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Effect of Different Accelerators on Some Mechanical Properties of Natural Rubber

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Abstract

This research aims to design a formula for natural rubber composites using different types and doses of secondary accelerators (N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) and Diphenyl Guanidine (DPG)). The bridge bearing pads are made from natural or synthetic rubber, such as chloroprene. Although natural rubber is abundant, high-quality natural rubber bridge bearing pads often fail compression set and accelerated aging requirements. Mechanical properties and swelling characteristics of NR composites were evaluated. Rheometer tests showed that using MBT and CBS as accelerators improved curing behavior and mechanical properties. Increased secondary accelerators raised maximum torque and decreased minimum torque. The results show that using the highest percentages of both accelerators, CBS and DPG, yields significant improvements in rheological and mechanical properties. The tensile strength improved from 18.3 MPa with zero CBS content to 31.53 MPa with the highest CBS content. Using DPG as a second accelerator improves tensile strength from 18.3 MPa to 27.37 MPa. Also, elongation at break for NR accelerated with CBS and DPG was improved. Rheometer characteristics showed that increased crosslinking with second accelerator absorption is directly proportional, as presented by scorch time measurements. Both accelerators achieved similar hardness values of 70 Shore A blending these accelerators significantly affects rubber properties.

Keywords: Bearing pads, Natural rubber, Rheological characterstics, Mechanical properties

1. Introduction

Strengthening bridges against earthquakes is important and involves developing advanced materials, especially rubber for bearings. Rubber bearings are key components in bridge construction, designed to absorb and dissipate seismic energy. Research has shown that using different types of accelerators in rubber significantly improves its physical properties, like hardness, tensile strength, and elongation, which are crucial for making durable and resilient bridge bearings [1-6]. These improvements help ensure that rubber bearings can withstand the stresses of an earthquake [7, 8].

Natural rubber, widely used in engineering, has advanced significantly with the addition of innovative additives. By adjusting rubber formulations with precise amounts of accelerators, engineers create materials that meet the tough requirements for earthquake resilience. This approach ensures that rubber bearings maintain their performance and integrity during seismic activity [9-15]. Advances in natural rubber have resulted in better mechanical properties, making it essential for developing earthquake-resistant infrastructure [16-18].

Our goal is to improve natural rubber used in bridge bearings by integrating accelerators and applying these advancements to larger volumes. This involves using accelerators to enhance natural rubber's performance, ensuring its durability and resilience [19, 20]. By focusing on the specific effects of accelerators, researchers have developed formulations that significantly improve rubber's response to seismic forces. Continuous innovation and adaptive material science are vital for sustainable engineering practices, enhancing the lifespan and effectiveness of bridge bearings, and ensuring resilient infrastructure in civil engineering [21-24].

2. Experimental
2.1. Materials

Natural Rubber (NR) in the form of Smoked Malaysian Rubber (SMR), specifically SMR 20, was employed. Key properties include low dirt content (max 0.20%), ash content (max 1.00%), N2 content (max 0.60%), and volatile matter (max 0.80%). It exhibited a minimum Wallace plasticity of 30 and a plasticity retention index of at least 40, provided by Transport and Engineering Company, Egypt serving as a vital material component in our study. Chemicals of commercial-grade supplied from Transport and Engineering Company such as stearic acid and zinc oxide (ZnO) as activators, parrafin oil as a Plasticizer,

N-Cyclohexyl-2-benzothiazole sulphenamide (CBS), 1,3-Diphenylguanidine (DPG), and 2-Mercaptobenzothiazole (MBT), as accelerators, and elemental sulfur as a curing agent were used without any further purification. 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) as antioxidants, paraffin wax as antiozonant agent are commercial-grade products. High abrasion furnace (HAF) carbon black N330 (CB) was obtained from Amerya Company for carbon black, Egypt.

2.2. Techniques
2.2.1 Preparation of NR rubber vulcanizates
Natural rubber (NR) was combined with additional compounding ingredients and curatives on an open two-roll mill with a diameter of 470 mm, a working distance of 300 mm, and a slow roll speed of 24 rpm, using a 1:1.25 gear ratio, in accordance with ASTM D3182-21a. The base formulation for (100 parts) NR rubber in this study included: 4 parts ZnO, 2 parts stearic acid, 1 part TMQ antioxidant, 3 parts paraffin oil, 1 part paraffin wax, 40 parts HAF, 1 part MBT accelerator, and 2 parts sulfur (all parts per 100 parts of rubber). Initially, NR was masticated on the two-roll mill for 2 minutes. ZnO, stearic acid, and TMQ antioxidant were then added sequentially, each mixed for 2 minutes. HAF330 filler was subsequently incorporated into the NR rubber and mixed for 5 minutes. Finally, different types of second accelerators (CBS, and DPG) in various ratios (0, 0.25, 0.5, 0.75, and 1) along with sulfur, were added to the rubber mixes, each mixed for 2 minutes. [25-26].

