

Effect of Vegetable-Derived Linoleic Acid in Passenger Car Radial (PCR) Tyre Tread, Sidewall and Ply Compound

Tirthankar Bhandary^{1*}, Sumit Singha Roy¹, Mukesh Paliwal¹, Mridul Dasgupta¹, Saikat Das Gupta¹, Dipankar Chattopadhyay², Mahuya Das³ and Rabindra Mukhopadhyay¹

¹Hari Shankar Singhanian Elastomer and Tyre Research Institute, India

²Department of Polymer Science and Technology, University of Calcutta, India

³Greater Kolkata College of Engineering and Management, India

ABSTRACT

Stearic acid, octadecanoic acid, is a primary ingredient used in the rubber industry as an activator for vulcanization. Linoleic acid, derived from vegetables, contains a similar number of carbon atoms and has a similar concentration of acid functional groups (193 mg KOH/g) with a higher unsaturation content, as indicated by its iodine number (134 g/100g) compared to stearic acid (2 g/100g). Gas chromatography mass spectrometry (GC-MS) analysis reveals the location of unsaturation at the 9th and 12th positions. When mixed with tread, sidewall, and ply compounds, linoleic acid exhibits lower activation energy (E_a) and a higher vulcanization reaction rate constant, and a higher order of the reaction compared to the control compounds. These unique properties of linoleic acid result in enhanced modulus at 300% strain with improved tensile strength. Dynamic mechanical analysis shows that the experimental tread compound achieves a higher modulus than the control compound. The fatigue properties of the experimental sidewall demonstrate a slightly longer lifespan (273 kc) compared to the control compound (268 kc), while both exhibit similar ozone protection. For the ply compound, the adhesion between the ply compound and the fabric is stronger in the experimental compound (16.25 Kg \bar{f}) than in the control (15.51 Kg \bar{f}).

*Corresponding author

Tirthankar Bhandary, Hari Shankar Singhanian Elastomer and Tyre Research Institute, India.

Received: January 13, 2026; **Accepted:** January 19, 2026; **Published:** January 28, 2026

Keywords: Tyre, Tread, Sidewall, Ply, Kinetics, Vulcanization, Sustainability, Tack, Ozone, Order of Reaction, Reaction Rate Constant

Introduction

Raw rubbers, in their natural state, typically lack the necessary strength to return to their original shape after undergoing significant deformation, which limits their usefulness in many applications. To address this issue and enhance their elastic properties, the vulcanization process was developed—a technique that involves crosslinking the polymeric chains within the rubber. This chemical process significantly improves the rubber's ability to return to its original form after deformation, increasing both its durability and overall performance [1].

The vulcanization process was first pioneered by Charles Goodyear in 1843, who discovered that by heating natural rubber and sulfur together, a chemical reaction occurred that resulted in a much stronger and more elastic material. Initially, the vulcanization process was slow and time-consuming, requiring up to eight hours at a temperature of 140°C to achieve the desired properties in the rubber. However, the addition of zinc oxide as an activator for the vulcanization reaction led to a significant reduction in the time needed for vulcanization, cutting it down to just three hours. Further improvements in the process came with the introduction of various accelerators, which reduced the vulcanization time even further to just 1–5 minutes, making the process much more efficient

and suitable for mass production. Despite these advancements, an interesting phenomenon was observed by Russell et al. when utilizing the zinc oxide–sulfur–accelerator vulcanization system in rubber compounds. It was found that while some types of rubber vulcanized efficiently, others failed to achieve the desired level of crosslinking and mechanical properties, even when the accelerator concentration was increased [2]. This observation prompted further investigation into the vulcanization process. The results of this investigation revealed that the addition of stearic acid to the vulcanization system significantly improved the overall quality of the vulcanizate, resulting in rubber compounds with enhanced strength, elasticity, and thermal stability.

A typical modern recipe for a vulcanization system in rubber compounds includes a precise blend of ingredients: 2–8 parts per hundred rubber (phr) of zinc oxide, 0.5–4 phr of stearic acid, 0.5–5 phr of sulfur, and 0.5–3 phr of accelerators. These ingredients work in tandem to facilitate the vulcanization process and create a high-performance rubber material that can be used in a wide range of applications, from automotive tyres to industrial seals and gaskets.

The vulcanization reaction itself is a multi-step process that can be broken down into five distinct stages. First, the accelerator forms an active complex with the rubber molecules, initiating the vulcanization reaction. Next, an active sulfurating agent is generated, which enables sulfur atoms to bond with the rubber's

polymer chains. This is followed by the formation of crosslinking intermediates, which link the individual polymer chains together, resulting in a network of interconnected molecules. The fourth stage involves the creation of polysulfide bonds, which further strengthen the rubber. Finally, the last step in the process is the final vulcanization stage, where the rubber is fully crosslinked and solidified, resulting in a material that is significantly stronger, more elastic, and more durable than its raw form[3,4].

Vulcanization remains a cornerstone of rubber production today, allowing for the creation of materials that exhibit superior strength, flexibility, and resistance to wear, heat, and chemicals. As a result, vulcanized rubber continues to be integral to a vast array of industries, from automotive and aerospace to manufacturing and healthcare. The continuous development and refinement of vulcanization methods ensure that rubber products meet the increasingly demanding standards of modern engineering and technology.

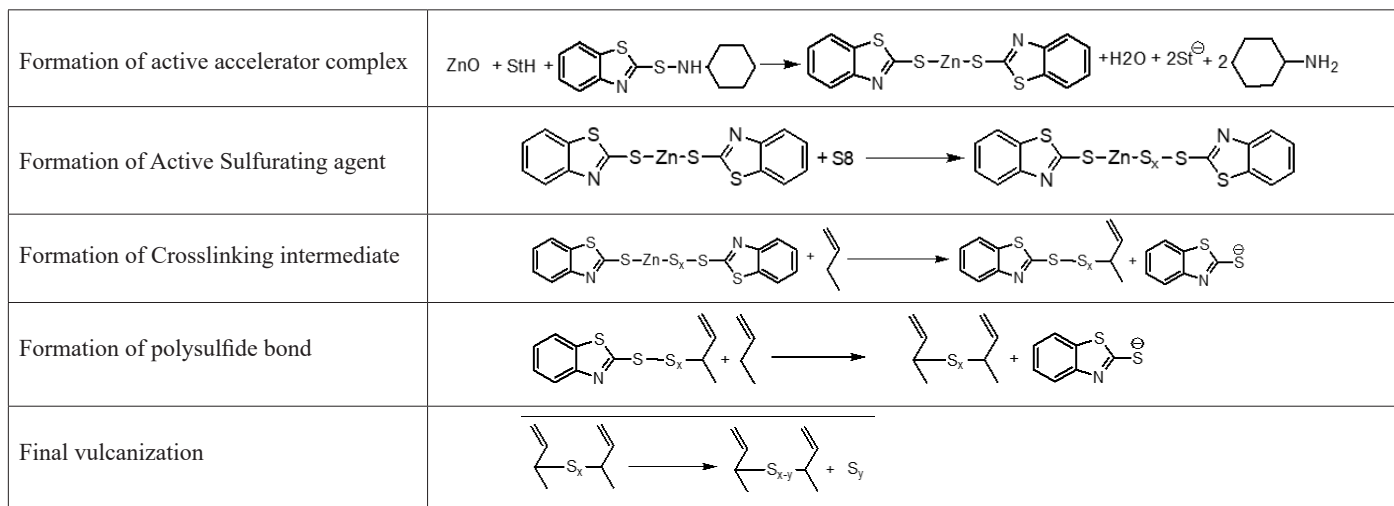


Figure 1: Reaction Mechanism of Zinc Oxide, Stearic Acid, Accelerator and Sulfur in Rubber Vulcanization

In the first step of the vulcanization process, the formation of the active accelerator complex begins. Here, zinc oxide interacts with stearic acid, leading to the formation of zinc stearate, a crucial intermediate. This zinc stearate then reacts with the accelerator system, forming a zinc-accelerator complex. This complex plays a vibrant role in initiating the vulcanization reaction by engaging with the vulcanizing agent. As a result, a crosslinking intermediate is produced, which is essential for the formation of sulfur bonds between polymer chains. These crosslinking intermediates subsequently interact with the unsaturation sites in the polymeric backbone, facilitating the creation of a more stable, elastic network structure within the rubber[1,5-8].

The role of stearic acid in the vulcanization system is widely recognized for its ability to enhance the overall efficiency of the process. It improves the dispersion of ingredients and optimizes the interaction between components, significantly influencing the quality of the final vulcanizate. However, to better understand the effects of other long-chain aliphatic acids in the vulcanization system, linoleic acid—derived from vegetable—has been investigated.

