



# The role of reduced graphene oxide as a secondary filler in improving the performance of silica-filled styrene-butadiene rubber compounds

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Received: 23 July 2021 / Revised: 7 September 2021 / Accepted: 13 September 2021  
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## Abstract

The present work discusses the effects of reduced graphene oxide (rGO) on the nonlinear viscoelastic behavior, or the Payne effect, of silica/styrene-butadiene rubber compounds. The volume fraction of unmodified silica was constant, while the amount of rGO in these hybrid filler compounds varied. Dynamic-mechanical analysis (DMA) in strain sweep mode showed that adding a small quantity of rGO to the silica-filled compounds resulted in diminished network formation of unmodified silica as well as a reduced Payne effect and corresponding energy dissipation. The state of silica dispersion in the presence of rGO in the rubber matrix was predicted by calculating the work of adhesion in a three-component system and detected by scanning electron microscopy. It was observed that the dispersion of the unmodified silica was improved by the addition of only 0.25 or 0.5 phr rGO, which may be due to the improved silica-rubber interactions that occur during mixing and/or reduced silica flocculation after mixing, as measured by DMA in time sweep mode. The synergy between silica and small quantities of rGO (0.25 or 0.5 phr) resulted in an enhancement in mechanical strength (45%) and abrasion resistance (63%), as well as a reduction in heat build-up (23%). This hybrid system can be considered an alternative to silane modification of silica in green tire technology.

## Introduction

Over the last two decades, silane-modified silica has been used as a reinforcing filler in rubber compounds used in tire treads and has emerged as the main basis for saving energy in green tire technology. The high surface energy of unmodified silica particles (due to the presence of hydroxyl groups on the surface) leads to strong filler-filler interactions and a poor unstable state of dispersion in silica-filled rubber compounds [1–3]. Specifically, when the compound is stored at room temperature after mixing or vulcanized at high temperatures, reagglomeration or so-called “flocculation” of dispersed silica occurs [4]. Flocculation of silica

aggregates forms a rubber-mediated filler network. Breakage and reformation of the filler network under small-medium dynamic deformations lead to nonlinear viscoelastic behavior and corresponding energy dissipation, known as the Payne effect. The Payne effect is the source of instability in mechanical properties and heat build-up in highly filled rubber compounds. Moreover, the Payne effect is responsible for energy dissipation and rolling resistance in tires and fuel consumption in automobiles [5–7].

To reduce filler flocculation and the Payne effect of silica-filled composites, the application of bifunctional silanes along with silica is mandatory in green tire technology, although it brings about challenges in the mixing process and raises the final price of the product [8, 9]. Recently, “hybrid filler systems” have been widely used as a new approach to obtaining homogeneous filler dispersion [10–13], synergy in mechanical and electrical properties [14–18], and reduced filler networking or the Payne effect in polymer composites [10, 12, 19, 20]. Carbon black (CB) and silica hybrid fillers, traditional fillers in rubber compounds, have been extensively studied [10, 16, 19]. Sattayanurak et al. [16] observed a synergistic effect on the overall properties of tire tread compounds by the replacement of silica with a small amount of

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CB (18 wt.%) in the natural rubber (NR) matrix. Further studies have explored other hybrid fillers, such as CB/expanded organo-montmorillonite (EOMt) [21], silica/multi-walled carbon nanotubes (MWCNTs) [22], MWCNT/EOMt [11], CB/molybdenum disulfide ( $\text{MoS}_2$ ) [12] and silica/graphene oxide (GO) [15]. Rooj et al. [21] reported a reduction in the crack growth rate of CB-filled NR in the presence of 5 phr EOMt. Another study [11] reported that strong thermodynamic interactions between EOMt and MWCNTs improved the dispersion of MWCNTs in an EOMt/MWCNT hybrid filler network in a nonpolar NR matrix. Formation of the hybrid filler network led to the enhancement of electrical and mechanical properties; however, the filler network or the Payne effect was also increased. Tang et al. [12] observed a diminished filler network, lower small-strain storage modulus, decreased Payne effect, and significantly improved dynamic-mechanical properties due to the partial substitution of  $\text{MoS}_2$  platelets in styrene-butadiene rubber (SBR)/CB compounds. They attributed these improvements to the strong thermodynamic interactions between CB and  $\text{MoS}_2$ . Feng et al. [10] obtained the same results by replacing the silica with CB in silica/CB/SBR compounds. They ascribed these results to the reduction of CB cluster branching in the presence of small amounts of silica.

Reduced graphene oxide (rGO) has attracted both academic and industrial attention due to its large specific surface area and excellent mechanical, barrier, thermal, and electrical properties [23]. Dispersion of rGO platelets in rubber matrices using conventional direct mixing is challenging owing to van der Waals forces between layers. One of the methods used to overcome this challenge is latex mixing. The *in situ* reduction of GO in the latex phase, followed by latex coagulation, provides well-dispersed rGO in rubber [24]. rGO has been used to form a core-shell hybrid filler system. Zhu et al. [20] obtained hybrid filler compounds by self-assembling silica and rGO in styrene-butadiene/butadiene rubber blends. The chemical interactions between these two fillers and the homogeneous distribution of small silica particles on large rGO platelets by 3-aminopropyltriethoxysilane (APTES) decreased the filler network formation and the Payne effect. In addition, stronger filler-rubber interfacial interactions improved the dispersion and mechanical properties. Synergistic properties were also reported with the substitution of small amounts of graphene in a silica/graphene hybrid filler system.

