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RESEARCH ARTICLE

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Vulcanization kinetics of styrene butadiene rubber reinforced by graphenic particles

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Abstract

The present study discusses the effects of graphenic particles on the kinetics of sulfur vulcanization in styrene butadiene rubber composites. Using data obtained from a cure rheometer and fitted by an autocatalytic model, it was verified that graphenic particles follow our recently established catalytic-networking model for the effect of particles on the sulfur vulcanization of rubber, regardless of the type of particles. The magnitude of the catalytic and networking effects depends on surface chemistry and interfacial interactions of particles with rubber that can be tailored by the chemical reduction of graphene oxide. Accordingly, the reduction process decreased the catalytic effect due to the elimination of surface functional groups and increased the networking effect due to the enhancement of filler–rubber interactions and immobilization of rubber. The latter was verified by differential scanning calorimetry and bound rubber measurements.

KEYWORDS

graphene oxide, interfacial interactions, rubber composites, surface chemistry, vulcanization kinetics, wettability

1 | INTRODUCTION

Incorporating reinforcing fillers into rubbers leads to alteration of vulcanization kinetics and ultimate crosslink density of the host rubber that can severely affect the final properties of the vulcanizate.[1,2] Many reports in the literature[3–10] consider chemical impacts of the reinforcing fillers and their interactions with the vulcanization ingredients as controlling factors on the vulcanization reaction. In this view, it has been speculated that functional surface groups in carbon-based reinforcing fillers such as carbon blacks and graphene could take part in the kinetics of sulfur vulcanization, so the vulcanization rate and crosslink density of host rubber are increased by the addition of these fillers.[3,6,11] Also, the incorporation of carbon-based particles into the rubber have been shown to enhance the rate of vulcanization because of increasing the thermal conductivity of filled composites.[11,12] Furthermore, the silica surface contains acidic groups, for example, hydroxyl, siloxane, and silanol that slows down the rate of vulcanization by adsorbing and deactivating the basic accelerators.[5,13–16] However, our recent works on the sulfur[17–19] vulcanization of rubbers demonstrated that vulcanization

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follows a unique mechanism consisting of a catalytic effect and a networking effect depending on the concentration of the filler, regardless of its type. The physical effects of reinforcing fillers on the mobility of the reactive macro-radicals could have significant effects on the kinetics (including rate and conversion) of the vulcanization process. At concentrations below the rheological percolation threshold, the rate of vulcanization increases due to the catalytic effect of functional groups on the surface of the fillers. However, at concentrations above the rheological percolation threshold of fillers, the rate of vulcanization slows down due to reduced mobility of reactive macro-radicals entrapped and immobilized in the filler network. Based on the proposed mechanism, our work showed that the final chemical crosslink density of rubber monotonically decreases by incorporating reinforcing fillers, even at low concentrations, in agreement with the works of other researchers.[15,20–24] Also, the proposed unique mechanism for the chemical and physical effects of reinforcing fillers on the vulcanization kinetics of rubbers has been confirmed by other researchers.[25–27]

In recent years, graphene oxide (GO) and reduced graphene oxide (rGO) have attracted much attention due to their ability to enhance mechanical, thermal, electrical, and especially gas barrier properties of rubber composites.[1,28–40] However, the effects of GO and its derivatives on the kinetics of sulfur vulcanization in such systems has not been studied. There is no appropriate affinity between nonpolar elastomers and highly polar GO. Nevertheless, the surface chemistry of GO and its compatibility with such elastomers can be easily improved by thermal or chemical reduction processes or via functionalization/grafting methods.[41] According to the literature, the latex mixing method and also in-situ chemical reduction of GO particles in such systems can bring about composites with an appropriate state of dispersion for GO and rGOs, but with different interfacial properties between rubber and particles.[29,42]

In this work, we extend the proposed vulcanization kinetics mechanism to the case of rubber composites filled with graphenic particles for the first time. We have chosen to study graphenic particles because of their easy surface modification by in-situ chemical reduction in the latex phase, outstanding reinforcing characteristics due to their high aspect ratio, and widespread applications. Styrene butadiene rubber (SBR) composites filled with different concentrations of GO and two rGO particles were fabricated to evaluate the chemical and interfacial effects of different surface characteristics of particles on the vulcanization kinetics of the host rubber.

2 | EXPERIMENTAL

2.1 | Materials

Graphite flakes, sulfuric acid, hydrochloric acid, potassium permanganate, aqueous hydrogen peroxide solution (30% wt.) and hydrazinium hydroxide for the synthesis and reduction of GO were purchased from Merck, Germany and used as-received. Latex styrene-butadiene rubber (SBR 1502) with a solid content of 20% was obtained from Bandar-Imam Petrochemical Company (BIPC), Iran. All vulcanization ingredients (sulfur, accelerator, anti-oxidant, zinc oxide, and stearic acid) were industrial grades obtained from Barez Industrial Group, Iran.

2.2 | Filler synthesis

GO particles in the water suspension were chemically reduced to prepare rGO particles for characterization that is thoroughly described in the previous work.[29] In this process, hydrazinium hydroxide was added to GO with the weight ratio of 1:1. The reduction process was conducted at two different reduction temperatures (40 and 60 °C) for 3 h and were named as rGO-X, where X is the reduction temperature. This nomenclature was used for both the particles and composites. Besides, the weight loss in the reduction process of GO to rGOs was approximated to be about 30%. Therefore, by considering the weight loss value, GO was added to the latex more than its actual amount.

2.3 | Composite fabrication

Initially, GO particles were synthesized by the Hummers' method, as described in our previous work.[29] Graphenic-filled SBR composites were prepared using a common latex compounding method. First, the chosen amount of SBR latex added to a flask. The diluted GO suspension in deionized water was sonicated for 20 min then added to the latex under stirring, while pH was adjusted to a ≥5 to avoid latex coagulation. For SBR/rGO composites, GO suspension was added to the latex and then in-situ reduced by hydrazine hydrate at two different process temperatures (40 and 60°C). Afterward, the mixture was coagulated by 5% wt. sulfuric acid and washed with deionized water several times. All composites were vacuum dried at 60°C for 24 h. Then, dried composites were subjected to an open two-roll mill mixer (Brabender-PM2000) with the

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TABLE 1 Recipes for the reference and filled composites (the values are based on phr)

	Master-batch		Anti-oxidant & vulcanization package				
Composite	**Rubber**	**Filler**	**IPPD[a]**	**Stearic acid**	**Zinc oxide**	**TBBS[b]**	**Sulfur**
Unfilled SBR	100	0	1	2	3	1	1
SBR/GO		0.5, 1, 2, 4					
SBR/rGO40		0.5, 1, 2, 4					
SBR/rGO60		0.5, 1, 2, 4					

Abbreviations: GO, graphene oxide; rGO, reduced graphene oxide; SBR, styrene butadiene rubber.
[a]*N*-isopropyl-*n*′-phenyl-p-phenylenediamine (antioxidant).
[b]*N*-tert-butyl-2-benzothiazole sulfenamide (vulcanization accelerator).

