



Effects of Zinc Stearate Replacement and Zinc Oxide/Zinc Stearate Ratio on Rheological Properties and Curing Characteristics of Carbon Black-Filled Rubbers

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Article Information	Abstract
<p>Article history:</p> <p>Received: 2024-04-05</p> <p>Accepted: 2024-12-28</p>	<p>This work aims to study the substitution of zinc stearate (ZS) as an activator and co-activator with stearic acid (SA), its mechanism of action, and also the influence of ZnO/ZS on the rheological and curing characteristics of styrene-butadiene (SBR), butadiene (BR), and nitrile-butadiene (NBR) rubbers-filled carbon black. Despite accelerating the curing reaction rate of SBR, BR, and NBR by ~119, 145, and 22%, the ZS chemical increased the maximum torque in the oscillating disc rheometer (ODR) by 13 and 17% for BR and NBR, respectively, with a slight change for SBR. The minimum torque in the ODR test also increased by ~25% and 11% for BR and NBR in the presence of ZS, while SBR experienced a ~8% reduction. The decrease in the ZnO/ZS ratio changed the rheological behavior of SBR to an insignificant over curing reversion in the maturing zone. The curing time of SBR was decreased from 15.09 to 11.31 min by reducing the ZnO/ZS amount from 2/1 to 1/1, while the scorch time was almost similar in the BR and NBR-based compounds. Reducing the ZnO/ZS amount raised the maximum vulcanization rate of SBR by ~50% (0.687 to 1.03 1/min), while its trend was descending in the BR and NBR compounds by ~53% and 20%. Moreover, the decrease of ZnO in the recipe containing the ZS chemical decreased the cross-linking by ~16% (from 8.065 to 6.768×10⁵ mol/g) and 4% (from 0.278 to 0.268×10⁵ mol/g) for the BR and NBR compounds, while it did not vary the SBR crosslink density.</p>
<p>Keywords:</p> <p>Rubber compound; Cure characteristics; Zinc oxide; Zinc stearate; Stearic acid.</p>	

1 INTRODUCTION

The unique properties of rubbers, *i.e.*, high absorbance of shocks, insulator of heat and electricity, good moldability, resistance to breaking, chemicals, and water, have made them fantastic candidates to use in various industrial fields [1], [2]. Pipe fitting, gardening applications, matting and flooring, medical accessories, insulating materials, and automobile

The SBR, BR, and NBR polymers by themselves do not have the required capability to be used in industries. Hence, they have been turned into a composite using different chemical additives and mineral fillers [8]. Various fillers, *i.e.*, carbon black [9], silicon carbide [10], silicon nitride [11], alumina [12], graphene [13], clay [14], as well as the silane coupling agent [15] have been applied to improve the properties of the aforementioned rubbers. Abdelsalam *et al.* [16] studied the impact of the carbon black (CB) content on

production are only some examples of the targeted applications for rubbers [3], [4]. So far, different types of rubbers have been manufactured for desired applications, from natural rubbers to synthetic ones [5]. Despite the existence of various rubbers, styrene-butadiene (SBR), butadiene (BR) and nitrile-butadiene (NBR) rubbers and also their blends, are the most widely used rubbery materials in different industries, from car accessories to rubber rings for sealing [6], [7].

the rheological and mechanical features of the SBR/NBR-based nanocomposites. Their results showed that the minimum and maximum torques, tensile strength, elongation at break, and crosslink density were enhanced by the filler content, while the curing times and the filler interactions with rubber were decreased. Rasouli *et al.* [17] proved the significant catalytic effect of the silicon carbide on the vulcanization reaction of the SBR/BR blend by adding 5 phr (parts per hundred rubber) of the filler. Moreover, they reported that

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silicon nitride as a high thermal diffusive material also improves the thermal diffusivity of SBR/BR by more than 90% [18]. Zirnstein *et al.* [19] promoted Young's modulus, hardness, and flame retardancy of NBR-filled carbon black by over 60%, 10% and 10%, respectively, using multilayer graphene made of only 10 sheets of graphene at a low content of 3 phr. Essawy *et al.* [20] increased the stress at yield by 2.5–5 times for the NBR/SBR blend by adding 20 phr of the montmorillonite clay as a reinforcement filler. Tang *et al.* [21] evaluated the natural rubber/SBR composites reinforced with hydrophobic silica and carbon black for a damping bearing application. In another research work, Akshay *et al.* [22] improved the mechanical characteristics, *i.e.*, tensile, abrasion, tear, and resilience, of SBR/NBR blends by using silicon carbide filler. In a comprehensive consideration, Jin *et al.* [23] investigated the influences of SBR/BR blend ratio, silica, and vulcanization parameters on the tire tread performance. According to the literature, polymer scientists have commonly focused on different types of fillers and their modified versions to improve the properties of SBR, BR, and NBR rubbers. Nevertheless, less attention has been paid to modifying and changing the required chemicals and reactants in the curing procedure during the compound preparation as the improvement agents of the rubber properties. While the fillers in the rubber compound formulation have made the processing harder, sometimes creating dispersion problems and leading to an increase in the composite density [24]. In rubber compound preparation, different chemicals are used for proper missions; antioxidants for aging and prolonging the service life, curing agents to form crosslinks between the rubber chains, plasticizers to improve processability, accelerators to raise the speed of the curing reaction, *etc.* [25]. Except for the mentioned chemicals, stearic acid (SA) and zinc oxide (ZnO) have been used in the rubber compounding as the mainstays of the recipe [26]. The SA chemical is utilized in the role of the activator of the reaction accelerators and the dispersing agent for fillers. Moreover, it has a positive effect on the processing by facilitating the mold flow by acting as a stock lubricant [27]. The ZnO promotes the strength of rubber compounds and donates a resistance against abrasion and heat, and also is one of the best guardians for ultraviolet degradation [28]. These two ingredients are usually applied at a low amount, almost 1–4 phr in the rubber formulation [29]. In comparison with the research done on the evaluation of filler effects on the improvement of the rubber compound properties, less research work has been conducted on the impact of chemicals on the features of rubber composites. Sirisinha *et al.* [30] increased the swelling percentage of isoprene rubber by adding 3–4 phr of SA. Hadi *et al.* [31] enhanced the curing rate index by 48% and rheometry torque by 4% by using 8 phr of the conventional ZnO. Zinc stearate, used as a substitute for 5 phr ZnO and 2.5 phr stearic acid in solid tire production, significantly improved curing efficiency by accelerating curing time (t_{90}) by 58.3–69% and scorch time (t_{s2}) by 22.4–95.5%, enhanced mechanical properties such as compression set by 28.6–57.1%, and promoted a more homogeneous material distribution in the vulcanized rubber matrix [32].

