



Article Effect of Cross-Linking Density on Non-Linear Viscoelasticity of Vulcanized SBR: A MD Simulation and Experimental Study

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Abstract: In recent years, there has been a growing interest in changes in dynamic mechanical properties of mixed rubber during dynamic shear, yet the influence of vulcanized characteristics on the dynamic shear behavior of vulcanized rubber, particularly the effect of cross-linking density, has received little attention. This study focuses on styrene–butadiene rubber (SBR) and aims to investigate the impact of different cross-linking densities (D_c) on dynamic shear behavior using molecular dynamics (MD) simulations. The results reveal a remarkable Payne effect, where the storage modulus experiences a significant drop when the strain amplitude (γ_0) exceeds 0.1, which can be attributed to the fracture of the polymer bond and the decrease in the molecular chain's flexibility. The influence of various D_c values mainly resides at the level of molecular aggregation in the system, where higher D_c values impede molecular chain motion and lead to an increase in the storage modulus of SBR. The MD simulation results are verified through comparisons with existing literature.

Keywords: vulcanized SBR; non-linear viscoelasticity; Payne effect; MD simulations



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1. Introduction

Rubber is a cost-effective viscoelastic material with exceptional elasticity performance that finds extensive applications in automobiles, aerospace, construction, and medicine [1–3]. Since rubber products are usually subjected to alternating loads [4], the processing technology has a significant impact on their mechanical properties, particularly their dynamic mechanical properties. Studying the influence of processing technology on rubber's dynamic mechanical properties is crucial to enhancing its mechanical performance.

Pure rubber cannot meet practical mechanical performance requirements. Thus, the most common method to improve rubber mechanics is adding microfillers. Silicon dioxide particles and carbon black (CB) are the most common microfillers used to improve rubber mechanics. Jong et al. [5,6] showed that adding silica fillers significantly improves natural rubber's tensile properties, while Hait et al. [7] demonstrated the enhanced mechanical effect of adding CB to polybutadiene rubber (BR). Lin et al. [8] prepared CB-filled powdered natural rubber (P (NR/N234)) by the method of latex–CB coagulation technology and deeply studied the influence of curing recipes and CB contents on the curing properties, mechanical properties, and dynamic properties, and the results were compared with those of NR/N234 compounds based on traditional dry mixing of bale natural rubber and CB. Robertson and Hardman discussed in detail the mechanism of CB reinforcing the mechanical properties of rubber and the generation mechanism of the Payne effect in the shear process of filling rubbers [9], and there is no doubt that this work is helpful for understanding the reinforcing mechanism and Payne effect of fillers on rubber.

The Payne effect relates to the elastic and storage moduli variation, which typically increase and decrease, respectively, under high shear strain. The phenomenon was first

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reported by Payne and has since garnered considerable attention. It has been extensively applied in dynamic mechanical analysis for polymer materials under medium-to-high strain. The addition of nanoparticles (NPs) to the mixed rubber has a significant impact on the Payne effect. Shi et al.'s research studied the enhancement mechanism of the Payne effect by using CB to fill natural rubber, and the results indicated the recoverability and hysteresis of the Payne effect, demonstrating the positive impact of high frequencies and low temperatures on enhanced Payne effect. The structural evolution of the filler phase was not the primary influence factor [10]. Similarly, Zhao et al. [11] applied CB as a filler to SBR to create a CB conductive network and studied the Payne effect of the filling system. The results revealed that the polymer matrix next to CB particles can accelerate the reconstruction of the filler–polymer network, thereby enhancing the reversibility of the Payne effect [12–14]. CB, along with other fillers, such as spherical [15–17] and fibrous [18–20], have excellent electrical and thermal conductivity, which significantly affects Payne effect improvement. Experimental research can satisfactorily explain the Payne effect of mixed rubber filling. However, the micromechanism of Payne effect formation remains challenging to explain.