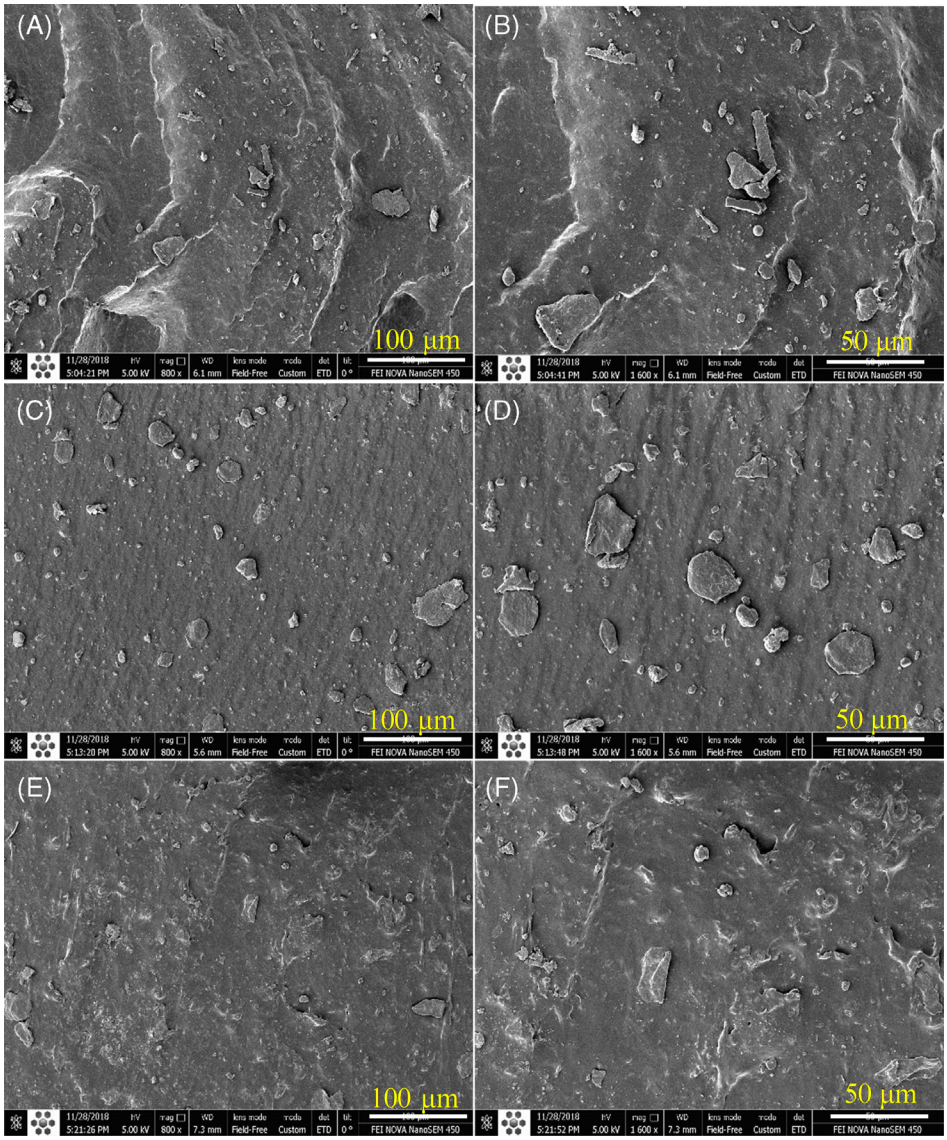


FIGURE 1 FESEM images of composites filled with 2 phr of (A, B) GO, (C, D) rGO40, and (E, F) rGO60 at two different magnifications

friction ratio of 1:1.2 for the addition of vulcanizing agents. The formulation for the reference (unfilled SBR), GO and rGOs-filled composites are given in Table 1.

2.4 | Characterization methods

Field emission scanning electron microscopy (FESEM) was performed to study the morphology of the

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TABLE 2 Contact angle values, surface energy and other thermodynamically parameters of the fillers and SBR

Sample	$\theta_{Glycerol}$ (°)	θ_{Water} (°)	γ^d (mJ/m^2)	γ^p (mJ/m^2)	γ_{total} (mJ/m^2)	γ_{rf} (mJ/m^2)
SBR	88	97	14.6	3.9	18.5	–
GO	64	45	0	76.5	76.5	60.3
rGO40	80	93	24.3	2.6	23.9	1.3
rGO60	94	104	14.5	2.0	16.5	0.4

Abbreviations: GO, graphene oxide; rGO, reduced graphene oxide; SBR, styrene butadiene rubber.

composites. Therefore, the cryogenically fractured surface of the samples was coated with gold and investigated by using FEI NOVA NANOSEM.

To evaluate the surface energy of the particles and SBR, static contact angle measurements were carried out by the sessile drop method. Water and glycerol were used as the test liquids. To prepare the samples, GO/water, rGO/tetrahydrofuran (THF) suspension, and SBR/toluene solution were coated onto separate glass slides and vacuum dried to evaporate the liquid phase and form a film with an almost smooth and non-porous surface.

Vulcanization of SBR composites were studied by an oscillating disc rheometer (ODR) (Gotech-GT-7070-S2) performed under an isothermal condition at 160°C.

The calorimetric glass transition process was studied using differential scanning calorimetry (DSC). Measurements were carried out in the temperature ranging from −80 to 25°C, under a nitrogen atmosphere using a Netzsch-200 F3 Maia DSC. The samples were cooled from room temperature to −80°C at 10 °C/min, held at this temperature for 10 min and the measurements were taken during subsequent heating at 5 °C/min.

To evaluate the filler–rubber interaction in the form of bound rubber content, about 0.5 g of un-vulcanized samples were cut into small pieces and put in stainless steel cages of mesh 400. The cages were properly locked and immersed into a bath of toluene. After 4 days, the cages were removed from the solvent and vacuum dried at 80°C until a constant weight was achieved. In this process, the toluene renewed every day. The content of bound rubber can be calculated by the following equations:

$$\text{Bd.R}\,(\%) = 100 \times \frac{m_0 - (m_2 - m_3)}{m_0} \tag{1}$$

$$m_0 = 100 \times \frac{m_2 - m_1}{w_{\text{compound}}} \tag{2}$$

where Bd. R is the value of bound rubber in percentage, m_0, m_1, m_2, m_3, and w_{compound}, are the rubber weight in the original sample, weight of the un-filled cage, weight of the cage plus the un-extracted sample, weight of the cage plus the extracted sample after drying process and the total formulation of compound (in phr), respectively.

