STUDIES ON CHARACTERIZATION OF ECO-FRIENDLY MATERIALS AND THEIR EFFECTS ON DIFFERENT PROPERTIES OF RUBBER COMPOUNDS

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CERTIFICATE

Its gives me immense pleasure in certifying that the thesis entitled **"STUDIES ON CHARACTERIZATION OF ECO-FRIENDLY MATERIALS AND THEIR EFFECTS ON DIFFERENT PROPERTIES OF RUBBER COMPOUNDS"** and submitted by **Mr. SHAMBHU LAL AGRAWAL** is based on the work research carried out under my guidance. He has completed the following requirements as per Ph.D. regulations of the University;

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DECLARATION

I, **Mr. SHAMBHU LAL AGRAWAL** S/o **Late Mr. PURANMAL AGRAWAL** resident of HIG, Ist Floor, Flat No. 29, Jeevan Anand Society, Plot No. 1, West Enclave, Pitampura, Delhi – 110034, hereby declare that the research work incorporated in the present thesis entitled **“STUDIES ON CHARACTERIZATION OF ECO-FRIENDLY MATERIALS AND THEIR EFFECTS ON DIFFERENT PROPERTIES OF RUBBER COMPOUNDS”** is my own work and is original. This work (in-part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources, wherever required. I solely own the responsibility for the originality of the entire content.

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PREFACE

Sustainability is “Acting responsibly to meet the requirements of the present without compromising the ability of future generations to meet their own needs”. Sustainable development is basically use of renewable raw materials for all kinds of products manufacturing as and when possible. Its aim is to assure conservation of fauna and flora species. Because fossil reserves are decreasing, and greenhouse gas emissions are increasing regularly day by day. Carbon dioxide emissions can be minimized using these raw materials in products of daily use. It also helps in reduction of toxicity of products.

However, it is a quite challenging task to use sustainable materials in place of petroleum-based materials due to cost-performance compromise and lack of knowledge about structure property relationship for these materials. Few materials used by rubber industry are not sustainable like petroleum based raw materials

Huge quantity of extender oil is used by the tire industry, so it is getting attention. Several large oil manufacturing companies (traditionally blenders of refinery products) have already jumped on the foray as the demand of some of the naturally occurring vegetable oils are increasing and this trend is going to continue. These vegetable oils are non-carcinogenic, better processing and are shown to improve tire performance properties like rolling resistance, traction and mileage in varied proportions as compared to mineral oil counterpart.

In the present work styrene butadiene rubber latex (normal and high styrene content) was extended with various vegetable oils. Oil-extended rubbers prepared with normal styrene content latex were evaluated in American Society for Testing and Materials (ASTM) standard recipes and passenger car radial (PCR) tire tread compound formulation. Oil-extended rubbers prepared with high styrene content latex were evaluated in motorcycle tire tread compound formulation. Detailed characterization of the compounds was done with respect to processing, stress-strain, performance properties and dynamic mechanical properties.

Few vegetable oils based SBRs exhibited improvement in processing, performance and dynamic mechanical properties. These oils may be used for commercialization to produce sustainable SBRs. Few vegetable oils based SBRs exhibited slow cure behaviour in rheometeric characterization. These oils extended SBRs based rubber compounds may be evaluated with higher dosage of curatives to adjust the cure rate and crosslink density. Research work may also be conducted with use of blend of oils in place of using single oil for extension of SBR. This may further optimize the properties of the rubber compounds.

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INTRODUCTION

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1.1 SUSTAINABILITY

Sustainability is “Acting responsibly to meet the requirements of the present without compromising the ability of future generations to meet their own needs”. Sustainable development is basically use of renewable raw materials for all kinds of products manufacturing as and when possible. Its aim is to assure conservation of fauna and flora species. Because fossil reserves are decreasing, and greenhouse gas emissions are increasing regularly day by day. Carbon dioxide emissions can be minimized using these raw materials in products of daily use. It also helps in reduction of toxicity of products[1].

