Effect of Peroxide Concentration on Cure Kinetics and Crosslink Density in EPDM Rubber

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Abstract

The study examines how peroxide concentration affects vulcanization behavior, cure kinetics, and crosslink density in oil–extended *EPDM* rubber. *EPDM* compounds containing 43 wt.% (75 phr - parts per hundred rubber) paraffinic oil were vulcanized with di (tert–butylperoxyisopropyl) benzene at concentrations from 4 to 9 phr. Vulcanization characteristics were evaluated using moving die rheometry over the 160–190 °C range, and kinetic parameters were determined by first–order kinetic analysis and Arrhenius modeling. Crosslink density was assessed by equilibrium swelling using the Flory–Rehner equation. Scorch safety was evaluated using Mooney scorch testing at 135 °C. The results showed that increasing peroxide concentration significantly increased the maximum torque and reduced the molecular weight between crosslinks, indicating the formation of a denser crosslinked network. In contrast, the minimum torque remained nearly unchanged. The vulcanization rate constant increased markedly with temperature but showed negligible dependence on peroxide concentration, whereas the activation energy remained within a relatively narrow range (120–125 kJ/mol). Higher peroxide concentrations resulted in more extensive crosslinking, suggesting improved radical utilization during vulcanization. At the same time, increasing peroxide concentration reduced scorch safety. Overall, the results demonstrate that peroxide concentration primarily controls the extent of network formation, whereas temperature predominantly governs the kinetics of vulcanization in oil–extended EPDM systems.

Keywords: peroxide vulcanization, EPDM, rheometry, cure kinetics, crosslink density, Arrhenius analysis.

1. Introduction

The demand for advanced materials that combine low density, appropriate hardness, and sufficient mechanical properties continues to grow rapidly. Alongside these requirements, modern engineering increasingly focuses on materials suitable for low–cost production, with properties that can be tailored through chemical and physical modifications [1]–[3]. Among these materials, elastomers such as ethylene–propylene–diene rubber (*EPDM*), isoprene rubber (*IR*), natural rubber (*NR*), styrene–butadiene rubber (*SBR*), chloroprene rubber (*CR*), and polysiloxanes (*Q*) have found extensive use in engineering applications [4]–[9].

EPDM is one of the most widely used and extensively studied elastomers worldwide. This is attributed to its excellent thermal stability, elasticity, low-temperature flexibility, and resistance to environmental factors, thermo-oxidative aging, and ozone degradation [10]–[14]. *EPDM* belongs to the group of unsaturated polyolefins and is produced by copolymerizing ethylene, propylene, and a small amount of a non–conjugated diene as a third monomer. The ratio of ethylene to propylene determines the elastomer's properties, while the presence of a diene

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monomer enables sulfur crosslinking. Typically, the third monomer content ranges from 3 to 9 wt.%, with ethylidene norbornene (*ENB*), dicyclopentadiene (*DCPD*), and related dienes being the most commonly used [15]–[17]. The chemical structure of *EPDM* is presented in Figure 1.

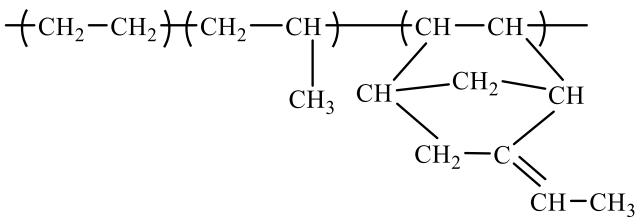

Figure 1. Chemical structure of the ethylene–propylene–diene terpolymer with 5–ethylidene–2–norbornene as the third monomer.

The application of elastomers is inherently linked to vulcanization. This process fundamentally alters elastomer properties by transforming them from a plastic to an elastic state through the formation of a three–dimensional crosslinked network between polymer chains. As a result, vulcanizates become insoluble in organic solvents and exhibit markedly improved mechanical properties [18], [19]. The most widely used vulcanization systems are based on sulfur or organic peroxides.

Peroxide crosslinking of elastomers was first reported by Ostromislensky in 1915. This reaction is primarily associated with saturated elastomers, where the absence of double bonds limits the effectiveness of sulfur vulcanization. However, peroxide systems can also be used with unsaturated elastomers and are therefore widely used in blends containing both saturated and unsaturated rubbers [20]. Peroxide vulcanization proceeds via a radical mechanism. Upon heating, organic peroxides undergo homolytic cleavage, generating free radicals that abstract hydrogen atoms from the polymer backbone, thereby producing macroradicals. Recombination (and, in elastomers containing residual unsaturation, radical addition followed by termination) yields predominantly covalent carbon-carbon (C–C) crosslinks between chains [21]–[30].

In contrast to mono–, di–, and polysulfidic bridges formed during sulfur vulcanization, C–C bonds have higher bond dissociation energy, resulting in improved thermo–oxidative stability of peroxide–cured elastomers. Consequently, such vulcanizates typically exhibit superior electrical properties, lower compression set, and enhanced resistance to thermal aging [21], [31].

Effective peroxide curing agents must remain thermally stable during mixing yet decompose rapidly at the selected vulcanization temperature. These requirements are best met by peroxides with a peroxy group attached to a tertiary carbon atom, because peroxides with primary or secondary carbon atoms are less thermally stable [22]. In peroxide vulcanization, the type and concentration of the curing agent, and the curing temperature are key factors governing reaction kinetics and, ultimately, the properties of the final composites [32].

Peroxide vulcanization offers several important advantages, including fast curing rates and the absence of reversion at elevated temperatures. The resulting vulcanizates typically exhibit good tensile strength, low compression set, and excellent resistance to thermal aging. Unlike sulfur vulcanization, peroxide systems are applicable to both saturated and unsaturated elastomers. Despite the well–established fundamental mechanism of peroxide vulcanization, several challenges remain. A major drawback is competing side reactions during network formation, which can reduce crosslinking efficiency. These side reactions are often associated with tertiary radicals and may involve main–chain scission and radical disproportionation [24], [33]–[35].