Swelling of the vulcanized samples was performed in toluene (representative of a good solvent) at room temperature for 7 days. After equilibrium was reached, excess solvent was wiped off from the sample surface. Then, the sample was weighed in the swollen state, dried at 80_°C under vacuum, and weighed again in the fully dried state. Crosslink density (CLD) was determined by the equilibrium swelling measurements based on the Flory–Rehner equation[43]:

$$-\left[\ln(1-\varphi_r) + \varphi_r + \chi\varphi_r^2\right] = V_0 n\left[\varphi^{\frac{1}{3}} - \frac{\varphi_r}{2}\right] \tag{3}$$

where $\varphi_r$is the volume fraction of polymer in the swollen mass, V_0 is the molar volume of the solvent (106.2 cm^3 for toluene), n is the number of active network chain segments per unit volume (crosslinking density), χ is the Flory-Huggins polymer-solvent interaction term, with the value of 0.44 for toluene-SBR. The value of $\varphi_r$was obtained according to the method used by Bala et al[44]:

$$\varphi_r = \frac{\frac{\omega_2}{\rho_2}}{\frac{\omega_2}{\rho_2} + \frac{(\omega_1 - \omega_2)}{\rho_1}} \tag{4}$$

where ω_1 and ω_2 are the weights of the swollen and deswollen samples, and ρ_1 and ρ_2 are the densities of the solvent and the polymer, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Morphology of the composites

Figure 1 (A, C, and E) demonstrate the state of dispersion and distribution of aggregates in the composites filled with different graphenic particles with a lower magnification. As shown in these figures, the size and distribution of aggregates are similar,[29] regardless of the reduction level

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in the latex phase. As seen at higher magnifications in Figure 1(B), GO particles have a poor affinity to the SBR matrix that can result in a weak interface with an abundance of voids in the interfacial area [29]; the lower adhesion between the filler and SBR, the higher pull-out phenomenon which leads to a lower affinity in the filler–rubber assembly and consequently a weaker interface. With increasing the level of GO reduction, the dispersion relatively remains unchanged due to the applied latex mixing method. Nevertheless, as seen in Figure 1(F), particles in rGO60 are covered by the rubber, showing that the partial removal of the surface functional groups has improved the interfacial adhesion between the rubber and filler. The reason for similar dispersion and intercalation of particles with different affinity to rubber in three types of composites is comprehensively described in our previous research by using FESEM images along with XRD test.[29]

3.2 | Surface energy of the constituents

In our previous work,[29] GO particles were synthesized and chemically reduced by hydrazine under similar conditions as done here. GO and rGO particles were characterized by energy dispersive spectroscopy, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy to evaluate the C/O ratio as a criterion of chemical reduction and quantitative appraisal of functional groups, the interlayer spacing of the GO/rGO particles, and qualitative assessment of the surface functional groups, respectively.[29] The C/O ratio and non-polarity of the particles increase with the reduction process due to elimination of oxygen containing groups from the surface of GO. The Fowkes' model[26] was employed to calculate the surface energies of the graphenic particles and SBR matrix. In this equation, the total surface energy is obtained by measuring the contact angles of two liquids as described in Equation (5):

$$\gamma_l(1+cos\theta) = 2\left(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p}\right) \quad (5)$$

where $\gamma_{l=}\gamma_l^d + \gamma_l^p$, γ_l^p and γ_l^d are the total, polar and dispersive components of the liquid surface energy, respectively (The γ_l^p and γ_l^d values for water are 51 and 21.8 mJ/m^2, respectively, also the correspondent values for glycerol are 30 and 34 mJ/m^2, respectively). γ_s^d and γ_s^p are the dispersive and polar components of the surface energy for solid surface, respectively. The obtained surface energy results are summarized in Table 2. As seen, the surface energies of the fillers are decreased through the chemical reduction process which clearly shows the removal of the GO polar surface groups. The highest values of the surface energy belong to GO, and GO demonstrates the incompatibility between the filler and SBR based on the data in Figure 1. On the contrary, with reducing the GO and eliminating the polar groups from the surface, the values of the surface energies for rGO particles are near that of SBR.