In this research, zinc stearate (ZS) as a combination of ZnO and SA chemicals, is used as a replacement for SA. The effects

of ZS and the ratio of ZnO/ZS on the cure characteristics, vulcanization rate and crosslink density of the most usable rubber compounds in the industries, SBR, BR and NBR-filled N330-type carbon black, are studied in this work.

2 MATERIALS AND METHODS

2-1 Materials

Styrene-butadiene rubber [type 1500, 23.5 wt.% remaining styrene, glass transition temperature of $-40\text{ }^{\circ}\text{C}$ and Mooney viscosity of 52 MU (at $100\text{ }^{\circ}\text{C}$)], butadiene rubber [type 1210S, 97 wt.% cis and Mooney viscosity of 45 MU (at $100\text{ }^{\circ}\text{C}$)] and acrylonitrile-butadiene rubber [type 1845, bound acrylonitrile 18% and Mooney viscosity of 51 MU (at $100\text{ }^{\circ}\text{C}$)] were purchased from Bandar Imam Petrochemical Co. (Khuzestan, Iran), Shazand Petrochemical Co. (Arak, Iran) and Kumho Petrochemical Co., Ltd. (Korea), respectively. Zinc oxide, stearic acid, sulfur, and aromatic DAES30-type oil [specific gravity of 1 g.cm^{-3} , flash point of $200\text{ }^{\circ}\text{C}$, kinematic viscosity of 20 cSt] were bought from Arian Tootia Co. (Shar e kord, Iran), Pars Pak Kimiya Co. (Tehran, Iran), Parto Googerd Asia Co. (Tehran, Iran) and Iranol Co. (Tehran, Iran), respectively. Moreover, zinc stearate [type EBSOP630, specific gravity of 0.994 g.cm^{-3} and acid value 0.8 mg KOH/g], DOP oil (2-ethylhexyl phthalate) [type 6751, specific gravity of 0.986 g.cm^{-3} , flash point of $230\text{ }^{\circ}\text{C}$] and antioxidant 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) [type 4020, purity of 96% min] were supplied by Pakchemical Co. (Tehran, Iran), Shokouhshimi Co. (Tehran, Iran) and Richon Chem Co. (Dalian, China), respectively. Pre-vulcanization scorch inhibitor of PVI (N-cyclohexylthio-phthalamide (CTP)) was supplied by Henan Kailun Chemical Co., Ltd. (Henan, China). The chemicals of accelerator CZ (N-cyclohexyl-2-benzothiazolesulfenamide), accelerator DM (2,2'-dibenzothiazole disulfide) and accelerator TBBS (N-tert-butyl-benzothiazole sulfonamide) were also purchased from Kemai Chemical Co., Ltd. (Tianjin, China). The carbon black powder [type N330, purity of 98%, particle size of 200–300 nm, bulk density of 1.80 g.cm^{-3}] was bought from Iran Carbon Co. (Tehran, Iran).

2-2 Preparation of rubber compound

In the present research, the compounds containing different rubbers, SBR, BR and NBR filled with carbon black, are prepared using the lab-scale internal mixer of Brabender Plasticorder (Netherlands) and the 6"×12" two-roll mill of Farrel Pomini (USA). The two-roll mill apparatus was equipped with water circulation at $25\text{ }^{\circ}\text{C}$ to cool the compound. The formulations used in this study are summarized in Table 1, which provides detailed information on the composition and specifications of each. The preparation steps for these formulations are illustrated in the accompanying flowchart (Figure 1), which outlines the process clearly and sequentially for ease of understanding.

Table 1 The rubber compound formulations for SBR, BR and NBR in phr (parts per hundred rubber)

Sample code	SBR			BR			NBR		
	S1	S2	S3	B1	B2	B3	N1	N2	N3
Rubber	100	100	100	100	100	100	100	100	100
Stearic acid	1	0	0	1	0	0	2	0	0
Zinc stearate	0	1	1	0	1	1	0	2	2
Antioxidant 6PPD	2	2	2	2	2	2	2	2	2
ZnO	2	2	1	2	2	1	4	4	2
Sulfur	3	3	3	3	3	3	3	3	3
DAES30 oil	7	7	7	7	7	7	0	0	0
DOP oil	0	0	0	0	0	0	7	7	7
Accelerator CZ	1	1	1	1	1	1	0	0	0
Accelerator DM	1	1	1	1	1	1	0	0	0
Accelerator TBBS	0	0	0	0	0	0	2	2	2
PVI	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Carbon black	30	30	30	30	30	30	30	30	30