In addition to intrinsic radical side reactions within the polymer, common compounding ingredients can also act as radical scavengers, competing for peroxide–derived radicals and thereby reducing crosslinking efficiency. Process oils and certain plasticizers can act as radical–reactive components (via hydrogen abstraction or chain transfer), lowering the number of radicals available for rubber–rubber crosslink formation and decreasing the final network density [36]–[40].

Despite the extensive use of peroxide-cured *EPDM* in industrial applications such as automotive seals, hoses, and insulation materials, the fundamental relationships among peroxide concentration, cure kinetics, crosslink network development, and processing safety remain incompletely elucidated, particularly in highly oil-

extended formulations. Although peroxide curing is widely recognized for producing thermally stable carbon–carbon crosslinks and improved aging resistance compared to sulfur-based systems, the complexity of the radical reactions involved poses significant challenges for predicting and controlling the final network structure. In most previous studies, attention has been primarily directed either toward the influence of curing temperature on reaction rates or toward the resulting mechanical and physical properties of the vulcanizates. In contrast, comparatively little effort has been devoted to systematically correlating rheometric kinetic parameters—such as scorch time, cure rate index, and torque development—with the evolution of crosslink density and network architecture during vulcanization.

This lack of understanding is especially critical for oil-extended *EPDM* compounds, in which substantial amounts of process oil are added to improve processability, flexibility, and cost efficiency. The presence of oil can significantly influence curing behavior by diluting reactive species, modifying chain mobility, and potentially participating in radical reactions, thereby affecting the efficiency of peroxide decomposition and crosslink formation. Consequently, the interplay between peroxide concentration and oil content may produce complex, nonlinear effects on cure kinetics, scorch safety, and the resulting network structure. From a practical perspective, insufficient control over these parameters may lead to premature vulcanization (scorch), non-uniform crosslink distribution, or suboptimal mechanical performance, all of which are critical concerns in industrial processing.

Therefore, a comprehensive understanding of how peroxide concentration affects rheometric behavior, kinetic parameters, and crosslink network development in oil-extended *EPDM* systems is essential. Such knowledge would enable more precise formulation design, better control of processing safety, and improved curing efficiency. Ultimately, this would facilitate the optimization of material performance by achieving a balanced combination of crosslink density, mechanical properties, and processing stability in peroxide-cured *EPDM* compounds.

Therefore, the aim of the present study is to investigate how the concentration of di (tert–butylperoxyisopropyl) benzene, used as a curing agent, affects the vulcanization kinetics, rate constants, activation energy, crosslink density, and Mooney scorch safety time of *EPDM*–based compounds prepared from an oil–extended *EPDM* containing 43 wt.% (75 phr - parts per hundred rubber) of paraffinic process oil.

The novelty of the present work lies in the integrated evaluation of rheometric cure behavior, kinetic parameters, crosslink density, and scorch safety in highly oil-extended *EPDM* compounds cured at varying concentrations of di (tert-butylperoxyisopropyl) benzene. Attention is given to the relationship between apparent cure kinetics and network development in the presence of high process oil content, providing additional insight into peroxide utilization efficiency and crosslink formation during peroxide vulcanization.

2. Materials and Methods

2.1. Materials

The elastomeric matrix used was *EPDM – Keltan 4577* from *ARLANXEO*. The polymer characteristics were: ethylene content 66 wt.%, third monomer ethylidene norbornene (*ENB*) 5.1%, and Mooney viscosity $M_L(1+4)$ at 125ºC – 46 MU. The elastomer was oil-extended with 75 phr of paraffinic oil. Carbon black *Corax N550*, supplied by *Cabot Corporation* (USA), served as the reinforcing filler. Peroxide vulcanization was carried out using *Perkadox 14–40 B–PD* (*Nouryon*, the Netherlands), a commercial formulation containing 40 wt.% di (tert–butylperoxyisopropyl) benzene supported on an inert mineral carrier (calcium carbonate). Other ingredients, such as zinc oxide and stearic acid, were commercial products and were used as received.

2.2. Methods

2.2.1. Vulcanization characteristics

The vulcanization characteristics of the studied rubber compounds were determined using a moving die rheometer (*MDR)*, *HD–R 811–1*, from *Haida International* (Figure 2), in accordance with ISO 6502–3:2018. The cure curves were obtained at 160 °C, 170 °C, 180 °C and 190 °C.

Figure 2. Moving die rheometer used for rheometric characterization of the investigated rubber compounds.

2.2.2. Kinetic parameters

Cure kinetics were investigated using a *MDR* under isothermal conditions. For each formulation, rheometric torque–time curves were recorded at four temperatures (e.g., 160 °C, 170 °C, 180 °C and 190 °C) using identical testing parameters (oscillation frequency, arc amplitude, and specimen geometry). Each experiment was continued until a quasi–plateau torque was reached, ensuring that the dominant peroxide decomposition and crosslink formation processes were substantially complete.

From each curve, the following characteristic torques were obtained:

- M_L minimum torque (initial viscosity–controlled torque);
- M_H maximum torque (plateau torque);
- M_t torque at time t.

Thermal decomposition of organic peroxides proceeds predominantly via homolytic first–order scission, allowing the cure kinetics to be approximated by a first–order rate expression. Under this approximation, the fraction of unreacted peroxide at time t decays exponentially:

$$\ln(a - x) = -kt + ln\, a \quad (1)$$

where: a is the initial amount of reactive peroxide; x is the amount reacted at time t; k is the apparent first–order rate constant.

Because absolute peroxide concentration is not directly measurable by rheometry, torque development was used as a relative proxy for reaction progress. The reacted and unreacted fractions were expressed as:

$$a = (M_H - M_L), \quad (a - x) = (M_H - M_t) \quad (2)$$

Substituting these relations into the integrated first–order expression yields:

$$\ln(M_H - M_t) = -kt + \ln\,(M_H - M_L) \quad (3)$$

This formulation enables direct extraction of kinetic parameters from rheometer data without requiring chemical analysis of residual peroxide.

For each curing temperature, torque values were sampled at multiple time points during the primary curing interval (excluding the initial instrument stabilization and any late–stage plateau artifacts). The quantity $\ln\,(M_H - M_t)$ was calculated and plotted as a function of curing time.