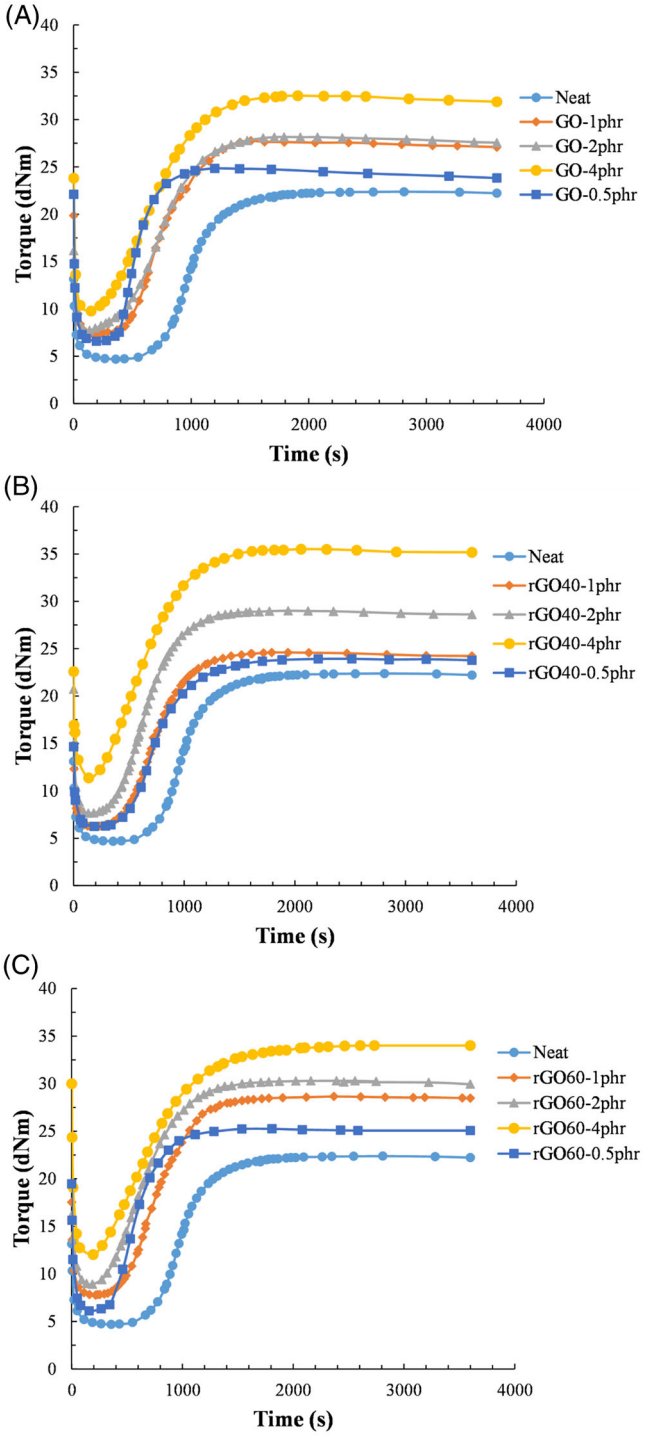


FIGURE 2 Vulcanization curves of: (A) GO/SBR, (B) rGO40/SBR, and (C) rGO60/SBR, composites obtained from rheometer

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TABLE 3 Kinetics characteristics of the composites obtained from rheometer

Composite	Graphene loading (phr)	t_{S2} (min)	t_{C100} (min)	Δt (t_{C100}- t_{S2}) (min)
Unfilled SBR	0	12.83	43.5	30.67
SBR/GO	0.5	6.08	21.76	15.68
	1	7.91	28.46	20.55
	2	7.20	31.95	24.75
	4	5.58	31.08	25.50
SBR/rGO40	0.5	8.91	26.33	17.42
	1	8.36	31.08	22.72
	2	6.83	31.61	24.78
	4	5.10	36.71	31.61
SBR/rGO60	0.5	5.95	29.10	23.20
	1	8.43	38.78	30.35
	2	6.23	37.40	31.17
	4	5.61	43.88	38.27

Abbreviations: GO, graphene oxide; rGO, reduced graphene oxide; SBR, styrene butadiene rubber.

For a deeper insight into the interfacial adhesion variation between fillers and matrix with the degree of chemical reduction, the values of the interfacial tension parameter were calculated via Equation (6) [45]:

$$\gamma_{RF} = \gamma_R + \gamma_F - 2\left(\sqrt{\gamma_R^d \gamma_F^d} + \sqrt{\gamma_R^p \gamma_F^p}\right) \quad (6)$$

where γ_R and γ_F are total surface energies of the rubber and the filler, respectively. γ^d and γ^p are dispersive and polar components of the surface energy for constituents. The interfacial tension parameter (γ_{RF}) is used as a criterion of rubber–filler energetic compatibility with lower values indicating stronger filler–rubber interaction.[45] As can be seen in Table 2, by increasing the degree of chemical reduction, the filler–rubber affinity increases and interfacial adhesion between the SBR and rGO particles improves. Further investigations will be presented in the next sections to verify the thermodynamic aspects of the interfacial adhesion on dynamics of the system.

3.3 | Vulcanization kinetics of composites

Vulcanization curves for all composites obtained from rheometry are presented in Figure 2(A–C). The rheometry method for characterizing vulcanization is based on the direct relationship between the formation of chemical cross-links and the increment of torque measured on the sample at a constant dynamic shear strain. Table 3 illustrates important vulcanization characteristics of the composites, extracted from Figure 2. As can be seen in Table 3, incorporating graphenic particles into the rubber at all loading levels reduced the induction time (t_{S2}), which represents the onset of cross-linking. A similar effect was observed for silica and carbon black reinforcing fillers in our previous studies.[17,18] Time to reach a fully vulcanized state (t_{C100}) or maximum torque was initially reduced by incorporating 0.5 phr of all three fillers into the composites, but increases as the concentration of fillers is increased. Moreover, the time period at which chemical cross-links are formed (t_{C100}–t_{S2}) shows a similar trend as t_{C100}. It can be concluded that incorporation of all three particles accelerates the overall rate of vulcanization, but as the concentration of particles increases, the rate slows. However, the induction time monotonically decreases as the concentration of fillers increases. The overall rate of vulcanization for three types of composites is in the order GO > rGO40 > rGO60. This observation challenges the previous works in the literature which consider the surface chemistry[7] or heat conductivity[11,12] of carbonic particles as the controlling effect of such particles on the kinetics of vulcanization since GO has more acidic nature but less heat conductivity than rGOs.[46,47]

In order to correlate these results to our previously explained theory,[17,18] the kinetics of cross-linking reactions needs to be studied in more detail. For this purpose, the degree of vulcanization conversion (α) based on the rheometry data can be defined as Equation (7):

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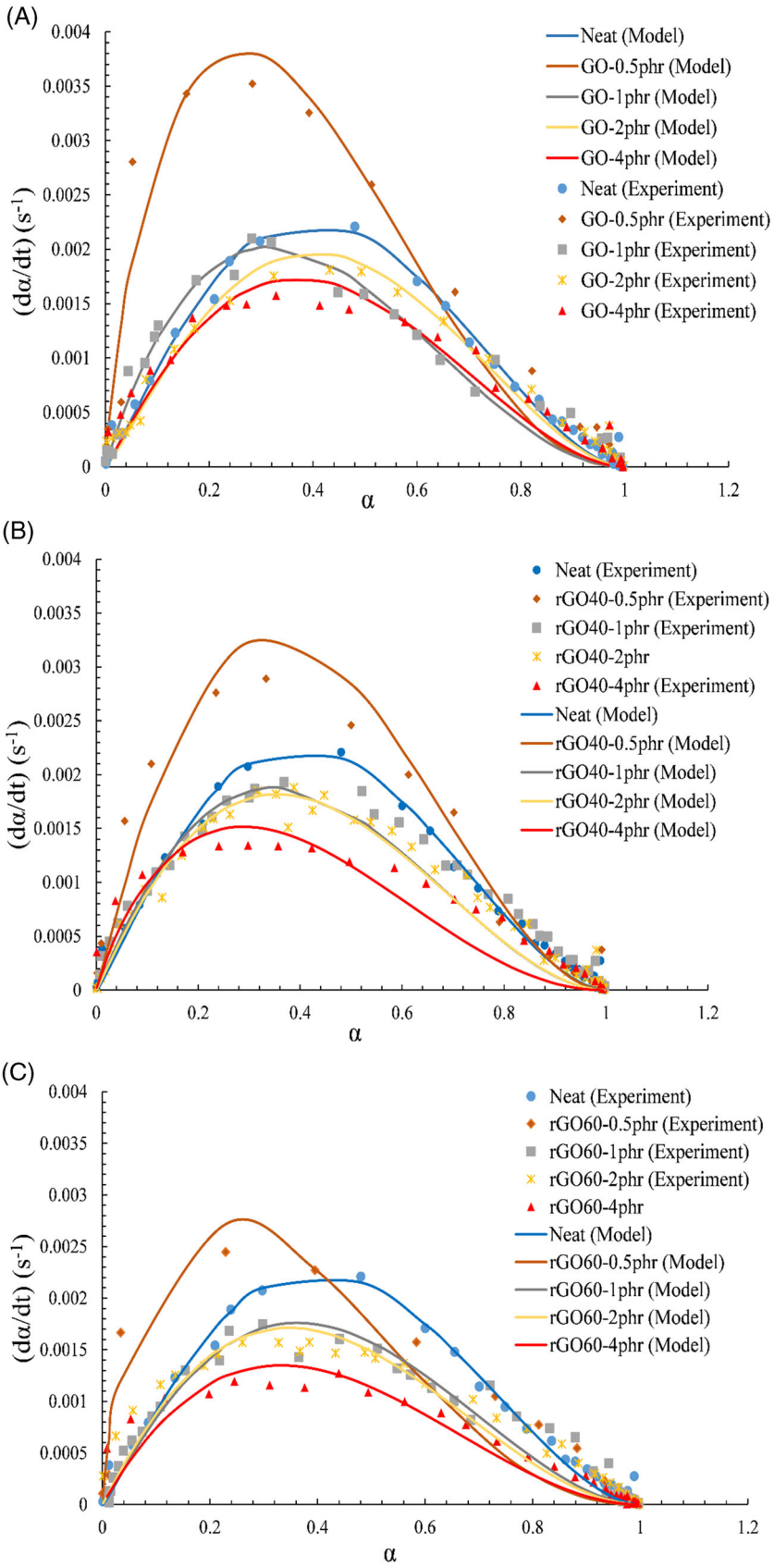