Reduction in usage of physical resources and enhancement of usage of more renewable resources may lead to achieve targets of sustainability. Hence avoid toxic materials[2], redesigning of the processes and products are mandatory. Tire and automobile industry is integral part of our mobility. Tire industry is the world’s biggest manufacturing industry among all industries. Tire provides grip, safety, comfort, durability, steering accuracy and fuel efficiency with main function as load carrying from one place to another place. Current compound annual growth rate (CAGR) prediction is 4% for tire industry for period 2021-26. World tire production volume is expected to reach 4.11 billion units per year during 2021-26. During COVID outbreak, tire industry was affected badly due to strict lockdown, however, it is recovered completely in year 2022. Raw materials consumption is growing in line with industries growth. Tire manufacturing flow diagram is shown in Fig. 1.1.

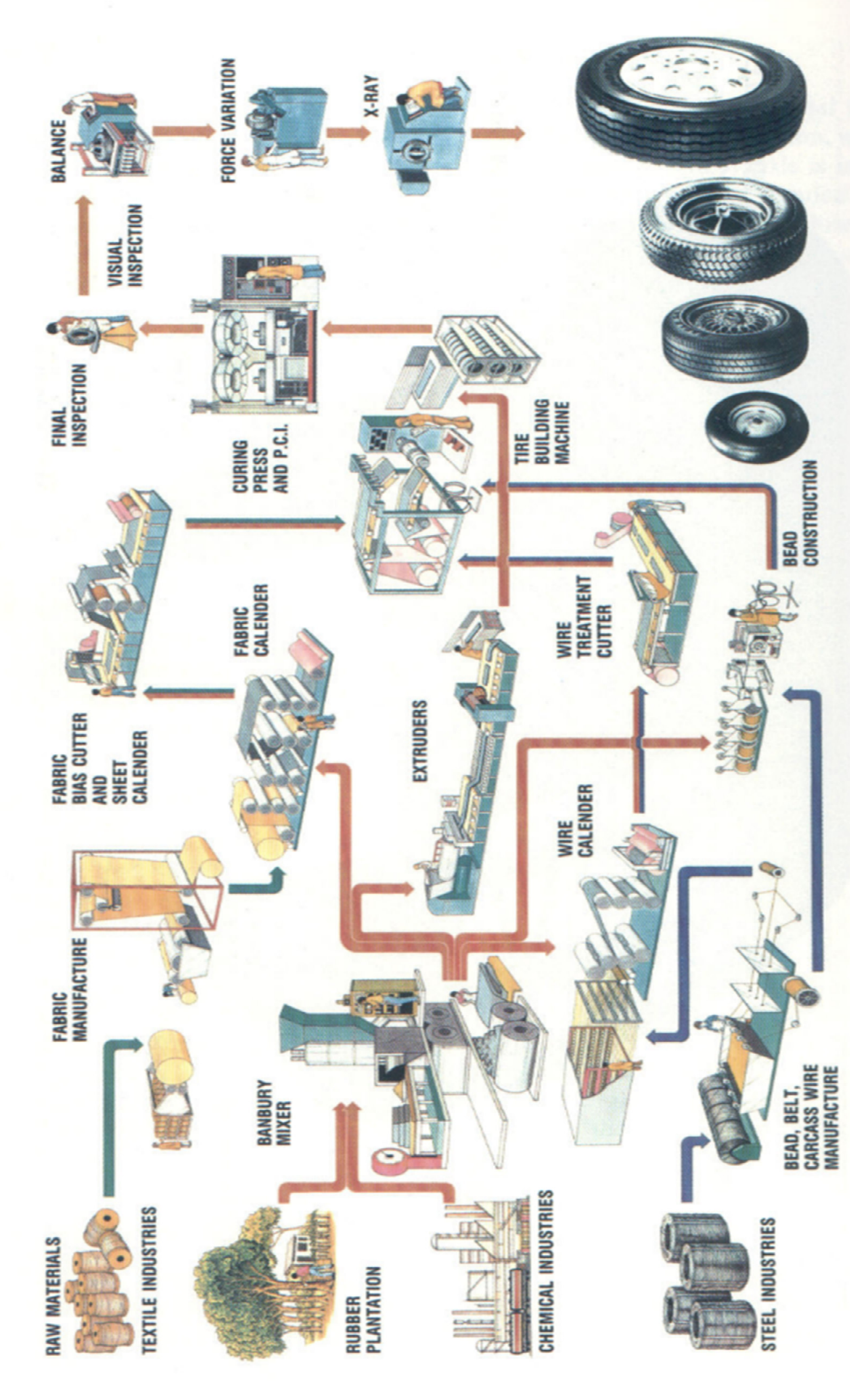

Fig. 1.1: Tire manufacturing flow diagram

(https://www.pinterest.co.uk/pin/689121180464246415/)

This industry spends approx. 65% of the production cost on various raw materials. Raw materials are classified as direct and indirect raw materials. Direct raw materials are consumed during tire manufacturing while others are called indirect raw materials. It induces natural and synthetic rubbers, carbon black and silica fillers, petroleum-based various process oils, nylon and polyester fabrics, brass and bronze coated steel wires, and various other chemicals like zinc oxide, stearic acid, resins, sulfur, accelerators, etc. Synthetic rubbers, carbon black, process oils, and fabrics are based on petroleum source, and they generate harmful product, by product, and end of life materials[3,4]. Natural resources are exploited unscientifically by humans, which lead to huge environmental pollution globally. Around 40% global pollution in the form of greenhouse gas emissions is contributed by automobile industry and out of this, 20 to 30% by tire during its production and use. There is tremendous pressure on tire industry to use new materials that are more sustainable with respect to nature and performance.