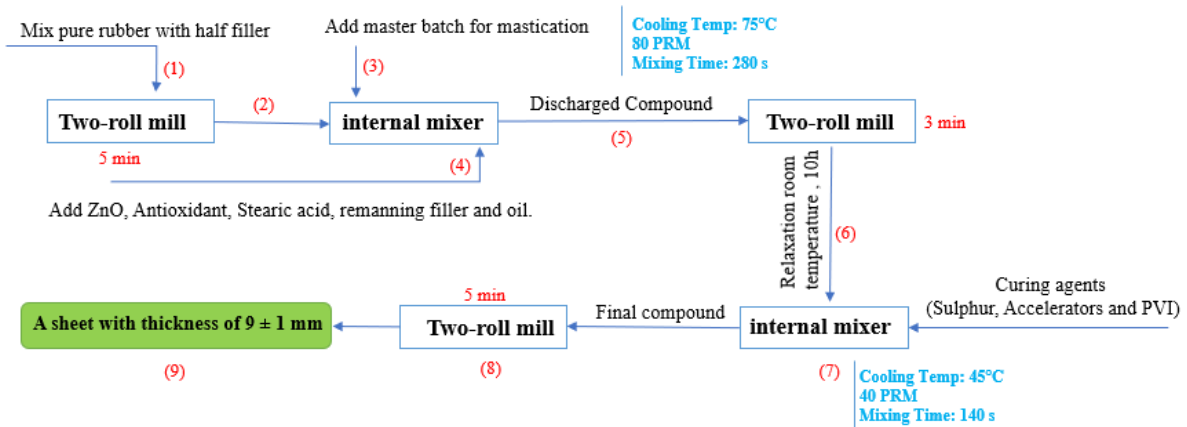


Fig. 1 Flowchart of the compound preparation steps

2-3 Vulcanization of rubber compounds

The prepared final compounds were compression molded in a hydraulic hot press at 10 MPa pressure and 160 °C based on their respective cure times. The curing time for all the compound formulations was obtained by the oscillating disk rheometer of Monsanto ODR 2000 (Ohio, USA) at a temperature of 160 °C.

2-4 Testing performed on rubber compound

2-4-1 Rheological test

A rheometry test was implemented on the cured compounds using the oscillating disc rheometer of Monsanto ODR 2000 (Ohio, USA) according to the standard of ASTM D-2084. The rheological test was done to find the cure characteristics, *i.e.*, the maximum and minimum torques, optimum cure time and the curing kinetics for each compound.

2-4-2 Swelling test

Swelling analysis in room temperature of 25 °C was done using the standard of ASTM D471, to quantify the crosslinking degree of the cured composites (with an average on the five different samples for each compound formulation). To accomplish the swelling test, each sample was cut into the dimensions of 20×20 mm² with a thickness of 6 mm and then the sample was weighed. Next, the samples were put into the

toluene aromatic solvent for 48 h, according to the aforementioned standard. The value of crosslink density is obtained based on the weighed samples before and after the 2 days (swelling period).

2-4-3 Density measurement

The density of the cured sample was achieved using the buoyancy method using the densimeter of DM3000 made by MonTech Company (Germany) according to the standard of ASTM D297. The density was determined based on an average of five different samples.

3 RESULTS AND DISCUSSIONS

In the present research, zinc stearate - the combination of zinc oxide and stearic acid - was considered a potential alternative for stearic acid in the activation of the curing accelerators to improve the cure characteristics of the rubber compounds. The study aims to reveal the role of the ZnO/ZS ratio in the curing features of the compounds as well.

3-1 Cure characteristics of rubber compound

3-1-1 Replacement of zinc stearate with stearic acid

To control the stiffness of rubbers during the curing procedure, the oscillating disc rheometer (ODR) test is usually

utilized. The ODR apparatus detects the required torque to oscillate a disc in a cavity filled with the rubber compound. The viscosity of the compound is enhanced due to the stiffening of the compound during the vulcanization, consequently, more torque is needed to rotate the disc. Therefore, the stiffness change of rubbers during the vulcanization process in the ODR test is used as an indicator of the curing degree of the rubber compounds. In this research, the torque-time curves extracted from the ODR test during the curing of the SBR, BR and NBR-filled 30 phr carbon black are used to quantify the curing features of the vulcanization reaction of the compounds. The torque-time graphs of the ODR test for all the compounds cured with the chemicals of SA and ZS are exhibited in Figure 2.

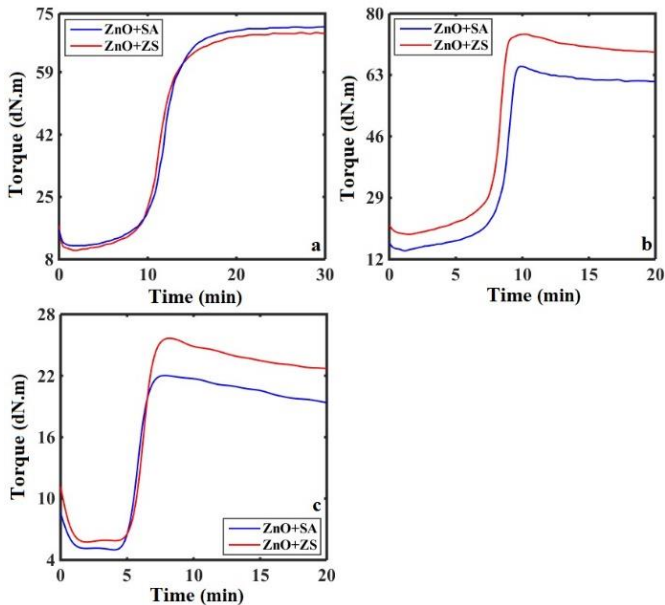


Fig. 2 The torque-time graphs extracted from the oscillating disc rheometer (ODR) for (a) SBR, (b) BR and (c) NBR -filled 30 phr (parts per hundred rubber) carbon black compounds during the vulcanization with both the stearic acid (SA) and zinc stearate (ZS) chemicals.