2.2.2 Rheometer characteristics of rubber
The rheological properties of the rubber mixes were evaluated using a moving die rheometer MDR–one rheometer (TA Instrument), at a temperature of $152 \pm 1°C$, in accordance with ASTM D2084-19a. The parameters measured included: maximum torque (M_H), minimum torque (M_L), scorch time (ts_2), optimum cure time (Tc_{90}), and cure rate index (CRI). Subsequently, the NR composites were vulcanized at their optimum cure times (Tc_{90}) using a hydraulic press in a clean, polished mold ($15cm \times 15cm \times 0.2cm$) under a pressure of 4 MPa at $152 \pm 1°C$. The cure rate index was calculated using the following equation [27, 28]:

$$Cure\ rate\ index\ (CRI) = \frac{100}{Tc_{90} - ts_2}\ \ min^{-1} \qquad (1)$$

2.2.3 Mechanical properties of NR vulcanizates
Using an ASTM cutter, natural rubber sheet vulcanizates were formed into dumbbell-shaped specimens that were 5 cm long and 0.4 cm wide.The thickness of each specimen was measured with a standard thickness gauge. Mechanical properties (tensile strength in MPa, elongation at break in %, and hardness in Shore A) of the rubber composite vulcanizates were determined, both before and after accelerated thermal aging, using a Zwick/Roell Z010 tensile tester machine with a load cell (Type: Xforce P and Nominal force: 10 KN), in accordance with ASTM D412-16 (2021). Mechanical data were measured in five replicates to obtain an average. Accelerated thermal aging was conducted in an air-circulated oven at 70°C for 7 days according to ASTM D573-04 (2019). The retained values of tensile strength (TS) and elongation at break (E%) after thermal aging were calculated using the following equations [29,31].

$$Retained\ Tensile\ strength, \% = \frac{Ts\ after\ aging}{Ts\ before\ aging} \times 100 \qquad (2)$$

$$Retained\ Elongation\ at\ break, \% = \frac{E\ after\ aging}{E\ before\ aging} \times 100 \qquad (3)$$

2.2.4. Swelling test for NR vulcanizates
Swelling behavior of the rubber vulcanizates was assessed by measuring their weight swell at equilibrium (Q%). The swelling test in toluene and was conducted at 25 °C for 48 h, according to ASTM D471-97. It was measured and calculated according to the following equation [32]:

$$Q\% = \frac{Ws - Wd}{Wd} \times 100 \qquad (4)$$

Where Ws is the weight of the specimen after swelling, and Wd is the weight of the dry specimen. The average of five replicates was considered.

2.2.5. Diffusivity
The diffusivity behavior in natural rubber formulations with (DPG) and (CBS) accelerators reveals distinct diffusion characteristics for these compounds. Diffusivity is influenced by the chemical interactions and structural changes induced by the accelerators. In the case of DPG, diffusivity is expected to exhibit a moderate rate due to its less reactive nature. DPG

promotes crosslinking in rubber compounds, which may lead to a denser network structure. This increased crosslinking hinders the mobility of polymer chains, resulting in a diffusion behavior characterized by a moderate rate. The formation of a stable but less flexible network influences the diffusion of molecules within the rubber matrix.

On the other hand, CBS, known for its efficient vulcanization and crosslinking capabilities, is likely to impact diffusivity differently. The accelerated crosslinking induced by CBS can create a more interconnected and rigid network. This enhanced network structure may restrict the diffusion of molecules, resulting in a lower diffusivity compared to the DPG-accelerated formulation. The increased density of crosslinks and reduced polymer chain mobility contribute to the observed diffusivity behavior. To quantify the diffusivity coefficient (D), we applied Fick's second law of diffusion in its simplified form for thin samples [33]:

$$D = n \left(\frac{h\,\theta}{4\,Q\infty} \right)^2 \qquad (5)$$

Where h is the rubber thickness, θ is the slope of the initial linear portion of the plot of Qt against √t, and Q∞is the equilibrium absorption.

2.2.6 Kinetics of diffusivity
Our study extends to the kinetics of diffusivity in natural rubber compounds modified with DPG and CBS, revealing distinct, time-dependent diffusion behaviors. The kinetics observed in DPG-modified rubber aligns with its moderate reactivity, leading to a gradual diffusion process. This slower kinetic profile suggests a more prolonged progression towards equilibrium, characterized by measured solvent absorption and release rates.

In contrast, the kinetics associated with CBS-modified rubber display a divergent pattern. The expedited crosslinking process inherent to CBS results in a swift achievement of diffusion equilibrium. This is indicative of a denser and more rigid network structure, emphasizing the need for materials that can rapidly adjust to changes in environmental conditions, particularly in applications like dynamic sealing. To study the mechanism of transport phenomenon the sorption data have been fitted into the relation [33]:

$$\log(Qt/Q\infty) = \log(k) + n \log(t) \qquad (6)$$

Where Qt denotes the swelling quotient at time t and Q∞ represents the equilibrium swelling, k is a constant that depends on the polymer morphology and the polymer-solvent interaction. The value of n characterizes the mode of toluene transport through the sample: n=0.5 corresponds to Fickian transport; n=1.0 indicates case 2 (relaxation controlled) transport; and values of n between 0.5 and 1.0 suggest anomalous transport behavior. The values of n and k were determined from the plot of log(Qt/Q∞) against log(t).

3. Results and discussions
With the increasing concerns over improving the properties for natural rubber using improving additives, there is always a growing need for more results analysis to redirect properly the formulations to the improving methods and updating testing mechanisms and methods. In this study an investigation for mechanical, curing and absorption properties was done using the previous methods and tools.