This investigation was carried out on various rubber compounds used in the manufacturing of passenger car radial tyres, including the tread, sidewall, and ply components. The study aims to explore how linoleic acid influences the vulcanization process and the overall performance of rubber products, particularly in terms of durability and wear resistance in automotive applications.

Material

For this study, a typical silica-based passenger car radial tyre tread compound was selected, incorporating a blend of solution-polymerised styrene-butadiene rubber (SSBR) and emulsion-polymerised styrene-butadiene rubber (ESBR). This combination was chosen to optimize the tread's performance in terms of durability, wear resistance, and wet traction. In addition, the sidewall compound was designed using a mixture of natural rubber (NR) and polybutadiene rubber (PBR) combined with N660-type carbon black to enhance the sidewall's strength, flexibility, and resistance to cracking. For the ply compound, a formulation that included NR was chosen, aiming to strike a balance between reinforcement and flexibility. The specific types and proportions of raw materials used in these compounds are detailed in Table 1, providing a comprehensive overview of the components involved.

Table 1: Details of Raw Material Used and its Supplier

Material	Supplier
SSBR (Styrene 27%, Vinyl 57%)	JSR BST Elastomer Co. Ltd, Thailand
ESBR 1739 (Styrene 39%, oil 27.3%)	Reliance Industries Ltd, India
PBR (Cis 96.5%)	Reliance Industries Ltd, India
NR (SMR 20)	Syarikat Tenaga (Gemas) Sdn BDH, Malaysia
Carbon Black (N234)	Philips Carbon black Ltd, India
Carbon Black (N330)	Philips Carbon black Ltd, India
Carbon Black (N660)	Philips Carbon black Ltd, India
Silica (Surface area 175 m ² /g)	Evonik United Silica (SIAM) Ltd, Thailand
Silane coupling agent [(Bis(triethoxysilylpropyl)disulphide)]	Evonik Industries Ltd, Germany
Process oil (Commercial grade)	Raj Petro Speciality Pvt Ltd, India
Zinc oxide (Commercial grade)	Himalaya Oxide Pvt Ltd, India
Stearic acid (Commercial grade)	Godrej Industries Ltd, India
Linoleic acid	Synthomer plc, England
MC wax (Commercial grade)	Raj Petro Speciality Pvt Ltd, India
6PPD (Commercial grade)	NOCIL Ltd, India
TMQ (Commercial grade)	NOCIL Ltd, India
PF Resin (Commercial grade)	SI Group India Pvt Ltd, India
Soluble Sulfur (Commercial grade)	The Standard Chemical Co Pvt Ltd, India
DPG (Commercial grade)	Finorchem Ltd, India
CBS (Commercial grade)	NOCIL Ltd, India
TBBS (Commercial grade)	Finorchem Ltd, India

Physico-Chemical Characterization of Vegetable-Derived Linoleic Acid

To assess the chemical characteristics of linoleic acid compared to commercial-grade stearic acid, various critical tests have been conducted. These tests include measurements of acid number and degree of unsaturation, as well as a detailed analysis using gas chromatography coupled with mass spectrometry.

Acid Number of Linoleic Acid and Stearic Acid

To estimate the concentration of acid functional groups in the linoleic acid and stearic acid, the acid number is determined. The acid number is a measure of the number of acid functional groups in a sample and is calculated based on the amount of base (sodium hydroxide) required to neutralize the acids present in the sample. For the determination, approximately 1.0 g of linoleic acid is dissolved in 75 mL of ethanol, creating a clear solution. This solution is then titrated with a standardized 0.1 N sodium hydroxide (NaOH) solution, using phenolphthalein as an indicator to identify the endpoint.

The acid number of the linoleic acid is calculated using Equation 01:

$$\text{Acid number (mg of KOH / g)} = \frac{\text{volume (ml) of NaOH consumed} \times \text{actual strength (N) of NaOH}}{\text{Sample weight (g)}} \times 56.1 \quad (1)$$

Results of the acid number of Linoleic acid vis-à-vis stearic acid have been plotted in Figure 2. The results reveal that both fatty acids, vegetable-derived linoleic acid and commercial-grade stearic acid, possess a similar quantity of acid functional groups, 193 mg KOH/g and 195 mg KOH/g, respectively, indicating similar efficacy in the formation of zinc salts in the vulcanization reaction. Furthermore, the degree of unsaturation and the mass spectrometry analysis are discussed in the subsequent study.

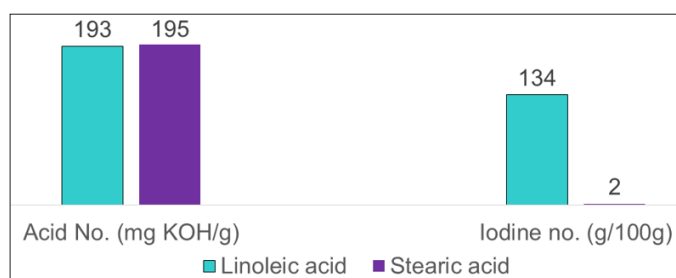


Figure 2: Acid Number and Degree of Unsaturation in Terms of Iodine Number in Vegetable-derived Linoleic Acid and Commercial-Grade Stearic Acid

Degree of Unsaturation in Linoleic Acid and Stearic Acid

The degree of unsaturation in linoleic acid is typically quantified by determining its iodine absorption number, which measures the amount of iodine that can be absorbed by the unsaturated bonds in the compound. In this procedure, the iodine number is determined using a back titration method, providing an accurate measurement of the unsaturation levels in the sample. To begin, approximately 0.5 grams of the linoleic acid sample was dissolved in 20 mL of dichloromethane, inside an iodine flask. To this, 25 mL of a 1.27% iodine solution was added. The flask was then sealed with a stopper that had been moistened with a 15% potassium iodide solution. The iodine solution was left to react with the unsaturation present in the linoleic acid, and the flask was kept in a dark place for one hour to prevent the degradation of iodine due to exposure to light. After the reaction time, the excess iodine that had not reacted with the sample was titrated with a standardized 0.1 N sodium thiosulfate solution using starch as an indicator. The volume of sodium thiosulfate required to reach the endpoint was noted. A blank titration is performed under the same conditions, but without the addition of the sample. The volume of sodium thiosulfate consumed in the blank titration was subtracted from the total volume used in the sample titration. This difference corresponds to the iodine that was consumed by the unsaturated bonds in linoleic acid.

The iodine absorption number of the linoleic acid is calculated using Equation 2:

$$\text{Iodine absorption number (g/100g)} = \frac{\text{Excess volume (ml) of thiosulfate} \times 12.69 \times \text{strength (N) of thio sulfate}}{\text{Sample weight (g)}} \quad (2)$$

Linoleic acid exhibited a significantly higher iodine absorption, as illustrated in Figure 2. The iodine absorption number for linoleic acid is recorded at 134 g/100 g, in contrast to only 2 g/100 g for commercial grade stearic acid. This higher iodine absorption in linoleic acid is attributed to the presence of double bonds in its molecular structure. The greater iodine absorption number makes linoleic acid, derived from vegetables, much more unsaturated than commercial grade stearic acid.

Gas Chromatography and Mass Spectroscopy Study

The chemical composition of the experimental linoleic acid and commercial-grade stearic acid was analyzed using gas chromatography coupled with mass spectrometry (GC-MS). To prepare the samples for analysis, linoleic acid underwent methylation to form its respective methyl ester. This was achieved by refluxing 0.5 grams of the sample in methanol solvent in the presence of sulfuric acid, which acts as a catalyst for the esterification reaction. The methylation process converts the free acids into methyl esters, making them more nonpolar and suitable for GC-MS analysis. Once the methyl ester was formed, it was injected into the gas chromatograph in a split ratio of 100:1. The analysis was carried out using a DB-5HT column (30 m x 0.25 mm, 0.10 μm). The GC-MS analysis began with an initial oven temperature of 50°C, which was maintained for a brief period to allow the sample to stabilize. The temperature was then ramped up at a rate of 10°C per minute until it reached 325°C. This gradual increase in temperature facilitates the separation of different components in the sample based on their boiling points and volatility. The mass spectrometer, coupled with the gas chromatograph, detected and characterized the individual components in the sample by measuring the mass-to-charge ratio of the ions produced during the ionization process [9].