As illustrated in Figure 2, three-time districts are observed in the torque-time graphs, *i.e.*, the first (or induction) zone with the completion of most of the accelerator reactions, the second (or curing) zone with the formation of cross-links between the polymer chains, and the third (or maturing) zone with the completion of the curing reaction. The maturing district is accomplished by three crosslinking supplements of over-curing reversion, equilibrium, and even slower vulcanization. These three types of crosslinking occur at the end of the curing of rubbers according to the quality of the materials' chemistry. This phenomenon was also observed by Kang *et al.* [2] in the ODR test of the natural rubber compounds during the curing reaction. According to Figure 2a, the equilibrium crosslinking supplemental [33] is seen in the maturing time district for the SBR-filled CB compounds. This means neither further curing nor degradation occurred at the end of the vulcanization reaction of the SBR compounds. Whereas, the reversion crosslinking supplement is observed for the BR and NBR-filled CB compounds. However, an equilibrium occurred after the reversion supplement for the BR-based compounds. In this regard, Pöschl *et al.* [34] presented two mechanisms for the interpretation of the observed post-reversion, *i.e.*, the creation of sulfidic crosslinks with the allylic C atoms of BR and NBR

by unreacted monosulfide precursors within the broken structures and the formation of Diels–Alder reactions [35] among the polymer chains. As shown in Figure 2a-c, the replacement of the ZS chemical with SA has not changed the crosslinking supplementals of the rubber compounds.

For deep consideration of the impact of the ZS chemical on the curing features of the rubber compounds, the curing times, *i.e.*, scorch (t_s) and optimum curing (t_{90}) times, were determined utilizing Figure 2. The achieved curing times for all the compound samples are demonstrated in Figures 3a and b.

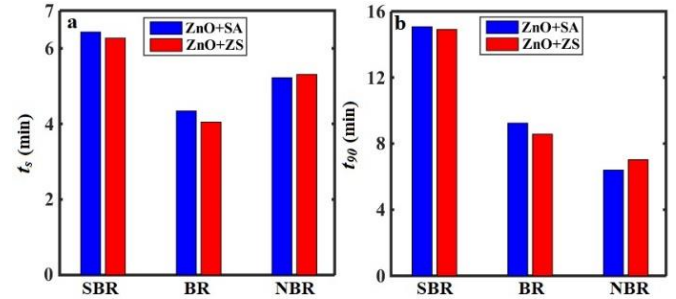


Fig. 3 The curing times: (a) scorch time (t_s) and (b) optimum curing time (t_{90}) for all the SBR, BR, and NBR-filled 30 phr CB samples cured with both the chemicals of stearic acid (SA) and zinc stearate (ZS)

As reported in Figure 3, the scorch and optimum curing times for the SBR and BR-based compounds were reduced by replacing the ZS chemical with the SA one. While the ZS led to a slight increase in the t_s and t_{90} values for the NBR compound. According to the rheometry results, the ZS chemical accelerated the curing reaction of the SBR and BR-filled CB compounds, which has a favorable effect on the vulcanization reaction. However, the ZS had a slightly worse effect on the curing times of the NBR compound. Therefore, the ZS can reduce the required time for the curing of the SBR and BR rubbers, which means saving energy and processing costs. According to Heideman *et al.* [36], the ZS chemical forms complexes with the applied accelerator improved the curing reaction kinetics.

To evaluate the ZS influence on the stiffening degree of the rubber compounds, the required minimum (ML) and maximum (MH) torque to rotate the disc during the rheometry were calculated based on Figure 2 and reported in Figure 4.

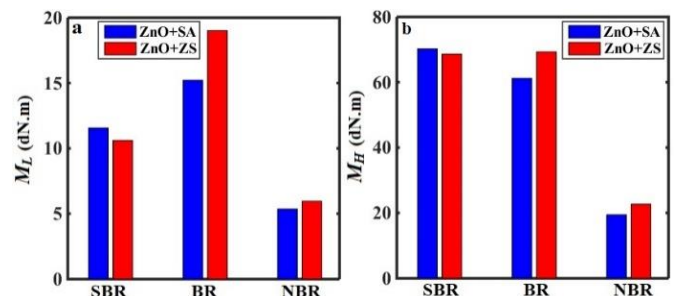


Fig. 4 The cure characteristics: (a) minimum (M_L) and (b) maximum (M_H) torques during the ODR test for all the SBR, BR and NBR-filled 30 phr CB samples cured with both the chemicals of stearic acid (SA) and zinc stearate (ZS)

According to Figure 4, the ZS chemical had an incremental effect on the ML and MH values of the BR and NBR-filled CB compounds, while the behavior was vice versa for the SBR-based compounds. As seen in the figure, the ML and MH amounts were increased by ~25% and 13% for BR and ~11%

and 17% for NBR, while they were reduced by ~8% and 3% for the SBR compound, respectively. Therefore, the ZS not only improved the curing times but also increased the ML and MH values for the BR rubber. However, zinc stearate had a desirable impact on the curing times of the SBR compound and the torques of the NBR sample. According to the calculated data, despite the improvement of the curing times of BR, the ZS chemical caused the stiffening of the BR and even the NBR compounds during the vulcanization procedure by increasing the crosslinking degree between the polymer chains.

In addition, to quantify the influence of the ZS on the rate of the vulcanization reaction of the SBR, BR, and NBR-filled CB compounds, first, the curing conversion was obtained for all the samples using the following equation [37]:

$$\alpha = \frac{M - M_L}{M_H - M_L} \quad (1)$$

In which M indicates the torque of the oscillating disc rheometer at time t. The conversion-time graphs of the vulcanization reaction for all the compounds during the curing reaction extracted from Figure 2 are shown in Figure 5.