A linear regression was performed according to:

$$ln\,(M_H - Mt) = b - kt \quad (4)$$

The slope of the fitted line equals $-k$, yielding the apparent first–order rate constant k (min^{-1}). The regression's linearity (e.g., R^2) was used to verify the validity of the first–order approximation over the selected cure window.

The temperature dependence of the rate constant was analyzed using the *Arrhenius* equation:

$$k = A \cdot exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where: E_a is the activation energy; A is the pre-exponential factor; R is the universal gas constant (8.314 J/mol.K); T is absolute temperature (K).

Taking the natural logarithm yields the linear *Arrhenius* equation:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \left(\frac{1}{T}\right) \quad (6)$$

The $\ln k$ values obtained at different curing temperatures were plotted against the reciprocal temperature ($1/T$). Linear regression of the *Arrhenius* plot yielded the slope m, from which the activation energy was calculated as:

$$E_a = -m \cdot R \quad (7)$$

Activation energy values were reported in *kJ/mol*. A similar approach has been reported in the scientific literature [41].

2.2.3. Mooney scorch safety time

Mooney scorch safety time was determined using a Mooney viscometer *HD–R 812* from *Haida International* in accordance with ISO 289–2:2020. A photograph of the equipment used for the measurements is shown in Figure 3. The measurements were performed at 135 °C, and the scorch time (t_5) was recorded. The scorch time is the time required for the Mooney viscosity to increase by five units above the minimum viscosity and is commonly used as an indicator of processing safety. This parameter indicates the onset of vulcanization and the available processing window before significant crosslink formation occurs. Consequently, the Mooney scorch test is widely employed to evaluate the risk of premature curing during mixing, extrusion, and molding operations.

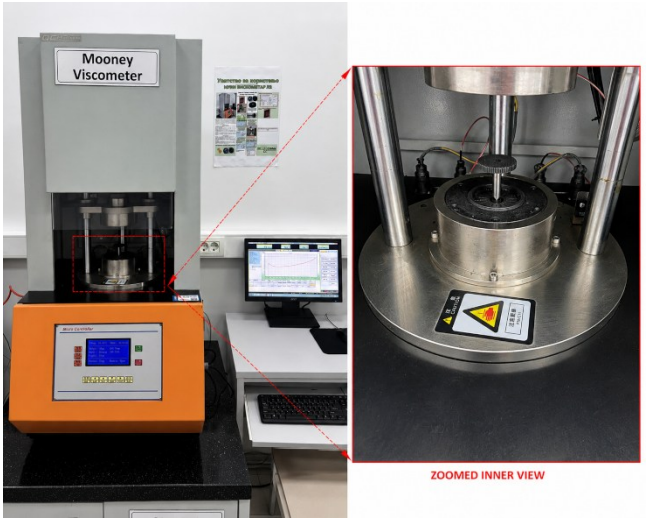

Figure 3. Mooney viscometer used to determine scorch safety characteristics.

2.2.4. Thermal aging and crosslink density

Thermo–oxidative aging of the obtained vulcanizates was carried out in accordance with ISO 188:2023 at 125 °C for 24 h.

The crosslink density of the composites was studied by determining the molecular weight of the rubber segments between two crosslinks, calculated using the *Flory–Rehner* (8) equation after measuring the equilibrium swelling degree in the organic solvent:

$$\frac{1}{M_c} = -\frac{[\ln(1-V_r)+V_r+\mu V_r^2]}{V_0 \cdot \rho \cdot \left(V_r^{1/3}-\frac{V_r}{2}\right)} \quad (8)$$

where: V_r is the volume fraction of rubber in equilibrium swollen vulcanizates sample; V_o is the molar volume of the solvent used; μ is the Huggins parameter; while ρ is the density of the solvent used.

The *Flory–Rehner* equation is widely used to characterize crosslinked elastomers because it relates equilibrium swelling behavior to the density of elastically active network chains. A decrease in the molecular weight between crosslinks (M_c) corresponds to an increase in crosslink density, indicating a more tightly crosslinked network. Therefore, equilibrium swelling measurements provide valuable information about the effectiveness of the vulcanization process and the extent of network formation.

Figure 4 illustrates the analytical balance used to measure the mass of the specimens before and after immersion in toluene.

Figure 4. The analytical balance used in equilibrium swelling measurements.

2.3. Preparation of the studied rubber compounds and vulcanizates

The rubber compounds were prepared on a laboratory rubber mixing mill (rolls L/D 320x160) using the formulations in Table 1.

Table 1. Composition of the investigated rubber compounds (phr).

Ingredient	1	2	3	4	5	6
EPDM Keltan 4577	175	175	175	175	175	175
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1
Carbon black N550	85	85	85	85	85	85
Perkadox 14–40 B–PD	4	5	6	7	8	9

The rubber compounds were vulcanized in an electrically heated hydraulic press at 160 °C, 170 °C, 180 °C, and 190 °C under a pressure of 10 MPa for the optimal curing time determined by their vulcanization characteristics. The prepared rubber compounds were stored at ambient temperature for 24 h before vulcanization. After vulcanization, the composites were conditioned for an additional 24 h at room temperature before testing. This conditioning period was intended to stabilize the rubber network and relax internal stresses generated during processing.

3. Results and Discussion

3.1. Curing characteristics

As described in the experimental section, di (tert–butylperoxyisopropyl) benzene (*Perkadox 14–40 B–PD*) was used as a crosslinking agent. Literature data indicate that the typical amount of this peroxide used for crosslinking ethylene–propylene–diene terpolymer (*EPDM*) ranges from 2.5 to 7.0 phr, depending on the required properties of the vulcanizates [42], [43]. To evaluate the influence of this peroxide on the vulcanization kinetics of the studied rubber compounds, its effect was investigated over the concentration range of 4 to 9 phr, with increments of 1 phr.

The *EPDM* elastomer used in this study is extended with more than 40 wt.% paraffinic oil. Such oils can partially scavenge radicals generated during the homolytic decomposition of the peroxide, thereby reducing crosslinking efficiency and, consequently, affecting the mechanical properties of the vulcanizates before and after aging. Therefore, slightly higher peroxide levels were used to compensate for radicals consumed by the oil during the early stages of vulcanization.