Molecular dynamics (MD) simulation is often preferred to experiments for studying the microscopic dynamic mechanisms of the Payne effect in rubber. MD has several advantages over experiments because it can explore the impact of molecular chain motion and filler–polymer interaction forces, which are typically unknown under experimental conditions. Hong et al. [21] demonstrated the utility of non-equilibrium molecular dynamics (NEMD) in exploring the viscoelastic properties of nanoplate-filled polymer composites as it relates to filler packing fraction, filler–polymer interaction forces, Rouse dynamics, chain constraint, and percolation networks. Gao et al. [22] used hydrodynamic effects, "clog rubber" and "filler network", to explain how polymer nanocomposites filled with nanorods experience dynamic modulus reinforcement and showed that the Payne effect becomes more pronounced with stronger interface interaction and increased nanorod fraction.

Currently, most research on the Payne effect has focused on mixed rubber, with little research done on vulcanized rubber. Vulcanization plays a critical role in rubber processing, but existing research about the impact of vulcanization characteristics on the Payne effect of rubber is limited. Therefore, it is necessary to investigate the effect of different vulcanization characteristics on the dynamic mechanical properties of rubber. Hou et al. [23] conducted experiments on the Payne effect of polyisoprene rubber vulcanized using thermooxidative aging, and the results revealed that thermooxidative aging significantly affected the vulcanized structure and Payne effect of polyisoprene rubber. Employing a highly efficient vulcanization method to prepare vulcanized polyisoprene rubber will remarkably enhance Payne dissipation, as for its microscopic mechanism, it was not mentioned in this report.

The application scope of vulcanized SBR is wide; therefore, the study of its Payne effect holds theoretical and practical significance. This research aims to utilize molecular dynamics methods to explore the Payne effect of vulcanized SBR in dynamic shear processes, providing new ideas for the study of the dynamic mechanical behavior of sulfurized rubber materials.

2. Results and Discussion

2.1. Verification of Simulation Correctness

The cross-linking densities (mol/mL) corresponding to each D_c in MD model obtained via calculation are presented in Table 1. The results of cross-linking densities obtained by experiments are also shown in Table 1.

The small difference between calculations and the experimental results suggests that MD simulation is able to realistically simulate the experiment, thereby demonstrating high reliability in this study.

In order to prove the accuracy of simulation model, we perform a comparison between T_g of SBR systems exhibiting varying D_c , utilizing both molecular simulation and experimentation approaches. Figure 1a–e depict the relationships between density and temperature of SBR systems at different D_c through molecular dynamic simulation. Figure 1f illustrates the

 $T_{\rm g}$ of each sample by experiments. Table 2 enumerates the $T_{\rm g}$ for SBR systems of different $D_{\rm c}$ acquired through both the experimental and molecular dynamic simulation methods, alongside the corresponding relative deviation.

Table 1. Cross-linking densities (mol/mL) in MD model and experiment results.

D_{c}	1.0	2.0	5.0	6.0	8.0
Content of S (phr)	1.04	1.99	5.03	6.29	8.28
Cross-link density by MD (10^{-4} mol/mL)	1.208	1.48	1.681	2.117	2.269
Cross-link density by experiment (10 ⁻⁴ mol/mL)	1.194	1.464	1.659	2.088	2.247

Table 2. $T_{\rm g}$ and relative error of SBR obtained by DSC and MD simulation.

Content of S (phr)	T _g by MD Simulation (K)	T _g by Experiment (K)	Relative Deviation (%)
1.04	231.23	219.17	5.5
1.99	235.79	223.13	5.65
5.03	238.13	227.47	4.69
6.29	241.74	232.02	4.19
8.28	243.84	236.10	3.28

By comparing the DSC results of different S contents with the T_g results obtained through simulation (Figure 1), it can be found that the results of MD simulation can predict the T_g relatively well.



Figure 1. Cont.



Figure 1. T_g of different D_c obtained by MD simulation (**a**–**e**) and DSC (**f**).

The tensile curve of pure SBR at strain rate of 0.01 ps^{-1} is shown in Figure 2, where snapshots captured at strains of 0, 1, and 2 are also provided. Additionally, Figure 2 presents the tensile curve obtained using the identical simulation parameters in reference [24]. It can be found in Figure 2 that the tensile strength of pure SBR is approximately 2 GPa at a strain rate of 0.01 ps⁻¹, consistent with the data reported in [24]. The high reliability of the *pcff* force field we selected is thus demonstrated.