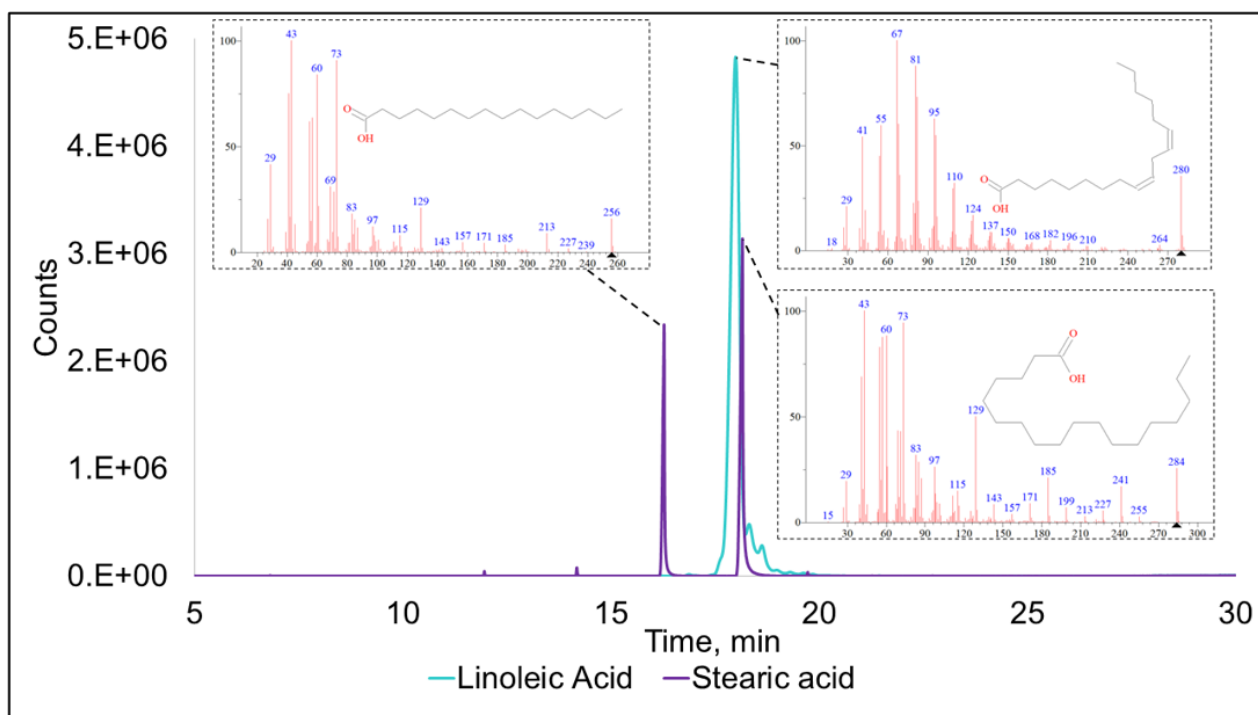


Figure 3: Chromatogram of Vegetable-Derived Linoleic Acid and Commercial-Grade Stearic Acid Obtained from GC-MS

Figure 3 presents a chromatogram that illustrates the relationship between retention time and counts for the gas chromatography-mass spectrometry (GC-MS) analysis of both linoleic acid and stearic acid. The chromatographic results were quite revealing: the stearic acid sample predominantly exhibited the presence of two compounds. These compounds eluted at distinct retention times of 16.275 minutes and 18.175 minutes. Subsequent mass spectrometry analysis confirmed these observations, identifying the compound eluting at 16.275 minutes as hexadecanoic acid, commonly known as palmitic acid, while the one eluting at 18.175 minutes was identified as octadecanoic acid, or stearic acid. In stark contrast, the chromatographic representation for linoleic acid revealed only a single compound, which was confirmed to elute at 17.99 minutes. Mass spectrometry further identified this compound as octadeca-9,12-dienoic acid, confirming its identity as linoleic acid. Despite both fatty acids having an equal number of carbon atoms, 18 in total, the molecular structure of linoleic acid is less heavy than that of stearic acid. This difference in molecular weight contributes to a lower elution temperature for linoleic acid during the GC analysis compared to its saturated counterpart, stearic acid[10,11].

The chemical characterization of linoleic acid and stearic acid reveals important differences in their structures. Both acids contain the same number of carbon atoms and functional groups, but linoleic acid, with its two double bonds, exhibits a higher iodine number, indicating greater unsaturation compared to the saturated stearic acid. The impact of these unsaturations on vulcanization behaviour and physical properties of rubber vulcanizate has been further investigated in a subsequent study.

Preparation of Rubber Compounds

The formulation of a typical passenger car radial tyre involves a multi-step mixing process to prepare the tread, sidewall, and ply compounds, ensuring optimal performance and durability. In this study, the compounds were mixed using a 1.8 litre Ferrel-made intermixer. The recipes for the control and experimental tread, sidewall, and ply are tabulated in Tables 2A, 2B, and 2C, respectively.

The mixing process for the tread began with masticating the primary rubber components, SSBR and ESBR, at a speed of 60 rpm for 10 seconds. After this initial masticating phase, the following ingredients were added: silica, a silane coupling agent, carbon black (N234), zinc oxide, wax, antidegradants (TMQ and 6PPD), and stearic acid or linoleic acid. These components were blended for 50 seconds before the injection of process oil. Additionally, ram scrap was introduced at 90 second. Once the temperature reached at 135°C, the time noted at zero for silanization reaction and continued missing for another 120 second maintaining the temperature between 135°C and 145°C. To get the desired viscosity of the compound, the master compound was then remixed at a speed of 30 rpm for 80 seconds, with ram scrap introduced at the 40-second mark. The final mixing, which includes the addition of soluble sulfur, DPG, and CBS accelerators, follows the same procedure used during the remixing phase.

Table 2: Recipe of Control and Experiment [A] Tread Compound, [B] Sidewall Compound and [C] Ply Compound

Table 2A		Recipe of Tread compound, phr		
Ingredients	Control			Experimental
SSBR		80.0		
ESBR 1739		27.5		
Silica		80.0		
Silane		10.0		
N234		10.0		
ZnO		2.5		
Wax		1.0		
TMQ		1.0		
6PPD		1.0		
Stearic acid	1.0			-
Linoleic acid	-			1.0
Plasticizer Oil		20.0		
Sulfur		1.5		
DPG		2.0		
CBS		1.8		
Table 2B		Recipe of Sidewall compound, phr		
Ingredients	Control			Experimental
NR		50.0		
PBR		50.0		
N660		60.0		
ZnO		3.0		
Wax		1.0		
TMQ		1.0		
6PPD		2.0		
PF Resin		7.0		
Stearic acid	1.0			-
Linoleic acid	-			1.0
Sulfur		2.0		
TBBS		1.0		
Table 2C		Recipe of Ply compound, phr		
Ingredients	Control			Experimental
NR		100.0		
N330		50.0		
ZnO		4.0		
PF Resin		3.0		
Stearic acid	1.5			-
Linoleic acid	-			1.5
Sulfur		3.5		
TBBS		1.0		

For the sidewall compounds, a 50:50 blend of NR and PBR were used. The rubbers were masticated for 10 seconds at 60 rpm, followed by the addition of carbon black (N660 grade), zinc oxide, wax, TMQ and 6PPD, phenolic resin, and stearic or linoleic acid. After mixing for 40 seconds, the process oil was introduced, and ram scrap was added at 90 seconds to ensure uniform dispersion. For the final mix, soluble sulfur and TBBS are incorporated, following a similar sequence to that in the final mixing of the tread compound.

The formulation of the ply compound starts with natural rubber, which was masticated at 60 rpm for 10 second, followed by the addition of carbon black (N330), zinc oxide, PF resin, and stearic or linoleic acid. Two ram scrap intervals at 50 and 90 seconds ensure uniform dispersion of the ingredients. To finalize the compound, insoluble sulfur and TBBS are incorporated, maintaining the same program used for the tread compound.

Physico-Chemical Characterization of the Compound

The compounds incorporating linoleic acid and stearic acid were rigorously evaluated across several key performance and processability metrics, essential for their application in tyre manufacturing.

Rheological Properties

In tyre manufacturing, the tread, sidewall and ply are shaped through extrusion and calendaring, which coats fabric with rubber. For effective processing, the rubber must remain soft, requiring a Mooney viscosity and scorch time (t5) to match those of a control compound. Mooney viscosity was measured at 100°C, with a t5 value indicating a 5-unit increase at 135°C. These properties were evaluated using M/s Alfa Technology's equipment. Additionally, curing behaviour with linoleic and stearic acids was analyzed at 160°C for 30 minutes, providing data on vulcanization cure times (ts2, tc10, tc50, tc90). Additionally, a strain sweep test at 50°C using a Premier RPA assessed polymer-silica interactions with fatty acids under varying strains from 0.1% to 100%.

Vulcanization Kinetics

To understand the effect of vegetable-derived linoleic acid on the activation energy (Ea), reaction rate constant (k), and order of reaction associated with the vulcanization were investigated employing conventional methodologies.