Figures 5–8 present the vulcanization curves of the investigated rubber compounds taken at 160 °C, 170 °C, 180 °C, and 190 °C, respectively. As shown in the figures, the minimum torque (M_L) of the studied rubber compounds, used as an indirect measure of their initial viscosity, remains essentially unchanged regardless of the amount of organic peroxide used or the temperature at which vulcanization is carried out. This result is not unexpected, given that the organic peroxide content in the compounds investigated is relatively low – approximately 2–4 wt.% – which is insufficient to produce noticeable changes in their viscosity. In addition, the M_L measurement is performed over a very short period (less than one minute), since crosslinking of the elastomer macromolecules begins shortly thereafter. This also explains the absence of a significant temperature effect on this parameter.

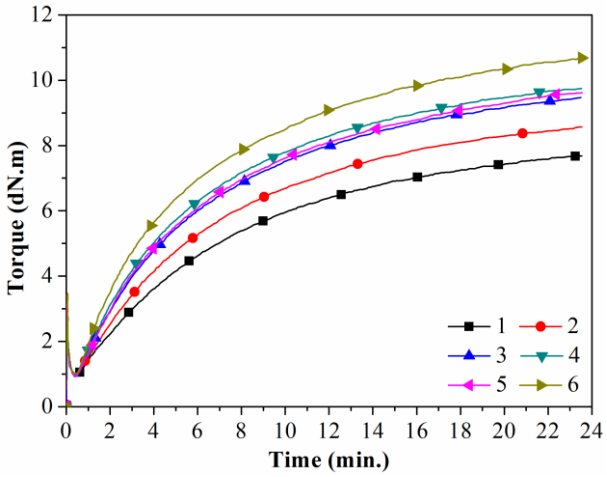

Figure 5. Cure curves of the investigated rubber compounds taken at 160 °C.

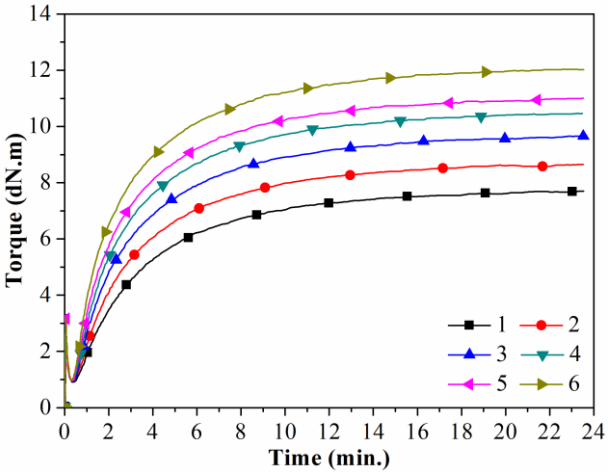

Figure 6. Cure curves of the investigated rubber compounds taken at 170 °C.

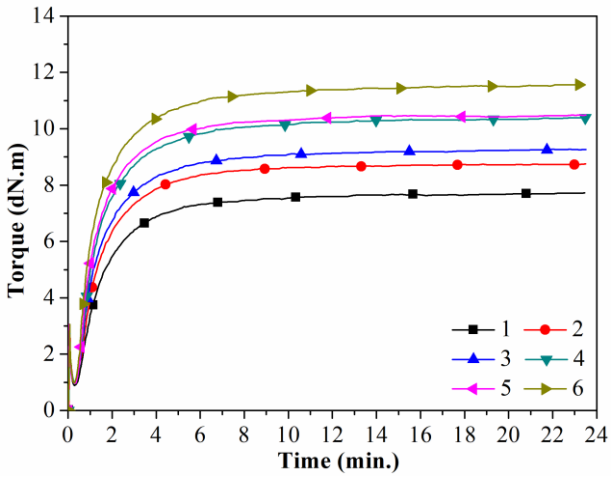

Figure 7. Cure curves of the investigated rubber compounds taken at 180 °C.

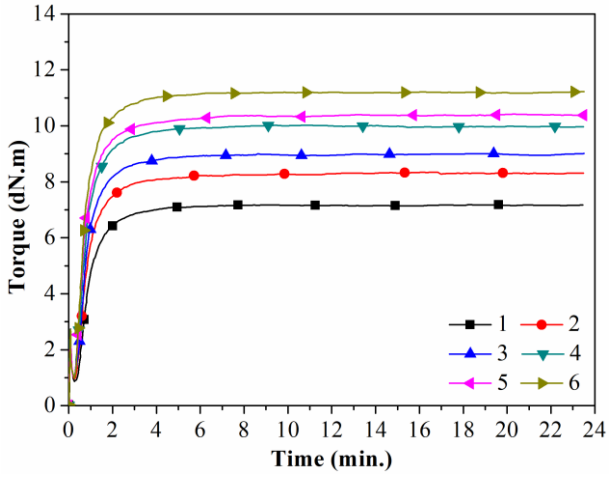

Figure 8. Cure curves of the investigated rubber compounds taken at 190 °C.

An increase in the amount of di (tert–butylperoxyisopropyl) benzene results in higher values of the maximum torque (M_H) and the torque difference ($\Delta M = M_H - M_L$). The latter provides insight into the extent of vulcanization in the obtained composites. This behavior indicates that increasing the amount of the curing agent leads to greater crosslinking in *EPDM*, as expected. The same trend is observed across all investigated temperatures. In addition, temperature exerts a pronounced influence on this parameter: at a constant peroxide level, higher temperatures yield higher M_H and ΔM values, indicating a stronger curing effect. This behavior can be attributed to the increased reactivity of the formed peroxy radicals at elevated temperatures [22].

The increase in maximum torque with peroxide concentration indicates that more peroxide-derived radicals were available for hydrogen abstraction from the *EPDM* backbone. Thermal decomposition of di (tert-butylperoxyisopropyl) benzene generates highly reactive peroxy radicals, which subsequently produce *EPDM* macroradicals by abstracting labile hydrogen atoms. Recombination of these macroradicals predominantly forms thermally stable carbon–carbon crosslinks. Consequently, increasing peroxide concentration increases the probability of intermolecular radical coupling and promotes the development of a more densely crosslinked network. The observed increase in ΔM therefore reflects not only a higher crosslink density but also a progressive restriction of molecular mobility associated with the formation of a more rigid three-dimensional network structure.