In the present study, unmodified silica and rGO, which are different in size, geometry and surface chemistry, are used simultaneously as a hybrid filler system. To thoroughly investigate the thermodynamic interactions between the components and maximize the surface energy differences between silica and rGO, pristine silica is used without any surface modification. Without any substitution of the first filler by the second filler, as other researchers have

done, different contents of rGO are added to the compounds containing a constant volume fraction of unmodified silica. The hybrid filler compounds of silica/rGO are compared with the reference compound filled with silica (without any rGO) to detect any synergy of the dynamic-mechanical properties of the hybrid filler compounds. We also attempt to explain the synergy and reinforcement in the hybrid filler system through thermodynamic parameters, such as the work of adhesion calculated by surface energies in the three-component system, which to the best of our knowledge have rarely been considered for this purpose. The effect of adding rGO on the network formation and breakage of the fixed volume fraction of silica, thus nonlinear viscoelastic behavior of unvulcanized and vulcanized compounds, is observed. Significant improvements in the mechanical properties, abrasion resistance, and heat build-up are reported with the addition of a small amount of rGO.

## Experimental

### Materials

The chemicals used in the synthesis of GO and rGO, which included graphite flakes, sulfuric acid, hydrochloric acid, potassium permanganate, aqueous hydrogen peroxide solution (30 wt.%), and hydrazine hydroxide were purchased from Merck, Germany and used without any further purification. Untreated precipitated silica, Ultrasil VN3 had a specific surface area of  $180 \text{ m}^2/\text{g}$  and was provided by Evonik-Degussa AG (Essen, Germany). Emulsion styrene-butadiene rubber (SBR-1502) was obtained from Bandar-Imam Petrochemical Company (BIPC, Iran). Two forms of SBR, in solid and latex (with solid content of 20%) forms, with a styrene content of 23.5 wt.%, specific gravity of 0.945, Mooney viscosity (ML4) of 84 at  $100^\circ\text{C}$ , and number average molecular weight of  $176000 \text{ g/mol}$ , were used. All vulcanization agents (sulfur, accelerators, antioxidants, zinc oxide, and stearic acid) were obtained from Barez Industrial Group (Iran).

### Compounds fabrication

Graphene oxide (GO) platelets were synthesized through Hummer's Method, as reported in detail in our previous work [25]. The important factors in the preparation of the compounds were the constant volume fraction of silica in all the compounds and the varied concentrations of rGO. The (rGO/silica)-SBR compounds were prepared in two steps. First, the rGO-SBR compounds were prepared by the latex mixing method. The required amount of GO suspension was sonicated for 20 min and added to the rubber in latex form while stirring, and the pH was adjusted to a reasonable value ( $\geq 5$ ) to avoid latex coagulation. Mixing was

continued for 2 h to obtain a homogeneous mixture. Subsequently, the in situ reduction was applied by hydrazine hydrate for 3 h at 60 °C. The weight ratio of hydrazine hydrate to GO was 1:1. Finally, the mixture of rGO-SBR latex was coagulated by 5 wt.% sulfuric acid, washed with deionized water several times and vacuum dried at 50 °C for 48 h. Second, silica-SBR compounds with a constant volume fraction of silica (14.66 vol.%) were prepared using an internal mixer (W50ETH, Brabender, Duisburg, Germany). The initial temperature of the internal mixer was 80 °C, and the rotor speed was 50 rpm. For all compounds, SBR was initially masticated for ~2 min, and then silica was added gradually. The mixture was continuously stirred for 10 min to reach a uniform state of dispersion. Afterward, the prepared “rGO-SBR” and “silica-SBR” compounds were mixed on a two-roll mill (Brabender PM2000) at a 15 rpm roll speed, 1:1.2 friction ratio, and 50 °C controlled temperature for ~10 min. In this study, the abbreviation (Si/xrGO) represents the compound containing x phr (parts per hundred rubber) rGO. For example, (Si/0.25rGO) is a compound containing 14.66 vol.% (~40 phr) silica and 0.09 vol.% (0.25 phr) rGO. Table 1 shows the compositions of the compounds. The curing agents were added to the compounds on the two-roll mill for 10 min, and the samples were vulcanized under compression molding at 160 °C for an optimum cure time ( $t_{c90}$ ) to prepare samples for scanning electron microscopy, heat build-up, Akron abrasion, and tensile tests. The curing package consisted of 2 phr sulfur, 2.5 phr N-cyclohexylbenzothiazole-2-sulfenamide, 0.5 phr diphenylguanidine, 3 phr ZnO, 2 phr stearic acid, and 1.5 phr N-isopropyl-N'-phenyl-p-phenylenediamine.

## Characterization methods

The state of dispersion and morphology of Si/xrGO in the SBR matrix were investigated using field emission scanning electron microscopy (FE-SEM). For this purpose, the cryogenically fractured surfaces of the vulcanized compounds were coated with a thin layer of gold, and cross-sectional images were taken on FEI NOVA NANOSEM450 (FEI, Czech Republic) and TESCAN MIRA3 (TESCAN, Czech Republic) instruments.

**Table 1** The formulation of compounds

Sample	Rubber		Silica		rGO
	phr	vol.%	phr	vol.%	phr
Si	100	14.66	40	0	0
Si/0.25rGO			40.05	0.09	0.25
Si/0.5rGO			40.10	0.18	0.5
Si/0.75rGO			40.15	0.27	0.75
Si/1rGO			40.21	0.36	1

The dynamic-mechanical properties of the compounds in the strain sweep were measured before and after vulcanization using a MonTech D-RPA 3000 (MonTech, Germany).

Static contact angle measurements were performed by the sessile drop method to calculate the GO, rGO and SBR surface energies. Water and glycerol were used as the test liquids. To prepare the samples, a GO/water mixture, an rGO/tetrahydrofuran suspension and an SBR/toluene solution were poured onto separate glass slides and vacuum dried to evaporate the liquid phase. Films of GO, rGO and SBR with an almost smooth and nonporous surface were formed on the slides. The contact angles were recorded within 2 s after the deposition of the liquid droplets. The contact angle measurements were conducted three times for three droplets of each liquid, and the average values were used to calculate the surface energies.

