



Preparation and Characterization of Varying Carbon Black Particle Sizes on Poly(Epichlorohydrin) Elastomer: I. Improving of Curing Kinetics and Mechanical Properties

Davut Aksüt¹ 

¹Hacettepe University, Department of Chemistry, Polymer Chemistry Division, 06800, Beytepe, Ankara, Türkiye

Abstract: This study investigates the effect of carbon black (CB) particle size on the curing kinetics and mechanical properties of poly(epichlorohydrin) (H55) elastomers. The curing behavior was analyzed at 170 °C, 180 °C, 190 °C, and 200 °C, using first-order and nth-order kinetic models to determine the activation energy (E_a) and cure rate constant (k). Results indicate that CB significantly accelerates the vulcanization process, reducing the scorch time (t_{s2}) and optimum cure time (t_{90}) while increasing delta torque (ΔT) values, which correlates with improved cross-link density. The H55-N330 formulation exhibited the fastest cure rate and the highest delta torque, highlighting its superior curing efficiency. Mechanical testing revealed that adding CB enhanced stiffness, tensile strength, and modulus of elasticity, with the H55-N330 blend showing the highest elastic modulus (9.90 ± 1.07 MPa), approximately 13 times higher than CB-free H55 (0.70 ± 0.14 MPa). Swelling studies confirmed that CB increases cross-link density, leading to a 54% reduction in swelling ratio for the H55-N330 blend. Additionally, Shore A hardness values doubled with CB incorporation, while compression set values increased. Despite no significant differences in elongation at break, the addition of CB improved overall toughness and durability. These findings suggest that carbon black, particularly N330, significantly improves the curing kinetics, mechanical properties, and cross-link density of H55 elastomers, making them ideal for high-performance rubber applications in automotive, aerospace, and industrial sealing systems.

Keywords: Poly(epichlorohydrin), Carbon Black, Cure Kinetics, Mechanical Properties.

Submitted: February 05, 2025. **Accepted:** March 05, 2025.

Cite this: Aksüt, D. (2025). Preparation and Characterization of Varying Carbon Black Particle Sizes on Poly(Epichlorohydrin) Elastomer: I. Improving of Curing Kinetics and Mechanical Properties. Journal of the Turkish Chemical Society, Section B: Chemical Engineering, 8(1), 123-136. <https://doi.org/10.58692/jotcsb.1633664>.

*Corresponding author. E-mail: davut.aksut@hacettepe.edu.tr.

1. INTRODUCTION

For about 150 years, developments in rubber technology have produced many useful products with rubber. Due to their elasticity, viscoelastic, mechanical, and chemical properties, rubbers are versatile, meaningful, and unique technological materials for widespread applications in the tire and, automotive, and aviation industries or general rubber products such as gloves, hoses, o-rings, etc. Two leading groups of rubber commonly used in industry are natural rubber and synthetic rubber.

Rubber materials consist of many components, such as activators, process oils, curing systems, and fillers. Fillers are a primary component in the rubber industry. They are added on purpose. They lower the material's cost and enhance the compounds' mechanical and dynamic qualities. Fillers add strength and rigidity to elastomers, increase rubber resistance to tearing, abrasion, and bending fatigue, and improve traction and endurance (Zhang et al., 2001). Silica and carbon black (CB) are the most widely used fillers in the rubber industry.

Decades ago, other fillers, such as silica and clay, were frequently utilized in situations where a high

level of reinforcement was not needed. There was a lesser polymer-filler interaction (Mark et al., 1994; Mowdood et al. 2000). Due to the silanol groups on its surface, silica has a high degree of polarity and a hydrophilic surface. Because of this, silica filler cannot be used with non-polar rubbers, including butadiene, styrene-butadiene, and natural rubber (NR), among others. It is well acknowledged that the molecular interactions between the filler and rubber particles cause the reinforcing effects. For the successful use of silica for rubber reinforcement, it has been widely used by modifying the silica surfaces with silane coupling agents to increase the silica-rubber interaction (Noordermeer et al., 2014; Hanifi et al., 2005; Manna et al. 1998).

Another standard filler is carbon black (CB). However, carbon black manufacturing generally leaves a significant carbon footprint. Carbon black is rubber industry's most widely used reinforced filler since World War I. More than 92 percent of CB production worldwide is used for rubber production, particularly in manufacturing tires; these components include inner liners, sidewall carcasses, air sources, belts, conveyor wheels, and specific vibration isolation devices. Around 8.1 million tonnes of carbon black are produced worldwide, ranking among the 50 most advanced industrial chemicals (Fan et al., 2020). Carbon black will be a filler that will continue to be used in rubber product production in the future. The literature on CB fortification of rubber has been reviewed over the last 100 years, and over 10,000 publications have been produced. Although this article includes the words "carbon black," "reinforcement," and "rubber" in its titles, the mechanical reinforcement effect of CB in rubber has been studied in papers generally (Robertson, C.G.; Hardman, 2021). Yan et al. (2021) found that the surface modification of graphene oxide (GO) nanosheets increased the strength at the break by 90% by showing a positive effect on the cross-link density of nitrile butadiene rubber containing carbon black (N220). Jovanovic et al. (2013) investigated the impact of N330 CB in different proportions on the activation energy, thermal stability, and mechanical properties of acrylonitrile-butadiene/ethylene-propylene-diene (NBR/EPDM) rubber mixtures. While the activation energy of the mix with 70 phr (parts per hundred rubber) CB was found to be the lowest, the best mechanical test results were seen in the NBR/EPDM mixture with 90 phr N330 carbon black added. Among viscoelastic materials, rubber materials have the unique feature of maintaining material integrity even when exposed to high deformation forces; these properties are widely used in energy-absorbing insulators. In a study by Bandyopadhyay et al., the effect of HAF N330 CB amount on the viscoelastic properties of vulcanized natural rubber was investigated. In the study, as the amount of CB increased, the viscoelastic properties of the blends decreased. It caused a decrease in the damping properties of

the vulcanizates with an increase in the amount of CB (Bandyopadhyaya et al. 2022). In a study by Sivaselvi et al., (2020) the effect of different N550 CB amounts on the mechanical properties of the windshield wiper blade was comparatively examined. They found that the mechanical properties of the front wiper blade enhanced with the increase in N550 CB (Sivaselvi et al., (2020) In a study by İsmail et al. (2019) in basic insulator systems, magnetorheological elastomers (MREs) systems provide information about the performance and other physical properties of the final products by adding N220 carbon black to natural rubber at different rates.

With the realization of the industrial revolution from the discovery of natural rubber to the present, the need for rubber material has increased since the beginning of the 20th century. In addition, Synthetic rubbers such as butadiene rubber (BR), Styrenebutadiene rubber (SBR), acrylonitrilebutadiene rubber (NBR), Chloroprene rubber (CR), Ethylene Propylene Diene rubber (EPDM), Silicone rubber (Q) have begun to be synthesized in industrial scale. Nowadays, different types of rubber are synthesized depending on their purpose and usage areas.