FIGURE 3 The vulcanization rate as a function of conversion for (a) GO/SBR, (B) rGO40/SBR, and (C) rGO60/SBR. The lines are the results of the fitting of autocatalytic equation on data

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TABLE 4 Kinetic parameters for the composites obtained from fitting the Equation (6) on experimental data

Composite	Graphene loading (phr)	Autocatalytic model constants					Gel point	
		N	m	$m+n$	k*1000 (s^{-1})	r^2	t_{Gel} (s)	α_{Gel} (%)
Unfilled SBR	0	1.80	1.19	~ 2.99	16.85	0.97	969	0.480
SBR/GO	0.5	2.21	0.78		21.29	0.99	462	0.283
	1	2.04	0.95		13.13	0.93	636	0.319
	2	1.80	1.19		14.76	0.94	698	0.432
	4	1.91	1.08		12.45	0.91	598	0.412
SBR/rGO40	0.5	1.94	1.05		22.72	0.94	660	0.333
	1	1.95	1.04		13.02	0.98	667	0.368
	2	1.93	1.06		12.77	0.99	586	0.376
	4	2.13	0.86		9.21	0.91	476	0.298
SBR/rGO60	0.5	2.29	0.70		13.91	0.94	462	0.229
	1	1.91	1.08		12.58	0.88	669	0.365
	2	1.96	1.03		11.87	0.88	562	0.367
	4	2.00	0.99		9.09	0.87	531	0.311

Abbreviations: GO, graphene oxide; rGO, reduced graphene oxide; SBR, styrene butadiene rubber.

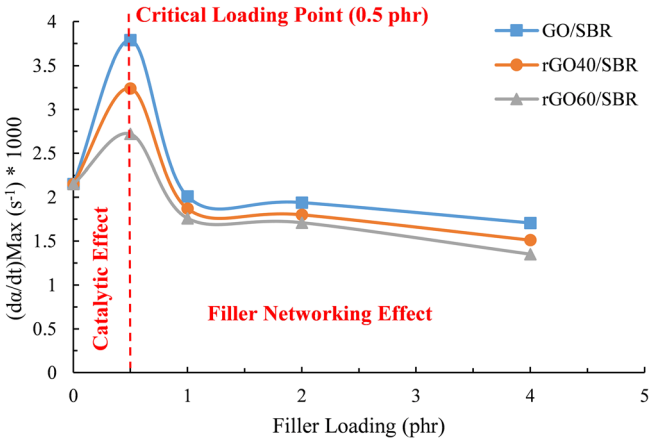


FIGURE 4 Effect of graphene surface chemistry and loading on the maximum vulcanization rate obtained from fitting experimental data on autocatalytic equation

$$\alpha(t) = \frac{T(t) - T_{min}}{T_{max} - T_{min}} \quad (7)$$

T_{min} and T_{max} represent the minimum torque (onset of the reaction) and the maximum torque value (end of the reaction) respectively, $T(t)$ is the torque value corresponding to arbitrary time (t) during the reaction. Equation (7) is based on the fact that the vulcanization conversion state is proportional to the stiffness of the vulcanizate. One well-known autocatalytic model that describes the kinetics of the vulcanization reaction in rubber composites,[48,49] was proposed by Piloyan et al.[50] according to Equation (8):

TABLE 5 The values of the fraction of immobilization along with bound rubber content in 4 phr graphene filled composites

Composite	Fraction of interfacial layer (χ_{im})	Bound rubber content (%)
Unfilled SBR	–	–
SBR/GO-4phr	0.028	27.7
SBR/rGO40-4phr	0.060	32.2
SBR/rGO60-4phr	0.125	38.1

$$\frac{d\alpha}{dt} = k\,\alpha^m(1-\alpha)^n \quad (8)$$

where dα/dt is the vulcanization rate, k is the reaction rate constant, m is the reaction order of autocatalytic part of the reaction, and n is the reaction order of non-autocatalytic part of the vulcanization. Generally, $m + n$ represents the order of the reaction. This model was fitted to the calculated rate of reaction and the results were depicted in Figure 3. Additionally, the values of m, n, $m + n$, and k for all composites were calculated by using a non-linear regression fit and summarized in Table 4. Figure 3 and Table 4 show clearly that this autocatalytic model fits well the vulcanization reaction rate obtained from experimental data for the unfilled and filled composites. Larger values of k mean faster vulcanization kinetics and higher conversions at shorter times. As presented in Table 4, by incorporating GO and rGOs into the SBR matrix the order of reaction ($m + n$) remains almost

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TABLE 6 The values of CLD for the composites filled with three graphenic fillers

Compound	Total CLD (mmol/cm^3)	Positive error	Negative error
Unfilled SBR	0.0067	0.0003	0.0003
SBR/GO-0.5	0.0094	0.0002	0.0001
SBR/GO-1	0.0141	0.0006	0.0008
SBR/GO-2	0.0153	0.0006	0.0005
SBR/GO-4	0.0199	0.0005	0.0002
SBR/rGO40-0.5	0.0088	0.0002	0.0003
SBR/rGO40-1	0.0119	0.0002	0.0002
SBR/rGO40-2	0.0150	0.0008	0.0004
SBR/rGO40-4	0.0202	0.0004	0.0005
SBR/rGO60-0.5	0.0098	0.0002	0.0002
SBR/rGO60-1	0.0114	0.0003	0.0003
SBR/rGO60-2	0.0129	0.0009	0.0005
SBR/rGO60-4	0.0123	0.0001	0.0001

Abbreviations: CLD, crosslink density; GO, graphene oxide; rGO, reduced graphene oxide; SBR, styrene butadiene rubber.