Cure rate index (K) can be demonstrated as Equation 3:

$$K = \frac{100}{TC_{90} - TS_2} \text{ min}^{-1} \quad (3)$$

Activation energy for vulcanization reaction of the three categories of the compounds mixed conventional stearic acid and linoleic acid, was estimated using the Arrhenius-type temperature dependence equation (Equation 4)

$$K = A e^{\frac{-E_a}{RT}} \quad (4)$$

Where K is cure rate index, A is pre-exponential factor of the reaction rate, Ea indicating the activation energy, R is the universal gas constant and T is absolute temperature of the reaction respectively. The Equation 4 can also be expressed as below:

$$\ln K = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (5)$$

To get insight into the reaction rate constant and order of reaction, further investigation was carried out using classical

reaction kinetics. The vulcanization kinetics can be described by a differential equation related to time (t) and temperature (T), irrespective of the reaction mechanism (Equation 4).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (6)$$

where,

α : conversion factor

t: time

$\frac{d\alpha}{dt}$: rate of vulcanization

k: kinetic constant at temperature T

f(α): function of α corresponding to the phenomenological model.

Conversion, α , in the vulcanization study using rheometer can be demonstrated as follows:

$$\alpha = \frac{M_t - M_L}{M_H - M_L} \quad (7)$$

where M_t , M_H , and M_L are represented as torque at time t, maximum torque and minimum torque, respectively.

Considering the vulcanization reaction is an autocatalytic reaction, f(α) can be denoted as

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad (8)$$

where m and n are the orders of reaction.

Consequently, Equation (6) can be established as

$$\frac{d\alpha}{dt} = k(T) \alpha^m (1 - \alpha)^n \quad (9)$$

The experimental data collected at temperatures of 150°C, 160°C, and 170°C from the rheological study of control and experimental tread, sidewall, and ply compounds have been accurately fitted to Equation 9. This fitting process provides results alongside the experimental data, including the resulting order of the vulcanization reaction, denoted as m and n.

Stress-Strain Properties

To understand how tyres react to diverse forces, researchers utilize stress-strain curves. These curves illustrate how a tyre material responds to applied stresses, allowing engineers to ensure that tyres maintain optimal grip, retain their intended shape, and provide stability across a range of driving conditions. To thoroughly evaluate the stress-strain characteristics of the tyre compounds, a Zwick universal testing machine was employed, adhering to the guidelines set forth by ASTM standards (ASTM D412). This testing involved measuring several key properties, including M100 (modulus at 100% strain), M300 (modulus at 300% strain), tensile strength, and elongation at the point of break.

Dynamic Mechanical Properties

A series of experiments were conducted using the DMA 2000 (Dynamic Mechanical Analyzer) to evaluate the dynamic mechanical properties of materials. Testing was performed at a frequency of 10 Hz and a strain level of 1%, focusing on tan δ values, which represent the ratio of the storage modulus (E') to the loss modulus (E''). Measurements were taken at three temperatures: 0°C indicating wet traction, 30°C, simulating dry traction conditions, and 70°C, reflecting rolling resistance. The tan δ values provide insights into the damping properties of the materials; higher values indicate greater energy loss and reduced efficiency, while lower values suggest better energy conservation and stability.

Abrasion Loss

The abrasion loss of both the regular and experimental tread compounds was rigorously evaluated using the DIN abrasion tester produced by Bareiss in Germany, in accordance with the methodology outlined in ISO 4649. For this analysis, a cylindrical specimen with a diameter of 16 mm and a height specified as 10 mm was subjected to abrasion. The testing involved placing the specimen on a rotating drum that was covered with an abrasive sheet. A consistent

$$\text{Abrasion loss, mm}^3 = \frac{\text{initial mass} - \text{final mass}}{\text{density}} \times \frac{\text{standard mass loss of the reference sample}}{\text{achieved mass loss of reference sample}} \quad (10)$$

vertical force of 10N was applied during the test to ensure uniform contact between the specimen and the abrasive surface. To quantify the abrasion loss accurately, the change in volume of the specimen was calculated using Equation 10, as specified in ISO 4649. This method provided precise measurements of the material loss due to abrasion, which is critical for evaluating the performance characteristics of the tread compounds under testing conditions.

Fatigue Properties

The fatigue-to-failure properties of the compound through the FTFT tester from M/s Alpha Technology, USA, were carried out adhering to the ASTM D4482 standards. This evaluation is crucial for understanding how the material behaves under repeated stress and its longevity throughout its service life.

Ozone Resistance Properties

The ozone resistance of the sidewall compound was assessed under controlled conditions of 40°C and 50 parts per hundred million (pphm) ozone exposure, utilizing the Ozone Tester developed by M/s Ektrontek in Taiwan, in accordance with IS 3400 standards. This testing method closely simulates real-world environmental conditions, providing crucial insights into the material’s durability against ozone-induced degradation. Such degradation can lead to the formation of cracks and significantly compromise the structural integrity of tyre components.

Tack Properties

Furthermore, the retention of tackiness in the ply skim compounds was thoroughly investigated using the Tackiness Checker HTC-1, manufactured by M/s Toyo Seiki Seisaku-sho, Ltd., Japan. Over a span of fourteen days, this test critically examines the tacky properties of the compounds, ensuring that they maintain their adhesive qualities throughout the tyre manufacturing process, even after extended periods of storage. This capability is essential for guaranteeing effective bonding during tyre building production.

H-Adhesion of Ply Skim Compound

The H-Pull Adhesion test, conducted as per ASTM D4776, is designed to evaluate the adhesion strength between a tyre cord and rubber compound under simulated service conditions. In this method, a cord is embedded longitudinally between two layers of rubber and vulcanized to replicate the actual tyre manufacturing process. The vulcanized specimen, typically shaped in an “H” configuration, is then subjected to tensile loading using a Universal Testing Machine (UTM). The machine pulls the rubber layers apart to determine the force required to extract the cord from the matrix. This test provides the maximum pull-out force and the associated failure mode, offering valuable insights into the quality and durability of the rubber–cord interface. The H-Pull test plays a vital role in quality control during production and is extensively employed in research and development to assess the influence of various rubber formulations, cord surface treatments, and coating technologies on adhesion performance. Ensuring robust adhesion is essential for maintaining the structural integrity and long-term reliability of tyres under dynamic operating conditions.

Result and Discussion

Rheological Properties

Figure 4 demonstrates the Mooney viscosity and t5 for the experimental and control compounds, tread, sidewall and ply, mixed with linoleic acid and stearic acid. The results indicate that across all - tread, sidewall, and ply compounds - the flowability characteristics and t5 are comparable to those of the control compound, confirming that the experimental formulations maintain the necessary properties for processing, such as extrusion of tread and sidewall and calendaring of ply.

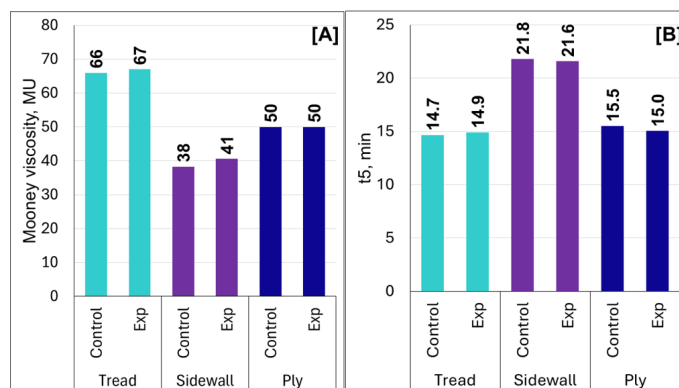


Figure 4: [A] Mooney viscosity and [B] t5, scorch safety time of control and experiment tread, sidewall and ply compound mixed with stearic acid and linoleic acid, respectively.