The vulcanization rate was measured using a Gotech-GT-7070-S2 (Gotech, Taiwan) rheometer to obtain the optimum cure time, and each compound was vulcanized to the optimum cure time ( $t_{c90}$ ) using a laboratory compression press (Gotech-GT-7014-S0, Gotech, Taiwan) at 160 °C. The tensile test was performed using a Gotech-TCS-2000 (Gotech, Taiwan) machine. Three specimens of each vulcanized compound were subjected to the uniaxial tension mode according to ASTM D638 at an elongation rate of 500 mm/min at room temperature. The average values and the range of error are reported.

Heat build-up tests were performed on vulcanized cylindrical samples with diameters and heights of 17.8 mm and 25 mm, respectively. Three specimens of each sample were tested under a constant load of 200 N and 30 Hz frequency at room temperature. The tests were conducted by a Doli compression flexometer (Goodrich, Germany), and the average of temperature increase and the range of error for three specimens were reported.

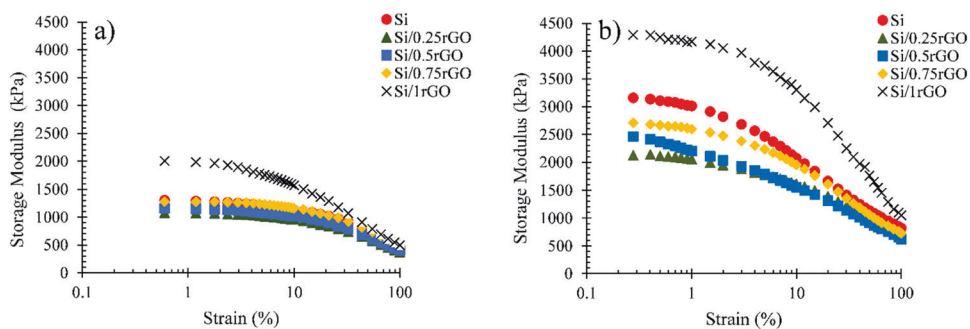
The abrasion resistance of the vulcanized compounds (three specimens of each sample) was measured by an Akron abrader (Gotech-GT-7012-A, Gotech, Taiwan) under a cornering angle of 15°, vertical load of 1.513 kg, and rotational speed of 74 rpm for 2000 rolling cycles. The average abraded volume and the range of error for the three specimens were reported. The abraded surfaces of the samples were photographed using a Dino-Lite microscope (AM7013MZ, AnMo Electronics, Taiwan) to obtain optical images of the abraded surfaces.

## Results and discussions

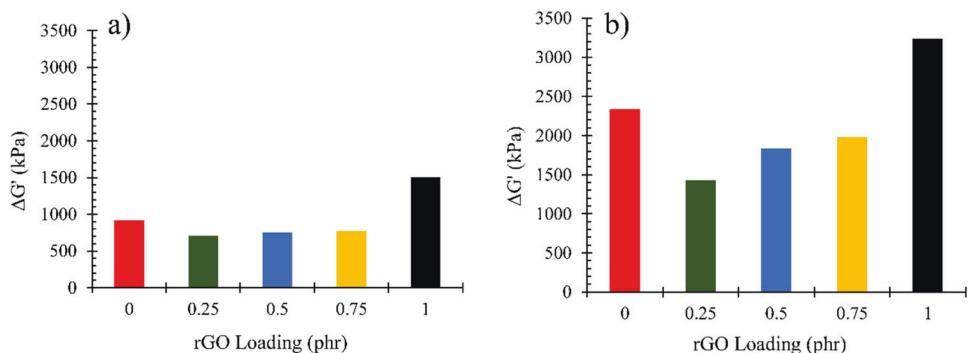
### Dynamic-mechanical properties of silica/rGO-SBR compounds

To investigate the effect of various quantities of rGO on the characteristics of the silica network in rubber, dynamic-mechanical measurements were performed by RPA at a

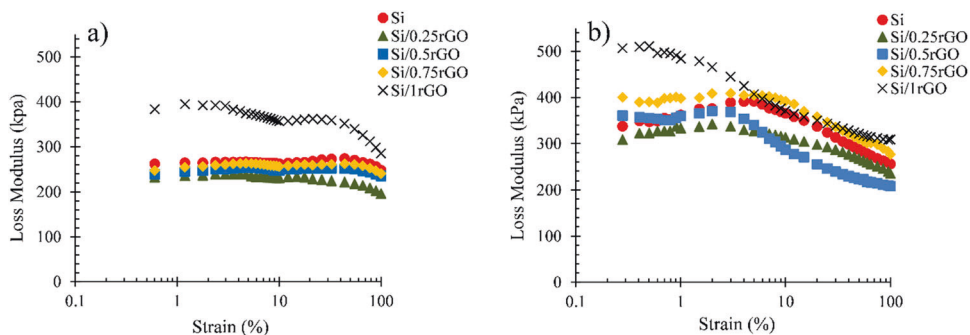
**Fig. 1** Strain dependency of  $G'$  in the Si/xrGO-filled SBR (a) before and (b) after vulcanization



**Fig. 2** Dependence of the Payne effect amplitude of silica-filled compounds on rGO content (a) before and (b) after vulcanization



**Fig. 3** Strain dependency of  $G''$  in the Si/xrGO-filled SBR (a) before and (b) after vulcanization



temperature of 60 °C and frequency of 1 Hz. Figure 1a and b display the storage modulus of the samples as a function of strain amplitude in unvulcanized and vulcanized compounds, respectively. The storage modulus at small strains ( $G'_0$ ), which represents the extent of the filler network, decreased considerably with increasing strain amplitude due to the break down of the filler network and the release of trapped rubber, known as the Payne effect [19]. In comparison to the silica-filled compound, the reference compound without rGO, the compound containing 0.25 phr rGO had the lowest  $G'_0$  of both the unvulcanized and vulcanized compounds. However,  $G'_0$  increased gradually as the concentration of rGO reached 0.75 phr, but it was still lower than that of the reference compound. Decreased values of  $G'_0$  are an indication of a diminished network of silica in the presence of rGO platelets. There was a sudden jump in  $G'_0$  at a concentration of 1 phr that exceeded that of the

reference compound. It is interesting to note that the magnitude of this effect is higher in the vulcanized compounds than in the corresponding unvulcanized compounds.