3.1 Rheometric characteristics
The curing behavior of prepared samples was analyzed by measuring minimum and maximum torque, scorch time, 90% cure time, and cure rate index. Torque is an important parameter that reflects the resistance of rubber formulations to deformation during curing. As the curing process progressed, the max torque values as shown in figure 1 increased with increasing in accelerators content, while Minimum torque values is slightly decreased with increasing in accelerators content. The samples' crosslinking is indicated by the torque difference readings' progressive increase.
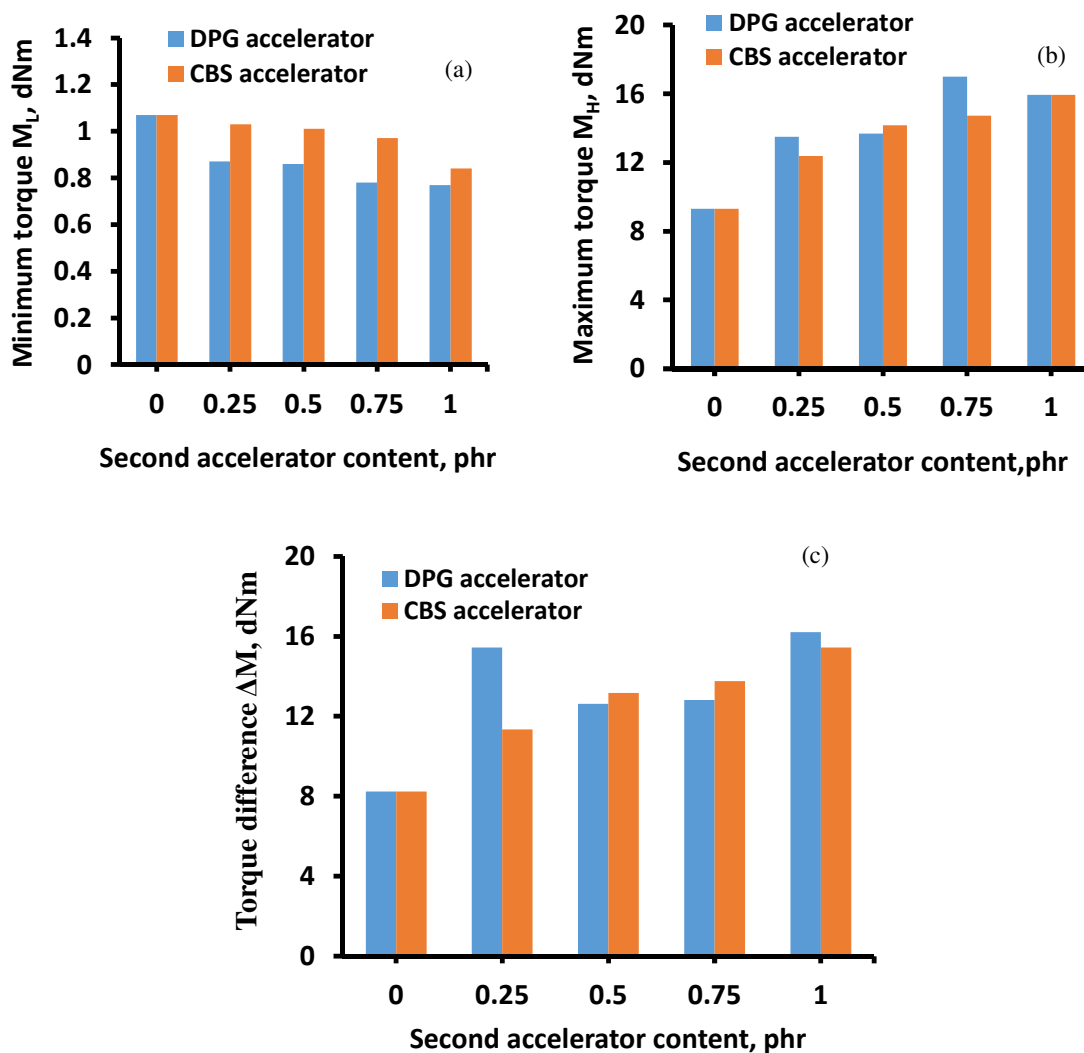
Figure 1: Impact of accelerators on Minimum (a), maximum torque (b) and torque difference (c) for NR composite

