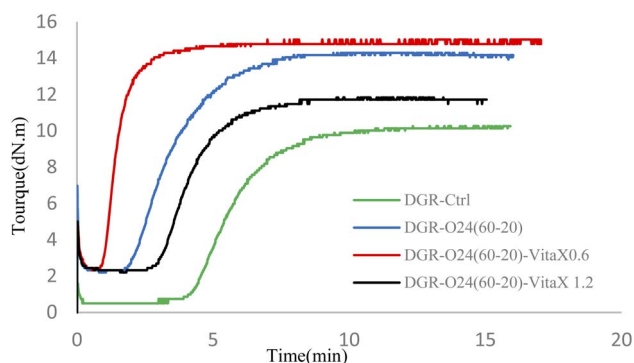


Fig. 9 Comparative ODR results of the devulcanized samples.



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