Figure 2. The comparison of the tensile curves of pure SBR at strain rate of 0.01 ps^{-1} and the snapshots at the strains of 0, 1 and 2 with the tensile curves of pure SBR obtained by identical simulation parameters in [24].

2.2. The Effects of D_c and γ_0 on Dynamic Mechanical Properties

The stress–strain curve of SBR with D_c of 8.0 at $\gamma_0 = 0.5$ is extracted to observe the phenomenon of strain lagging behind stress. Figure 3 presents the stress–strain curve, which shows the strain curve is constantly delayed behind the stress curve by a constant time δ_t of 20 fs. Notably, the stress curve's first two peaks are higher than the others. The phenomenon is predominantly attributed to the hindered movement of the entangled polymer chains by an external force, i.e., the shear stress. The interference results in relatively high viscosity and stress, leading to slightly higher peak values for the first two peaks. The originally entangled polymer chains' entanglement points are released with the continued shearing, reducing the viscosity and leading to the gradual stabilization of the stress curve's peak values.



Figure 3. Shear stress – strain curve (**a**) and equilibrium stress peak (**b**) of SBR system with $D_c = 8.0$ at $\gamma_0 = 0.5$.



The *G*' and tan δ at different γ_0 are presented in Figure 4.

Figure 4. G' (**a**) and tan δ (**b**) of SBR with different D_c under γ_0 of 0.05–0.5.

Figure 4 illustrates that SBR with varying D_c manifests conspicuous Payne effects under varying γ_0 . Specifically, the G' experiences a drastic decline with the augmentation of γ_0 , as depicted in Figure 4a. Additionally, Figure 4a shows that the G' escalates with the intensification of D_c . Figure 4b indicates that the tan δ of different D_c displays an increasing tendency as γ_0 increases. To explore the formation mechanism of Payne effects and the D_c impact on dynamic performance during the shear process, detailed analysis from both a static and dynamic outlook are operated.

2.2.1. Static Equilibrium Process

MSD and RDF of C atoms on the main chain are extracted from D_c systems with differing properties at equilibrium at the NPT for a period of 2 ns and presented in Figures 5 and 6. The purpose of this extraction is to investigate the impact of movement of molecular chains and arrangement of atomic components on mechanical characteristics.



Figure 5. MSD function with time of 2 ns NPT balance in SBR systems with different D_c .

Observations from Figure 5 reveal that the MSD exhibits a decreasing trend with an increasing D_c . Upon attaining equilibrium, the MSD of $D_c = 1.0$ SBR system is roughly 6 times more considerable than that of the $D_c = 8.0$ system. This is due to the abundance of C-S-C bonds, which progressively limit the movement of molecular chains, restricting their motion range and consequently their rigidity. This phenomenon, in turn, explains the increasing trend in G' with D_c increment, as illustrated in Figure 4a.



Figure 6. RDF (**a**) and local magnification at the red box in (**a**,**b**) at NPT equilibrium for SBR systems with different D_c .

The RDF depicted in Figure 6 reveals an increased density of C atoms present on the SBR main chain with an increment of D_c . Specifically, for the $D_c = 8.0$ system, this density level is observed to be 10% higher than for the $D_c = 1.0$ counterpart. The reason for this occurrence is primarily attributed to the presence of more C-S-C bonds that support a tighter coupling between the SBR chains, as depicted in Figure 5.

2.2.2. Microscopic Mechanism of Payne Effect

In this work, we sought to examine the influence of cross-links on the shearing process by calculating the rate of broken cross-linking bonds, or *P*, after10 cycles of shearing. The calculation is performed as follows. If the length of a C-S bond linked with an S atom exceeded 1.8 Å, it is designated as "broken" and considered unrepairable during the shearing process. *P* is calculated from the ratio of broken cross-links (N_b) to the total number of cross-linking bonds (N_s), as given by $P = N_b/N_s$, where the subscript "b" represents "broken". We present the relationship between *P* and γ_0 for various SBR systems with differing *D*_c values in Figure 7.



Figure 7. Relationship between *P* and γ_0 in SBR systems with different D_c .