One is Polyepichlorohydrin (PECH), which was synthesized in the 1950s. Polyepichlorohydrin is a polyether with a functional alkyl chloride side group. Epichlorohydrin (ECH) is currently produced using "green" methods, which convert glycerine, a byproduct of biofuel production, into ECH, making it much more environmentally friendly and reducing production costs than traditional synthesis methods (Martin et al., 2016). Due to their unique characteristics, including low-temperature flexibility and heat and oil resistance, PECH elastomers are utilized in various trading products, such as fuel hoses, gaskets, and air ducts (Ferrier et al., 2021). In the decades between its initial synthesis and the present, PECH and derived materials from PECH have been used for cost, functionality, chemically robust and pliable ether backbone, inexpensive polymer electrolytes (Hu et al., 2015), gas separation (Tu et al., 2021), ion exchange membranes (Tuan et al., 2020) and cold climate performances (Sokolova et al., 2019).

The flexible ether backbone of epichlorohydrin rubber allows for cold-climate applications. Zeon Chemicals L.P. (USA) developed the product code Hydrin T6000, which has the lowest glass transition temperature ($T_g = -60\text{ }^\circ\text{C}$) for use in cold climates or frost-resistant rubber based on epichlorohydrin. Haldeeva et al. (2019) prepared Hydrin T6000 elastomer and N774 and N550 carbon black blends at different ratios and investigated the effect of CB type and amount on residual deformation and mechanical properties. They found that the blend containing 65 phr N774 carbon black best maintained elastic properties. Bukowski et al. found that multi-walled carbon nanotubes (CNTs) at the rate of 1-2% w/w to be

added to the hydrin elastomer increase the abrasion resistance (Bukovskiy et al.,2019) In the study of Fedorova et al., (2021) viscoelastic properties of hydrin elastomer containing two different accelerator systems, such as thiuram and guanidine containing N550 carbon black, were investigated. In a similar study, Davydova et al. showed that the cooking system is a prominent parameter in determining the mechanical and physical properties of the hydrin elastomer (Davydova et al., 2021).

This study was carried out to determine the effect of carbon black size on the vulcanization kinetics and mechanical properties of epichlorohydrin rubber blends. For this aim, blends were prepared with the same amount of carbon blacks in different sizes (N220, N330, and N550). The effects of carbon black on the curing characteristics were investigated. However, the effects of the size of the carbon black on the curing kinetics and activation energy of the Poly(epichlorohydrin) elastomer were investigated with the 1st and nth-order kinetic models. Finally, it aims to examine the effects of the test samples prepared from each mixture on Shore A hardness values, compression set, rebound resilience, and tensile strength properties.

2. EXPERIMENTAL SECTION

2.1. Materials

Poly(epichlorohydrin)(CO) homopolymer, trade name H55, was obtained from Zeon Co. (USA). The H55 has a homopolymer of Epichlorohydrin (ECH) polymers. The Mooney viscosity value of polymers is (@100 °C ML (1 + 4)) and a viscosity range of 50-60, and the monomer content of the homopolymer is 100% epichlorohydrin (ECH). The relative density of H55 is 1.37 g/cm³, and the chlorine content is 36% by weight. Carbon blacks (HAF N220/330/550) used as filler were supplied from Omsk Carbon Group (Russia). The particle size of N220 carbon black ranges from 20 to 25 nm, N330 from 28 to 36 nm, and N550 from 39 to 55 nm. Their respective average surface areas are 112-115 m²/g, 76-80 m²/g, and 39-41 m²/g. The vulcanization system was based on ethylene thiourea (Zisnet F-PT) and Diphenyl Guanidine (DPG). Other ingredients are commercial chemicals commonly used in the rubber and tire industry.

2.2. Preparation of Blends

Table 1 presents the component ratios of the mixtures, expressed in phr. All blends were prepared at 40 °C at 50 rpm/min for 20 minutes using a laboratory two-roll mixing mill.

Table 1. Formulations of the H55/CB compounds.

Component	H55	H55-220	H55-330	H55-550
H55	100	100	100	100
N220	0	40	0	0
N330	0	0	40	0
N550	0	0	0	40
Naphtenic oil Octopus N418	5	5	5	5
Alkylphenol resin	20	20	20	20
6PPD, N-(1,3-Dimethylbutyl)-N'phenyl-p-phenylenediamine	1	1	1	1
Magnesium oxide (MgO)	3	3	3	3
Stearic Acid	1	1	1	1
DPG, N, N'- Diphenylguanidine	0.5	0.5	0.5	0.5
TTCA(TMT), Zisnet 2,4,6-Trimercapto-s-triazine (Trithiocyanuric acid)	0.8	0.8	0.8	0.8
TDQ, 2,2,4 - trimethyl - 1,2 - dihydroquinoline	1	1	1	1

2.3. Cure Characteristics and Swelling Study

The optimal cure time and curing parameters of blends were determined using a moving die rheometer (Alpha 2000 MDR) at 170/180/190/200 °C according to **ASTM D5289-12**. Tests were

carried out by taking three samples from 3 different points of each blend series.

The crosslinking density of rubber often affects swelling in that it can absorb more solvent molecules due to the less dense crosslink density.

Conversely, higher crosslink densities make polymer chains complex to flexibility; for this reason, it reduces chain gaps and restricts solvent molecule absorption into the networks (Darko, 2022) The swell ratio, the greatest equilibrium swelling condition attained during the soaking of the solvent molecules, may be calculated via the swelling technique (Kraus, 1957, Poller et al., 1962) This approach measures the swelling ratio by monitoring swelling polymers' volume or weight increase until swelling equilibrium is achieved (Liu et al., 2020). In this study, the swelling ratio was defined as follows:

$$Q = \left[\frac{(W_s - W_d)}{W_d} \right] \times 100\% \quad (\text{Eq. 1})$$

where; The weights of the dry specimen are represented by w_d and the swollen specimen by w_s , respectively. Rubber samples of a specific weight were soaked in toluene at room temperature for seven days to test for swelling.

2.4. Mechanical Properties of H55/CB Series Elastomers

For all the compounds' optimum cure times, vulcanization was carried out in a pressurized hot press (Brabender) at 200 °C.

Shore A hardness was measured according to ASTM D 2240 standard. Hardness values were calculated using a Westop brand Type A durometer (Nishi Tokyo Seimitsu, Japan) by preparing eight samples from 6 mm thick and 16 mm diameter smooth surface samples.

The rebound values of each elastomer were measured using 12.5 mm thick and 30 mm diameter samples with smooth surfaces. The samples were measured using the ZwickRoell 5109 Rebound Resilience Tester (Zwick Roell, Germany). Rebound resilience measurements were taken from 4 samples from each elastomer batch prepared according to ASTM D7121 standard.