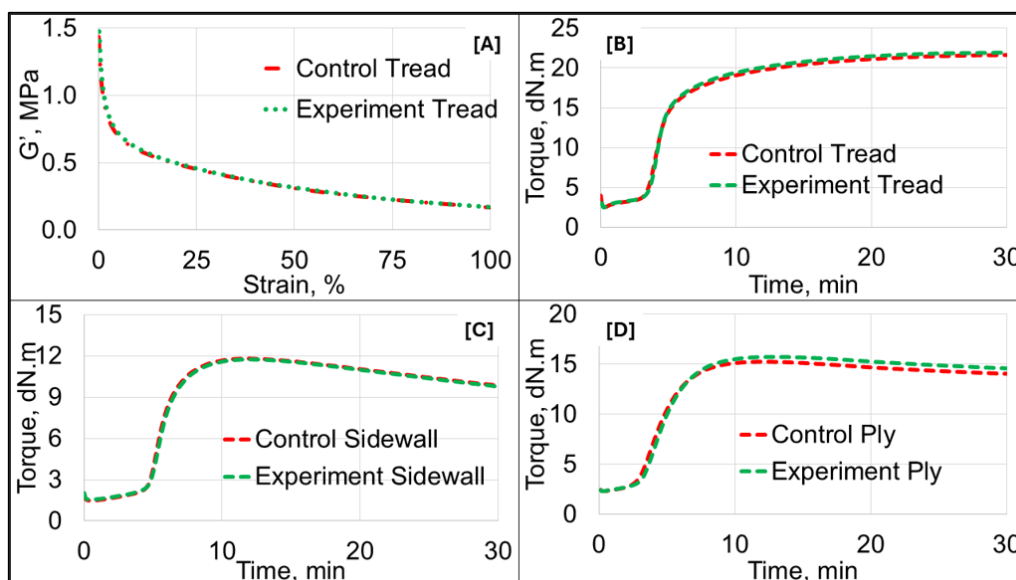


Figure 5: [A] Strain vs stress curve of uncured compound tread compound mixed with stearic acid (control) and linoleic acid (experiment). Time vs torque curve of control and experiment [B] tread, [C] sidewall and [D] ply compound at 160°C

Figure 5[A] represents the storage modulus (G') vs strain curves obtained from the Payne effect test, comparing both the control tread compound and the experimental tread compound incorporating linoleic acid. Upon analysis of the data, it can be observed that the G' vs strain curves for both the control and experimental compounds overlap with each other, which indicates that the addition of linoleic acid does not lead to any discernible detrimental effects on the re-agglomeration of silica within the green compound.

The primary role of fatty acids in the rubber matrix is to react with zinc oxide and enhance the vulcanization process[12]. The effectiveness of linoleic acid has been evaluated in terms of tc_{10} , tc_{50} , and tc_{90} at a temperature of 160°C. The results from both control and experimental treads, sidewalls, and ply compounds, which were made from various types of rubber and rubber ingredients, are presented in Table 3. Furthermore, to provide a clearer understanding of the rheological properties, the time versus torque curves for the control and experimental tread, sidewall, and ply compounds are illustrated in Figures 5[B], 5[C], and 5[D], respectively.

Table 3: Impact of Vegetable-Derived Linoleic Acid on the Vulcanization Rate Compared to Commercial-Grade Stearic Acid

Parameter	Tread		Sidewall		Ply	
	Control	Exp	Control	Exp	Control	Exp
ts2, min	3.58	3.45	4.98	5.06	3.54	3.30
tc10, min	3.41	3.35	4.56	4.63	3.22	2.93
tc50, min	4.37	4.46	5.56	5.66	4.71	4.44
tc90, min	11.32	11.48	7.78	7.86	7.50	7.17
Cure rate index, min^{-1}	12.92	12.70	35.7	35.7	25.3	25.8

Table 3 shows that the values of ts_2 , tc_{10} , tc_{50} , and tc_{90} remained consistent across all three types of applications in the experimental compound. Additionally, the cure rate index, calculated using Equation 03, also exhibited no such changes in the experimental compound. Furthermore, the rheological graphs illustrated in Figures 5[B], 5[C], and 5[D] demonstrate an increase in torque for both the tread and ply compounds[13–16]. The sidewall compound exhibited a slightly higher torque[17]. Further investigations into these properties were conducted during the analysis of the effect of linoleic acid on vulcanization kinetics [18].

Vulcanization Kinetics

Figure 6 demonstrating the effect of linoleic acid on activation energy of vulcanization reaction, reveals that activation energy of all the experiment compounds are lower than that of their respective control samples.

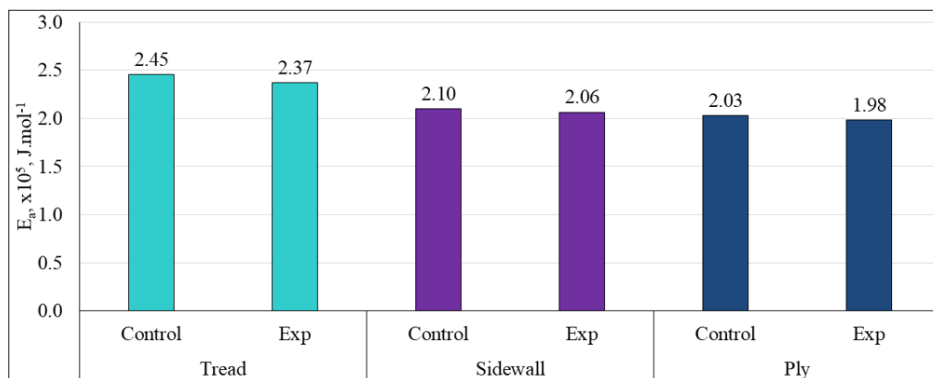


Figure 6: Activation Energy of Control (Mixed with Conventional Stearic Acid) and Experimental (Mixed with Linoleic Acid) Tread, Sidewall and Ply Compound

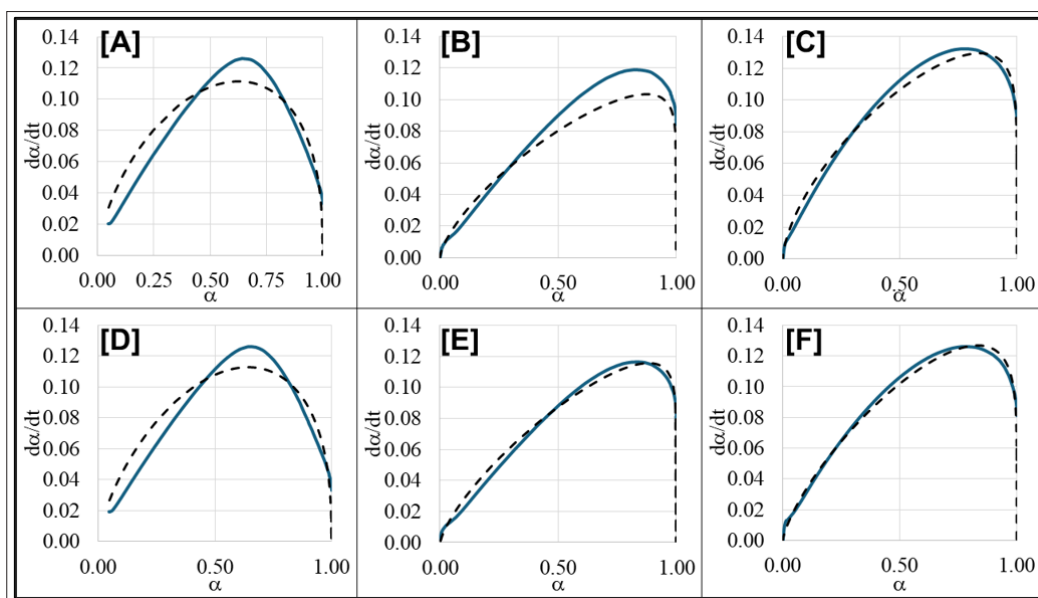


Figure 7: Fitting the Experimental Data Obtained from the Rheology Study of Control

- [A] Tread,
- [B] Sidewall,
- [C] Ply and experimental
- [D] Tread,
- [E] Sidewall and
- [F] Ply

To further investigate the impact of linoleic acid on the vulcanization rate constant (k) and the order of the vulcanization reaction (m and n), the fitting of rheological data to Equation 9 serves as a foundational model for understanding the kinetics of the vulcanization process. The results of the fitting procedure are represented in Figure 7. Additionally, Table 4 provides a summary of the effective fitting parameters derived, presenting values that highlight the nuances of the vulcanization kinetics.

The findings from this study indicate a discernible trend toward an increase in the kinetic rate constant (k) in conjunction with a slight elevation in the order of the reaction with decrease in the activation energy of vulcanization reaction. This suggests that linoleic acid is positively influencing the efficiency of the vulcanization process, potentially enhancing the overall cross-linking reaction rates [15-17,19,20]

Table 4: Kinetic Parameters, k, m and n Obtained by Fitting the Curve in Equation 9

Compound Details		k	m	n	m+n
Tread	Control	0.22	0.65	0.39	1.04
	Experimental	0.23	0.70	0.39	1.09
Sidewall	Control	0.14	0.77	0.10	0.87
	Experimental	0.16	0.77	0.12	0.89
Ply	Control	0.18	0.76	0.12	0.88
	Experimental	0.19	0.75	0.15	0.90

Physical Properties

The stress-strain curve of tread, sidewall and ply compounds have been represented in Figure 8[A], 5[B] and 5[C], respectively.