It should be noted that peroxide-derived radicals are not used exclusively for crosslink formation. Radical termination, disproportionation reactions, and hydrogen abstraction from paraffinic process oil may also occur. Nevertheless, the continuous increase in M_H observed across the investigated peroxide concentration range indicates that the increase in radical generation exceeded losses associated with these competing reactions. This suggests that radical utilization efficiency remained sufficiently high to promote additional network formation despite the substantial presence of process oil.

Figures 5–8 show that the vulcanization rate increases significantly with temperature. For example, the vulcanization time (t_{90}) of the investigated rubber compounds is approximately 12 min at 160 °C, about 8 min at 170 °C, about 4 min at 180 °C, and ~2 min at 190 °C. Based on these results, the most appropriate vulcanization temperature in this case is 170–180 °C. At lower temperatures (160 °C, Figure 5), a continuous increase in torque is observed during the post–vulcanization stage, indicating that this temperature is insufficient to fully consume the crosslinking agent. Conversely, higher temperatures (190 °C, Figure 8) result in excessively rapid curing, which may create difficulties during the industrial manufacturing of rubber products based on these compounds. Such conditions can promote excessive crosslinking of the elastomer and side reactions, including main–chain scission and disproportionation of elastomer radicals, which may ultimately lead to deterioration of the mechanical properties of the resulting composites [24], [33].

3.2. Vulcanization kinetics

In the chemistry of rubber vulcanization, the rate constant (k) and the activation energy (E_a) are key kinetic parameters that characterize the curing process. The rate constant k quantifies the rate of crosslink formation at a given temperature and can be determined from rheometer cure curves by fitting an appropriate kinetic model [41]. The activation energy (E_a) is the minimum energy required for the reaction to proceed and is derived from the temperature dependence of the rate constant. These parameters provide complementary information: a higher k at the curing temperature indicates faster network formation and shorter curing times, whereas a higher E_a implies greater sensitivity of the curing process to temperature variations [44], [45].

Figures 9–14 show the time dependence of the logarithm of the torque drop, $ln(M_H–M_t)$, for the investigated rubber compounds containing 4 phr (Figure 9), 5 phr (Figure 10), 6 phr (Figure 11), 7 phr (Figure 12), 8 phr (Figure 13), and 9 phr (Figure 14) of peroxide, measured at four temperatures. The rate constant k was calculated from the slope of the linear fit to the experimental data.

As shown in the figures, the rate constants (k) for the vulcanization process increase with temperature. This indicates that the rate of vulcanization of the investigated rubber compounds also increases with temperature, consistent with the optimum cure time (t_{90}) values obtained from the vulcanization curves presented in Figures 5–8. However, variations in the amount of di (tert–butylperoxyisopropyl) benzene used as a crosslinking agent do not significantly affect the rate constants of the vulcanization process. For example, the values of k at 160 °C vary between 0.147 and 0.152 min^{-1}, which fall within the experimental error of the measurement. Although this result may at first appear inconsistent, it is not. According to the principles of physical chemistry and chemical kinetics, the rate constant of a chemical reaction is determined by the reaction temperature and is independent of the concentrations of the reacting species [46], [47].

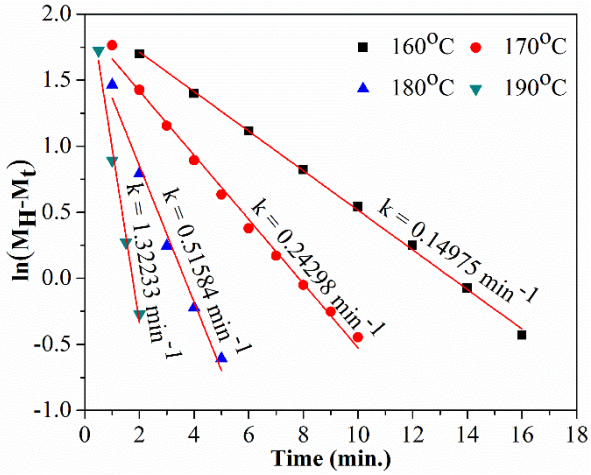

Figure 9. First–order kinetic analysis of peroxide vulcanization at different temperatures for the compound comprising 4 phr *Perkadox 14–40 B–PD*.

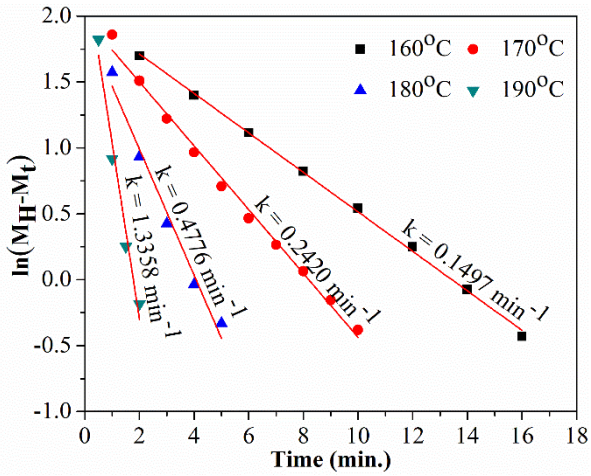

Figure 10. First–order kinetic analysis of peroxide vulcanization at different temperatures for the compound comprising 5 phr *Perkadox 14–40 B–PD*.