Ups and downs in automotive industry affects the tire industry so balance between profitability and sustainability is very difficult task nowadays. However, researchers are working rapidly to use eco-friendly materials and develop technologies with lowest impact on environment. They are developing the green materials for small household item to high-end product[5]. Tire industry is encouraged to create sustainability culture to reduce carbon footprint or circular economy by replacing tire components for sustainable products and replacing mineral oil by natural oils in last few years[6]. Urge of carbon footprint reduction is leading researchers to use more natural and sustainable materials. This sustainable dimension is getting more attention because petroleum-based products are contributing to environmental issues such as global warming and pollution.

However, it is a quite challenging task to use sustainable materials in place of petroleum-based materials due to cost-performance compromise and lack of knowledge about structure property relationship for these materials. Few materials used by rubber industry are not sustainable like petroleum based raw materials. Carbon black is produced by incomplete combustion of petroleum feedstock and required very high energy for its production. So, carbon black manufacturing is not environmentally friendly as it increases greenhouse gas emissions responsible for climate change. More focus is given to compatible, lightweight, and environmentally sustainable filler nowadays due to improve sustainability of materials. Nanocellulose can be used as an alternate to carbon black filler due to huge availability of cellulose in nature, renewability, biodegradability, low density, non-toxicity, and high strength. Also, this filler will reduce greenhouse gas emissions and environment impact due to less energy consumption with respect to carbon black and silica[7].

Huge quantity of waste polymeric materials is used as landfills. Their decomposition rate is very slow, and they may emit toxic products. Decomposable materials should have good strength and stability during their service, and non-toxicity in raw materials and residue after decomposition. Biodegradable polymers degrade fully through micro-organisms present in soil within 6 months and form carbon dioxide, ammonia, methane and water[8].Trans-β-farnesene is produced through bio-based route by fermentation of sugar feedstock. It can be polymerized by both anionic and cationic routes. It has shown unique thermal and rheological properties[9]. Green tire development is key contributor in tire industry for sustainable development. This tire is produced using sustainable materials with low rolling resistance, improved wet grip and wear resistance performance. Compound annual growth rate (CAGR) is expected to be around 11% during 2021-27 for global green tire market and market value is expected to reach 175 billion USD[5].