Scorch time refers to the time required for the rubber to start crosslinking during curing. The scorch time values obtained for the samples showed in Figure (2). These results indicate that samples with highest percentages of DPG have the shortest scorch time, indicating that they started crosslinking earlier than the other DPG lower content samples also sample with lower CBS contents exhibit the shortest scorch time earlier than other CBS samples. Again, because of using accelerators there is a significant difference of all scorch time results than the control samples without second accelerator. CBS is a sulfenamide-type rubber accelerator known for its long induction period during rubber vulcanization. This accelerator must first decompose into thiazole and amine, with the thiazole acting as the rubber accelerator and the amine serving as the activator (coagent) (34).
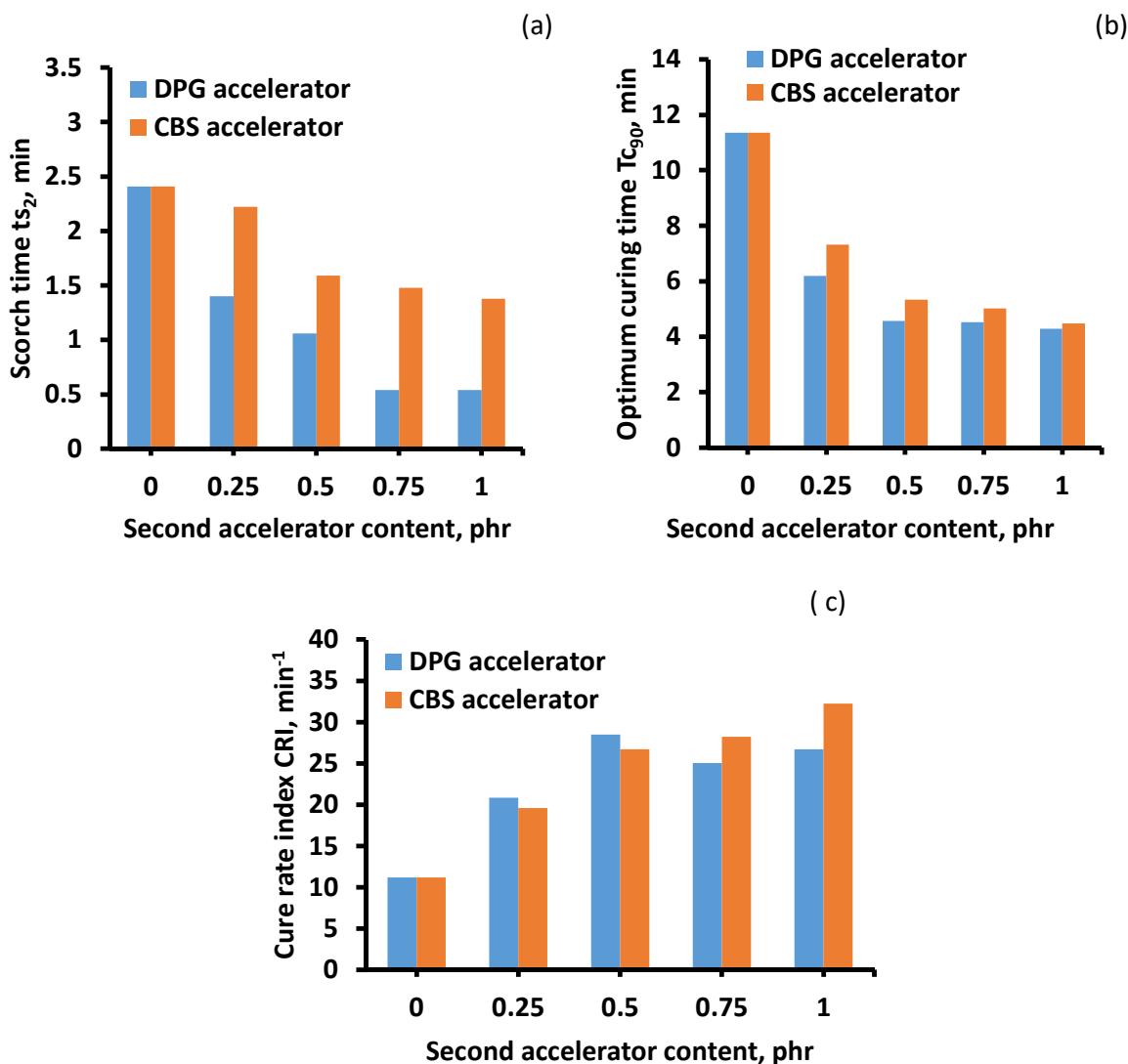
Figure 2: Curing properties for NR composites
a)Scorch time ts_2, b)Optimum curing time Tc_{90}, c) Cure rate index CRI

By analyzing scorch time values, scorch time decreased with increase in the percentages of both accelerators considering that in case of CBS it is an acceptable decrease while in DPG samples it is a dramatic decrease which is not suitable for big volume applications like bridges bearing pads.90% cure time shown in Figure 2(b) refers to the time required for the rubber to reach 90% of its maximum torque value during curing. The 90% cure time values obtained for the CBS showed that sample with the highest CBS content had the shortest 90% cure time, indicating that it reached 90% of its maximum torque value faster than the other CBS samples while for DPG samples, By analyzing scorch time values, scorch time decreased with increase in the percentages of both accelerators considering that in case of CBS it is an acceptable decrease while in DPG samples it is a dramatic decrease which is not suitable for big volume applications like bridges bearing pads.90% cure time shown in Figure 2(b) refers to the time required for the rubber to reach 90% of its maximum torque value during curing.The 90% cure time values obtained for the CBS showed that sample with the highest CBS content had the shortest 90% cure time, indicating that it reached 90% of its maximum torque value faster than the other CBS samples while for DPG samples,the 90% cure time values obtained showed that sample with the highest DPG had the shortest 90% cure time, indicating that it reached 90% of its maximum torque value faster than the other DPG samples. Both accelerators decrease the optimum curing time by increasing their concentrations which is desired behavior to save energy, for CBS it is an acceptable decrease with

respect to scorch time unlike DPG decreasing behavior which is not matched with the scorch time. The cure rate index shown in figure 2c is a measure of the rate of crosslinking during the curing process. It was calculated as the slope of the torque curve as a function of time. The cure rate index values obtained for the samples. These results indicate that sample with highest CBS content had the highest cure rate index, indicating the fastest crosslinking rate among CBS samples also the highest DPG content showed the fastest crosslinking rate among DPG samples.