By analyzing Figure 7, it is evident that an increase in γ_0 value leads to a corresponding increase in *P*. Larger γ_0 values in a vulcanized SBR system cause the breakage of C-S-C bonds, which increases as γ_0 increases. When γ_0 exceeds 0.1, all SBR systems demonstrate a sharp rise in *P* value, consistent with the observation in Figure 4a. Therefore, it can be concluded that larger values of γ_0 lead to a sudden increase in the number of broken crosslinking bonds, resulting in the occurrence of Payne effects during the shearing process, affecting the mechanical properties of the SBR system. Furthermore, the P value decreases as $D_{\rm c}$ increases. This implies that higher cross-linked densities exhibit lower P values after shearing. A plausible explanation for this observation is that larger $D_{\rm c}$ values can enhance the overall mechanical performance of SBR. During the shearing process, systems with lower D_c values tend to break more easily than those with higher D_c values, resulting in lower P values. The breakage of cross-linking bonds during the shearing process is mainly related to the movement of molecular chains. Therefore, taking the system with $D_c = 8.0$ as an example, the MSD during the shearing process is extracted under different values of γ_0 , as shown in Figure 8. In addition, Figure 8 also includes the MSD of different SBR systems with $\gamma_0 = 0.5$ and varying D_c .





Figure 8. The variation function of MSD of SBR system with $D_c = 8.0$ at different γ_0 (**a**) and variation function of MSD at different D_c at $\gamma_0 = 0.5$ (**c**) with shear period; (**b**) is the local amplification at the red box in (**a**,**d**) and the local amplification at the red box in (**c**,**e**–**g**) are snapshots of the SBR system at shear strain limit with $D_c = 8.0$ at $\gamma_0 = 0.05$, 0.1 and 0.5, respectively.

It can be observed in Figure 8a that MSD is approximately 7.0 at $\gamma_0 = 0.09$, but it significantly increases when γ_0 exceeds 0.1, as seen in Figure 8e–g. For example, when $\gamma_0 = 0.5$, MSD reaches approximately 230, which is 33 times that of $\gamma_0 = 0.09$. Higher γ_0 values move the system away from equilibrium, increasing the probability of cross-linking bond breakage and potentially decreasing mechanical performance, as explained by the significant decline in *G*' shown in Figure 4a when γ_0 is greater than 0.1. Furthermore, MSD decreases as D_c increases under the same γ_0 value, as shown in Figure 8c,d. This is primarily due to the partial restriction of molecular chain movement by the formation of the cross-linking network, consequently slowing the occurrence of bond breakage. Hence, when γ_0 remains the same, an increase in D_c results in a higher *G*'.

To analyze the energy variation in SBR systems during the shearing process, we calculate both the non-bonding energy (E_{pair} , which describes the repulsive or attractive forces between two non-bonded atoms and can be calculated by the sum of the van der Waals energy and Coulomb energy) as well as the bonding energy, which included bond energy (E_{bond} , which represents the stretching energy of a bond and characterizes the energy change resulting from the movement of each chemical bond in the direction of the molecular axis), angle energy (E_{angle} , which represents the bending energy of a bond angle, caused by changes to the bond angle) and dihedral energy (E_{dihed} , which represents the energy change caused by the rotation of a single bond and resulting in molecular skeleton distortion) over the period of shearing. Initially, we extracted *E*_{total}, *E*_{pair}, *E*_{bond}, *E*_{angle}, and E_{dihed} of SBR systems with different values of D_c during the shearing process at $\gamma_0 = 0.5$, as depicted in Figure 9 (where $E_{\text{total}} = E_{\text{pair}} + E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihed}}$). We also present the energy variation of a non-cross-linking system SBR system ($D_c = 0$) during the shearing process in Figure 9 for comparing the specific effects of different cross-linking densities on energy changes. We consider the energy difference (E- E_0) at each moment of the shearing process relative to the system's initial energy [25] to facilitate analysis.



Figure 9. The change function of E_{total} (**a**), E_{pair} (**b**), E_{bond} (**c**), E_{angle} (**d**) and E_{dihed} (**e**) with shear period of different D_{c} SBR systems at $\gamma_0 = 0.5$.