Approx. seven gallons of oils are used in manufacturing of a tire. Out of these, five gallons are used for synthetic rubber production and two gallons are used for energy requirement. Also tire uses two pounds' petroleum oil as plasticizer. Hence, large amount of petroleum oil is used in tire industry. However, petroleum oil sources are going to be probably depleted by 22nd century[10]. In the quest to generate sustainability in operation, tire manufacturers and researchers across the globe are working for the suitable alternatives of fossil fuel-based products. Huge quantity of extender oil is used by the tire industry, so it is getting attention. Several large oil manufacturing companies (traditionally blenders of refinery products) have already jumped on the foray as the demand of some of the naturally occurring vegetable oils are increasing and this trend is going to continue. These vegetable oils are non-carcinogenic, better processing and are shown to improve tire performance properties like rolling resistance, traction and mileage in varied proportions as compared to mineral oil counterpart. Fig. 1.2.

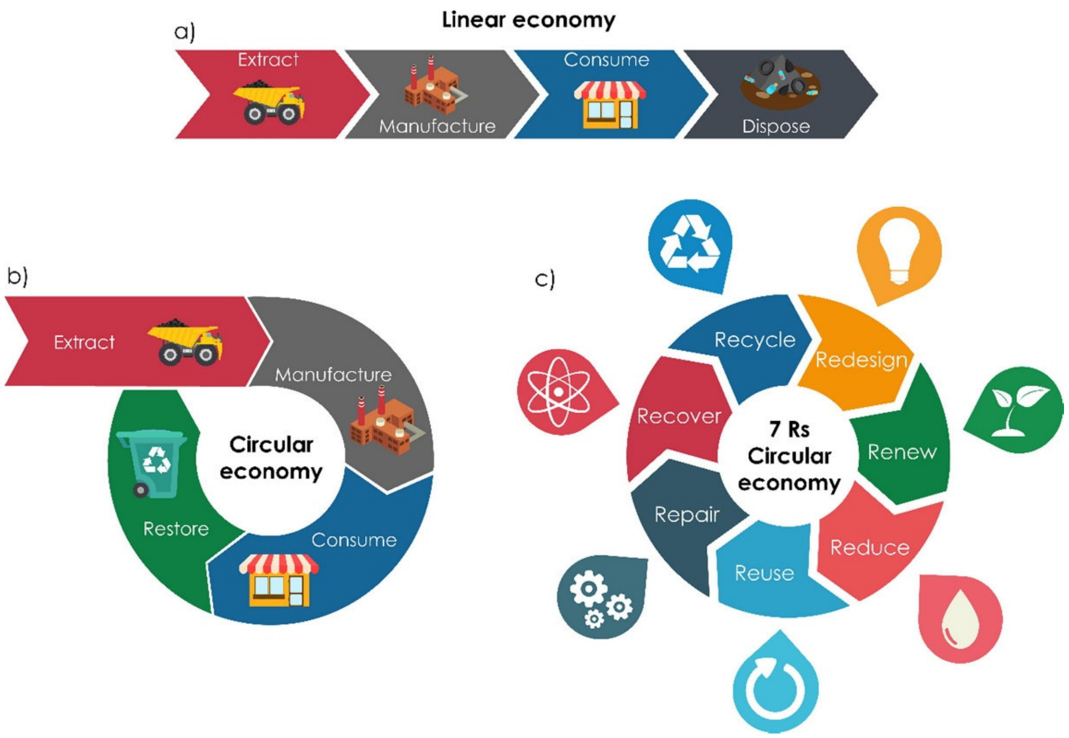

Fig. 1.2: (a) Linear economy model, (b) Circular economy model and (c) Circular economy model with 7R approach