3.2 Mechanical behavior

The tensile properties of the mixes were evaluated by measuring the tensile strength, elongation at break (EB), and hardness shore A. Tensile strength is a measure of the maximum stress that a rubber sample can withstand at break as shown for each accelerator in figure 3(a), while EB for NR samples which explained in figure 3 (b).
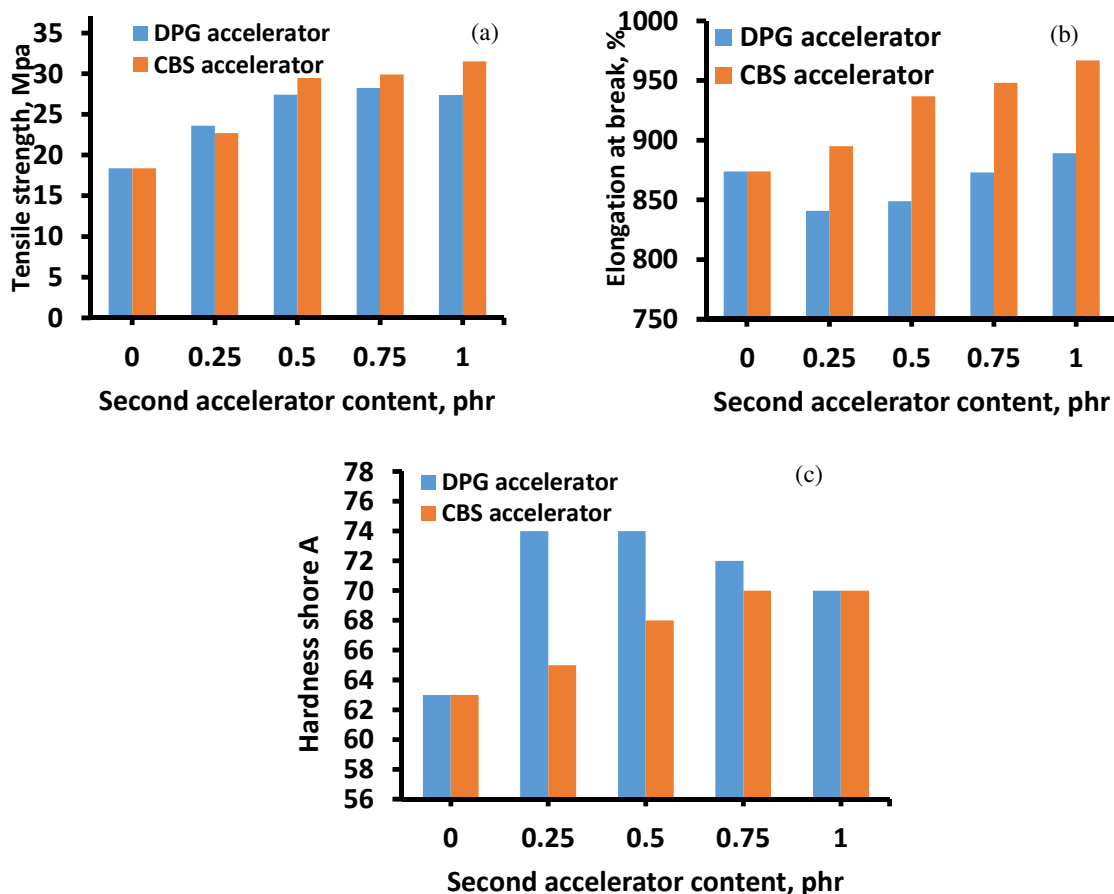

Figure 3: Mechanical properties for NR composites
a) Tensile strength, b) Elongation at break %, c) Hardness shore A

The tensile strength values obtained for the rubber mixes with different accelerators were as showed in Figure 3: the highest content for DPG exhibited tensile strength 27.37 MPa which is the highest value in DPG samples while sample for the highest content for CBS exhibited tensile strength 31.53 MPa which is the highest value in CBS samples. These results suggest that CBS exhibited the highest tensile strength, while DPG showed the lowest.

The EB values obtained for the mixes were as shown in Figure 3 (b), for the highest content for DPG sample 889 % EB which is the highest value for DPG samples and for the highest content for CBS sample 967% EB which is the highest value for CBS samples. These results indicate that CBS samples had the highest EB, while DPG samples had the lowest.

The results show that the tensile strength and EB of the mixes were influenced by the type of accelerator used. CBS samples exhibited the highest tensile strength and EB, while DPG samples showed the lowest values. The differences in the tensile properties may be attributed to the different crosslinking densities of the rubber mixes, as well as the different types of bonds formed between the rubber chains.

3.3   Thermal oxidative aging

The influence of aging on the retained values of elongation and tensile strength of natural rubber (NR) formulations containing (DPG) and (CBS) accelerators was investigated to understand the long-term performance characteristics of these materials. For formulations incorporating DPG, aging studies revealed notable effects on retained value of elongation and tensile strength.Over time, DPG-rich compositions exhibited a reduction in retained value of elongation at break, indicative of a diminishing ability to undergo deformation before failure(35). Concurrently, the tensile strength of aged DPG formulations exhibited a decline as shown in figure 4, suggesting a compromise in the material's ability to withstand maximum stress. This aging-induced deterioration in both retained value of elongation and tensile strength could be attributed to changes in crosslinking density and intermolecular interactions within the rubber matrix, highlighting the importance of considering aging effects in applications requiring sustained mechanical integrity.
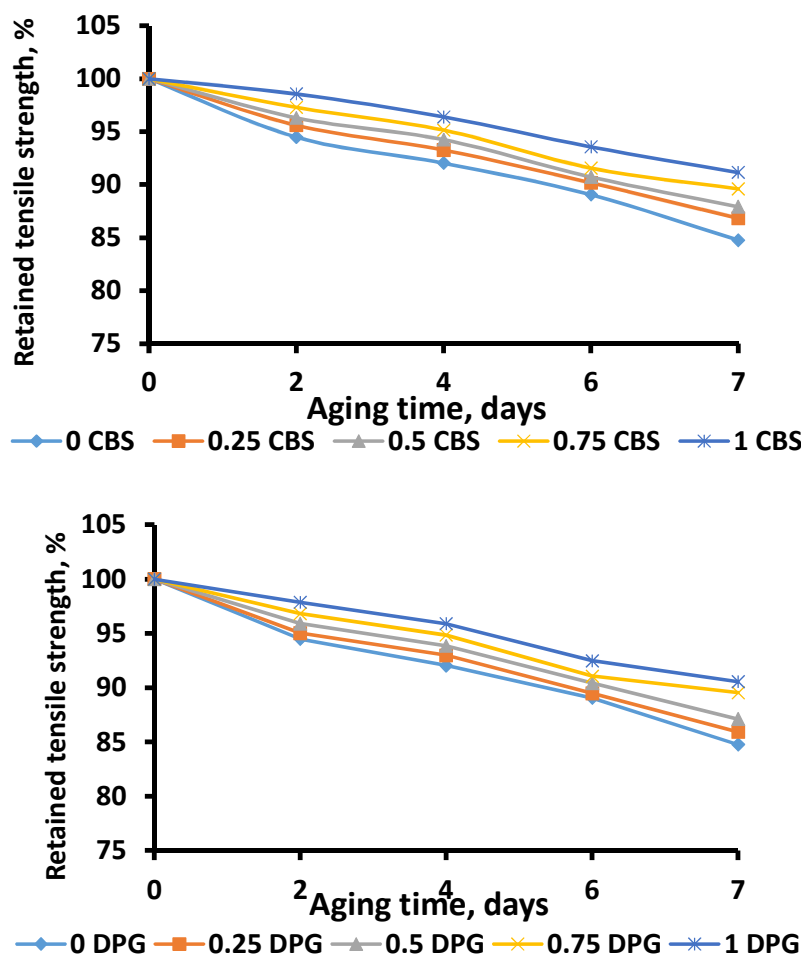