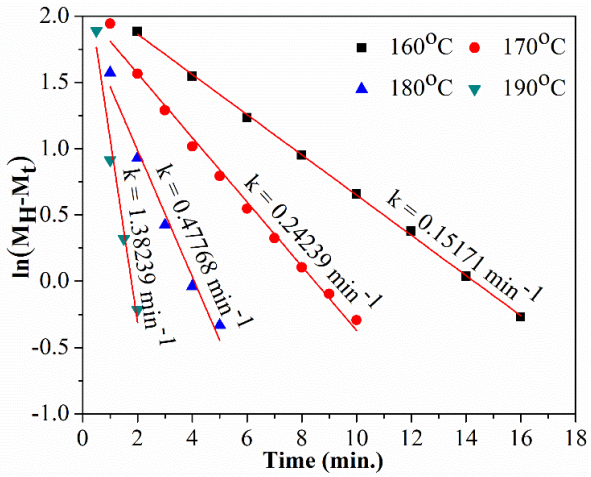

Figure 11. First–order kinetic analysis of peroxide vulcanization at different temperatures for the compound comprising 6 phr *Perkadox 14–40 B–PD*.

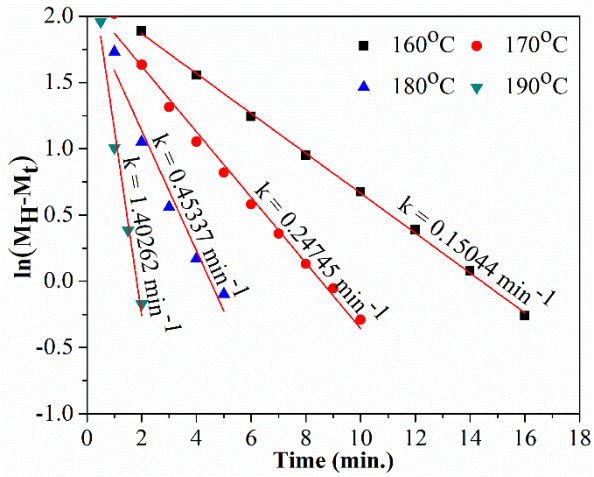

Figure 12. First–order kinetic analysis of peroxide vulcanization at different temperatures for the compound comprising 7 phr *Perkadox 14–40 B–PD*.

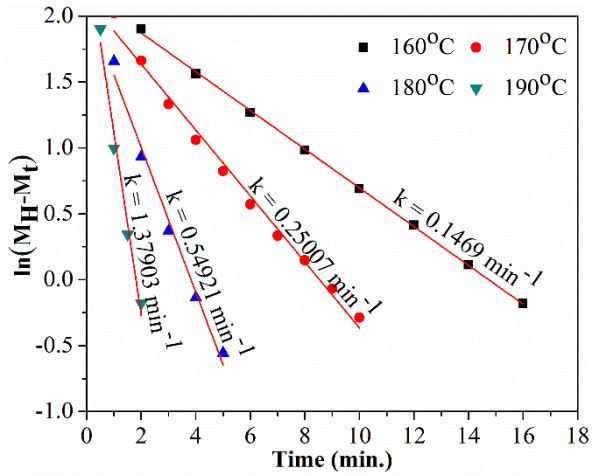

Figure 13. First–order kinetic analysis of peroxide vulcanization at different temperatures for the compound comprising 8 phr *Perkadox 14–40 B–PD*.

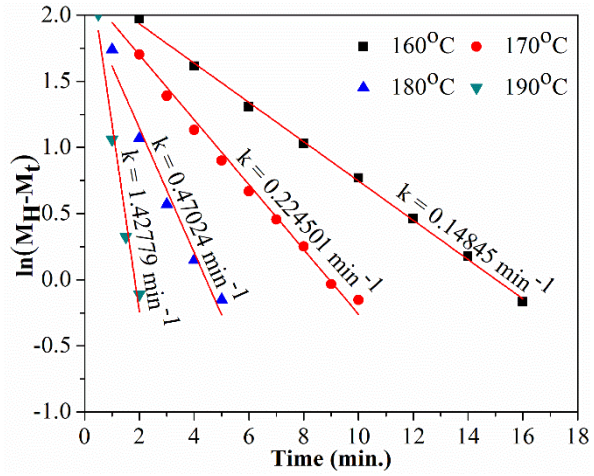

Figure 14. First–order kinetic analysis of peroxide vulcanization at different temperatures for the compound comprising 9 phr *Perkadox 14–40 B–PD*.

Figure 15 shows the dependence of ln*k* on temperature. Linear regression of the *Arrhenius* plot yielded the slope *m*, from which the activation energy of the vulcanization process was calculated for the investigated rubber compounds. The resulting activation energy values are presented in Figure 16. The results indicate that the minimum energy required for the vulcanization of this type of ethylene–propylene–diene terpolymer in the presence of di (tert–butylperoxyisopropyl) benzene as a crosslinking agent is essentially independent of its concentration.

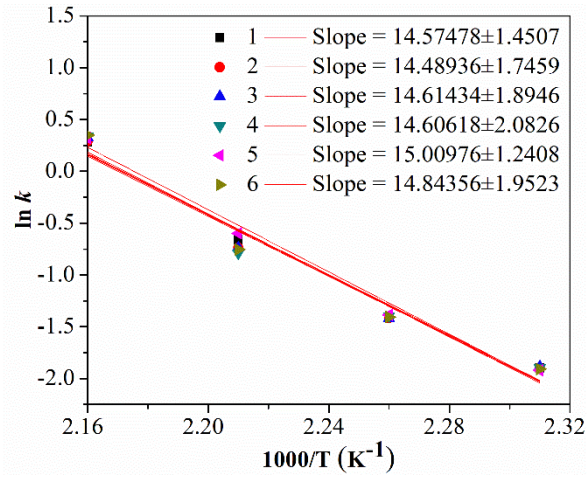

Figure 15. *Arrhenius* analysis of the vulcanization rate constant *ln k* vs *1/T*.

As shown in Figure 16, the activation energy determined in our study ranges from 120 to 125 kJ/mol. Literature data indicate that the activation energy for the vulcanization of ethylene–propylene–diene terpolymers typically ranges from 90 to 150 kJ/mol. Several factors may influence this parameter, most commonly including:

- the type of ethylene–propylene–diene terpolymer, particularly the ethylene-to-propylene ratio and the content of the third diene monomer;
- the type and amount of plasticizer present in the rubber;
- the type of peroxide used as a curing agent;
- the presence or absence of a coagent in the rubber formulation used as an activator for peroxide vulcanization.