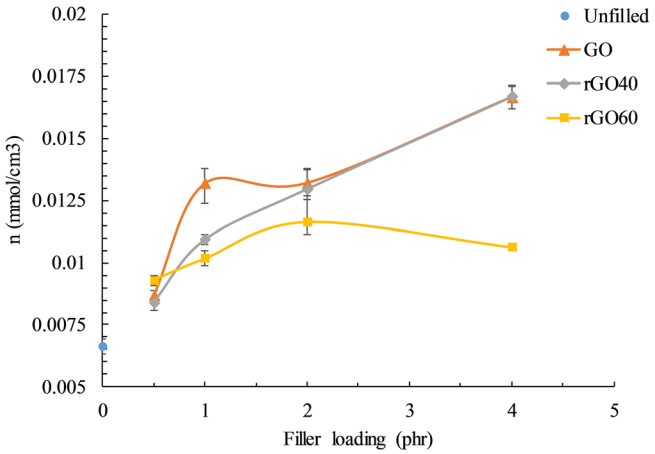


FIGURE 5 The trend of CLD of the composites using Flory–Rehner equation

constant. Constant order of the reaction demonstrates that the mechanism of the reaction is the same for all composites, regardless of the surface characteristics and loading level of particles. However, k, the rate of reaction, initially increases at low concentrations and then decreases at high amounts for the three fillers. Also, as shown in Figure 3, the trend of variation in the maximum rate of vulcanization, $(d\alpha/dt)_{max}$ or peak values, versus filler loading is similar to the changes of k and it has the order of: GO > rGO40 > rGO60. The trend of change in the $(d\alpha/dt)_{max}$ and k are in agreement with the results of Table 3. Noteworthy, the time to reach the maximum of vulcanization rate or the gel time,[17,18,48,49] drastically reduces by the addition of particles, as seen in Table 4. Changes in the gel time are in the order of GO > rGO40 > rGO60.

The reaction rate constant (k in the Equation (8)) is defined by the probability of reactions between the reactive sites, and is directly related to the mobility of reactants.[51] In small molecule systems, the mobility of reactants is a function of temperature, but high concentrations of filler and entrapment and immobilization of chains in the rubber-mediated filler network shows the same behavior as the lower temperatures.[15,20,21,23,24,52,53] Therefore, immobilized macro-radical chains in the highly-filled composites during the reaction require more thermal energy to overcome their mobility restrictions for enhancing the vulcanization conversion.[17]

Variations in the maximum rate of vulcanization against the filler loading as shown in Figure 4 can be interpreted based on our previous observations in composites filled with nanosilica,[17] carbon black,[18] and organo-clay[19] in which a unique mechanism with a critical loading point for fillers was explained for the kinetics of sulfur vulcanization of rubber. Accordingly, the kinetics of sulfur vulcanization in rGO-filled SBR composites follows similar trends as those filled with GO, but the catalytic effect in rGOs is much lower than GO because of less functional groups on the surface of rGOs that catalyze reactions between vulcanizing agents. Above the critical loading point for all three graphenic particles, the addition of more particles decelerates the vulcanization reaction due to the formation of bound rubber. In the case of GO, strong filler–filler interaction forms more loosely bound rubber, whereas in rGOs, strong filler–rubber interaction forms more tightly bound rubber. In both cases, immobilization of bound rubber leads to deceleration of the vulcanization rate.

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According to the literature,[7] it was expected that the acidic nature of GO cannot promote the kinetics of sulfur vulcanization in rubbers. Furthermore, by reducing the GO surface which eliminates polar groups, the acidity of particles decreases and the thermal conductivity of the filled composites increases,[46,47] Therefore, according to the previous theories,[7,11,12] the kinetics of vulcanization should be faster, but the opposite is seen here.

3.4 | Retarding effect of graphenic particles in highly filled composites

3.4.1 | Evaluating the extent of interfacial rubber

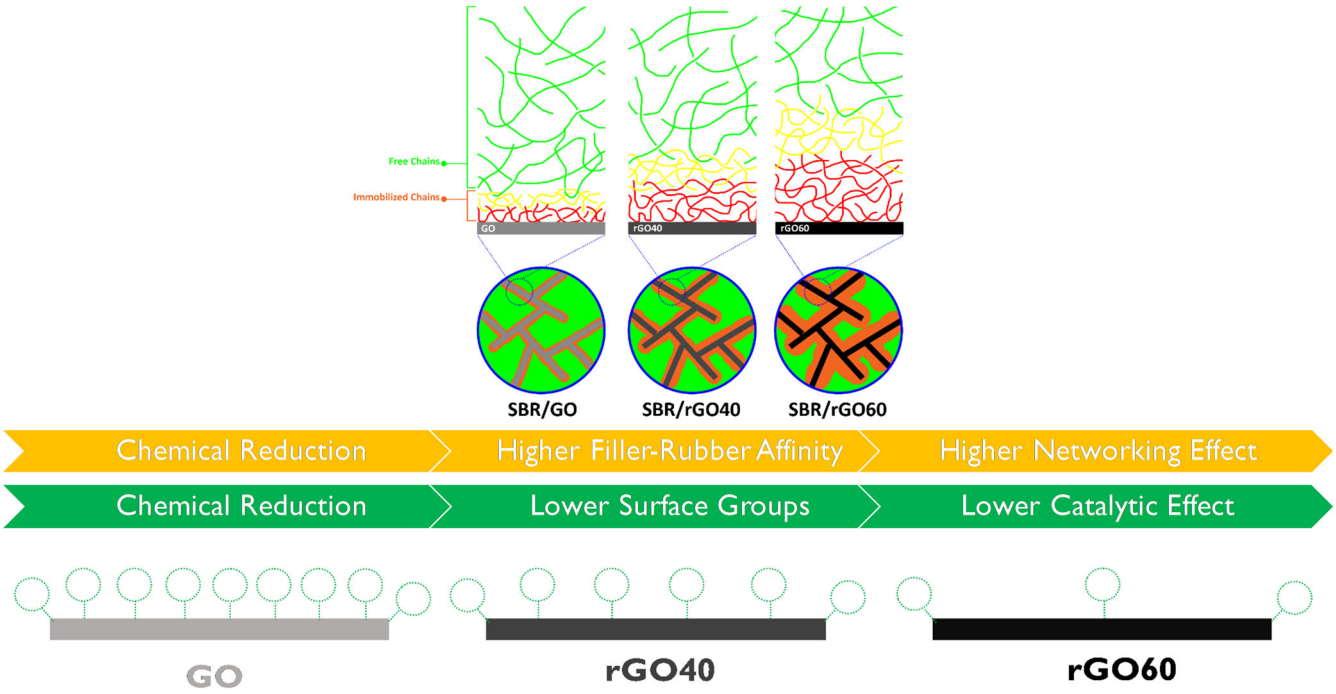
In this section, attempts were made to characterize the interfacial effects of GO and rGOs on chain mobility in the SBR composites. For this purpose, selected composites containing 4 phr of graphenic particles were tested.