The magnitude of the Payne effect can be quantified by the values of  $\Delta G' = G'_0 - G'_\infty$  [26], as illustrated in Fig. 2a and 2b for unvulcanized and vulcanized compounds. It is shown that in the presence of 0.25, 0.5 and 0.75 phr rGO, the Payne effect is reduced to that of the reference compound in both the unvulcanized and vulcanized compounds.

Increasing the content of rGO to 1 phr leads to the formation of a rGO network, which also traps a very large amount of rubber, and a sudden rise in  $G'_0$  occurs, increasing the extent of the Payne effect before and after vulcanization.

The strain dependency of the loss modulus ( $G''$ ) in the reference compound and those with different amounts of rGO are presented in Fig. 3. The loss modulus represents the energy dissipated by the breakage and reformation of a

**Table 2** Surface energies of SBR, GO, rGO and silica

Sample	$\gamma^d$ (mJ/m <sup>2</sup> )	$\gamma^p$ (mJ/m <sup>2</sup> )	$\gamma$ (mJ/m <sup>2</sup> )
SBR	14.60	3.90	18.50
GO	0	76.56	76.56
rGO	14.52	1.88	16.50
silica	37.27	30.40	67.65

filler network in a highly filled compound under dynamic loading. The peak of  $G''$  in the presence of 0.25 and 0.5 phr rGO decreases, especially after vulcanization, indicating a weakened network of silica under dynamic strain [19].

To explain the observed phenomena in the nonlinear viscoelastic behavior of hybrid filler compounds, a more detailed analysis is required.

### Prediction of filler dispersion by surface energies

Some of the thermodynamic characteristics of filled rubber systems, such as filler wettability, filler-rubber adhesion and filler reagglomeration, are strongly affected by the surface energy of the components. Therefore, the surface energy of components can be used to predict filler dispersion and rubber reinforcement. For this purpose, the surface energies of SBR, GO, rGO, and silica were calculated by measuring the contact angles of water and glycerol and using the Fowkes method as described in Eqs. 1 and 2, and the results are given in Table 2.

$$\gamma_l(1 + \cos \theta) = 2 \left( \sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p} \right) \quad (1)$$

$$\gamma_l = \gamma_l^d + \gamma_l^p \cdot \gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

$\gamma_l$ ,  $\gamma_l^p$  and  $\gamma_l^d$  are the total, dispersive and polar parts of the liquid surface tensions, respectively. The  $\gamma_l^p$  and  $\gamma_l^d$  values for water are 51 and 21.8 mJ/m<sup>2</sup>, and these values for glycerol are 30 and 34 mJ/m<sup>2</sup>, respectively [27]. The  $\gamma_s^d$  values are dispersive parts, and the  $\gamma_s^p$  values are polar parts of the solid surface energy. As seen in Table 2, chemical reduction of GO and removal of the oxygen-containing groups leads to lower polar but higher dispersive components of the surface energies of rGO. The large difference between the surface energies of rGO and silica indicates the incompatibility of these two fillers. To evaluate the compatibility of each filler with the SBR matrix, the interfacial tension between each filler and matrix is calculated using Eq. 3 and given in Table 3:

$$\gamma_{pf} = \gamma_p + \gamma_f - 2 \left( \sqrt{\gamma_p^d \gamma_f^d} \right) - 2 \left( \sqrt{\gamma_p^p \gamma_f^p} \right) \quad (3)$$

**Table 3** Interfacial tension between each filler (GO, rGO and silica) and rubber (SBR)

Sample	$\gamma_{pf}$ (mJ/m <sup>2</sup> )
GO-SBR	60.50
rGO-SBR	0.46
silica-SBR	17.71

According to the values given in Table 3, the high interfacial tension between silica-SBR shows the incompatibility of silica and SBR. Thus, the wettability of silica by SBR is low, the dispersion of silica in this rubber is not stable, and the dispersed particles tend to reaggregate or flocculate after mixing. In contrast, by the chemical reduction of GO, the interfacial tension between SBR and rGO is greatly reduced, and SBR becomes more compatible with silica.

To investigate thermodynamic interactions in the silica/rGO-SBR hybrid filler compounds, the interactions were examined in a three-component system. The attraction or repulsion between two dissimilar media (first and second fillers) immersed in a third common medium (rubber) are investigated by calculating the “work of adhesion in a third medium” ( $W_{123}$ ). The value of  $W_{123}$  provides effective insight into the filler dispersion and wetting of two fillers by the rubber matrix in a three-component system during mixing [28]. The energy of  $W_{132}$  required to separate two dissimilar media 1 and 2 in medium 3 is calculated using Eqs. 4 and 5:

$$W_{132} = W_{12} + W_{33} - W_{13} - W_{23} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (4)$$

$$W_{xy} = 2 \left( \sqrt{\gamma_x^d \gamma_y^d} + \sqrt{\gamma_x^p \gamma_y^p} \right) \quad (5)$$

The value of  $W_{132}$  can be positive or negative. Negative values indicate repulsion between media 1 and 2 in medium 3, and positive values indicate attraction between media 1 and 2 in medium 3. The value of  $W_{132}$  calculated for the silica/rGO-SBR hybrid filler system is -4.33. This negative value suggests that SBR (medium 3) wets both the rGO platelets (medium 2) and silica particles (medium 1) during mixing [28, 29]. Furthermore,  $\gamma_{13} + \gamma_{23} < \gamma_{12}$  indicates that the summation of the interfacial tension energies of SBR-silica and SBR-rGO is lower than that at the silica/rGO interface. In other words, in the presence of the SBR matrix, the silica/rGO interface is separated into two interfaces by the penetration and spreading of rubber on the silica and rGO surfaces [28]. The wettability of the fillers by the rubber matrix enhances the dispersion of silica/rGO hybrid filler in the compounds.