It is obvious in Figure 9 that the energy of the various D_c systems fluctuates sinusoidally during shear and gradually decreases. This behavior can be adequately explained by combining Figure 3b which results from the peak stress increase. Additionally, an increase in D_c leads to a rise in E_{total} , which increases by approximately 12% for $D_c = 8.0$ compared to the non-cross-linking system. This can mainly be attributed to the fact that the higher D_c system has more cross-linking bonds, thus increasing the E_{total} of the system. Furthermore, it can be observed from Figure 9b that E_{pair} does not significantly change as D_c increases. This is due to SBR chains being mainly cross-linked by C-S-C bonds, meaning that interatomic interaction forces do not show significant differences.

In contrast to E_{pair} , both E_{bond} and E_{angle} corresponding to Figure 9c,d exhibit correlation with D_{c} . The peak values of E_{bond} and E_{angle} increase and show an increase of 19.4% and 6.5%, respectively as D_{c} increases, when compared to the non-cross-linking system. Figure 9e shows that there is no significant correlation with respect to changes in D_{c} for E_{dihed} .

To sum up, from an energy perspective, changing D_c mainly affects the stretching of bonds and the rotation of bond angles during the shearing process under the same γ_0 conditions. As for the rotation of bond angles, D_c has a more significant impact on bond stretching in the cross-linking SBR system. In order to investigate the impact of different γ_0 on the energy during the shearing process, we extract the energy variation of the system with $D_c = 8.0$ under different γ_0 , as illustrated in Figure 10.



Figure 10. E_{total} (**a**), E_{pair} (**b**), E_{bond} (**c**), E_{angle} (**d**) and E_{dihed} (**e**) of SBR system with D_c 8.0 at different γ_0 .

According to Figure 10a, the E_{total} displays periodic variation with two peaks during each shear cycle, corresponding to the maximal and minimal strains of the action, respectively. As the parameter γ_0 increases, the peaks of E_{total} also increase. This finding has been previously discussed. The process of shearing depletes E_{total} gradually, primarily due to the viscoelasticity of SBR absorbing energy through overcoming the frictional force of molecu-

lar chains [26]. Consequently, the energy reduction rate tends to be slower under lower strain conditions, when molecular movement gets more limited, and resulting in lower frictional resistance between chains, causing slower dissipation of energy. Figure 10c,d report alterations in E_{bond} and E_{angle} during shearing. The shift trends of these values lead to the conclusion that the energy change during shearing is mainly driven by bond stretching and angle variation. The sum of E_{bond} and E_{angle} accounts for more than half of E_{total} , making these the primary contributors to the shearing status of the system. During the shearing process, stretching bonds and rotating bond angles mainly determine the deformation mode of the system. E_{bond} tends to reach equilibrium at 20,000 kcal/mol and E_{angle} at 14,000 kcal/mol. These findings suggest that bond stretching has a superior role concerning bond angles rotation in the shearing process. Dihedral angle distortion plays a relatively minor part in contrast, Figure 10e shows that E_{dihed} exhibits periodic variation and increases with γ_0 , while gradually decreasing with an increase in shearing cycle. When $\gamma_0 = 0.05$, E_{dihed} is around -400 kcal/mol and when $\gamma_0 = 0.5$, E_{dihed} is around 4000 kcal/mol. The principal reason for the raised value of E_{dihed} is the increase in the distance between the molecular chains and their initial position due to a larger γ_0 .

To study the changes in molecular chain conformation during the shearing process, we extract the mean square radius of gyration (R_g) of the molecular chain at $D_c = 8.0$ under different γ_0 , calculated by Equation (1) and shown in Figure 11.

$$R_{\rm g}^2 = \frac{1}{M} \sum_{i} m_i (r_i - r_{\rm cm})^2 \tag{1}$$

where *M* is the total of the model, r_{cm} is the center-of-mass position, and the sum is over all atoms in model.

The T_g is the primary mechanism for examining the impact of molecular chain flexibility on dynamic mechanical properties. A larger R_g indicates poorer flexibility and molecular chains with poorer flexibility correspond to higher T_g and poorer dynamic mechanical performance at the same temperature [27,28].