3.4.2 | Calorimetric glass transition and bound rubber measurements

As described in the previous study,[29] incorporation of the fillers cause slight changes in the calorimetric glass transition temperature. A decrease in the magnitude of the heat capacity change at the glass transition (ΔC_p) for filled composites is due to immobilized rubber that does not participate in the glass transition process.[26,27,54] Fragiadakis et al.[54] proposed a relation to estimate the quantity of immobilized rubber (χ_{im}), i.e. tightly-bound rubber, in the filled system:

$$\chi_{im} = 1 - \frac{\Delta C_p}{\Delta C_p^0 (1 - w_{Filler})} \quad (9)$$

where ΔC_p^0, ΔC_p, and w_{Filler} are the heat capacity change of unfilled rubber, heat capacity increment of filled composites and weight fraction of the filler, respectively. The calculated values of χ_{im} are shown in Table 5. As can be seen, the fraction of the tightly-bound rubber greatly increases with chemical reduction. Bound rubber is the sum of tightly and loosely-bound rubber and is the fraction of rubber chains that cannot be extracted from the unvulcanized composite by a good solvent.[53] and is considered to play a major role in the reinforcement of filled rubber.[24] Reduction of GO increases filler–rubber interactions and tightly bound rubber. In general, total bound rubber increases as the degree of chemical reduction increases, but not as much as that predicted by DSC for the fraction of interfacial layer. Bound rubber, as dense immobilized chains with lower free volume than the matrix, can be considered as a substantial parameter in reducing the rate of vulcanization.[17,18,49] All results in the Table 5 agree well with our hypothesis correlating



SCHEME 1 Mechanism for sulfur vulcanization of graphene-filled rubber composites

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the rate of vulcanization to the physical effect of fillers on immobilizing the rubber chains at high concentrations of fillers.

3.5 | Crosslinking density

The CLD, measured by the equilibrium swelling method, is the sum of physical crosslinks between filler and rubber and chemical crosslinks formed during vulcanization. Table 6 summarizes the amount of CLD of the composites. Also, Figure 5 shows the trend of CLD changes in the composites filled with three different graphenic fillers. In general, CLD increases with loading fillers. However, with increasing the degree of chemical reduction, the rate of growth in CLD decreases due to the decrease in the degree of vulcanization, as explained in our previous work.[18] As seen in both Table 6 and Figure 5, rGO60 has the lowest CLD, which can be attributed to the higher fraction of the immobilized rubber that was found in DSC and bound rubber measurements.

For elucidating the mechanism of the sulfur vulcanization in graphene-filled rubber composites, we have proposed a mechanism that can be seen in Scheme 1. In one hand, with increasing the chemical reduction, surface groups are eliminated and the catalytic effect would be less pronounced. On the other hand, the partial removal of the surface groups would lead to increase in the interfacial layer in the form of immobilized rubber.

4 | CONCLUSIONS

Kinetics of rubber vulcanization was studied for nanocomposites formed by SBR and graphenic particles with different surface chemistries. In-situ chemical reduction of GO particles in SBR latex provided a convenient method to modify the interfacial effects of fillers. The catalytic effect of GO was higher than the rGOs due to more functional groups on the surface of the former. More reduced particles show stronger interaction with rubber, and the interfacial or networking effect on decreasing the rate of vulcanization was more important. The networking effect of graphenic particles on vulcanization was verified by the presence of interfacial layers and bound rubber, which are higher for more reduced rGO's. This study confirms the unique mechanism (catalytic and networking) for the effect of particles on the sulfur vulcanization of rubber composites regardless of the filler surface chemistry.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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REFERENCES

[1] S. Thomas, R. Stephen, in *Rubber Nanocomposites* (Eds: S. Thomas, R. Stephen), John Wiley & Sons, Ltd, Chichester, UK **2010**.

[2] N. Torbati-Fard, S. M. Hosseini, M. Razzaghi-Kashani, *Polym. J.* **2020**, *52*, 1223.

[3] Z. H. Li, J. Zhang, S. J. Chen, *Express Polym. Lett.* **2008**, *2*, 695.

[4] M. A. López-Manchado, M. Arroyo, B. Herrero, J. Biagiotti, *J. Appl. Polym. Sci.* **2003**, *89*, 1.

[5] J. Ramier, L. Chazeau, C. Gauthier, L. Guy, M. N. Bouchereau, *Rubber Chem. Technol.* **2007**, *80*, 183.

[6] M. A. Semsarzadeh, G. R. Bakhshandeh, M. Ghasemzadeh-Barvarz, *Iran. Polym. J. (English Ed.)* **2005**, *14*, 573.

[7] J. Wu, W. Xing, G. Huang, H. Li, M. Tang, S. Wu, Y. Liu, *Polymer (Guildf.)* **2013**, *54*, 3314.

[8] S. Maghami, W. K. Dierkes, J. W. M. Noordermeer, *Rubber Chem. Technol.* **2016**, *89*, 559.

[9] A. K. Zachariah, A. K. Chandra, P. K. Mohammed, S. Thomas, *Polym. Test.* **2019**, *76*, 154.

[10] H. Dong, Y. Luo, B. Zhong, J. Bai, D. Jia, *Polym. Test.* **2020**, *81*, 106169.

[11] A. Allahbakhsh, S. Mazinani, M. R. Kalaee, F. Sharif, *Thermochim. Acta* **2013**, *563*, 22.