(With permission from Araujo Morera et al., Waste Manage., 126, 309-322, 2021)

It shows linear economy model, circular economy model and circular economy models with 7R approach. The linear economy model was adopted since industrial revolution worldwide. Huge urban solid waste was generated following this model globally as this model suggested to dispose the product at the end of life. Due to this, new model was proposed as circular economy model, which replaces disposability with restoration. The new model starts with sustainable, recyclable, and renewable raw materials selection and will help in value repeatedly due to rational and efficient use. New model will enhance durability and improve tire performance with reduction in final disposal to nature. Carbon neutrality is planned by reducing raw materials consumption, reducing tire weight, increasing use of renewable resources, and increasing energy efficiency by various inventions. To achieve these targets taken by tire majors, upgraded version 7R (4R + Redesign, Repair and Recover) principles are very important now. The schematic diagram of sustainable life cycle of a tire is presented in Fig. 1.3.

Fig. 1.3: Sustainable life cycle of a tire

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Sustainable practices are required to follow starting from raw materials selection, production, use and waste product disposal without affecting environment[5]. Few advance tires in market as green tags are introduce like Tweel (by Michelin) and Airless (by Toyo and Bridgestone) to achieve sustainability and carbon neutrality targets[3,11.] Sumitomo Rubber Industries has launched Enasave 100 tire made from 100% fossil fuel free and all natural materials,[12]. Over 86% of environment impact occur for passenger car radial tire during its use due to rolling resistance. Tire accounts for 20% energy consumption for passenger car and 50% for electric car total vehicle energy consumption. Tread of passenger car radial tire contributes to 40-50% in rolling resistance. Rolling resistance for electric vehicle is reduced by increasing air pressure in tire, increasing diameter and reducing width, and reducing tread pattern width, etc.

In electric car, Governments of various countries are offering supports to electric vehicle manufacturer and users. It is expected that electric vehicle will share around 30%

of the total automobile sales globally. This will lead to take forward the tire industry in future[13]. The European tyre commission implemented the revised tire labeling regulations in line with sustainability from May 2021. Next innovation horizons will be difficult after further tightening of rolling resistance by 50% in 2024. Tire majors like Bridgestone, Goodyear and Michelin have committed to use 100% sustainable materials by 2050[14]. Tire materials compositions are given in Fig. 1.4.

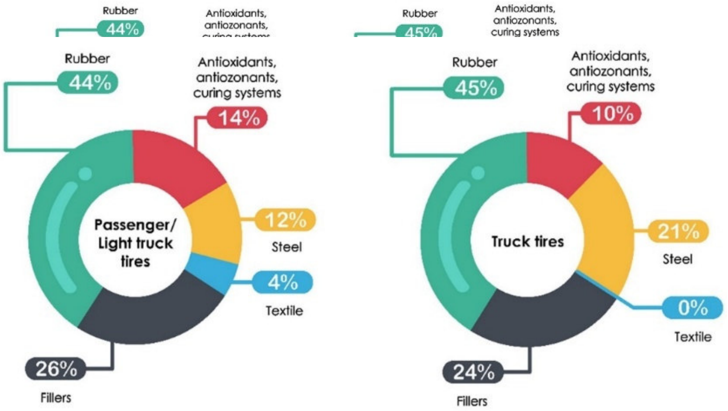

Fig. 1.4: Tire material compositions for passenger/light tires and truck tires

(With permission from Araujo Morera et al., Waste Manage., 126, 309-322, 2021)

For passenger/light tires and truck tires. Approx. 45% is rubber and 25% is filler usage for this kind of tires.