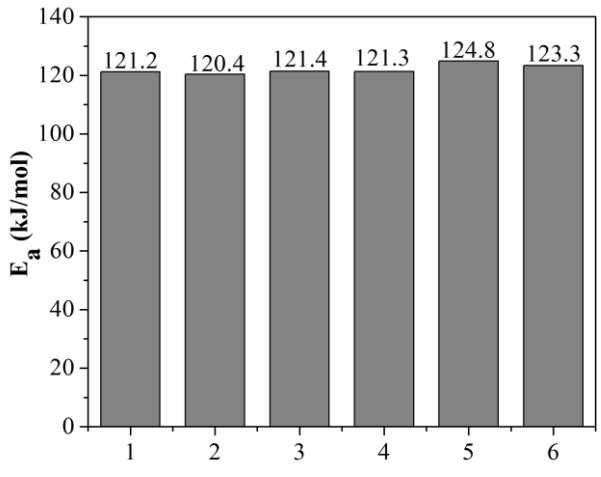

Figure 16. Activation energy of the vulcanization process of the studied *EPDM* based rubber compounds.

The kinetic parameters obtained in this work are consistent with previously reported values in the literature [48], [49].

The apparent rate constant and activation energy remained essentially unchanged as peroxide concentration increased, providing important insight into the mechanism of peroxide vulcanization. These results indicate that the energy barrier associated with peroxide decomposition and radical generation was not significantly influenced by peroxide loading. Instead, the primary effect of increasing peroxide concentration was to increase the number of radicals generated per unit volume of the compound, rather than altering the intrinsic reaction pathway. Consequently, the temperature dependence of the vulcanization process remained largely unaffected.

This observation further suggests that peroxide concentration primarily governs the extent of network formation rather than the fundamental kinetics of radical generation. In other words, the decomposition mechanism of di (tert-butylperoxyisopropyl) benzene remains consistent across the investigated concentration range, while the likelihood of effective radical–radical interactions that lead to crosslink formation increases as more peroxide molecules are introduced. Such behavior is characteristic of peroxide-cured elastomer systems, in which network density is predominantly controlled by radical availability rather than by changes in activation energy.

3.3. Crosslink density

According to *Flory*, the degree of crosslinking of a vulcanizate can be determined by measuring its maximum swelling in an appropriate solvent. By evaluating the equilibrium swelling ratio (Q_p), the average molecular weight between crosslinks (M_c) can be calculated, which, in turn, provides information on the crosslink density of the studied vulcanizates [50], [51].

Figures 17 and 18 show the dependence of the molecular weight between crosslinks (M_c) of the investigated vulcanizates before and after accelerated heat aging, measured at two vulcanization temperatures: 170°C (Figure 17) and 190°C (Figure 18). The aim of this analysis, conducted on composites with identical compositions but cured at different temperatures, is to evaluate the effect of vulcanization temperature on the extent of crosslinking of the rubber compounds and, consequently, on the efficiency of di (tert–butylperoxyisopropyl) benzene as a crosslinking agent.

As shown in the figures, the molecular weight between crosslinks (M_c) of the investigated composites decreases with increasing crosslinking agent content, indicating an increase in the extent of crosslinking of the ethylene–propylene–diene terpolymer. After accelerated heat aging, higher M_c values are observed than before aging, suggesting that network degradation, rather than additional crosslinking, occurs. This behavior can be attributed to side reactions such as main–chain scission and disproportionation of elastomer radicals. These reactions are likely enhanced by the absence of peroxide coagents (e.g., ethylene glycol dimethacrylate, triallyl cyanurate, triallyl isocyanurate), which are known to improve the crosslinking efficiency of organic peroxides by suppressing such degradation reactions [52]–[59].

It should be noted that in the present study, the rate constant (k) and the activation energy (E_a) of the vulcanization process do not appear to change significantly with increasing peroxide content. The term “apparent” is used deliberately, since even at similar values of these kinetic parameters, higher peroxide loadings lead to the formation of vulcanizates with a more developed crosslinked structure. The reduction in molecular weight between crosslinks with increasing peroxide concentration indicates that the average distance between network junctions decreases. This finding

confirms that additional peroxide molecules contributed primarily to the formation of new crosslink sites rather than merely accelerating the curing reaction. Consequently, a denser crosslinked network was formed.

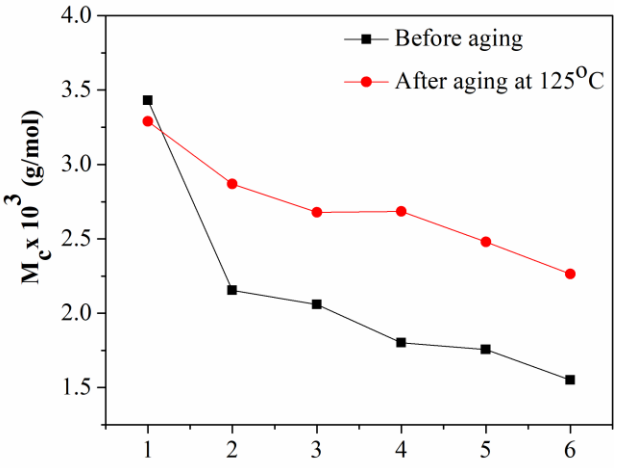

Figure 17. Molecular weight of the rubber segments between two crosslinks of the composites vulcanized at 170 °C.

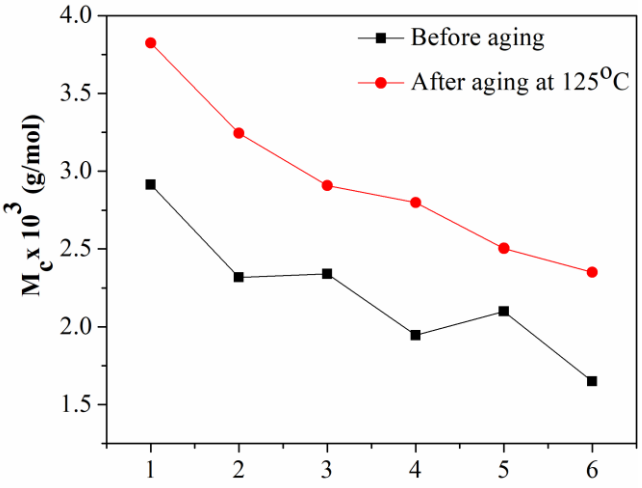

Figure 18. Molecular weight of the rubber segments between two crosslinks of the composites vulcanized at 190 °C.