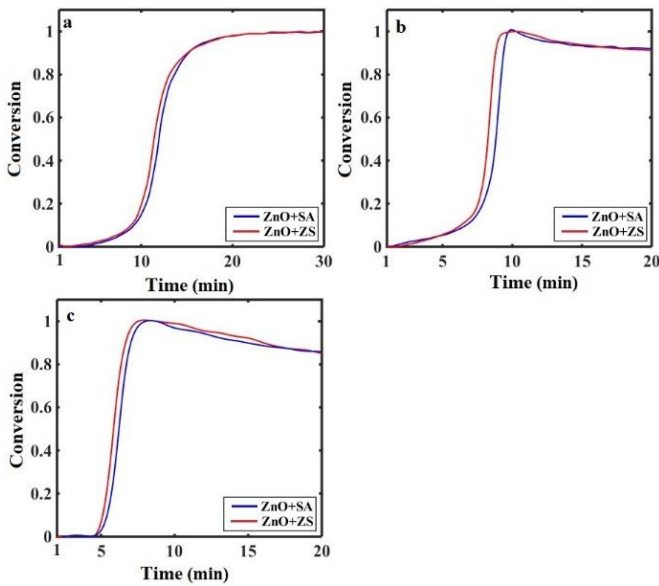


Fig. 5 The conversion of the curing reaction as a function of the rheometry time for (a) SBR, (b) BR and (c) NBR-filled 30 phr CB compounds containing both the stearic acid (SA) and zinc stearate (ZS) chemicals

As exhibited in Figure 5, the ZS chemical increased the conversion of the vulcanization reaction of the SBR, BR, and NBR-based compounds at each time. Also, zinc stearate led to the completion of the reaction in lower times. On the other hand, the replacement of ZS with the SA chemical moved the conversion-time curves to a lower time, which means the completion of the curing reaction of the samples occurs sooner. This phenomenon occurred due to a better activation role of the ZS chemical than the SA to accelerate the creation of the sulfur bonds. The role of the ZS in rubber compounds is like a catalyst to complete a chemical reaction in lower time. According to Coleman et al. [38], the complex formed by zinc and stearic acid (ZS) is further reacted with the applied accelerator in the recipe compared to SA. For this reason, the curing times shifted to lower times. Using ZS instead of SA

saved time by removing the required time for the creation of the Zn-SA complex because it already exists.

To examine the kinetics of the curing reaction for all the compounds, the conversion-time graphs are used to determine the rate of the vulcanization (R_v) reaction using the following equation [39]:

$$R_v = d\alpha/dt \quad (2)$$

The calculated curing rates for the vulcanization reaction of the rubber compounds based on Eq. 2 are exhibited in Figure 6 as a function of the reaction time.

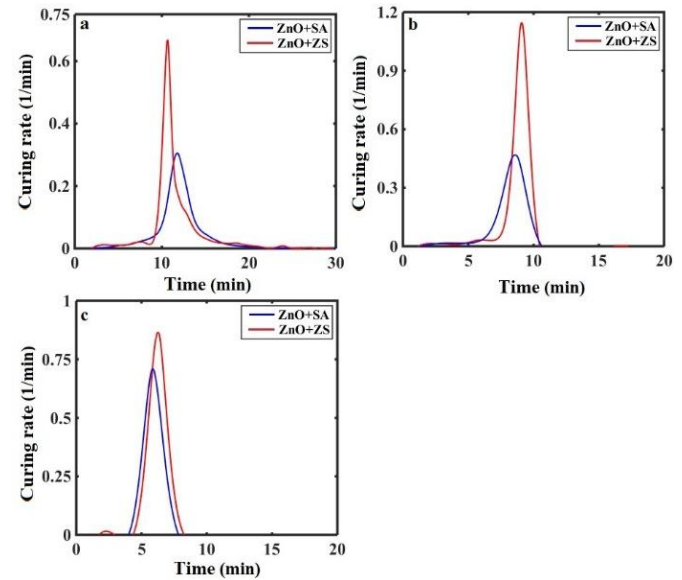


Fig. 6 The values of the curing reaction rate ($d\alpha/dt$) for (a) SBR, (b) BR, and (c) NBR-filled 30 phr of CB containing both stearic acid (SA) and zinc stearate (ZS) versus the curing time

As demonstrated in Figure 6, the replacement of the ZS with the SA chemical causes an obvious variation in the vulcanization rate of all the rubber compounds. The presence of the ZS chemical in the compound recipe instead of SA led to a significant enhancement in the maximum curing rate (the peak of the $d\alpha/dt$ -time curve) by ~119%, 145% and 22% for the SBR, BR, and NBR-filled CB compounds, respectively. Therefore, the ZS had a strong effect on the acceleration of the vulcanization reaction of the rubber compounds. Because the activation impact of the ZS chemical on the curing reaction was further than stearic acid. Pargoletti et al. [40] also reported the same observation about the effect of Zn-SA and ZS on rubber vulcanization. The changes were much more drastic in the BR-based compounds.

3-1-2 Impact of the ZnO/zinc stearate ratio

In the last section, the impact of the replacement of the zinc stearate with stearic acid on the cure characteristics of the SBR, BR, and NBR-filled carbon black compounds was deeply investigated. In this section, the effect of the ZnO/zinc stearate (ZnO/ZS) ratio on the curing features of the rubber compounds is evaluated. For this reason, the compounds consisting of two ZnO/ZS ratios of 2/1 and 1/1 were prepared according to the preparation method presented in Section 2.2. The recipe for the compounds is listed in Table 1. First, to find the effect of the ZnO/ZS ratio on the rheological properties of the compounds, the ODR test was performed on the SBR, BR,

and NBR-based compounds. The torque-time graphs for all the compounds are demonstrated in Figure 7.