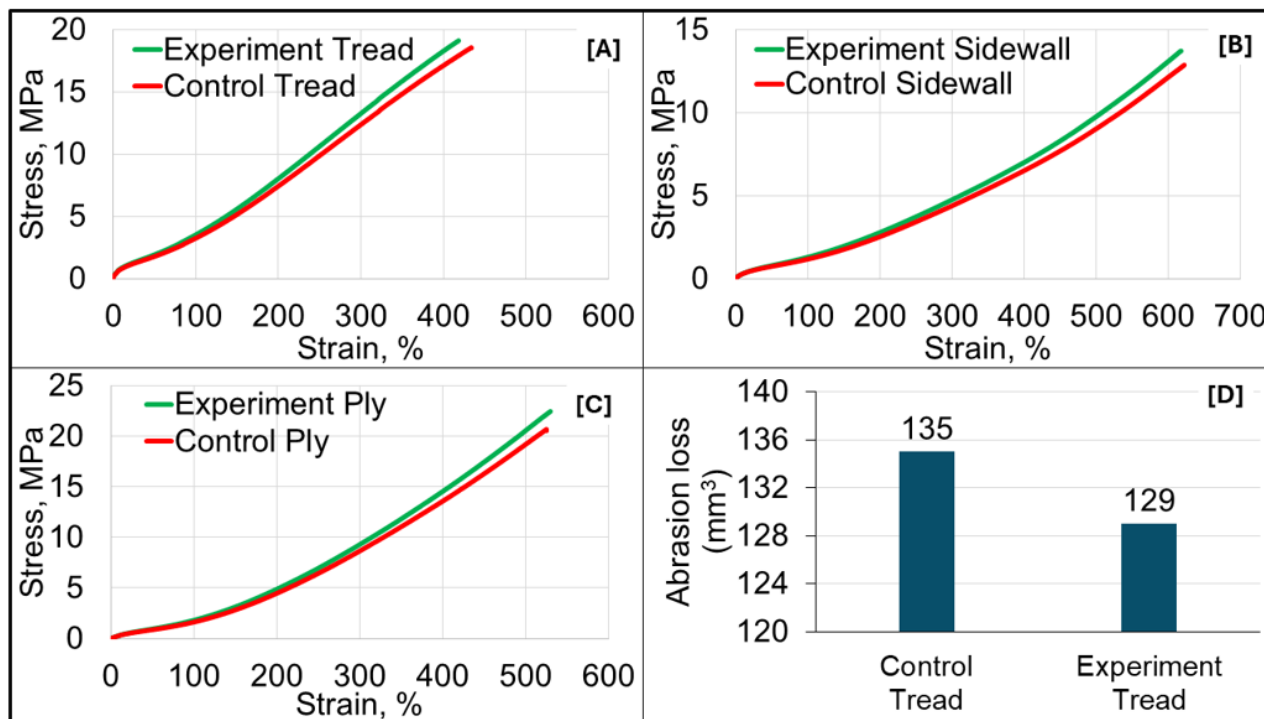


Figure 8: Strain vs Stress Curve of Control and Experiment

[A] Tread,

[B] Sidewall and

[C] Ply Compound.

[D] Abrasion Loss of Control and Experiment Tread Compound Mixed with Commercial-Grade Stearic Acid and Vegetable-Derived Linoleic Acid

A detailed analysis presented in Figure 8 reveals the stress levels at various strain percentages for both the regular compound and the experimental sample, as summarized in Table 5.

For the regular tread compound, the recorded stress values were as follows: at 100% strain, the stress was 3.2 MPa; at 200% strain, it increased to 7.4 MPa; and at 300% strain, it reached 12.4 MPa. Notably, the tensile strength of this compound was measured at 18.6 MPa, and it exhibited an elongation at break of 434%. In comparison, the experimental sample demonstrated slightly higher stress values at the same strain levels. Specifically, the recorded stress values for the experimental sample were 3.5 MPa at 100% strain, 8.0 MPa at 200% strain, and 13.3 MPa at 300% strain. However, the tensile strength of the experimental tread was slightly lower than that of the regular sample, measuring 19.1 MPa, with an elongation at break of 417%.

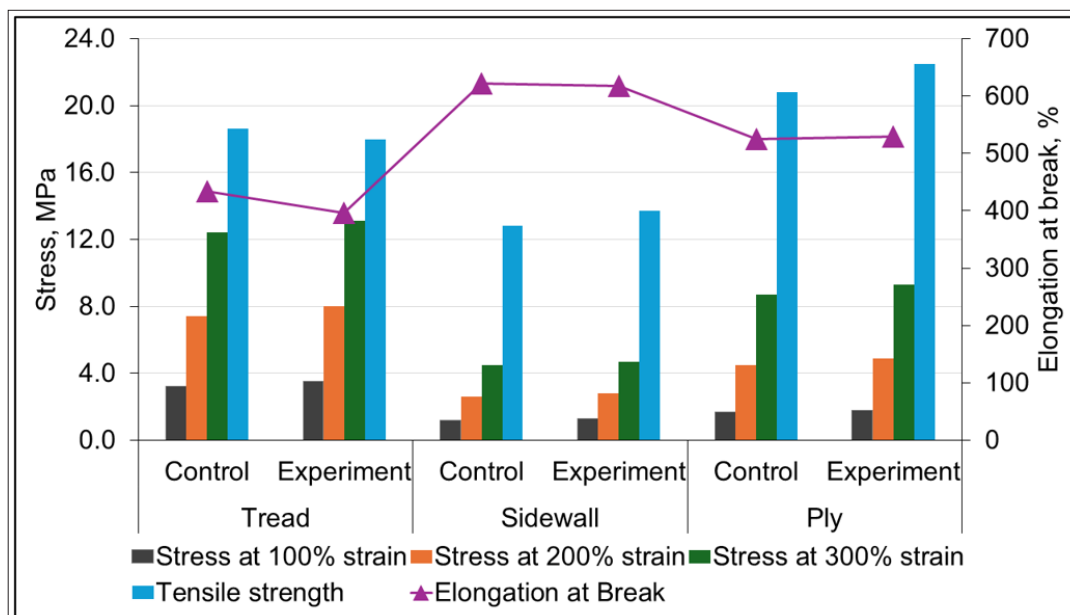


Figure 9: Detailed Analysis of Stress at Various Strain Percentages for the Regular Tread, Sidewall and Ply Compound with their Experimental Sample

Similar results were observed in the experimental sidewall and ply compound compared to the regular sidewall and ply compound.

In both cases, the experimental compound demonstrated higher stress at various percentages of strain when compared to the regular sample.

Table 5: Physical Properties of Control and Experiment Tread, Sidewall and Ply Compound in Terms of Stress at Different Strains, Tensile Strength and Elongation at Break

Parameter	Tread		Sidewall		Ply	
	Control	Exp	Control	Exp	Control	Exp
Stress at 100% strain, MPa	3.2	3.5	1.2	1.3	1.7	1.8
Stress at 200% strain, MPa	7.4	8.0	2.6	2.8	4.5	4.9
Stress at 300% strain, MPa	12.4	13.3	4.5	4.7	8.7	9.3
Tensile strength, MPa	18.6	19.1	12.8	13.7	20.8	22.5
Elongation at Break, %	434	417	622	617	525	529

Upon examining Table 5, it became clear that the stress levels corresponding to various levels of strain, along with the tensile strength measurements of the experimental rubber compounds, surpass those of conventional compounds mixed with commercial-grade stearic acid[21]. This significant increase can be attributed to the unique characteristics of linoleic acid, particularly its unsaturation. This facilitates a more extensive curing reaction, which, in turn, enhances stress resilience at specific strains and significantly improves the tensile strength of the experimental rubber formulations[13,22].

Dynamic Mechanical Properties

The dynamic mechanical properties of the experimental tread, when compared to those of the regular tread, are illustrated in Figure 10. Specifically, the storage modulus (E') and loss modulus (E'') were evaluated at three distinct temperatures: 0°C, 30°C, and 70°C. At all these temperatures, the experimental tread exhibited higher values for both E' and E'' compared to the regular sample, indicating enhanced stiffness and energy dissipation characteristics. Furthermore, the ratio of the loss modulus to storage modulus, known as $\tan\delta$, was analyzed to assess performance under different conditions. Interestingly, $\tan\delta$ remained relatively constant across these temperature conditions, suggesting that while there was a notable increase in the storage modulus (E') of the experimental compound, the changes did not translate to significant differences in wet grip, dry grip, or RRC behaviour for the rubber compound[13]. Despite the elevated E' in the experimental tread, the consistent $\tan\delta$ values indicate that the inclusion of linoleic acid had minimal effect on altering the performance characteristics related to traction and resistance in varying temperature conditions.