Figure 4: Retained tensile strength % of NR composites accelerated with CBS & DPG after aging7 days at 90℃

In contrast, aging studies on formulations containing CBS revealed interesting results. CBS-rich compositions demonstrated a relatively more stable retained value of elongation at break over time compared to DPG formulations as shown in figure 5. This suggests that CBS may contribute to a more robust resistance to aging-induced retained value of elongation degradation. Additionally, the tensile strength of CBS formulations showed a comparatively slower decline with aging, signifying a better retention of material strength over an extended period. The distinct aging behaviors observed in CBS-containing formulations may be attributed to its impact on crosslinking dynamics and the resulting mechanical properties. These findings underscore the potential benefits of CBS in applications where sustained retained value of elongation and tensile strengthproperties are critical, emphasizing the importance of accelerator selection in designing durable rubber materials.

Aging studies revealed nuanced effects on the retained value of elongation and tensile strength of natural rubber formulations containing DPG and CBS accelerators. While DPG formulations exhibited a pronounced aging-induced deterioration in both

properties, CBS formulations displayed a relatively more stable performance, suggesting superior resistance to aging-related mechanical degradation. These insights are crucial for industries requiring durable rubber materials over extended service life, guiding the selection of accelerators for optimal long-term performance (36).
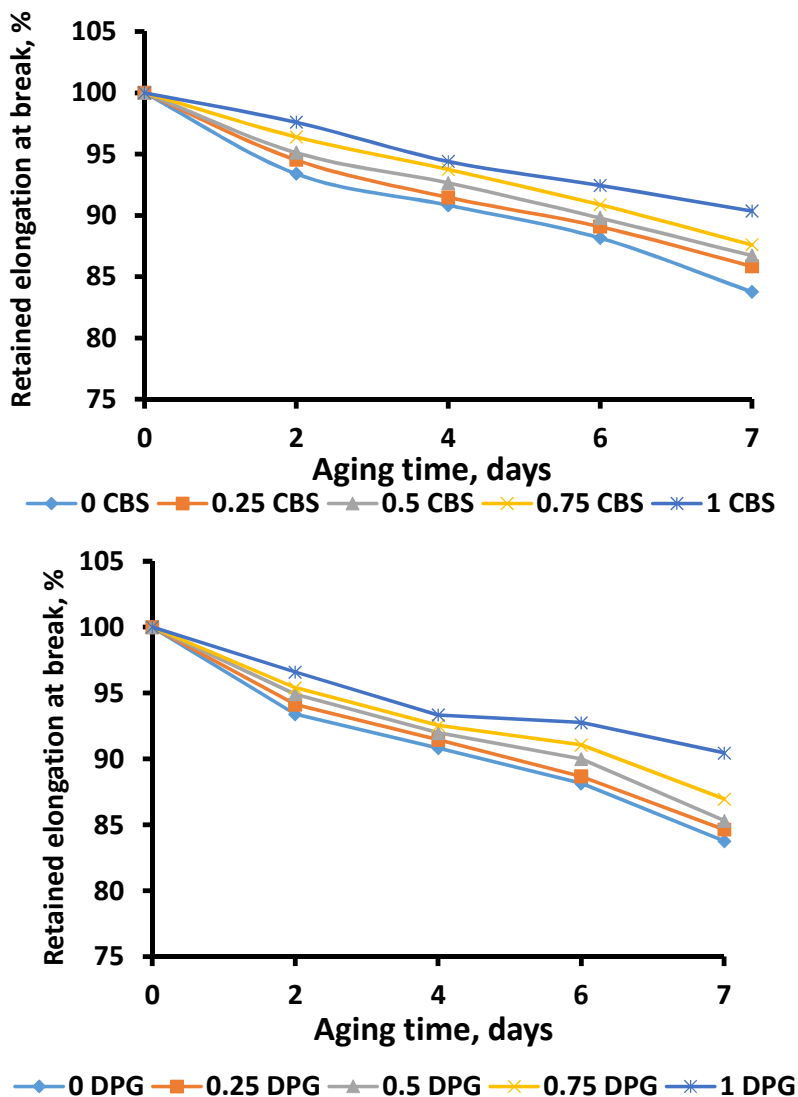