The Compression Set was measured according to the ASTM D395 standard. Permanent deformation tests are performed using five 6 mm thick and 16 mm diameter smooth surface samples. The samples exposed to 25% compression for 22 hours were removed from the test setup, and measurements were taken after they were relaxed for 30 minutes.

The tensile properties of the H55/CB blend vulcanizates were measured with a universal test tensile test machine (UTM, Zwick Z010, by Zwick/Roell, Germany) according to ASTM D412, in the 0.5-2.5% elongation zone with a mechanical extensometer at 100 mm/min and the rest of the test at 500mm/min. Eight samples were tested from each batch of blends. The tensile properties are given with deviation values.

3. RESULTS AND DISCUSSION

3.1. Cure characteristic and kinetic study of H55/CB blends

The size of the carbon blacks employed makes the most difference in the blends made according to the formula listed in **Table 1**. Curing curves of H55/CB series compounds at different temperatures are given in Figure 1 below. In addition, the measured curing parameters are given in **Table 2**.

As seen in **Figure 1**, the curing curves increase with the addition of carbon black at each temperature value, regardless of the carbon black size.

As the torque increases by two units over the minimum torque during the cure period, scorch time ts_2 is recorded. Scorch occurs when the rubber partially vulcanizes before the product is completely shaped and prepared for vulcanization (Al-Nesrawy et al.,2016). Even at 170 °C, the ts_2 value was not observed during the 20 minutes of curing of the **H55** blend, which does not contain carbon black. However, ts_2 values of mixtures containing CB were observed at 170 °C. The lowest ts_2 value was observed in the mixture of **H55-N330** with a value of 2.75 ± 0.01 minutes. This study shows that CB positively affects curing at the lowest temperature value of 170 °C. It was observed that ts_2 and t_{90} times of all CB mixtures were shortened.

Even at 170 °C, the ts_2 value was not observed during the 20 minutes of curing of the **H55** blend, which does not contain carbon black. However, ts_2 values of mixtures containing CB were observed at 170 °C. The lowest ts_2 value was observed in the mixture of **H55-N330** with a value of 2.75 ± 0.01 minutes. This study shows that CB positively affects curing at the lowest temperature value of 170 °C. It was observed that ts_2 and t_{90} times of all CB mixtures were shortened. In addition, Δ torque values were higher than the reference blend **H55**. The delta torque value is directly proportional to the crosslink density. Regardless of the size structure of all mixtures containing CB, the Δ torque value at all temperatures was approximately 2/2.5 times higher than the Δ torque value of the H55 mixture without CB. As expected, the curing rate increases with the increase in temperature for all mixtures with CRI values. As illustrated in **Figure 1** and **Table 2**, CB-containing poly (epichlorohydrin) blends have been demonstrated to enhance crosslinking reactions and promote crosslink formation. Carbon black improves the vulcanization process by acting as a reinforcing filler that aids in better heat dissipation and speeds up the curing reaction. It is thought to lead to more efficient and faster curing by mitigating side reactions such as transfer and rearrangement reactions that would otherwise compete with crosslinking.

Table 2. Cure values of H55, H55 N220, H55 N330 and H55 N550 blends.

Temperature	Compound Code	t_{s2} (m)	t_{90} (m)	$\Delta Tork$ (dNm)	CRI(m ⁻¹)
170 °C	H55	0.00±0.00	16.40±0.05	1.82±0.01	6.10±0.02
	H55-N220	3.33±0.06	14.81±0.09	6.18±0.12	8.71±0.03
	H55-N330	2.75±0.01	14.70±0.01	6.67±0.01	8.37±0.01
	H55-N550	4.30±0.03	15.58±0.06	5.09±0.01	8.87±0.03
180 °C	H55	13.42±0.08	15.30±0.10	2.36±0.00	53.48±0.40
	H55-N220	2.09±0.01	12.87±0.04	7.03±0.01	9.28±0.02
	H55-N330	1.70±0.00	12.94±0.01	7.61±0.04	8.90±0.01
	H55-N550	2.64±0.15	14.07±0.12	5.98±0.16	8.75±0.02
190 °C	H55	8.13±0.20	13.16±0.04	2.67±0.03	19.91±0.64
	H55-N220	1.43±0.04	10.38±0.17	7.33±0.01	11.17±0.17
	H55-N330	1.16±0.02	10.29±0.11	7.88±0.23	10.95±0.15
	H55-N550	1.65±0.02	11.80±0.13	6.60±0.03	9.85±0.10
200 °C	H55	5.05±0.03	8.85±0.01	2.73±0.01	26.32±0.29
	H55-N220	1.03±0.01	7.09±0.01	7.26±0.00	16.49±0.02
	H55-N330	0.83±0.00	2.21±0.00	7.87±0.02	16.14±0.02
	H55-N550	1.15±0.00	2.64±0.01	6.58±0.02	13.98±0.04

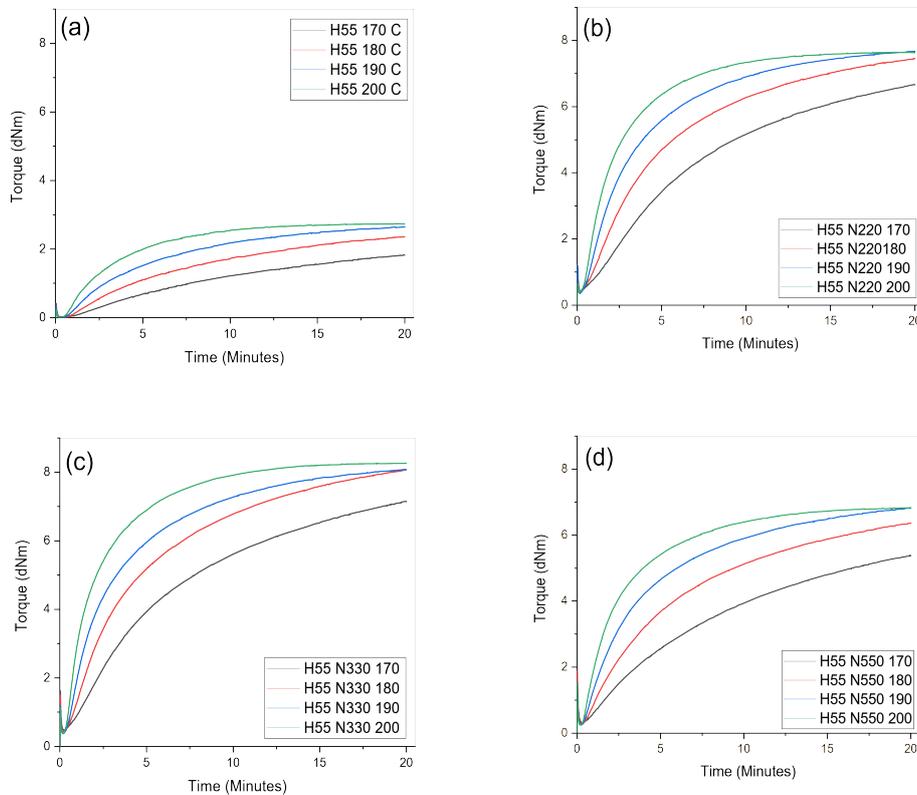


Figure 1. Curing curves of H55 (a), H55 N220 (b), H55 N330(c), and H55 N550 (d) Blends at 170 °C, 180 °C, 190 °C, and 200 °C.