[12] S. M. Park, Y. W. Lim, C. H. Kim, D. J. Kim, W.-J. Moon, J.-H. Kim, J.-S. Lee, C. K. Hong, G. Seo, *J. Ind. Eng. Chem.* **2013**, *19*, 712.

[13] S.-S. Choi, *Polym. Int.* **2001**, *50*, 524.

[14] S.-S. Choi, B.-H. Park, H. Song, *Polym. Adv. Technol.* **2004**, *15*, 122.

[15] A. Mujtaba, M. Keller, S. Ilisch, H.-J. Radusch, T. Thurn-Albrecht, K. Saalwächter, M. Beiner, *Macromolecules* **2012**, *45*, 6504.

[16] M. A. Ansarifar, J. P. Chugh, S. Haghighat, *Iran. Polym. J. (English Ed.)* **2000**, *9*, 81.

[17] S. M. Hosseini, M. Razzaghi-Kashani, *Polymer (Guildf.)* **2014**, *55*, 6426.

[18] S. M. Hosseini, M. Razzaghi-Kashani, *Soft Matter* **2018**, *14*, 9194.

[19] A. Sepehri, M. Razzaghi-Kashani, M. H. R. Ghoreishy, *J. Appl. Polym. Sci.* **2012**, *125*, E204.

[20] J. G. Meier, M. Klüppel, *Macromol. Mater. Eng.* **2008**, *293*, 12.

[21] A. Mujtaba, M. Keller, S. Ilisch, H.-J. Radusch, M. Beiner, T. Thurn-Albrecht, K. Saalwächter, *ACS Macro Lett.* **2014**, *3*, 481.

[22] G. A. Bohm, W. Tomaszewski, W. Cole, T. Hogan, *Polymer (Guildf.)* **2010**, *51*, 2057.

[23] J. Fritzsche, M. Klüppel, *J. Phys. Condens. Matter* **2011**, *23*, 35104.

[24] Y. Yue, H. Zhang, Z. Zhang, Y. Chen, *Compos. Sci. Technol.* **2013**, *86*, 1.

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[25] L. Song, Z. Li, L. Chen, H. Zhou, A. Lu, L. Li, *RSC Adv.* **2016**, *6*, 101470.
[26] B. Zhong, Z. Jia, D. Hu, Y. Luo, B. Guo, D. Jia, *Appl. Surf. Sci.* **2016**, *366*, 193.
[27] B. Zhong, Z. Jia, Y. Luo, D. Jia, *Compos. Sci. Technol.* **2015**, *117*, 46.
[28] S. Verma, S. Mohanty, S. K. Nayak, *Soft Matter* **2020**, *16*, 1211.
[29] M. Raef, M. Razzaghi-Kashani, *Polymer (Guildf.)* **2019**, *182*, 121816.
[30] S. Wilczewski, K. Skórczewska, J. Tomaszewska, K. Lewandowski, *Polym. Test.* **2020**, *81*, 106282.
[31] V. Kumar, N. Alam, D.-J. Lee, U. Giese, *Rubber Chem. Technol.* **2020**, *93*, 172.
[32] B. Ucpinar Durmaz, C. Ozturk, A. Aytac, *Polym. Eng. Sci.* **2020**, *60*, 2606.
[33] N. L. Batista, E. Helal, R. S. Kurusu, N. Moghimian, E. David, N. R. Demarquette, P. Hubert, *Polym. Eng. Sci.* **2019**, *59*, 675.
[34] S. Yaragalla, C. Sarath Chandran, N. Kalarikkal, R. H. Y. Subban, C. H. Chan, S. Thomas, *Polym. Eng. Sci.* **2015**, *55*, 2439.
[35] J. Jose, M. A. Al-Harthi, M. A. A. AlMa'adeed, J. B. Dakua, S. K. De, *J. Appl. Polym. Sci.* **2015**, *132*, 41827.
[36] Muthusankar, E.; Ragupathy, D. *Nano-Structures and Nano-Objects* **2019**, *20*, 100390.
[37] Sarkar, N.; Sahoo, G.; Swain, S. K. *Nano-Structures and Nano-Objects* **2020**, *23*, 100507.
[38] Z. Yang, H. Liu, S. Wu, Z. Tang, B. Guo, L. Zhang, *Chem. Eng. J.* **2018**, *342*, 112.
[39] M. G. Maya, J. Abraham, S. C. George, S. Thomas, *J. Appl. Polym. Sci.* **2019**, *136*, 48168.
[40] Yaragalla, S.; Thomas, S.; Maria, H. J.; Mishra, R. K.; Kalarikkal, N. *Carbon-Based Nanofiller and their Rubber Nanocomposites*; Elsevier, Amsterdam **2019**.
[41] B. V. Basheer, J. J. George, S. Siengchin, J. Parameswaranpillai, *Nano-Struct. Nano-Obj.* **2020**, *22*, 100429.
[42] V. Phetarporn, S. Loykulnant, C. Kongkaew, A. Seubsai, P. Prapainainar, *Mater. Today Commun.* **2019**, *19*, 413.
[43] L. Qu, G. Yu, L. Wang, C. Li, Q. Zhao, J. Li, *J. Appl. Polym. Sci.* **2012**, *126*, 116.
[44] Bala, P.; Samantaray, B. K.; Srivastava, S. K.; Nando, G. B. *J. Appl. Polym. Sci.* **2004**, *92*, 3583.
[45] M. Alimardani, M. Razzaghi-Kashani, R. Karimi, A. Mahtabani, *Rubber Chem. Technol.* **2016**, *89*, 292.
[46] Y. Yang, J. Cao, N. Wei, D. Meng, L. Wang, G. Ren, R. Yan, N. Zhang, *Molecules* **2019**, *24*, 1103.
[47] C. B. Kim, J. Lee, J. Cho, M. Goh, *Carbon N. Y.* **2018**, *139*, 386.
[48] R. Ding, A. I. Leonov, *Rubber Chem. Technol.* **1999**, *72*, 361.
[49] S. M. Hosseini, M. Razzaghi-Kashani, *Polymer (Guildf.)* **2017**, *133*, 8.
[50] G. O. Piloyan, I. D. Ryabchikov, O. S. Novikova, *Nature* **1966**, *212*, 1229.
[51] Christov, S. G. *Collision Theory and Statistical Theory of Chemical Reactions*; Springer-Verlag, Berlin **1980**.
[52] K. W. Stöckelhuber, S. Wießner, A. Das, G. Heinrich, *Soft Matter* **2017**, *13*, 3701.
[53] S. Choi, E. Ko, *Polym. Test.* **2014**, *40*, 170.
[54] D. Fragiadakis, L. Bokobza, P. Pissis, *Polymer (Guildf.)* **2011**, *52*, 3175.

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