## Effect of rGO on the final state of dispersion and flocculation of silica

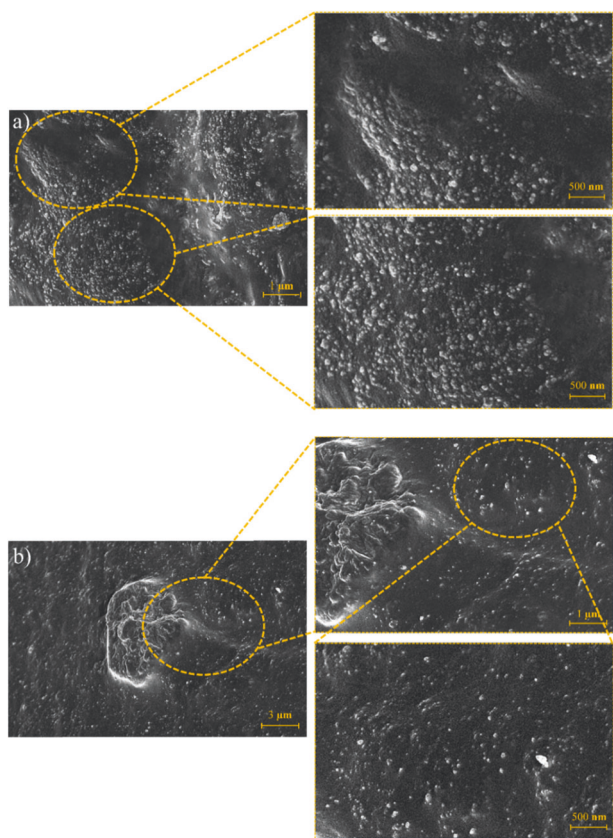
The final state of dispersion of filler in rubber matrix is defined by 1- initial dispersion of the filler particles during the mixing process and 2- flocculation of the filler particles during the storage or high-temperature vulcanization process [30]. The dispersed silica aggregates tend to flocculate after mixing because of the strong filler-filler interactions. Such a thermodynamically unstable system forms a 3D filler network, which leads to a large  $G'_0$ , the Payne effect, and corresponding energy dissipation [31]. To investigate the

effect of adding rGO platelets to the silica-filled compounds on the final state of dispersion, FE-SEM was conducted on the cryogenically fractured surface of the vulcanized compounds. Figure 4 demonstrates the distribution and dispersion of silica aggregates with or without rGO. The volume fractions of silica in all compounds were maintained. The improper dispersion of silica in the SBR matrix of the reference compound can be seen in Fig. 4a. Large aggregates of silica, ~100–200 nanometers in size, and some free parts of the rubber matrix indicate the poor dispersion and distribution of silica in the SBR matrix. When a small quantity of rGO (here 0.25 phr) was added to the reference compound, the distribution of silica aggregates was more uniform throughout the matrix, and the average size of silica aggregates was reduced to below 100 nanometers, as seen in Fig. 4b. The average dimension of the rGO platelets in this figure is ~3–4 microns.

The high modulus and large size of the added rGO platelets can also cause higher shear stress during mixing, which improves the dispersion of silica. Moreover, as mentioned earlier,  $\gamma_{13} + \gamma_{23} < \gamma_{12}$  and a negative value of  $W_{132}$  indicates lower interfacial tension in the filler-rubber interface compared to the filler-filler interface. Due to the separation of the two fillers and the spread of the rubber on both of them, filler-filler interaction is decreased, and the filler dispersion is improved during mixing.

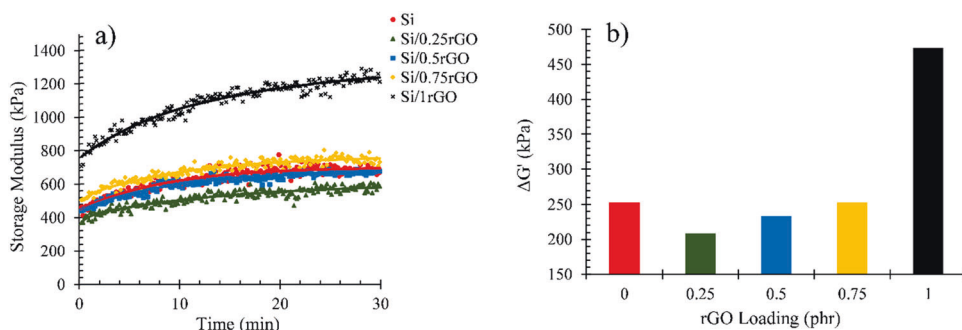
To investigate the effect of adding various amounts of rGO on the flocculation or reagglomeration of silica particles after mixing and during the vulcanization process, the dynamic storage modulus was swept against time using RPA. In this test, compounds are initially conditioned under a large (25%) strain amplitude for 30 min to break down the previously flocculated filler structure. Then, a time sweep of the dynamic modulus at 160 °C under a small strain amplitude (0.28%) was carried out to simulate the flocculation of silica during the vulcanization process, as shown in Fig. 5a.

The difference between the initial and final modulus ( $\Delta G'$ ), as an indication of the intensity of flocculation, is shown in Fig. 5b. The  $\Delta G'$  value of the reference compound decreases when 0.25 phr rGO is added, but it gradually increases as the



**Fig. 4** FE-SEM images of the cryogenically fractured surface of SBR filled with (a) silica and (b) Si/0.25rGO

**Fig. 5** a Flocculation investigation of Si/xrGO-filled SBR. b Dependence of  $\Delta G'$  on rGO content in silica-filled compounds



content of rGO increases to 0.75 phr. A sudden increase in  $\Delta G'$  is observed upon addition of 1 phr rGO due to either the formation of an rGO network in the silica-filled compound or a more compact network of silica in the presence of rGO. The rate of filler flocculation ( $dG'/dt$ ) is presented in Fig. 6. As seen in this figure, the rate of flocculation decreases upon addition of 0.25, 0.5 and 0.75 phr rGO.