The Cure Rate Index (CRI) is a parameter used in rubber and elastomer processing to quantify the rate of vulcanization or curing. It indicates how quickly a rubber compound transitions from uncured to fully cured when subjected to heat and curing agents (such as peroxides or sulfur-based systems). The cure index (CRI) indicating the cure rate of the blends is defined in **Equation 2**.

$$CRI = \frac{100}{(t_{90} - t_{s2})} \quad (\text{Eq. 2})$$

To analyze the curing kinetics of the prepared H55-CB blends, α -time graphs were generated using **Equation 3** based on the curing curve data for all blends. The α -time plots for these blends are presented in **Figure 2**. Furthermore, to determine the cure rate content and activation energy of elastomers according to the first-order kinetic model, the state of cure (α) values were calculated by evaluating the cure curves of ECHR-CB blends at four different temperatures using Equation 3.

$$\alpha(t) = \frac{Mt - ML}{MH - ML} \quad (\text{Eq. 3})$$

where MH is the maximum torque, ML is the minimum torque, and Mt is the torque at the time. k values were calculated according to the first-order kinetic model using **Equation 4** by evaluating the area between $\alpha=0.25-0.45$ in the cure curve.

$$\ln(\alpha) = k(T) \times t \quad (\text{Eq. 4})$$

Activation energies of elastomers have been calculated with k values obtained at different temperatures using the Arrhenius equation.

$$K = k_0 \exp(-Ea/RT) \quad (\text{Eq. 5})$$

Ea is the activation energy, R is the universal gas constant, and T is the absolute temperature.

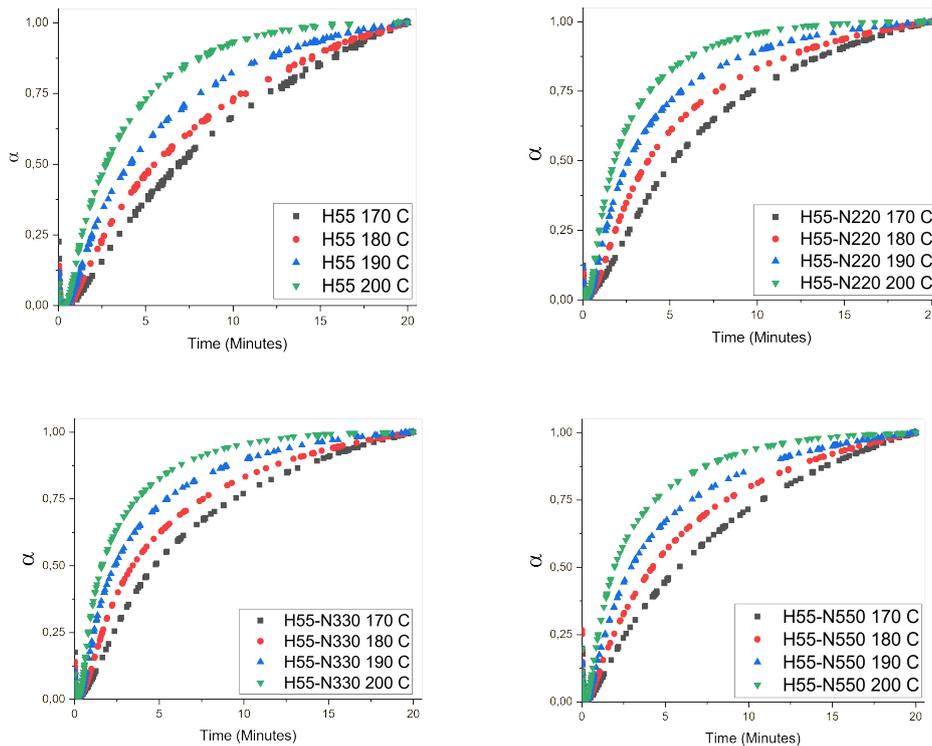


Figure 2. α -time curves of H55, H55 N220, H55 N330, and H55 N550 blends at 150 °C, 160 °C, 170 °C, and 180 °C.

Figure 2 shows the state of cure (α) values versus cure time of H55 series compounds curves. The region between $\alpha=0.25-0.45$ in the α -time curve was evaluated to calculate k values according to the first-order kinetic model using **Equation 4**.

The cure rate was calculated using the slope of the $\ln\alpha$ -time curves of the blends of H55, H55-N220, H55-N330, and H55-550 used to evaluate the (k) value of the content.

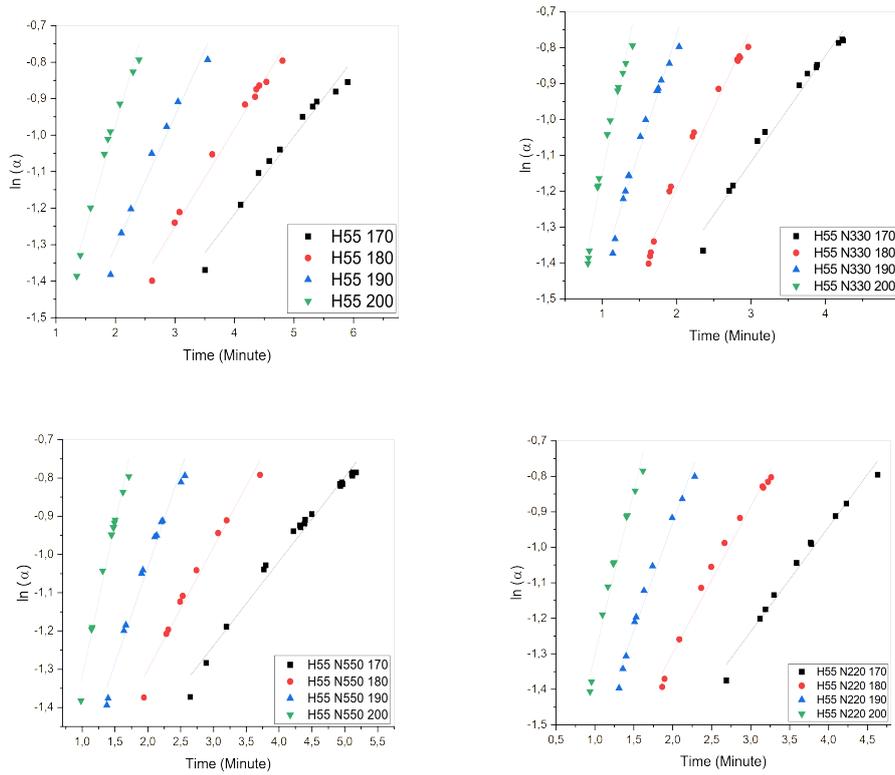


Figure 3. $\ln \alpha$ -time curves of H55, H55 N220, H55 N330, and H55 N550 blends.