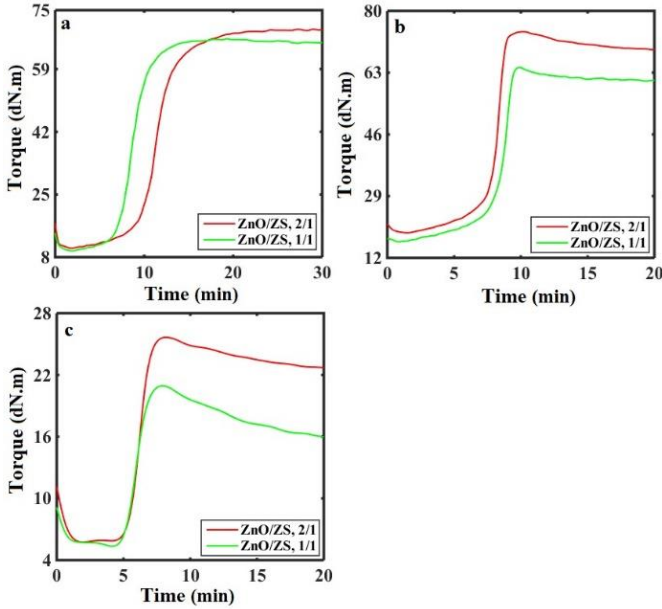


Fig. 7 The torque-time graphs extracted from the oscillating disc rheometer (ODR) for (a) SBR, (b) BR and (c) NBR-filled 30 phr (parts per hundred rubber) carbon black compounds during the vulcanization with both the ZnO/zinc stearate ratios of 2/1 and 1/1

As seen in Figure 7, the rheological behaviors of the SBR-filled CB were changed in the maturing zone, from equilibrium supplemental to an insignificant reversion crosslinking, by reducing the ZnO/ZS ratio. Also, decreasing the ZnO/ZS amount from 2/1 to 1/1 enhanced the overcuring reversion phenomenon in the third time district of the NBR compound. However, the reversion supplement in the last time zone for the BR compound was slightly reduced to the ZnO/ZS ratio of 1/1. To create a better understanding of the effect of the ZnO/ZS ratio on the curing times of the rubber compounds, the t_s and t_{90} values for all the compounds were extracted from Figure 7 and reported in Figures 8a and b, respectively.

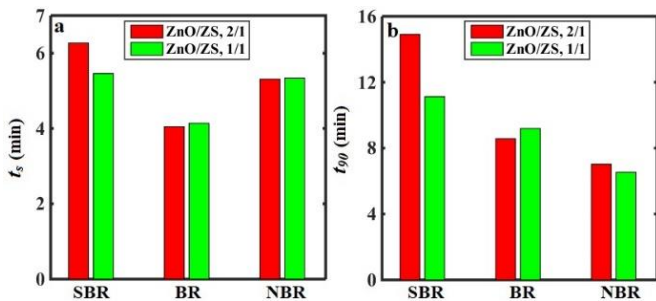


Fig. 8 The curing times; (a) scorch time (t_s) and (b) optimum curing time (t_{90}) for all the SBR, BR, and NBR-filled 30 phr CB samples cured with both the ZnO/zinc stearate ratios of 2/1 and 1/1

As shown in Figure 8a, the scorch time of the curing process was reduced by ~13% for SBR by changing the ZnO/ZS ratio from 2/1 to 1/1, while the t_s value was almost constant for the BR and NBR compounds. Moreover, the optimum curing times of the SBR and NBR compounds containing lower amounts of ZnO/ZS had a lower value; a ~25% and 7%

reduction compared to ZnO/ZS=2/1, respectively (see Figure 8b).

Additionally, the minimum and maximum torques of the ODR test for all the compounds are exhibited in Figure 9.

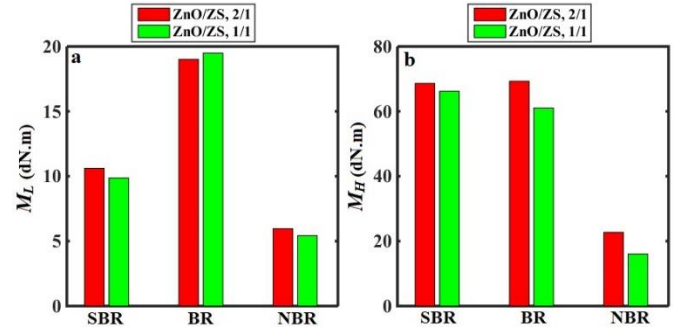


Fig. 9 The cure characteristics; (a) minimum (M_L) and (b) maximum (M_H) torques during the ODR test for all the SBR, BR and NBR-filled 30 phr CB samples cured with both the ZnO/zinc stearate ratios of 2/1 and 1/1

In general, the reduction of the ZnO/ZS ratio from 2/1 to 1/1 led to a decrease in the required torques to rotate the disc during the ODR test (see Figure 9). Therefore, the compounds containing a lower amount of ZnO/ZS had a lower level of stiffness, which means a lower crosslinking. However, this phenomenon was not significant.

Furthermore, to consider the role of the ZnO/ZS ratio in the conversion of the curing reaction during the vulcanization procedure, the α value versus time for all the compounds was obtained and illustrated in Figure 10. According to Figure 10, reducing the ratio of ZnO/ZS from 2/1 to 1/1 caused the curing reaction to start and to be completed earlier for the SBR compound across the whole range of the curing time. Nevertheless, the ZnO/ZS=1/1 led to a small delay in the vulcanization of the BR and NBR-filled CB compounds.