According to Mihara et al. [4], filler flocculation depends on three parameters: filler-filler interactions, filler-rubber interactions, and the movability of filler particles in the rubber matrix. The high tendency of silica particles to flocculate can be considered the result of all three parameters [31]. The size, geometry and surface energy of silica and rGO are very different. As a result, the presence of rGO in the rubber matrix can reduce silica-silica interactions and increase silica-rubber interactions, as shown by the work of adhesion in the three-component system,  $W_{123}$ . In addition, the presence of large rGO platelets in the compound can decrease the movability of silica particles, which leads to a reduction in the flocculation tendency. The higher silica flocculation due to a small amount of rGO and the stability of the silica dispersion after mixing result in a smaller filler network with less trapped rubber and a smaller Payne effect in comparison to the network containing a single filler compound, as demonstrated in Fig. 1.

It was shown that the rate of filler flocculation and the Payne effect increased significantly as the concentration of

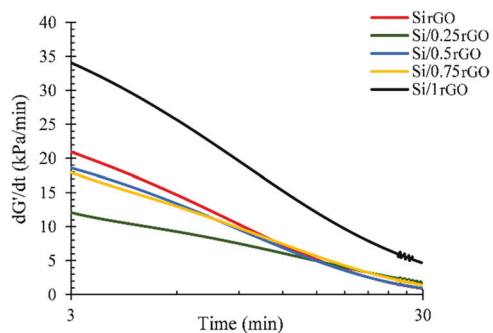


Fig. 6 Flocculation rate of Si/xrGO-filled SBR

rGO reached 1 phr. Figure 7 shows the trend in the morphological changes of the compounds filled with a constant volume fraction of silica in the presence of 0.25 up to 1 phr of rGO. The inter-rGO distance decreases as its concentration increases. As seen in Fig. 7d, by further addition of rGO, they form a secondary filler network, interpenetrating the silica network, and a hybrid filler network (silica/rGO) is formed. The average size of the platelets seems to be a few microns, while the aspect ratio of platelets is  $\sim 100$  [25]. Figure 8 schematically shows the development of filler morphology on a small scale of observation as the concentration of rGO increases in the compounds at a constant volume fraction of silica. Figure 8a shows the self-aggregation of silica in the reference compound, which generates large silica agglomerates in the rubber matrix and traps a large amount of immobilized rubber. In this window of observation, one of the agglomerates is shown. The trapped rubber, which loses its identity as rubber and behaves as a part of the filler, is called “dead rubber” [19]. Dead rubber is loosely rubber trapped in the filler agglomerates, and it is unstable under dynamic loadings. Figure 8b and c demonstrate diminished silica flocculation and network in the presence of low concentrations of rGO platelets (0.25 and 0.5 phr). A small number of rGO platelets interrupt the silica aggregates and prevent them to create large agglomerates, improve the silica dispersion, and release the trapped rubber, leading to a decrease in  $G'_0$ . When the content of rGO was increased to 0.75 and then 1 phr (Fig. 8d and e), the formation of the rGO network along with the silica network increased the amount of trapped rubber in the hybrid filler structure. Rubber trapped in the compact structure of the hybrid filler turns into dead rubber again and increases the value of  $G'_0$  (Fig. 8e).

### Mechanical properties of hybrid filler compounds

Typical stress-strain curves of all vulcanized compounds are illustrated in Fig. 9a, and important characteristics of the curves, such as the Young's modulus, tensile strength, and elongation at break, are given in Fig. 9b, c, and d,