Figure 4 gives the $\ln k$ versus $(1/T)$ of H55, H55-N220, H55-N330, and H55-N550 blends from the Arrhenius equation at 170 °C, 180 °C, 190 °C, and 200 °C.

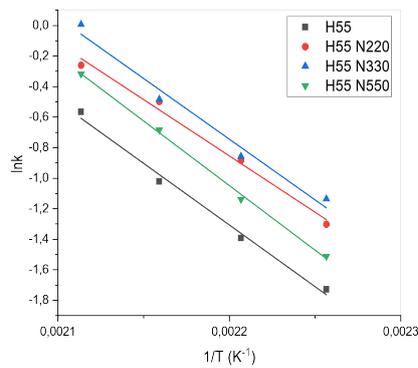


Figure 4. 1st order cure kinetics; $\ln k$ versus $(1/T)$ of H55, H55 N220, H55 N330, and H55 N550 blends from Arrhenius equation, at 170 °C, 180 °C, 190 °C, and 200 °C.

Then, using **Equation 5**, the activation energies of each mixture were found. **Tables 3** and **4** present

the cure rate content and activation energy of H55 elastomers.

Table 3. First order kinetic model; Cure rate content of H55 N220, H55 N330 and H55 N550.

1 st order "k" values				
Temp (°C)	H55	H55-N220	H55-N330	H55-N550
170	0.178±0.005	0.272±0.008	0.321±0.010	0.221±0.007
180	0.248±0.007	0.413±0.012	0.424±0.017	0.320±0.010
190	0.360±0.011	0.608±0.012	0.617±0.019	0.505±0.025
200	0.568±0.017	0.771±0.023	1.007±0.022	0.728±0.022

Table 4. Activation energy of H55 N220, H55 N330 and H55 N550 blends.

Blend Code	Ea (kJ/mol)
H55	67.13±3.36
H55 N220	61.30±4.29
H55 N330	66.09±2.64
H55 N550	70.35±3.52

According to the first-order kinetic model of the cure curves of the H55-CB series elastomer, **k** values increased with temperature. As seen in **Table 3**, the **k** value increased with the use of CB, and this increase was more pronounced at high temperatures. The rise in the **k** constant with the use of CB is that CB prevents reactions other than crosslinking, such as transfer and rearrangement, which compete with the cross-linking reaction. The highest **k**-constant value is seen in the **H55-N330** coded blend, while the lowest **k**-constant value is in the **H55** coded blend. When the **Ea** values were examined, it was seen that the highest activation energy value was in the **H55-N550** coded blend.

For *n*th-order curing kinetics, the α -time curves of the mixtures at different temperatures were iteratively fitted to the curing curves using **Equation 6**. The *n*th-order kinetic model serves as the second method for calculating the reaction rate constant (**k**), activation energy (**Ea**), and reaction order (*n*). To determine the values of **k** and *n*, the state-of-cure time curves were analyzed

using the OriginLab program based on **Equation 6**:

$$\alpha = \frac{k(t-t_s)^n}{1+k(t-t_s)^n} \quad (\text{Eq. 6})$$

Where, t_s is scorch time.

Equation 5 was then used to calculate the activation energies of the elastomers. **Figure 6** presents the α -time curves for the H55, H55-N220, H55-N330, and H55-N550 blends. According to **Equation 5**, the reaction rate constants (**k**) and reaction order (*n*) for each mixture at different temperatures were determined using the Isayev-Deng model (Isayev et al., 2009; Farid et al., 2007; Mansilla et al., 2006), applying a scientific graphing program and nonlinear curve fitting. The reaction rate constants (**k**) and reaction order (*n*) for the H55, H55-N220, H55-N330, and H55-N550 blends are summarized in **Tables 5** and **6**.

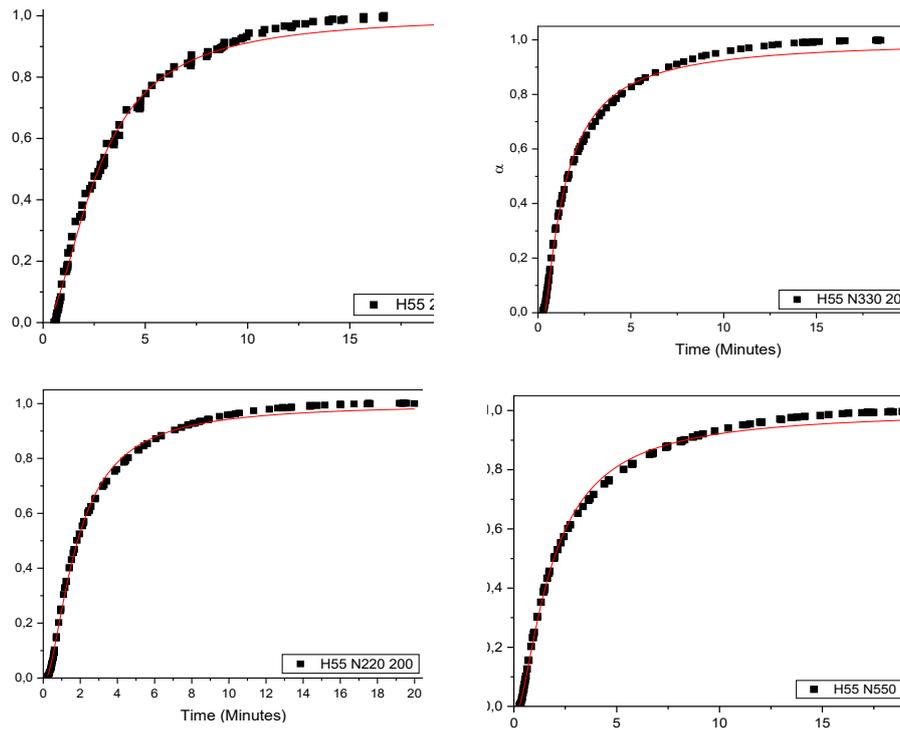


Figure 6. α -time curves of H55, H55 N220, H55 N330 and H55 N550 a with curve fitting at 200 °C.

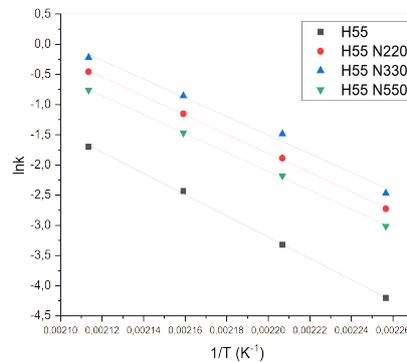


Figure 7. nth order cure kinetics; $\ln k$ versus $(1/T)$ of H55, H55 N220, H55 N330, and H55 N550 blends from Arrhenius equation, at 170 °C, 180 °C, 190 °C, and 200 °C.