In line with various international environmental protection agreements and protocols to reduce greenhouse gas emission and carbon footprints, tire companies across the globe are putting up resolute efforts to use materials, which are environment friendly, renewable, and sustainable. Some of the set targets by the international tire majors are:

- Continental tire has committed to use 100% sustainably generated materials in their tire products by 2050 to achieve full carbon neutrality. Company is using renewable and recycled materials, developing light weight tire design, and switching to raw materials from sustainable sources for tire production to achieve this target. Continental has developed a tire with use of 17% recycled materials like reclaimed steel, recovered carbon black and polyester from recycled plastic bottles. Conventional passenger car tires (4) use 1.6 Kg of polyester yarn so approx. 60 recycled polyethylene terephthalate (PET) bottles can be reused[15].

- Bridgestone has taken a long-term environmental vision to use 100% sustainable materials by 2050 and beyond. The company will perform sustainability activity by reducing overall materials use in tire manufacturing through weight saving technology, process loss reduction and by using more recycled materials (Retread technology and regenerated carbon black) and new type of renewable materials (Alternate source of natural rubber like Guayule, Dandelion). Company will also reduce waste generation and recycling in their processes. Company has taken target of using 40% recycled and renewable materials by 2030. Currently they are using 37% of these materials[16].
- Michelin aims to use 80% sustainable materials and 100% recycling of used or waste tires by 2048. As per company, current tire recycling rate is 50% only. So, company is investing in advanced tire recycling technologies to increase the share of recycled materials in tire. Company is working to develop bio source materials like synthetic rubbers using wood, straw, etc. They are making micronized rubber powders from used or waste tires. which may reduce use of non-renewable materials in tire manufacturing. With these targets, company will save 33 million barrels of oil per year. Company is working on 4R approach (Reduce, Reuse, Recycle and Renew) to achieve its commitment towards circular economy[17]. Under BioButterfly project, company will produce butadiene from biomass like scrap wood, rice husk and corn stover. The objective is to manufacture butadiene using ethanol generated from biomass to replace petroleum generated butadiene. This may lead to consume 4.2 million tons of waste wood[18].
- Goodyear has already commercialized tire containing soybean oil. They used modified soybean oil as a processing oil for styrene-butadiene rubber tire tread compounds. This new processing oil has improved tire performances in different conditions like dry, wet, and winter. Also, this processing oil is derived from nature, cost-effective, carbon-neutral, and renewable. Company found that this process oil is mixed more easily in silica-based compounds and improved productivity and reduced mixing energy consumption. Company is also working

on use of sustainable materials like silica from rice husk ash, carbon fiber, volcanic sand, etc.[19]

- Pirelli has taken sustainability target to use more than 60% renewable, less than 30% fossil fuel-based and more than 7% recycled materials by 2030. Company has already started extensive use of rice husk-based silica in 2021 in selected categories, paper pulp-based lignin antioxidants in 2022 in selected car products and recovered carbon black obtained by pyrolysis of used tires in 2021 in limited applications[20].
- Yokohama has developed World's first technology to produce isoprene from biomass (Sugar), which is carbon neutral. This isoprene monomer is used for production of synthetic polyisoprene, which is used for tire and other rubber products manufacturing[21].
- Hankook Tire is listed in Dow Jones Sustainability Indices World (DJSI World) for 4th consecutive year. This was reported in Tire Technology International[22].
- CEAT has taken sustainability target to source 100% of agriculture raw materials by 2030. Company will use fossil free and reclaim rubber, reusable packaging materials and biodegradable stickers & labels on tires to achieve this target. Company is also working to reduce rolling resistance (improve fuel economy), enhance tire life (minimize tire scrap) and tire weight reduction (optimize resources)[23].

Sustainable circular economy idea has given lot of attention recently from environment, social and economic point of view. It properly utilizes green and renewable materials for various commercial applications, so it provides environmental and economic benefits to current and future generations. Researchers in the globe are forced to search more green materials for rubber products manufacturing due to increasing environmental consciousness. Hence, rising trend is observed for utilization of vegetable oils in rubber industry and it has become interesting approach for sustainability[24].