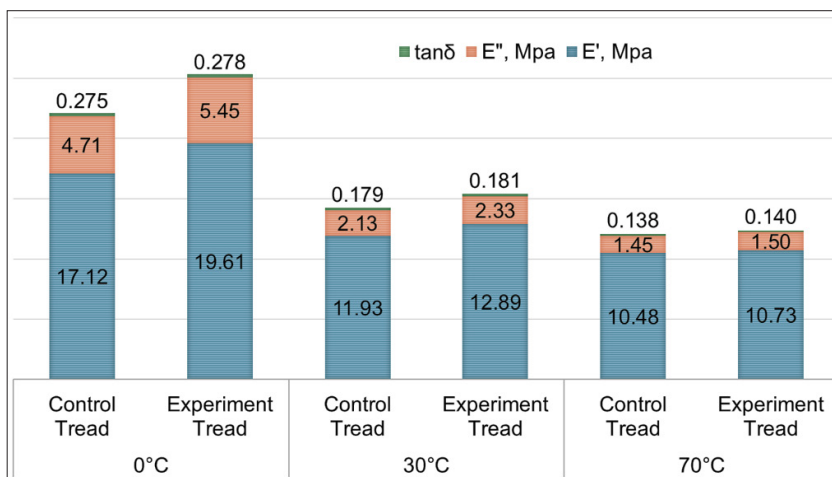


Figure 10: Dynamic Mechanical Behaviour of Tread Compound Mixed with Stearic Acid (control) and Linoleic Acid (Experiment) at Different Temperatures with 11Hz Frequency and 1% Dynamic Strain

Abrasion Loss

The abrasion loss of the tyre tread compound serving a laboratory indicator for predicting tyre mileage, is illustrated in Figure 8[D]. Analyzing the collected data reveals that the abrasion loss for the regular sample measures 135 mm³, while the experimental sample demonstrates an improvement, exhibiting an abrasion loss that is 129 mm³. This reduction in abrasion loss in the experimental compound appears to stem from its ability to withstand higher stress at varying strain levels, as well as its enhanced tensile strength.

Fatigue Properties

The fatigue properties of the control and experimental sidewalls are clearly illustrated in Figure 11. In Figure 11[A], the data reveal that the sidewall compound formulated with linoleic acid demonstrates an enhanced lifespan when subjected to a challenging condition of 100% strain, compared to the control compound. This improvement in durability indicates that the addition of linoleic acid may provide beneficial properties that enhance the material's resistance to fatigue. Further examination in Figure 11[D] depicts the surface characteristics [B] Optical Images at 8x Magnification of Failed Portion of Fatigue Failed Samples of Sidewall Compound Mixed with Stearic Acid (Control) and Linoleic Acid (Experimental) the failed portions after conducting rigorous testing, specifically after enduring 268 kilocycles (kC) for the control compound and 273 kilocycles for the experimental compound. The optical microscopic image captured at an 8x magnification divulges notable differences in the surface textures: the experimental compound displays a rougher profile compared to the surface of the control compound. The combination of a greater fatigue life and the rougher surface in the experimental compound likely contributes to the extended durability of the sidewalls during their operational use.

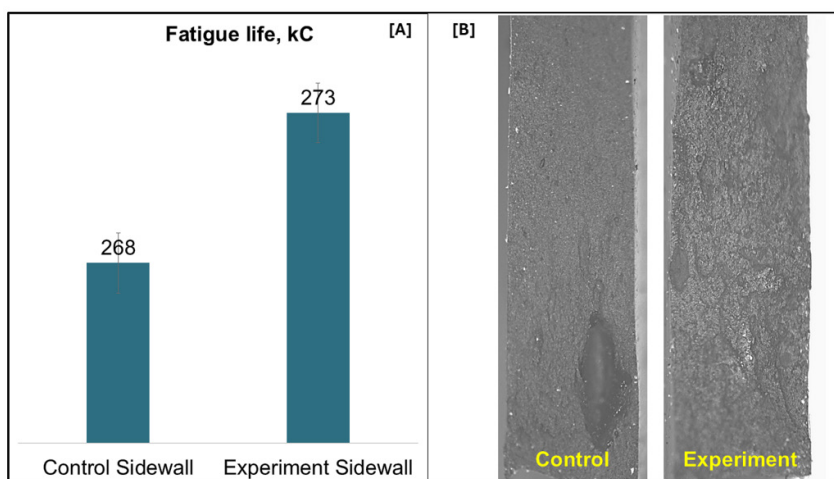


Figure 11: [A] Fatigue to Failure Properties

Ozone Resistance Properties

Figure 12[A] presents the visual representations of the samples subjected to ozone testing, comparing the control sidewall with the experimental sidewall. Both the control and experimental sidewall compounds exhibit a notable resistance to ozone degradation when exposed to a temperature of 40°C and an ozone concentration of 50 ppm for a duration of 72 hours. Remarkably, neither sample displayed any signs of ozone-induced cracking in the bent loop samples, indicating that the material integrity was maintained throughout the testing conditions. This resistance suggests a significant efficacy of the compounds in preventing ozone-related deterioration, highlighting their potential for applications where exposure to ozone-prone environments is a concern [23,24].

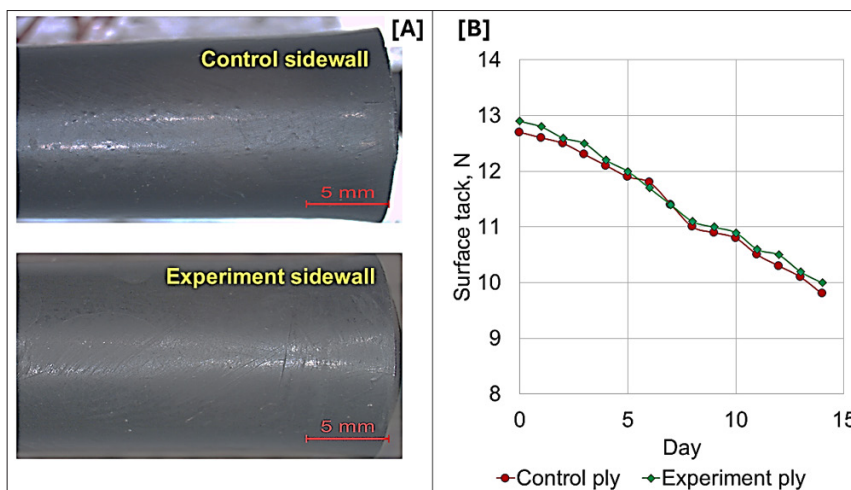


Figure 12: [A] Optical microscopic image of control and experiment sidewall sample after 72 hour of 50 ppm ozone exposure at 40°C, [B] Surface tack study of control ply and experimental ply for 14 days

Tack Properties

Figure 12[B] shows the surface tack of both the control and experimental ply compounds over a period of fourteen days. The initial tack of the control compound was recorded at 12.7 N, and the experimental compound showed a tack of 12.9 N, which is comparable to that of the control. The presence of phenol formaldehyde (PF) resin in the compound enhances its tack. However, the surface tack decreases over time as the plasticizer oil and organic acids, such as stearic acid and experimental linoleic acid, migrate to the surface and reduce the tackiness of the compound. This phenomenon is observed in both the control and experimental compounds, as both gradually lose their tackiness over time. The rate of decrease in tack for the control compound was recorded at 0.215 N/day, while the experimental compound decreased at a slightly higher rate of 0.216 N/day, resulting in surface tack values of 9.8 N and 10.0 N, respectively, on the 14th day.

H-Adhesion of Ply Skim Compound

Figure 13[A] presents the H-adhesion results for both the control and experimental ply skim compounds, while Figure 13[B] shows images of the tested samples, demonstrating 100% coverage in both cases. The control ply skim compound, which is mixed with commercial-grade stearic acid, exhibits an adhesion force of 15.51 kgf. In contrast, the experimental ply skim compound shows a higher adhesion force of 16.25 kgf. The notable increase in the H-adhesion force observed in the experimental compound can be attributed to the unique chemical [B] image at 40x magnification of samples after H-adhesion testing of control ply skim compound and experimental ply skim compound mixed with conventional stearic acid and experimental linoleic acid structure of linoleic acid, which contains double bonds at the 9th and 12th carbon positions. These double bonds may play a critical role in enhancing the interaction between the ply cord and the ply skim compound through improved molecular bonding. The findings from the H-adhesion study emphasizes the importance of incorporating linoleic acid into the ply skim formulation[25-27]. This modification not only bolsters the adhesion between the material layers but also contributes to the overall durability and longevity of the tyre throughout its operational lifespan. Enhancing adhesion in tyre compounds is crucial, as it directly impacts tyre safety, performance, and resistance to wear and tear during usage.