According to the n^{th} kinetic model of the cure curves of H55-CB blends, When the k values were examined, it was seen that the value of the k rate constant increased with the increase in temperature for all blends. The highest k value was seen in the **H55-N330** coded blend, as in the first-order kinetic model, while the lowest k value was seen in the **H55** coded blend. When the E_a values were examined, it was seen that the highest activation energy value was in the **H55-coded** blend. Carbon black interacts with curing agents such as sulfur and accelerators, modifying

the overall kinetics of vulcanization. The type and structure of carbon black affect how it absorbs these chemicals, influencing cure speed and efficiency. Carbon black enhanced the cure rate by suppressing competing reactions, such as transfer and rearrangement, that are distinct from cross-linking reactions. CB plays two roles in the vulcanization kinetics (Razzaghi-Kashani et al., 2018): first, it exhibits a catalytic effect that accelerates the initial reactions among vulcanization agents.

Compd	170 °C		180 °C		190 °C		200 °C	
	k	n	k	n	k	n	k	n
H55	0.02±0.02	2.22±0.05	0.04±0.01	1.98±0.04	0.09±0.04	1.79±0.03	0.18±0.03	1.76±0.11
H55-N220	0.41±0.06	1.78±0.03	0.15±0.01	1.64±0.03	0.32±0.01	1.43±0.02	0.63±0.01	1.37±0.02
H55-N330	0.09±0.01	1.72±0.05	0.23±0.01	1.41±0.03	0.43±0.01	1.29±0.02	0.80±0.016	1.21±0.02
H55-N550	0.05±0.01	1.84±0.05	0.11±0.01	1.62±0.04	0.23±0.01	1.51±0.03	0.47±0.01	1.41±0.02

Table 5. n order kinetic model; Cure rate content of H55-REF, H55-N220, H55-N330 and H55-550.

Table 6. Activation energy of H55 N220, H55 N330 and H55 N550 blends.

Blend Code	Ea (kJ/mol)
H55-REF	146.4±7.3
H55 N220	131.7±7.9
H55 N330	128.8±4.5
H55 N550	130.4±9.1

Figure 8 below shows a comparative bar graph of activation energy values calculated from 1st– and nth-order kinetic models of H55, H55-N220, H55-N330, and H55-N550.

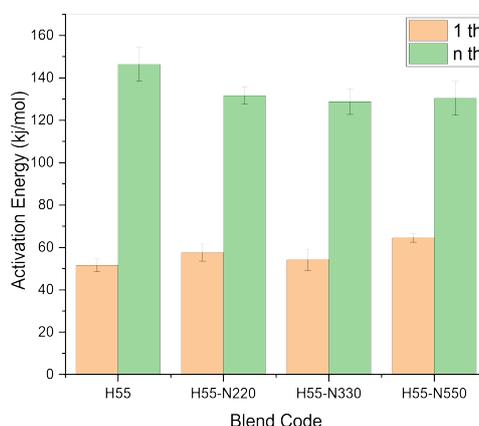


Figure 8. Calculated 1st and nth order activation energy values of H55, H55 N220, H55 N330 and H55 N550.

The 1st-order kinetic model's activation energy values were discovered to be lower than those of the nth-order kinetic model, as shown in **Figure 8**. The activation energy levels of all blends, it was noted, did not significantly differ. This is because only data from α -time graphs between 0.25 and 0.40 are considered in the first-order kinetic model. With the addition of carbon black, the activation energy value is reduced by around 19% when considering the nth-order kinetic modeling. Carbon black interacts with curing agents such as sulfur and accelerators, modifying the overall kinetics of vulcanization. The type and structure of carbon black affect how it absorbs these chemicals, influencing cure speed and efficiency.

3.2. Swelling studies of H55/CB Blends

The swelling ratio is a key indicator of an elastomer's cross-link density and interaction with solvents. A lower swelling ratio suggests higher cross-link density, which restricts the penetration of solvents into the polymer network. The swelling ratios given in Figure 9 show that adding carbon black (CB) to the hydriin elastomer (H55) leads to a decrease in the swelling ratio. While the highest swelling ratio was observed in the blend coded H55 (without CB) with 3.327 ± 0.0274 , the lowest was observed in the blend coded H55-N330 with 1.466 ± 0.003 .

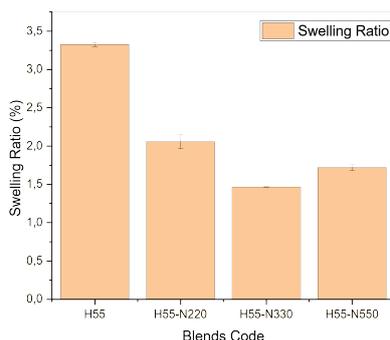


Figure 9. Swelling ratio of H55, H55 N220, H55 N330 and H55 N550 blends.

This phenomenon can be attributed to multiple factors. Carbon black is a reinforcing filler, enhancing mechanical stability and reducing free volume within the polymer matrix. Additionally, it promotes the formation of a highly cross-linked polymer network after curing, further restricting solvent penetration. Consequently, the interaction between polymer chains and the solvent is significantly diminished, reducing the elastomer’s solvent absorption capacity. With the addition of carbon black, the free volume within the polymer matrix decreases, leading to a more compact structure. Moreover, rheometer studies indicate an increase in delta torque values, suggesting that

carbon black also contributes to an enhanced cross-link density in the elastomer network.

3.3. Mechanical Properties of H55/CB series blends

Shore A hardness, Rebound Resilience, Compression Set, and tensile strength tests were performed to examine the effect of different sizes of carbon black on the mechanical properties of Epochlorohydrin elastomer. Shore A hardness, Compression Set, and Rebound resilience value of Epichlorohydrin Rubber with carbon black in different sizes are given in **Table 7** below.

Table 7. Basic Mechanical Properties of Epichlorohydrin Rubber with Carbon Black in Different Sizes.

Blend Code	Shore A	Compression Set	Rebound Resilience
H55	20±1	11.4±5.0	6.8±0.5
H55-N220	60±1	44.9±3.8	6.5±0.6
H55-N330	64±2	47.4±1.0	7.5±0.6
H55-N550	60±1	27.7±2.8	6.0±0.2

With the addition of CB to ECHR, the shore A value of all blends increased approximately twofold. There was no significant difference in Rebound Resilience values in all blends. The compression set values of H55/CB Blends increased with the addition of carbon black.

Figure 10 provides stress-strain curves for the H55, H55-N220, H55-N330, and H55-N550 coded compounds.