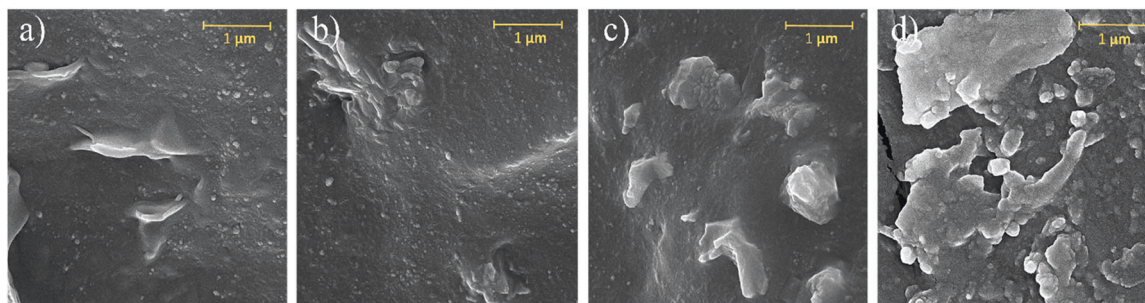
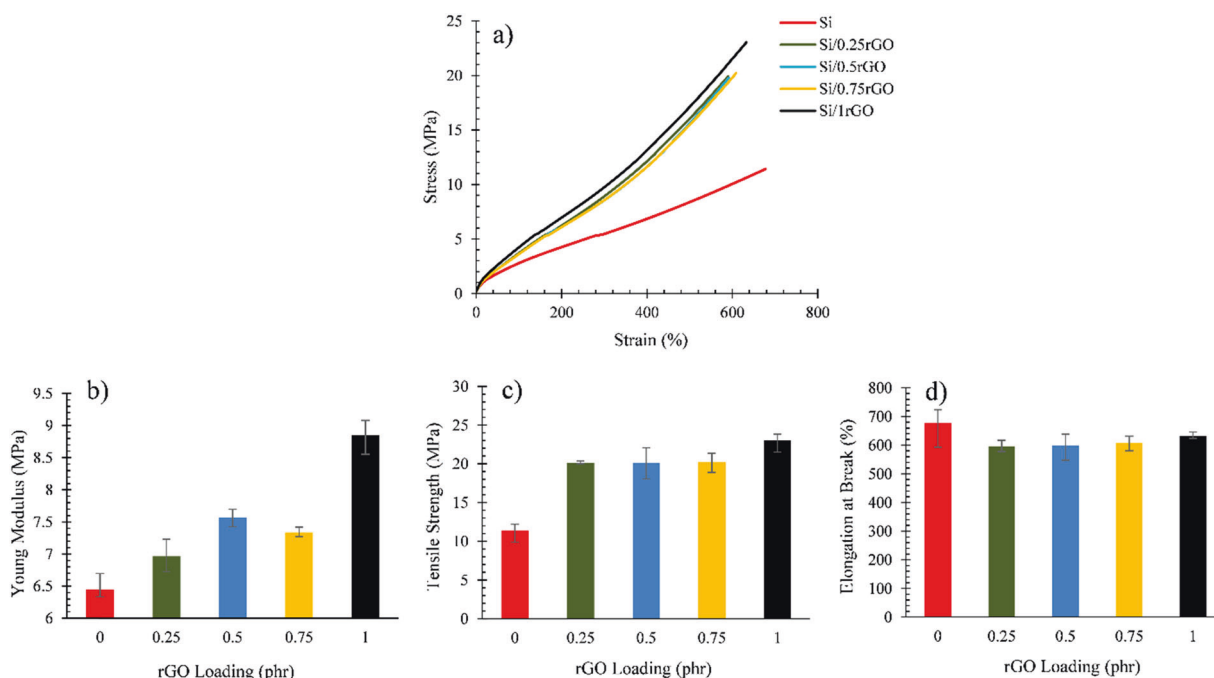
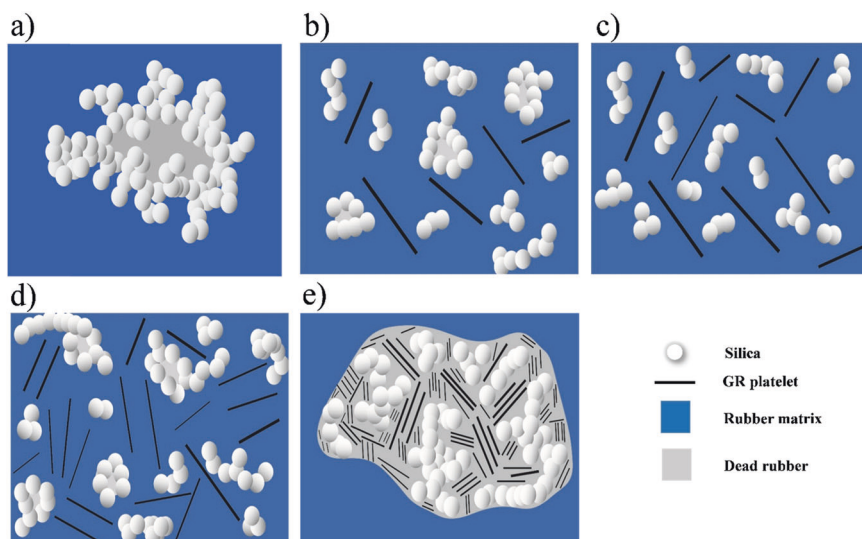


Fig. 7 FE-SEM images of the cryogenically fractured surface of SBR filled with the constant volume fraction of silica (14.66 vol.%) and (a) 0.25 phr, (b) 0.5 phr, (c) 0.75 phr, and (d) 1 phr rGO

**Fig. 8** Schematic of the dependence of the silica filler network (constant volume fraction) on the addition of different amount of rGO in the rubber matrix. (a) pure silica, (b) silica/0.25rGO, (c) silica/0.5rGO (d) silica/0.75rGO (e) silica/1rGO



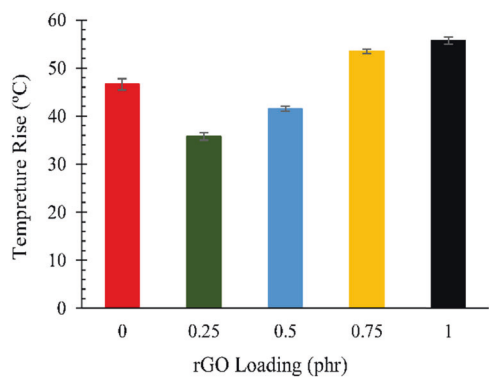
**Fig. 9** Mechanical behavior of the Si/xrGO filled compounds. Dependencies of (a) typical stress-strain curves, (b) Young's modulus, (c) tensile strength and (d) elongation at break on the rGO content of the silica-filled compounds

respectively. Figure 9b indicates that incorporating rGO into the silica-filled compound increases the Young's modulus of the hybrid filler compound with respect to that of the reference compound. The increase in the low-strain modulus of rubber compounds can be attributed to the improved dispersion and uniform distribution of aggregates [32].

As evidenced in Fig. 9c and d, despite the increase in tensile strength, elongation at break of the compounds does

not decrease significantly by adding rGO, which is a great sign of reinforcement. It should be noted that the reasons for the increase in the Young's modulus of the Si/0.25rGO and Si/1rGO compounds are different. In compounds containing low concentrations of rGO, improved dispersion enhances the Young's modulus. However, addition of 1 phr rGO to the silica-filled compound forms a strong filler network with a high amount of trapped rubber in the hybrid filler structure, which increases the Young's modulus.