From Figure 11a–c, it is evident that the R_g of the molecular chain undergoes periodic variation during the shearing process, with two peaks in one shear cycle, corresponding to the two displacement limits during the shearing process. With the increase in parameter γ_0 , the R_g peaks increase, implying a decreased flexibility of molecular chains during shearing, ultimately leading to diminished dynamic mechanical properties of vulcanized SBR.



Figure 11. Cont.



Figure 11. R_g of the system under different γ_0 (**a**–**c**) varies with the shear period and the difference between the R_g and the initial R_g ((R_g)_T–(R_g)₀) after 10 shear periods under different γ_0 (**d**).

The results from Figure 11 reveal that R_g remains almost unchanged, i.e., independent of the γ_0 when γ_0 is less than 0.1 (Figure 11c). On the contrary, R_g demonstrates a noticeable upward pattern with γ_0 , as determined by the difference between the initial R_g and the value after 10 shearing cycles, when γ_0 exceeds 0.1 (Figure 11b,d). As the value of γ_0 increases, the molecular chains become progressively inflexible, causing a significant increase in R_g and a reduction in the mechanical properties. This trend is further demonstrated in Figure 4a, which illustrates the G' of SBR, showing no obvious reduction when γ_0 falls below 0.1. However, when γ_0 reaches and surpasses 0.1, the G' of SBR dwindles considerably.

3. Materials and Methods

3.1. Verification of Simulation Correctness

The cross-linking densities (mol/mL) corresponding to each D_c in MD model obtained via calculation are presented in Table 3. The results of cross-linking densities obtained by experiments are also shown in Table 3.

Monomer	Styrene	1,4 Butadiene	Cis-1,2 Butadiene	Trans-1,2 Butadiene
Contents (wt. %)	23.5	14	12.5	50

Table 3. Monomer components in single-chain SBR.

A model of vulcanized SBR is established by changing the cross-linking density (D_c) according to the method in Equation (2). D_c values of 1.0, 2.0, 5.0, 6.0, and 8.0 are assigned for the model.

$$Dc = Ns/Mc$$
 (2)

where *N*s is the number of cross-link bonds and *M*c is the number of single chains.

The cross-linking criteria are defined as follows. If the distance between two carbon atoms (C) on the main chain falls within the range of 1.6 to 3.45 Å, a sulfur atom (S) is added to the geometric center of the two C atoms and a C-S-C bond is formed [29]. Additionally, since every two C atoms on a single chain can create a C-S-C bond, the phenomenon of self-cross-linking is considered in the actual cross-linking process [30]. Once a C atom on the main chain establishes a cross-link bond, it can no longer bind to other S atoms. To implement the complete cross-linking process, this study utilized *Perl* scripts inside Materials Studio software.

The *pcff* force field is utilized to describe the intermolecular and intramolecular interactions in SBR. Equation (3) depicts the formula of the *pcff* force field.

$$\begin{split} E_{pot} &= \sum_{b} [k_{2}(b-b_{0})^{2} + k_{3}(b-b_{0})^{2} + k_{4}(b-b_{0})^{2}] \\ &+ \sum_{\theta} [H_{2}(\theta-\theta_{0})^{2} + H_{3}(\theta-\theta_{0})^{3} + H_{4}(\theta-\theta_{0})^{4}] \\ &+ \sum_{\varphi} [V_{1}(1-\cos\varphi) + V_{2}(1-\cos2\varphi) + V_{3}(1-\cos3\varphi)] + \sum_{\chi} K_{\chi}\chi^{2} \\ &+ \sum_{b,b'} F_{bb}(b-b_{0})(b'-b'_{0}) + \sum_{b,\theta} F_{b\theta}(b-b_{0})(\theta-\theta_{0}) + \sum_{\theta'\theta'} F_{\theta\theta'}(\theta-\theta')(\theta-\theta') \\ &+ \sum_{b,\varphi} (b-b_{0})(V\cos\varphi + V_{2}\cos2\varphi + V_{3}\cos3\varphi) \\ &+ \sum_{b,\varphi} F_{b\theta\varphi}(b-b_{0})(\theta-\theta_{0})\cos\varphi \\ &+ \sum_{b,\beta,\varphi} F_{b\theta\varphi}(b-b_{0})(\theta-\theta_{0})\cos\varphi \\ &+ \sum_{i,j} \left[\frac{A_{ij}}{er_{ij}} - \frac{B_{ij}}{r_{ij}^{6}} \right] \end{split}$$
(3)