Figure 5: Retained elongation at break % of NR composites accelerated with CBS & DPG after aging 7 days at 90°C

3.3 Swelling behavior of NR composites

On analyzing the swelling characteristics of natural rubber accelerated with DPG and CBS, it's evident that the choice of accelerator significantly impacts its properties. Rubber modified with DPG shows consistent swelling, indicating a stable network structure with moderate crosslink density. This stability is crucial for applications needing predictable dimensional behavior in various conditions. Conversely, rubber accelerated with CBS demonstrates reduced swelling due to a denser network and higher crosslink density. This decreased swelling is beneficial for applications requiring minimal volume expansion and enhanced chemical resistance. These observations underscore the importance of accelerator selection in developing materials for specific industrial applications where swelling properties are critical.
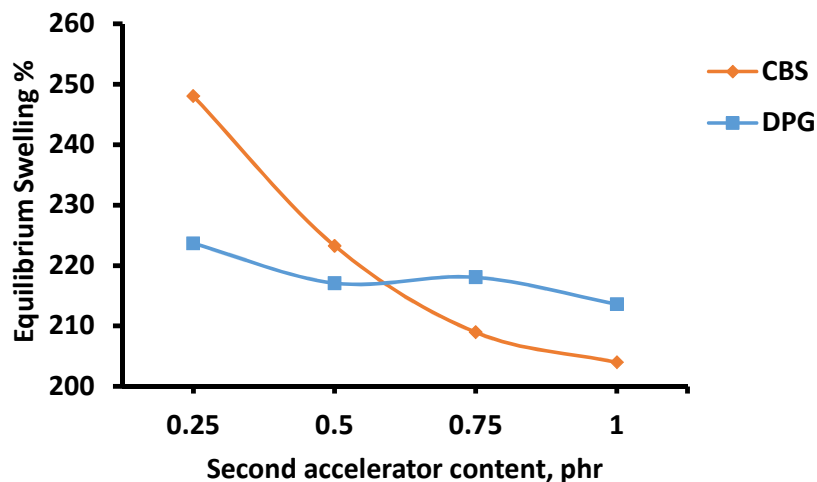
Figure 6: Equilibrium swelling % for NR composites accelerated with DPG and CBS

3.3.1 Diffusivity behavior

Exploring the diffusivity behavior of natural rubber when modified with DPG and CBS, showcases notable differences in the rate of mass transport within the material. DPG, due to its less reactive nature, promotes a moderate rate of diffusivity. Its influence on crosslinking leads to a denser network structure within the rubber, which in turn moderates the mobility of polymer chains. This results in a stable, yet less flexible network, impacting the overall diffusion of molecules within the rubber matrix. Conversely, CBS, known for its efficient vulcanization properties, significantly alters diffusivity. The accelerated crosslinking and dense network formation attributed to CBS result in a more constrained molecular diffusion pathway, leading to a lower diffusivity rate compared to DPG-treated rubber. This distinction is critical for applications where controlled diffusion rates are essential, such as in certain sealing or barrier applications.
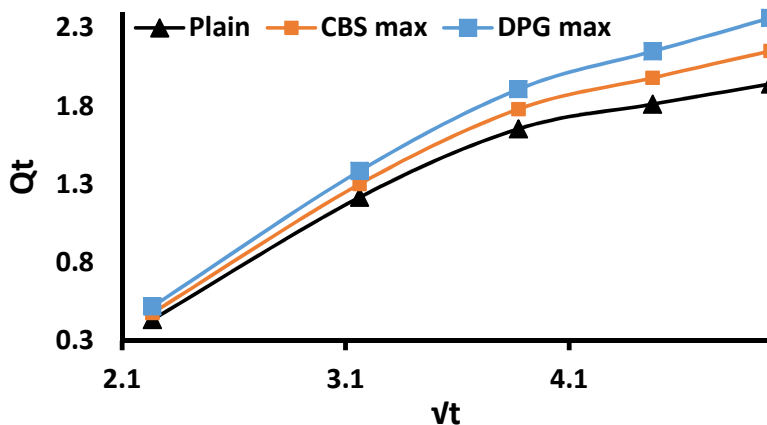

Figure 7: Plot of QtVs√t for plain NR, NR containing CBS max and NR containing DPG max

In analyzing the diffusivity behavior of natural rubber modified with DPG and CBS, compared to pure natural rubber, we observed significant differences in mass transport rates. Figure 7presents a combined plot for DPG, CBS, and pure natural rubber. This graph elucidates the comparative diffusivity rates across different treatments. The DPG-modified the rubber shows a moderated diffusivity rate due to its less reactive nature influencing the crosslinking process. This results in a denser network structure, restricting polymer chain mobility and affecting molecular diffusion. CBS-treated rubber, on the other hand, exhibits a notably reduced diffusivity rate, as CBS accelerates crosslinking and forms a denser network, constraining molecular diffusion pathways.

3.3.2. Charact Kinetics of diffusivity

On studying the diffusivity kinetics of natural rubber compounds modified with DPG and CBS reveal dynamic and time-dependent diffusion processes. In DPG-treated rubber, the kinetics indicates a gradual progression of diffusion, consistent with the moderate reactivity and resultant network structure of the rubber. The diffusivity kinetics suggests a slower approach to equilibrium, indicating a more gradual solvent uptake and release.