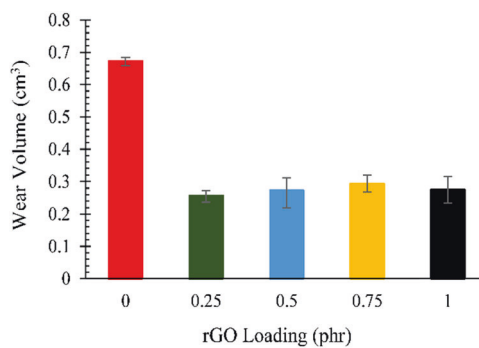


**Fig. 10** Dependence of heat build-up on the rGO content in silica-filled compounds

### Heat build-up and abrasion resistance of hybrid filler compounds

The heat generated during dynamic deformation mainly results from energy dissipation in the compound. As mentioned earlier, the Payne effect is involved in energy dissipation due to breaking and reformation of the filler network during dynamic deformation [33]. As shown in Fig. 10, the temperature rise during the heat build-up test is remarkably reduced from ~47 °C for the vulcanized reference compound to 36 °C and 42 °C for vulcanized compounds Si/0.25rGO and Si/0.5rGO, respectively. This result is in line with the results of the Payne effect and loss modulus tests shown in Figs. 2 and 3. The presence of a small content of large rGO platelets separates the silica particles from each other, hinders the reformation of the silica network after mixing and reduces the friction between the silica particles. However, increasing the rGO concentration to 0.75 and 1 phr leads to the penetration of the rGO network into the silica network and a significant increase in heat build-up and temperature rise. The ~23% reduction in heat build-up, achieved by using a small amount of rGO, can be considered a great alternative to the silanization of silica in silica-filled tire tread compounds.

To examine the abrasion resistance of the vulcanized compounds, the Akron abrasion test was carried out. Rubber abrasion directly depends on the quality of filler dispersion and filler-rubber interactions [20]. As presented in Fig. 11, the abraded volume of the Si/0.25rGO compound is reduced by 63% with respect to the reference compound, which is a significant improvement in rubber abrasion resistance. However, the abrasion resistance of the hybrid filler compounds does not improve by further addition of rGO to the compound. The chemical decomposition of rubber and mechanical fatigue fracture are two main mechanisms for rubber abrasion [34, 35]. The first mechanism is usually absent in SBR compounds, and as seen from the heat build-up results, a high-temperature rise



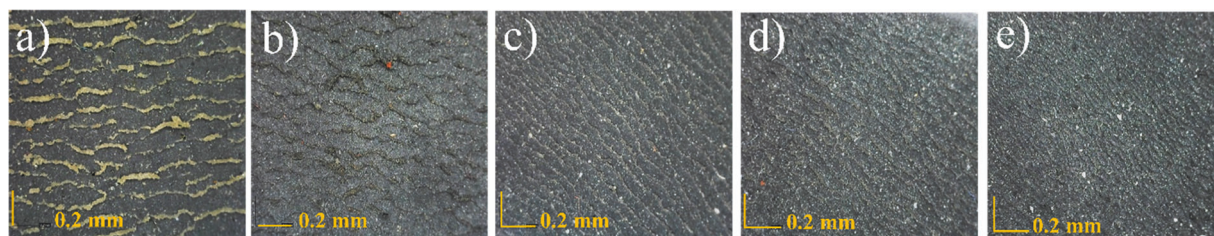
**Fig. 11** Dependence of abrasion loss volume on the rGO content in silica-filled compounds

in the compound containing 1 phr rGO does not lead to high abrasion loss in this compound. As a result, the abrasion resistance of the compounds mainly depends on the resistance to mechanical fatigue fracture [32]. The reduction in the abrasion loss of the silica/0.25rGO and silica/0.5rGO compounds can be attributed to the improvement in the silica dispersion and mechanical properties, as shown in the previous sections. The improved dispersion and reduced size of silica aggregates greatly reduce the probability of initiation and propagation of cracks at the filler-rubber interface under periodic loading. With further increase in the rGO concentration (0.75 and 1 phr), the abrasion loss volume is still less than that of the pure silica-filled vulcanizates. This result can be attributed to the proper dispersion of silica in the presence of rGO and the high modulus of vulcanizates due to the formation of a hybrid filler network.

Figure 12 shows the abrasion patterns known as Schallmach waves. [36]. These patterns represent the rate of abrasion under different service conditions. As seen in Fig. 12a for the reference compound, large ridges are indicative of high rubber abrasion. By adding rGO to the silica-filled compounds (Fig. 12b–e), the height and spacing between ridges decrease; thus, abrasion loss decreases [16, 37].

### Conclusions

In summary, different contents of rGO platelets were incorporated into compounds filled with a constant volume fraction of silica to investigate the extent of the silica network and dispersion and the dynamic-mechanical properties of the silica/rGO-SBR hybrid filler compounds. The addition of a small quantity of rGO to the silica-filled compound improves the silica dispersion and stabilizes the final state of silica dispersion, which leads to a reduction in silica flocculation, the Payne effect, and the corresponding energy dissipation in dynamic loadings. This synergy is limited to low concentrations of rGO (below 0.75 phr) prior to the formation of rGO network. The mechanism for the



**Fig. 12** Effect of adding (a) 0 phr, (b) 0.25 phr, (c) 0.5 phr, (d) 0.75 phr, and (e) 1 phr rGO to the silica-filled compounds on the abrasion pattern of the abraded surface

improvement in dispersion of silica and synergy in non-linear viscoelastic behavior was explained thermodynamically through the work of adhesion in the three-component system of silica/rGO-SBR and the enhanced interactions between the fillers and rubber in the presence of rGO. Considerable synergy in the final properties of compounds, which included mechanical properties, heat build-up, and abrasion loss, was also shown. With the addition of 0.25 phr rGO, heat built-up and abrasion loss were reduced 23% and 63%, respectively. Enhancement of the key properties of the compounds was obtained without any surface modification of silica with silane, which can be considered an alternative method in green tire technology.

## Compliance with ethical standards

**Conflict of interest** The authors declare no competing interests.

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