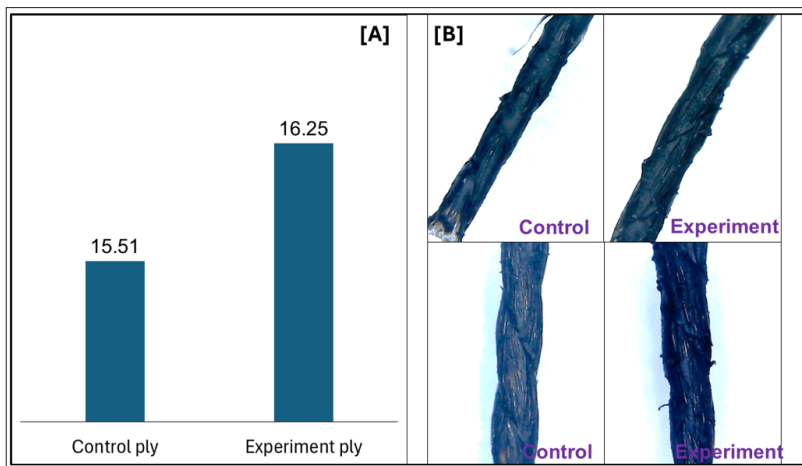


Figure 13: [A] H-adhesion force in kgf and [B] image at 40x magnification of samples after H-adhesion testing of control ply skim compound and experimental ply skim compound mixed with conventional stearic acid and experimental linoleic acid structure of linoleic acid, which contains double bonds at the 9th and 12th carbon positions. These double bonds may play a critical role in enhancing the interaction between the ply cord and the ply skim compound through improved molecular bonding. The findings from the H-adhesion study emphasizes the importance of incorporating linoleic acid into the ply skim formulation[25-27]. This modification not only bolsters the adhesion between the material layers but also contributes to the overall durability and longevity of

the tyre throughout its operational lifespan. Enhancing adhesion in tyre compounds is crucial, as it directly impacts tyre safety, performance, and resistance to wear and tear during usage.

Conclusion

Physicochemical characterization of linoleic acid and conventional stearic acid shows both have a similar number of acid functional groups for vulcanization. However, linoleic acid has a higher degree of unsaturation, measuring 134 g/100 g compared to 2 g/100 g for stearic acid, as confirmed by gas chromatography. Experimental compounds made from linoleic acid for the tread, sidewall, and ply demonstrated similar flowability at 100°C to those made with stearic acid. Their vulcanization properties, including scorch safety time and cure rate index, were comparable to the controls. Kinetic studies indicated decreased activation energy for the vulcanization reaction and increased reaction rate constants. Strain sweep analysis showed that linoleic acid did not adversely affect silica re-agglomeration. Rheology curves indicated higher torque increases in experimental compounds, with higher modulus and tensile strength. It has also been noticed that the reaction rate constant and the order of the vulcanization reaction has been increased. Dynamic mechanical analysis revealed no significant effect on $\tan \delta$, but a notable increase in storage modulus (E'). The abrasability of tread compounds using linoleic acid was better (129 mm³ vs. 135 mm³), and sidewall compounds showed improved fatigue life (273 kc vs. 268 kc) while maintaining ozone resistance. Ply compounds displayed similar tackiness, but those with linoleic acid had a higher adhesion force (16.25 kgf vs. 15.51 kgf).

This study indicated that linoleic acid possesses a similar number of acid functional groups to conventional stearic acid, with two unsaturation groups. These unsaturation groups may take part into the vulcanization reaction, resulting in higher modulus, increased tensile strength, improved storage modulus, greater fatigue life, and enhanced adhesion force. Further, the efficacy of this vegetable-derived linoleic acid over stearic acid can be explored in tyre level.

References

1. Coran AY (2013) Vulcanization. *The Science and Technology of Rubber* 337-381.
2. Russell WF (1929) Early experiments with stearic acid in rubber compounding. *Ind Eng Chem Res* 21: 727-729.
3. Kohjiya S, Tosaka M, Furutani M, Ikeda Y, Toki S, Hsiao BS, et al. (2007) Role of stearic acid in the strain-induced crystallization of crosslinked natural rubber and synthetic cis-1,4-polyisoprene. *Polymer (Guildf)* 48: 3801-3808.
4. Helaly FM, El Sabbagh SH, El Kinawy OS, El Sawy SM (2011) Effect of synthesized zinc stearate on the properties of natural rubber vulcanizates in the absence and presence of some fillers. *Mater Des* 32: 2835-2843.
5. Dinsmore RP (1929) Stearic and oleic acids as rubber-compounding ingredients. *Ind Eng Chem* 21: 722-723.
6. Gradwell MHS, McGill WJ (1994) The interaction of sulfenamide accelerators with sulfur, ZnO, and stearic acid in the absence of rubber. *J Appl Polym Sci* 51: 177-185.
7. Das Gupta S, Satpathi H, Bhandary T (2024) Reverse engineering: a tool for the chemical composition analysis of finished rubber products. *Rubber Products: Technology and Cost Optimisation* 279-322.
8. Luyt AS, McGill WJ, Shillington D (1990) DSC study of the interaction of 2-mercaptobenzothiazole, sulfur, ZnO and stearic acid in the absence of rubber. *Br Polym J* 23: 39.
9. Bhandary T, Satpathi H, Banerjee A, Pal K, Pal A, et al. (2023) Development of a test method for the estimation of SBR-BR blend ratio in tyre tread formulation and validation through robust statistical tools. *Org Polym Mater Res* 5: 1-11.
10. Joshua O, Ayo R, Adegbe EA, Iekhaize J (2019) Physicochemical and GC-MS analysis of selected plant seed oils: castor, neem and rubber seed oils. *Fuw Trends Sci Technol J* 3: 644-651.
11. Aigbodian AI, Bakare IO (2005) Rubber seed oil quality assessment and authentication. *J Am Oil Chem Soc* 82: 465-469.
12. Musto P, Larobina D, Cotugno S (2013) Confocal Raman imaging, FTIR spectroscopy and kinetic modelling of the zinc oxide–stearic acid reaction in a vulcanizing rubber. *Polymer (Guildf)* 54: 685-693.
13. Ismail H, Kamal SK, Mark SE (2001) Comparison of palm oil fatty acid and stearic acid in natural rubber compounds. *J Elastomers Plast* 33: 100-113.
14. Junkong P, Morimoto R, Miyaji K (2020) Effect of fatty acids on the accelerated sulfur vulcanization of rubber by active zinc/carboxylate complexes. *RSC Adv* 10: 4772-4785.
15. García DB, Mansilla MA, Crisnejo M (2019) Effect of carbon nanotube content on vulcanization kinetics in styrene–butadiene rubber compounds. *Polym Eng Sci* 59: E327–E336.
16. Fard-Zolfaghari G, Abbasian A, Razzaghi-Kashani M (2021) Compatibility of vegetable-based plasticizers in filled rubber vulcanizates. *Polym Eng Sci* 61: 1379-1391.
17. Bhandary T, Satpathi H, Dutta A (2023) Effect of unsaturation content in bromo-butyl rubber on cure kinetics. *Polymer Science: Peer Review Journal* 5: 1-2.
18. Bera O, Pavličević J, Ikončić B, Jelena Lubura, Dragan Govedarica, et al. (2021) Kinetic modeling and optimization of rubber molding. *Polym Eng Sci* 61: 879-890.
19. Milani G, Leroy E, Milani F (2013) Mechanistic modeling of reversion phenomena in sulphur-cured natural rubber vulcanization kinetics. *Polym Test* 32: 1052-1063.
20. Mensah B, Bensah YD, Nbelayim PSF (2022) Vulcanization kinetics of acrylonitrile-butadiene rubber reinforced with graphene oxide. *Polym Eng Sci* 62: 4156-4172.
21. Chukwu M, Ekebafé L, Madufor IC (2011) Effect of stearic acid level on the physical properties of natural rubber vulcanisate. *Pac J Sci Technol* 344.
22. Zhou Y, Kosugi K, Yamamoto Y (2017) Effect of non-rubber components on the mechanical properties of natural rubber. *Polym Adv Technol* 28: 159–165.
23. Agrawal SL, Mandot S, Bandyopadhyay S, R Mukhopadhyay, AS Deuri, et al. (2005) Effect of waxes on rubber vulcanisates.
24. Bhandary T, Dey S, Dasgupta S, Ajay Chengalaveedu, Mahuya Das, et al. (2025) Sustainable replacement of petroleum wax in tyre compounds. *Polymer Science: Peer Review Journal* 6: 1-9.
25. Tian H, Yao Y, Wang C, Rui Jv, Xiang Ge, et al. (2020) Essential work of fracture analysis for surface-modified carbon fiber/polypropylene composites. *Polym Compos* 41: 3541-3551.
26. Jeon GS, Han MH, Seo G (1999) Adhesion properties of stearic acid-loaded rubber compounds to brass-plated steel cords. *Chem Eng*.
27. Ziegler E, Macher J, Gruber D (2012) Influence of stearic acid on rubber–brass adhesion. *Rubber Chem Technol* 85: 264-276.

Copyright: ©2026 Tirthankar Bhandary, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.