Van der Waals forces are calculated by truncated Lennard-Jones (L-J) 9-6 equation, illustrated in Equation (4).

$$V_{LJ}(r) = \begin{cases} 4\varepsilon \left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^6 & (r \le r_c) \\ 0 & (r > r_c) \end{cases}$$
(4)

where ε is the bond energy at the equilibrium position where the force F(r) = 0, σ is the collision diameter, r_c is the truncation radius of 9.5 Å, and r refers to the interatomic distance. Figure 12 presents the molecular formula, process and results of cross-linking.

After the completion of cross-linking, we perform relaxation annealing on the model. The specific method is as follows. Firstly, a 2 ns NPT relaxation is carried out at 300 K and 1 atm, then the model is heated to 600 K and then cooled to 300 K in NVT ensembles to simulate the annealing process. This process lasted for 4 ns and is repeated 4 times. Finally, a 2 ns NPT relaxation is performed at 300 K and 1 atm, during which the radial distribution function (RDF) and mean square displacement (MSD) of the system are extracted. The obtained model is used for studying the dynamic shear process.

This study investigated the dynamic mechanical properties of SBR with varying density of cross-linking (D_c) through cyclic shear deformation of simulated box. The shear deformation is performed in the *XY* plane by moving the simulation box along the $\pm X$ directions with a fixed shear rate of 0.01 ps⁻¹. The shear strain amplitude (γ_0) varied from 0.05 to 0.5 and the system underwent 10 complete shear cycles. The changes over time in shear stress (σ) and strain (γ) are expressed using Equations (5) and (6). Consequently, the storage modulus (G') and loss factor (tan δ) of SBR with varying D_c are obtained through Equation (7).

$$\sigma = \sigma_0 \sin\left(\omega \, t + \delta\right) \tag{5}$$

$$\gamma = \gamma_0 \sin(\omega t) \tag{6}$$

$$G' = \frac{\sigma_0}{\gamma_0} \cos(\delta) \quad \tan \delta = G'' / G' \tag{7}$$

An Anderson thermostat and Berendsen barostat are employed to control temperature and pressure, respectively, for all simulation in this study, while the velocity Verlet algorithm is used for kinetic integration. Molecular dynamics simulations are performed



using the LAMMPS package on a 24-core supercomputer [31]. The visualizing results are analyzed through Open Visualization Tool (OVITO) software [32].

Figure 12. The modeling details of the cross-linking include four monomers in SBR chain (**a**), single chain containing 60 monomers (**b**), the model after cross-linking (**c**), molecular formula (**d**) and the local amplification (**e**) at the red box in (**c**). In (**c**,**e**), the magenta beads are C atoms on the main chain, the gray beads are C atoms of the benzene ring, the white beads are the H atoms and the yellow beads are the S atoms.

3.2. Experimental Methods

The amounts of sulfur addition in vulcanized SBR are determined based on the S atomic mass fraction (phr) in different D_c models. The determined amounts are 1.04, 1.99, 5.03, 6.29, and 8.28, respectively. The mixed SBR is obtained by adding compounding agents to pure SBR. Table 4 illustrates the content of each component.

Table 4. The content of each component in mixed SBR.

Components	SBR	SA	Accelerant DZ	Accelerant TT	ZnO	S
Contents (phr)	100	1	1	0.1	4.0	Variable

Pure SBR is premixed for 2 min on an open mill with a diameter of Φ 152.4 mm. Subsequently, ZnO, SA, accelerant DZ, accelerant TT, and insoluble sulfur (S) are added in sequence to produce mixed SBR. The mixed rubber is allowed to stand for 24 h before testing the vulcanization properties and recording T_{90} using a non-rotor vulcanizer produced by Gotech. Vulcanizations of each mixed rubber are carried out at 150 °C to create a 2 mm vulcanized SBR sheet with a temperature of 150 °C, and the time of vulcanization is calculated based on T_{90} value.