The combination of nearly constant activation energy and decreasing M_c suggests that peroxide concentration influenced the efficiency of network formation rather than the energetics of peroxide decomposition. Higher peroxide loadings generated more radicals, increasing the likelihood of intermolecular radical coupling and carbon–carbon bond formation. As a result, a larger fraction of the *EPDM* chains became incorporated into the elastically active network. This interpretation is further supported by the increase in rheometric torque, which is commonly associated with reduced chain mobility and increased crosslink density.

The results also indicate that peroxide utilization efficiency remained sufficiently high even in the highly oil-extended *EPDM* system investigated. Although paraffinic oils may participate in chain-transfer reactions and consume some of the generated radicals, the observed increase in torque and decrease in M_c demonstrate that a substantial fraction of the radicals remained available for effective crosslink formation. Therefore, within the investigated concentration range, peroxide addition promoted crosslink formation rather than radical loss through competing side reactions.

3.4. Mooney scorch safety

The time during which a rubber compound can be safely processed at elevated temperatures is a critical parameter in rubber technology. This parameter, commonly referred to as scorch safety time, depends strongly on temperature and on the type and concentration of the crosslinking agent. In the present study, this parameter was determined using a *Mooney* viscometer at 135 °C. The results are presented in Figure 19.

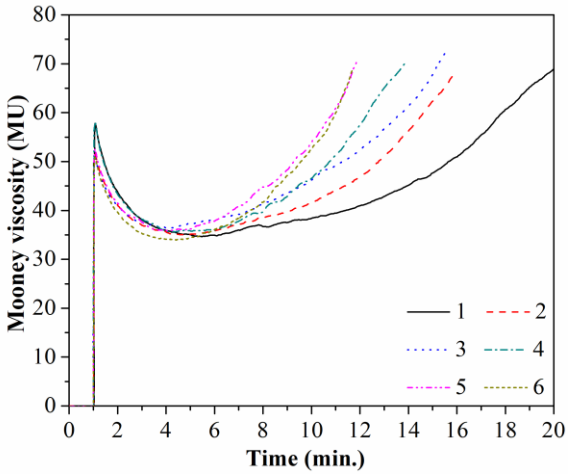

Figure 19. Mooney scorch safety of the studied composites at 135 °C.

As shown in Figure 19, increasing peroxide concentration reduced the scorch safety time from approximately 16 to 10 min. This behavior is attributed to the higher concentration of peroxide–derived radicals generated during the early stages of vulcanization, which

promotes an earlier onset of crosslink formation and shortens the safety processing time window.

The observed reduction in scorch safety time indicates that curing begins earlier during heating with increasing peroxide concentration. This behavior is associated with a higher concentration of peroxide-derived radicals, which accelerates the formation of reactive macroradicals and promotes earlier network formation. While this effect improves crosslink density and overall curing efficiency, it also shortens the time available for processing operations such as mixing, shaping, and molding. As a result, the findings illustrate the typical trade-off in peroxide-cured systems, where enhanced curing performance is achieved at the expense of reduced processing safety and a narrower processing window.

4. Conclusion

In this study, the effects of peroxide concentration on the vulcanization behavior, cure kinetics, scorch safety, and crosslink density of highly oil-extended *EPDM* compounds were investigated. Increasing the concentration of di (tert-butylperoxyisopropyl) benzene increased the maximum torque and torque difference, indicating the formation of a more densely crosslinked network. This was confirmed by a decrease in the molecular weight between crosslinks, as determined by equilibrium swelling measurements. In contrast, the minimum torque remained essentially unchanged, indicating that peroxide concentration does not significantly affect the compounds' initial viscosity.

The vulcanization rate constant increased markedly with curing temperature but was nearly independent of peroxide concentration. Likewise, the activation energy varied only within a narrow range of 120–125 kJ/mol. These results indicate that curing temperature governs the rate of vulcanization, whereas peroxide concentration affects the degree of crosslinking. Increasing peroxide content promoted the formation of additional carbon–carbon crosslinks, resulting in a more developed network structure. At the same time, the scorch safety time decreased, indicating reduced processing safety.

From a practical standpoint, the results demonstrate that peroxide concentration can be used effectively to control crosslink density and processing characteristics in oil-extended *EPDM* compounds. The findings may help select appropriate peroxide levels for applications that require a balance among curing efficiency, thermal stability, and processing safety.

Several limitations of the present study should be noted. Only one oil-extended *EPDM* grade was investigated; therefore, the results should not be generalized to all *EPDM* materials. In addition, only one peroxide curing agent was examined, and no peroxide coagents were included in the formulations. Because coagents are known to influence crosslinking efficiency and network formation, their effects were not considered in the present work. Furthermore, the investigation focused on vulcanization behavior, kinetic parameters, and crosslink density, but did not evaluate the mechanical properties of the resulting vulcanizates.

Future work should focus on establishing relationships between crosslink density and mechanical performance, including tensile properties, elongation at break, hardness, compression set, and dynamic mechanical behavior. Further studies should also examine the influence of peroxide curing agents and long-term aging resistance to provide a more complete understanding of peroxide-cured *EPDM* systems.

Competing Interest Statement

The authors declare that there are no known financial or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request. For access, please contact the corresponding author via *m_c_mihaylov@uctm.edu.*

Statement on the Ethical Use of AI Tools

Generative AI tools were used solely to improve language clarity and readability during manuscript preparation. The authors reviewed and edited all content and assumed full responsibility for the final manuscript.

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Author Contribution Roles

Mihail Mihaylov: Conceptualization, methodology, experimental design, formal analysis, data interpretation, writing-original draft preparation, writing-review and editing, and supervision.

Simona Nikolova: Investigation, experimental work, data collection, validation, and writing-review and editing.

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