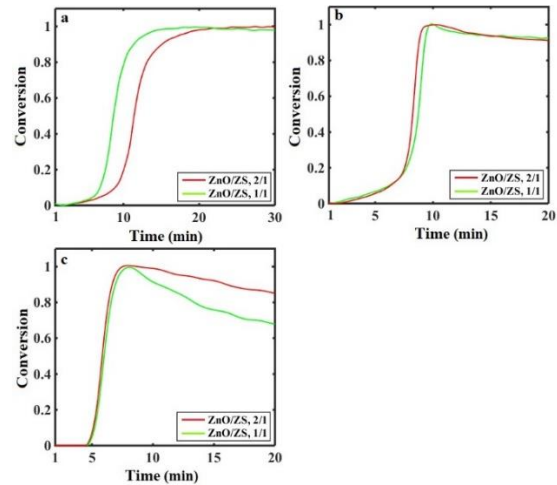


Fig. 10 The conversion of the curing reaction as a function of the rheometry time for (a) SBR, (b) BR and (c) NBR-filled 30 phr CB compounds containing both the ZnO/zinc stearate ratios of 2/1 and 1/1

To reveal the effect of the ZnO/ZS amount on the curing rates of SBR, BR, and NBR compounds, the Rv value during the ODR test was calculated using Eq. 2 and Figure 10, and the results were shown in Figure 11.

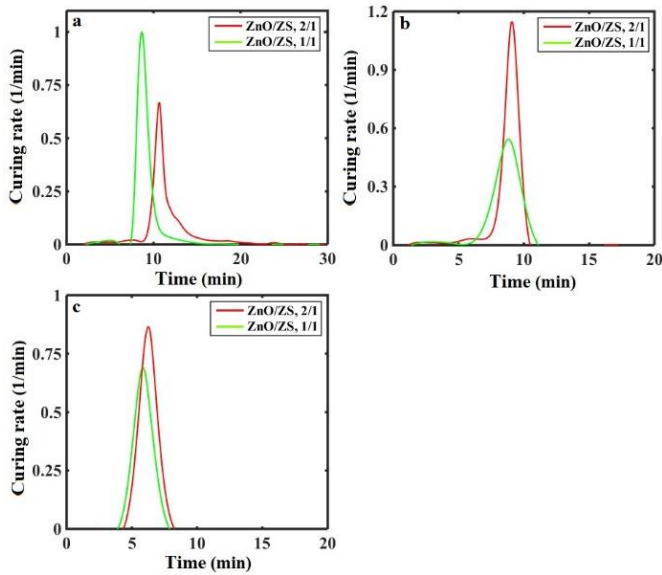


Fig. 11 The values of the curing reaction rate ($d\alpha/dt$) for (a) SBR, (b) BR and (c) NBR-filled 30 phr of CB containing both the ZnO/zinc stearate ratios of 2/1 and 1/1

Based on Figure 11, reducing the ZnO/ZS ratio to 1/1 increased the maximum curing rate (the peak of the curing rate-time curve) of the SBR-filled CB compound by ~50%. This amount of the ZnO/ZS led to a reduction in the maximum curing rate of the BR and NBR compounds by ~53% and 20%, respectively. In fact, the decrease in the ZnO/ZS ratio means the reduction of the ZnO amount or the increase of the ZS portion in the compound recipe. According to the results, reducing the ZnO amount did not have any negative effects on the cure characteristics of the SBR compound. Because the ZS material is the dominant chemical in the SBR compound, to activate the activators of the curing reaction. Hence, the activator activation (by ZS) is more effective than the sulfur activation (by ZnO) in the SBR compounds. Even though the inorganic ingredient of ZnO is an activator of the sulfur curing reaction [41], it also has thermal diffusivity capability with a thermal conductivity of ~50 W/m.K [42] due to its metallic oxide nature. Therefore, reducing its amount compared to the ZS in the BR and NBR compounds reduced the cure characteristics because of the domination of the ZnO in the ZS. Accordingly, decreasing the ZnO/ZS value in the BR and NBR compounds had a worse effect on the curing features of the compounds.

3-2 Crosslink density of rubber compound

In thermoset polymers, the number of created crosslinks between the polymer chains per unit volume is defined as the crosslinking density (CD) [43], which is well-known in the quantification of the curing degree in polymer science [44]. Based on the Phomrak et al. [45] research, most of the

characteristics of thermoset composites, i.e., stiffness and microstructural features, significantly depend on the crosslinking of the composite. In the present research, the crosslink density of the SBR, BR, and NBR composites containing a constant 30 phr of CB is determined based on the utilized swelling method according to the equation (Eqs. 3-5) of Flory–Rehner (FR) [46]:

$$-\left[\ln(1 - V_p) + V_p + \chi V_p^2\right] = \rho_p V_s M_c^{-1} V_p^{1/3} \quad (3)$$

$$CD = \frac{1}{2M_c} \quad (4)$$

$$V_p = \frac{\left(\frac{m_i - m_f}{\rho_p}\right)}{\left(\frac{m_i - m_f}{\rho_p}\right) + \left(\frac{m_e - m_i}{\rho_s}\right)} \quad (5)$$

In the FR equation, the parameters of V_p , m_i , and m_e are defined as the volume fraction of the rubbery part in the swelling analysis, and the mass of the composites before and after the swelling test (see Section 2.4.2), respectively. The constant of $\rho_s=0.866$ g/cm³ [47] indicates the density of the toluene solvent. The densities of the SBR, BR, and NBR rubbers were obtained by the buoyancy method and listed in Table 2. In this research, the weight of the CB filler (m_f) was also involved in the CD computation process. In the Flory–Rehner equation, the parameters of M_c and $V_s=106.4$ cm³/mol are the concentration of the physical crosslinking and the molar volume of the aromatic solvent toluene, respectively. Moreover, to calculate the Flory–Huggins interaction parameter (χ), the following equation is utilized [48]. The term χ in the FR equation takes the intermolecular interactions between the toluene and polymer molecules into account [49].