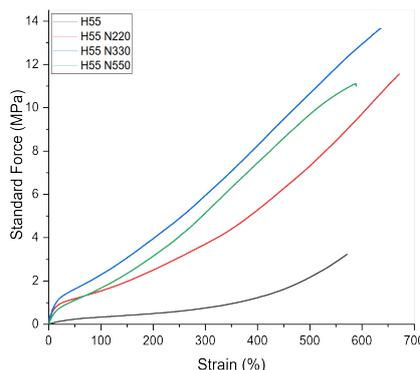


Figure 10. Strain-Stress curves of H55, H55 N220, H55 N330 and H55 N550 coded compound.

The stress-strain curve values of the H55/CB mixtures given in **Table 8** show that adding CB significantly improved the mechanical values of H55.

Table 8. Tension test results of H55, H55-N220, H55-N330 and H55-N550 coded elastomers.

Blend Code	E _{mod} (MPa)	E _{mod @ 100% strain} (MPa)	E _{mod @ 300% strain} (MPa)	Tensile strength (MPa)	Elongation at break (%)
H55	0.70±0.14	0.34±0.01	0.78±0.02	3.0±0.4	553±26
H55-N220	8.90±1.11	1.49±0.11	3.58±0.16	10.8±0.8	663±22
H55-N330	9.90±1.07	2.12±0.09	5.71±0.25	13.9±0.6	656±34
H55-N550	5.90±0.36	1.70±0.11	5.35±0.49	10.6±0.8	591±56

The stress-strain curves in **Figure 10** demonstrate that the stiffness of the epichlorohydrin elastomer increases with the addition of carbon black. This trend is further supported by the Shore A hardness test values, which confirm the material's enhanced rigidity. The elastic modulus, an indicator of cross-link density, exhibited an average eightfold increase, irrespective of CB particle size. Additionally, swelling ratios decreased in CB-containing blends, reinforcing that CB enhances cross-linking and restricts solvent penetration (Bezzazi et al.,2021). Among the tested formulations, the H55-N330 elastomer exhibited the highest proportional increase in elastic modulus, measured at 9.90 ± 1.07 MPa, making it approximately 13 times more elastic than the CB-free H55 elastomer, which had a modulus of 0.70 ± 0.14 MPa. Moreover, modulus values at 100% and 300% elongation indicate that CB significantly enhances the mechanical properties of epichlorohydrin rubber. While there was no substantial difference in elongation at break values, a general increase in elongation at break was observed with incorporating CB, suggesting improved toughness and flexibility.

4. CONCLUSION

Adding carbon black (CB) to H55 elastomers improves curing kinetics and mechanical performance. Scorch time (ts₂) was reduced, accelerating the onset of vulcanization, while t₉₀ values decreased, leading to a more efficient

curing process. The delta torque (ΔT) values increase, suggesting a higher cross-link density, enhancing overall material strength. Mechanical testing confirmed that CB improves stiffness, tensile strength, and modulus of elasticity, with the H55-N330 blend showing the best mechanical performance. Specifically, the elastic modulus increased by up to 13 times, and the swelling ratio decreased by 54%, confirming improved solvent resistance and durability. The activation energy (E_a) required for curing decreased by approximately 15% with CB addition, indicating a more energy-efficient vulcanization process. The Shore A hardness of all CB-filled blends nearly doubled, confirming increased material rigidity. Although no significant differences were observed in elongation at break, the overall toughness and resilience of the elastomer were improved. Among all formulations, H55-N330 exhibited the best balance between cure rate, mechanical strength, and solvent resistance, making it highly suitable for industrial applications requiring enhanced durability and performance. These findings suggest that CB-reinforced H55 elastomers can be effectively utilized in high-performance sealing, automotive, and aerospace applications.

5. CONFLICT OF INTEREST

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

5. REFERENCES

- A F Fedorova and M L Davydova 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1079** 032046
DOI 10.1088/1757-899X/1079/3/032046
- A. Almena, M. Martín.,(2016). *Ind. Eng. Chem. Res.*, 55, 3226.
<https://pubs.acs.org/doi/10.1021/acs.iecr.5b02555>
- Ajay K. Manna, A.K. Bhattacharyya, P.P. De, D.K. Tripathy, S.K. De, Dennis G. Peiffer. (1998).Effect of silane coupling agent on the chemorheological behaviour of epoxidised natural rubber filled with precipitated silica, *Polymer*, Volume 39, Issue 26, Pages 7113-7117. [https://doi.org/10.1016/S0032-3861\(98\)00155-4](https://doi.org/10.1016/S0032-3861(98)00155-4).
- Al-Nesrawy, Sameer Hassan Hadi, Mohammed H. Al-maamori and Hamad Rahman Jappor. (2016).Effect of Temperature on Rheological Properties of SBR Compounds Reinforced by some Industrial Scraps as a Filler. *international journal of chemical sciences* 14: 1285-1295.
<https://doi.org/10.1088/1742-6596/1973/1/012161>.
- Arrillaga A, Zaldua AM, Atxurra RM, Farid AS. (2007). Techniques used for determining cure kinetics of rubber compound. *Eur Polym J.*; 43:4783-99.
<https://doi.org/10.1016/j.eurpolymj.2007.08.024>
- Bandyopadhyaya, S.; Kitey, R.; Upadhyay, C.S., (2022).The Effect of Carbon Black Content on Viscoelastic Properties of Vulcanized Natural Rubber.,*Phys. Sci. Forum* 2022, 4, 9. <https://doi.org/10.3390/psf2022004009>
- Boukfessa, H., & Bezzazi, B. (2021). The effect of carbon black on the curing and mechanical properties of natural rubber/acrylonitrile- butadiene rubber composites. *Journal of Applied Research and Technology*, 19(3), 194-201.
<https://doi.org/10.22201/icat.24486736e.2021.19.3.168>
- Buckley DJ, Berger M, Poller D (1962) The swelling of polymer systems in solvents. I. Method for obtaining complete swelling-time curves. *J Polym Sci* 56:163-174.
<https://doi.org/10.1002/pol.1962.1205616315>
- Bukovskiy, P.O., Morozov, A.V., Petrova, N.N. et al.(2019). Study on the Influence of Activated Carbon Nanotubes on the Tribological Properties of Frost-Resistant Rubber. *Mech. Solids* 54, 1250-1255.
<https://doi.org/10.3103/S0013788X19080156>
- Chu HZ, Liu D, Cui ZW, Wang K, Qiu GX, Liu GY (2020) Effect of crosslink density on solubility parameters of styrene butadiene rubber and the application in pre-screening of new potential additives. *Polym Testing* 81:106253.
<https://doi.org/10.1016/j.polymertesting.2019.106253>
- Darko, C. (2022). The link between swelling ratios and physical properties of EPDM rubber compound having different oil amounts. *J Polym Res* 29, 325.
<https://doi.org/10.1007/s10965-022-03179-z>
- Davydova, M.L., Shadrinov, N.V., Khaldeeva, A.R. et al.(2021) Influence of Vulcanizing System on Properties and Structure of Rubbers Based on Hydrin T6000 Epichlorohydrin Rubber. *Inorg. Mater. Appl. Res.* 12, 859-865.
<https://doi.org/10.1134/S2075113321040110>
- Geetanjali Shukla, Robert C. Ferrier Jr.(2021). The versatile, functional polyether, polyepichlorohydrin: History, synthesis, and applications, *J Polym Sci.* 2021; 59:2704-2718. <https://doi.org/10.1002/pol.20210514>
- H. Hu, W. Yuan, Z. Jia, G. L. Baker.(2015). Ionic liquid-based random copolymers: a new type of polymer electrolyte with low glass transition temperature, *RSC Adv.* 2015, 5, 3135. <https://doi.org/10.1039/C4RA13432J>
- Haldeeva AR, Davydova ML, Sokolova MD. (2019). Development of Frost-Resistant Rubber Based on Epichlorohydrin Rubber of Hydrin T6000 Brand. *MSF* 2019; 945:356-61.
<https://doi.org/10.4028/www.scientific.net/msf.945.356>.
- Ismail, H., Rusli, A., Rashid, A.A., 2005. Maleated natural rubber as a coupling agent for paper sludge filled natural rubber composites. *Polymer Testing*, 24(7): 856-862. DOI: 10.1016/j.polymertesting.2005.06.011
- Jovanovic. V., Budinski. S., Samardzija. J., Gordana. M., Marinovic. C., The influence of carbon black on curing kinetics and thermal aging of acrylonitrile-butadiene rubber, *Chemical Industry & Chemical Engineering Quarterly*, 2009, 15(4):283-289
- Jun Qiu, Hongfei Wang, Jingwen Shao, Kefu Zhang, Juan Wu, Lifeng Yan.(2021). S4-Containing hyperbranched polymer modified graphene oxide as strong linker for both rubber and carbon black to enhance the