3.2.1. Cross-Linking Density Test

After allowing the vulcanized SBR to stand for 24 h, the cross-linking density analyzer with the model XLDS-15 is used to test the cross-linking density by the method of nuclear magnetic resonance (NMR). The SBR samples are tested under specific conditions of 90 °C for the temperature, 0.35 T for the magnetic field intensity and 15 MHz for the resonance frequency. The cross-linking density is calculated by measuring the relaxation time (T_2) of the SBR samples with varying sulfur contents. The same formulae are tested five times and the average values are adopted as the final result.

3.2.2. DSC Test

The differential scanning calorimeter model DSC 200 F3 is utilized to quantify the glass transition temperature (T_g) of the vulcanized SBR. The sample weighing 8–10 mg is then loaded into the calorimeter and heated to 100 °C for 5 min to eliminate the thermal history. Next, the temperature is lowered to -75 °C and held for five minutes before being heated back to 100 °C. The test parameters include both the heating and cooling rates of 10 °C/min.

3.2.3. RPA Test

The RPA2000 rubber processing analyzer (RPA) is employed for evaluation of the dynamic mechanical properties of each sample. Initially, the temperature is set to 150 °C and the samples are subsequently put into the testing equipment while recording the time taken. Upon reaching the corresponding T_{90} to simulate the vulcanization process, the instruments' temperature is decreased to 20 °C, after which the samples undergo a shearing test, the test frequency is set at 10 Hz and strain range is 0–55%.

3.3. Experimental Validation

Figure 13 shows the vulcanization curve of SBR with different contents of S and the variation of G' with γ_0 tested by RPA.



Figure 13. Vulcanization curve of SBR with different contents of S (**a**) and the variation of G' with γ_0 tested by RPA (**b**).

Figure 13 shows an increase in the Payne effect in all groups of SBR with an increase in γ_0 . As observed from combining these findings with the results presented in Figure 5, it is apparent that higher S content enhances the deformation resistance of SBR, which is demonstrated by a noticeable upward trend in *G*' (Figure 13). Furthermore, as γ_0 exceeds 0.1, *G*' reduction increases in all groups of SBR.

However, the experimental and simulated results presented in Figures 4 and 13 display a difference of five orders of magnitude in their G' values; nevertheless, the overall trends remain consistent. This means that both experimental and simulated outcomes confirm that vulcanized SBR exhibits a distinct Payne effect. The significant difference in magnitude

is due to the scale effect of MD simulation. Consequently, the experimental results can provide more reliable evidence to support our simulation approach.

4. Conclusions

In this study, molecular dynamics (MD) simulations are conducted to study the SBR models with different D_c , which are then subjected to shear deformation experiments for verification. The main conclusions of this study are as follows.

- 1. As D_c increases, the T_g of the SBR also increases. When $D_c = 8.0$, T_g is 243.84 K, which is 5.45% higher than the T_g of 231.23 K obtained for $D_c = 1.0$. The maximum difference between experimental and simulation results is 5.65%.
- 2. An increase in D_c limits the movement of molecular chains. When $D_c = 1.0$, MSD is about six times that of $D_c = 8.0$. RDF analysis proves that the larger D_c makes the atomic distribution in the system more compact, which is one of the reasons for higher D_c having a higher G'.
- 3. Dynamic shear deformation dissipates about 48% of the system's energy through bond stretching and 37% through bond angle rotation. Changes in D_c and γ_0 all have a significant impact on bond stretching, but little impact on bond angle rotation. In addition, the dihedral rotations have the lowest contributions in the Payne effect.
- 4. SBR with different D_c show significant Payne effect under dynamic shear deformation. This is primarily due to the deviation of molecular chains from the initial position, leading to bond breaking and reduced flexibility of molecular chains. When $\gamma_0 > 0.1$, the difference between $(R_g)_0$ and $(R_g)_T$ corresponding to each shear period increases significantly.
- 5. In summary, this study provides theoretical guidance and methodological insights for future research on sulfurized SBR.

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