$$\chi = \chi_\beta + \frac{V_s(\delta_s - \delta_p)^2}{RT} \quad (6)$$

In the above equation presented for the calculation of the interaction parameter, the constant of $\chi_\beta=0.34\pm 0.08$ is the entropic part of the Flory–Huggins parameter, which was reported by Sperling [47]. The quantities of $\delta_s=18.35$ and δ_p (presented in Table 2) are the solubility parameters of the toluene solvent and the rubbers, respectively. In Eq. 6, the temperature and gas constant were shown with the symbols of T and $R=8.314$ J/mol.K, respectively. In addition, to evaluate the swelling capability of the rubber composites, the swelling ratio with the symbol of SR is calculated as follows [12]:

$$SR = \frac{m_e - m_i}{m_i} \quad (7)$$

The calculated values of the composites' crosslink density, the χ parameter, concentration of the physical crosslinking, and swelling ratio are illustrated in Table 2.

Table 2 The results of the crosslink density (CD), the concentration of the physical crosslinking (M_c) and swelling ratio (SR) for the SBR, BR and NBR-filled 30 phr carbon black compounds cured by stearic acid and zinc stearate with different ratios of ZnO/ZS

Sample code	SBR			BR			NBR		
	S1	S2	S3	B1	B2	B3	N1	N2	N3
Polymer density (g/cm ³)	0.98	0.98	0.98	0.94	0.94	0.94	0.96	0.96	0.96
χ	0.446	0.446	0.446	0.465	0.465	0.465	0.365	0.365	0.365
$M_c \times 10^{-3}$ (g/mol)	6.187	6.213	6.232	7.741	6.199	7.387	1.864	1.794	1.860
$CD \times 10^5$ (mol/g)	8.080	8.047	8.022	6.458	8.065	6.768	0.268	0.278	0.268
SR	2.272	2.278	2.282	2.826	2.286	2.397	1.342	1.304	1.340

As listed in Table 2, the replacement of the ZS with the SA chemical caused an enhancement in the crosslink density of the BR and NBR-filled CB compounds by ~25 and 4%, respectively. However, it has not had any tangible effect on the crosslink density and swelling ratio of the SBR compound. In addition, the ZS chemical led to a reduction in the SR value by ~19 and 3% for the BR and NBR compounds, respectively. The use of ZS - simultaneously as an activator as well as a coactivator - in the rubber curing process enhanced the accelerator performance to create more cross-links [50]. This issue accelerated the vulcanization reaction time and crosslinking degree (see Table 2). According to the presented results in the table, changing the ZnO/ZS ratio almost did not have any impact on the crosslinking and swelling of the SBR compound. Because the variation was ~0.3 and 0.1% for the crosslink density and swelling ratio of the SBR compound by reducing the ZnO/ZS ratio from 2/1 to 1/1. In conjunction with other rubber compounds, the decrease of the ZnO/ZS ratio to 1/1 reduced the CD and SR values by ~16 and 4% for the BR and NBR-based compounds, respectively. The crosslink density results conform to the achieved resultant data in the last section. Because more crosslinking results in a stiffer rubber compound. Therefore, a rubber compound with a further CD value needs a higher amount of torque to rotate the disc during the ODR test. Although the reduction of the ZnO/ZS ratio from 2/1 to 1/1 decreased the CD and SR amounts in the BR and NBR compounds, their values were similar to the compounds consisting of the SA chemical.

4 CONCLUSIONS

In the present research, the effect of the chemical zinc stearate as an alternative to stearic acid – a widely used chemical as an accelerator, activator, and dispersing agent – on the cure characteristics of the SBR, BR, and NBR-filled 30 phr CB compounds was studied. The impact of the ZnO/ZS ratio on the curing features as well as the vulcanization kinetics of the rubber compounds was also evaluated. The ODR graphs showed that the replacement of the ZS chemical with the SA did not have any impact on the rheological behavior of the compounds in the maturing zone. The curing times for the SBR and BR-filled CB compounds were decreased by replacing the ZS with the SA chemical, while the ZS led to a slight increase in the curing times of the NBR compound. Therefore, the ZS accelerated the vulcanization of the SBR and BR-based compounds. The required torques to rotate the disc during the ODR test are raised by ~13-25% for BR and ~11-17% for NBR, while they are reduced by ~3-8% for the SBR compound. According to the rheometry results, zinc stearate improves the curing times and also increases the ML and MH amounts for the butadiene rubber. Moreover, the ZS causes completion of the curing sooner for all the compounds and moves the conversion-time graphs to lower times. This issue was the origin of the drastic increase in the maximum curing rate by ~119%, 145% and 22% for the SBR, BR, and NBR compounds, respectively. The decrease of the ZnO/ZS ratio changed the rheological behavior of the SBR compound to a slight overcuring reversion in the maturing zone. According to the resultant data, the curing times were reduced by ~13% for SBR, while the scorch time was almost the same for the BR and NBR compounds by changing the ZnO/ZS amount. The parameter of t90 had a ~25% and 7% reduction in the SBR and NBR compounds containing lower amounts of ZnO/ZS,

respectively. The results indicated that the decrease of the ZnO/ZS ratio made the compounds softer. The maximum curing rate for the SBR compound was increased by ~50% by lowering the ZnO/ZS ratio, while it was reduced for the BR and NBR compounds by ~53% and 20%, respectively. In addition, the decrease in the ZnO/ZS amount lowered the crosslinking level by ~16 and 4% in the BR and NBR-based compounds, respectively, while it did not have any effect on the CD value of SBR. Accordingly, using the ZS chemical instead of SA and reducing the ZnO/ZS ratio is a perfect way to manufacture a rubber compound with accelerated vulcanization without any change in the compound crosslinking degree.

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