- crosslinking and mechanical properties of nitrile butadiene Rubber. *Chemical Engineering Journal* 417, 129336. <https://doi.org/10.1016/j.cej.2021.129336>
- Kashani M. R.-., Hosseini S. M., Catalytic and networking effects of carbon black on the kinetics and conversion of sulfur vulcanization in styrene butadiene rubber. *Soft Matter*, 2018,14, 9194. DOI: 10.1039/c8sm01953c
- Karnda Sengloyluan, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer, "Silica-reinforced tire tread compounds compatibilized by using epoxidized natural Rubber", *European Polymer Journal* 51 (2014) 69–79, <http://dx.doi.org/10.1016/j.eurpolymj.2013.12.010>
- Kraus G (1957) Degree of cure in filler-reinforced vulcanizates by the swelling method. *Rubber Chem Technol* 30:928-951. <https://doi.org/10.5254/1.3542738>
- Mark, J. E.; Erman, B.; Eirich, F. R. (1994). *Science and Technology of Rubber*, 2nd ed.; Academic Press: New York, p 388.
- Marzocca AJ, Mansilla MA.(2006). Vulcanization kinetic of styrene-butadiene rubber by sulfur/TBBS. *J Appl Polym Sci.*;101: 35-41. <https://doi.org/10.1002/app.23173>
- R. Ismail, Nurul Husna Binti Rajhan, Hanizah Abdul Hamid, Azmi Ibrahim.(2019). "Experimental data for effect of carbon black loading on tensile, hardness and rebound of magnetic iron filled natural rubber composites.", *Data in brief* 25, 104166. <https://doi.org/10.1016/j.dib.2019.104166>
- Robertson, C.G.; Hardman, N.J. (2021). Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite. *Polymers*, 13, 538. <https://doi.org/10.3390/polym13040538>
- Schaal, S.; Coran, A. Y.; Mowdood, S. K.(2000). The effects of certain recipe ingredients and mixing sequence on the rheology and processability of silica- and carbon black-filled tire compounds, *Rubber Chem. Technol.* 2000, 73, 240. <https://doi.org/10.5254/1.3547588>
- Sivaselvi K., Kandasamy Gopa,(2020). Study to enhance the mechanical properties of natural rubber by using the carbon black (N550). *Materials Today: Proceedings*, Volume 26, Part 2, Pages 378-381. <https://doi.org/10.1016/j.matpr.2019.12.059>
- Sokolova, M. D., Fedorova, A. F., & Pavlova, V. V. (2019). Research of Influence of Plasticizers on the Low-Temperature and Mechanical Properties of Rubbers. *Materials Science Forum*, 945, 459-464. <https://doi.org/10.4028/www.scientific.net/msf.945.459>
- Tuan, C. M., Cong Tinh, V. D., & Kim, D. (2020). Anion Exchange Membranes Prepared from Quaternized Polyepichlorohydrin Cross-Linked with 1-(3-aminopropyl)imidazole Grafted Poly(arylene ether ketone) for Enhancement of Toughness and Conductivity. *Membranes*, 10(7), 138. <https://doi.org/10.3390/membranes10070138>
- Vojislav Jovanovic', Suzana Samarz'ija-Jovanovic', Jaroslava Budinski-Simendic', Gordana Markovic', Milena Marinovic'-Cincovic', Filler in Rubber Industry Silica and CB which purpose they uses in Rubber industry", *Composites: Part B* 45 (2013) 333-340, <http://dx.doi.org/10.1016/j.compositesb.2012.05.020>
- X. Sun, A.I. Isayev.(2009). Cure kinetics study of unfilled and carbon black filled synthetic isoprene rubber, *Rubber Chemistry and Technology* 82 (2) 149-169. <https://doi.org/10.5254/1.3548241>
- Yimin Zhang, S. Ge, B. Tang, T. Koga, M. H. Rafailovich, J. C. Sokolov, D. G. Peiffer, Z. Li, A. J. Dias, K. O. McElrath, M. Y. Lin, S. K. Satija, S. G. Urquhart, H. Ade and D. Nguyen, (2001). Effect of Carbon Black and Silica Fillers in Elastomer Blends, *Macromolecules*, 34, 7056-7065. <https://doi.org/10.1021/ma010183p>
- Yiran Fan a, b, Geoff D. Fowler b, Ming Zhao. (2020). The past, present and future of carbon black as a rubber reinforcing filler e A review. *Journal of Cleaner Production* 247 119115. <https://doi.org/10.1016/j.jclepro.2019.119115>
- Zhuoheng Tu, Mingzhen Shi, Xiaomin Zhang, Pingping Liu, Youting Wu, Xingbang Hu. (2021). Selective membrane separation of CO2 using novel epichlorohydrin-amine-based crosslinked protic ionic liquids: Crosslinking mechanism and enhanced salting-out effect. *Journal of CO2 Utilization*, Volume 46, 2021. <https://doi.org/10.1016/j.jcou.2021.101473>.