In contrast, CBS-modified rubber exhibits a different kinetic profile. The accelerated crosslinking leads to a rapid attainment of diffusion equilibrium, reflecting the more rigid and densely crosslinked network. This kinetic behavior is crucial in applications where rapid response to environmental changes is necessary, such as in dynamic sealing applications. These observations in diffusivity and its kinetics under different accelerator treatments underscore the importance of accelerator choice in designing rubber compounds with tailored transport properties. This knowledge aids in optimizing rubber formulations for specific industrial applications, where the control over molecular transport is a key performance criterion.

The kinetics of diffusivity in natural rubber compounds modified with DPG and CBS, as well as in pure natural rubber, were systematically investigated using equation no. 3. Figure 8 combines the results for DPG, CBS, and pure natural rubber, plotting $\log(Q_t/Q_\infty)$ against log t. This graph highlights the distinct kinetics profiles for each type of treatment.

$$\log(Q_t/Q_\infty)= \log (k)+ n \log(t)$$

The kinetics in DPG-treated rubber suggests a gradual progression towards equilibrium, aligning with its moderate reactivity. CBS-accelerated rubber, however, shows a rapid attainment of equilibrium due to the more rigid and densely crosslinked network formed by CBS. The comparison with pure natural rubber provides a baseline to understand the impact of these accelerators.
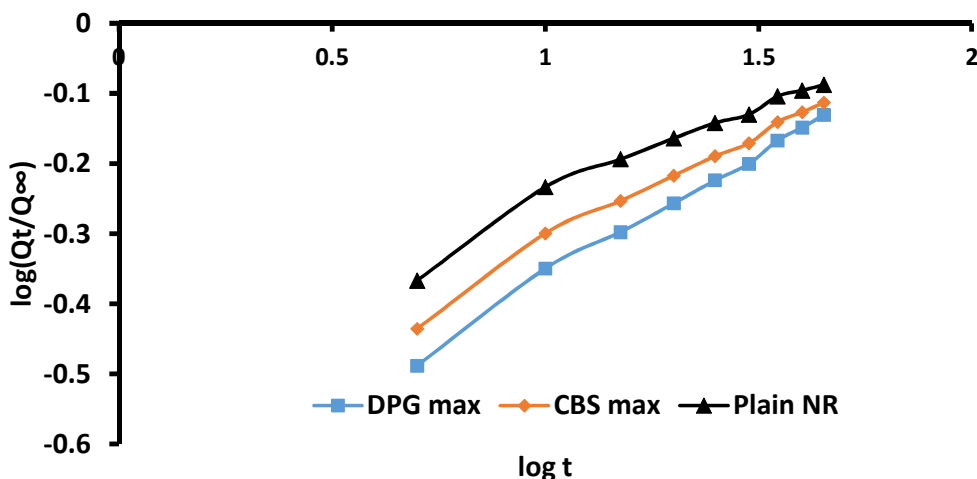

Figure 8: Plot of log (Q_t/Q_∞)vs log tfor plain NR, NR containing CBS max and NR containing DPG max

The diffusivity coefficient (D), rate constant (K), and diffusion exponent (n) for each sample were calculated and are presented in Table 1. This table provides a clear summary of these parameters, facilitating a comparison of the impacts of DPG and CBS. With n values ranging between 0.29 and 0.36, it suggests a transport mechanism that deviates from purely Fickiandiffusion. The significantly low N values indicate an anomalous or non-Fickian diffusion process, implying that diffusion is influenced by more complex interactions and factors beyond simple concentration gradients, potentially involving polymer relaxation or other dynamic behaviors within the material. [37-38].

Table 1: Diffusion kinetics for plain rubber with accelerators

Samples	D, cm^2/min	N	log k	K
NR without secondary accelerator	4.8E-05	0.2992	-0.5565	0.573212
CBS-0.25%	6.2E-05	0.3088	-0.5835	0.557942
CBS-0.5%	8E-05	0.3179	-0.6087	0.544058
CBS-0.75%	5.2E-05	0.3266	-0.6323	0.531368
CBS-1%	4.6E-05	0.3349	-0.6544	0.519754
DPG-o.25%	4.3E-05	0.3179	-0.6087	0.544058
DPG-0.5%	3E-05	0.3349	-0.6544	0.519754
DPG-0.75%	1.9E-05	0.3504	-0.6949	0.499124
DPG-1%	3.5E-05	0.3635	-0.7299	0.481957

4. Conclusion

Rheological analyses revealed the dynamic nature of curing processes influenced by DPG and CBS. The torque measurements demonstrated that both accelerators promote crosslinking, with DPG leading to a significant increase in maximum torque values. Scorch time results indicated that DPG initiates crosslinking earlier than CBS, highlighting the accelerators' divergent kinetics. The 90% cure time and cure rate index underscored the distinct behaviors of CBS and DPG, with CBS exhibiting a faster crosslinking rate.

Swelling tests illuminated the accelerators' substantial influence on NR's solvent interaction. DPG-rich formulations exhibited higher swelling, while CBS-rich compositions displayed lower swelling percentages. These findings can be attributed to the differing chemical properties of the accelerators, with CBS enhancing crosslinking and reducing swelling, while DPG exhibited the opposite effect. Mechanical assessments unveiled the pivotal role of accelerators in determining tensile strength and elongation at break. CBS formulations exhibited superior tensile strength, while DPG formulations displayed enhanced elongation at break. These variations in mechanical properties stem from differences in crosslinking density and the types of bonds formed within the rubber matrix.

The investigated materials have significant implications for industries relying on rubber-based materials, offering opportunities for tailored rubber compound formulations to meet specific application requirements. Further research could delve into the underlying chemical intricacies, providing a roadmap for optimizing accelerator selection and enhancing natural rubber's performance across a spectrum of applications.

5. Conflicts of interest
The authors declare no conflict of interest.

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