1.2 COMPATIBILITY

The compatibility of oil with elastomer matrix is the principal determining factor to be used as an extender. In this context, Hansen solubility parameter assumes importance. This parameter is based on like dissolves like theory. As per basic equation of Hansen solubility parameters, total cohesion energy between two molecules (E)is sum of the energies of non-polar (ED), molecular dipolar (EP) and hydrogen bonding (EH) interactions. This equation is:

$$E = ED + EP + EH \qquad \dots (1.1)$$

If one divides this equation by molar volume on both the sides, is obtained from equation square of Hildebrand solubility parameter:

$$\delta^2_T = \delta^2_D + \delta^2_P + \delta^2_H \qquad \dots (1.2)$$

where

δ_T = Total Hildebrand solubility parameter,

δ_D = Hansen dispersion component,

δ_P = Hansen polar component, and

δ_H = Hansen hydrogen bonding component

Hildebrand has measured the solubility parameter as the square root of cohesive energy density (CED). This is applicable for the system in which cohesive energy arises only from dispersion forces. Hansen solubility parameter can also be measured through intrinsic viscosity measurement. Inverse Gas Chromatography (GC) can be used to measure solubility parameter of various petroleum oils.

Rubber and rubber chemicals are having specific solubility parameter value, they are mixed together to achieve certain target properties because of proper miscibility. Hansen solubility parameter for vegetable oils helped to select suitable vegetable oil for rubber in more convenient and cost-effective way. Compatibility between rubber and vegetable oil can be calculated through the difference in solubility parameters of rubber and vegetable oil. Close solubility parameter for both these materials indicates better compatibility. Hansen solubility parameters of commonly used oils of mineral origin and selected vegetable origin and few elastomers are reported it Table 1.1[25-30].

Table 1.1: Solubility parameter (δ)

S. No.	Materials	Value
1	Styrene butadiene rubber	17.0 - 17.5
2	Aromatic. Il	18.0 - 20.0
3	TDAE oil	17.2 - 18.9
4	Paraffinic oil	13.0 - 16.0
5	Naphthenic oil	15.0 - 19.0
6	Palm oil	17.5 - 17.7
7	Coconut oil	14.9 - 16.7
8	Soybean oil	15.4 - 16.5
9	Castor oil	13.6 - 15.9
10	Peanut oil	15.3

Many naturally occurring raw materials like natural rubber, wood resin, natural fillers like silica, etc. are used by rubber product manufacturers as they are compatible with petroleum-based materials. Polar nature of fatty acid present in vegetable oil causes poor compatibility with general purpose no polar rubbers[31]. Increase in oil polarity strongly affect the rubber infiltration rate. Addition of oil affects the carbon black dispersion more in non-polar rubber with polar oil than polar rubber. This can be checked using electrical conductivity meter[32].

1.3 FREE OIL AS PROCESS AID

Organic compounds contain oils, fats, phosphor lipids, sulpho lipids, cyano lipids, etc. Oils and fats are obtained from plant and animals, respectively. Oils are liquid at room temperature whereas fats are solid or semisolid. Vegetable oils can be classified as fixed and essential oils. Essential oils are mixture of low molecular weight volatile organic compounds like alcohols, aldehydes, and ketones. Fixed oils are esters of long chain fatty acids with glycerol. If same fatty acids are present in glyceride, it is called simple triglyceride, otherwise it is called mixed triglyceride. Chemically, vegetable oils are mixture of mixed triglycerides. Molecular formula and structure of saturated and unsaturated fatty acids present in various vegetable oils are shown in Table 1.2 and 1.3 respectively.

Table 1.2: Saturated fatty acids present in various vegetable oils

S. No.	**Fatty acid type**	**Molecular formula**	**Structure**
1	Caproic acid	$C_6H_{12}O_2$	CH_3-$(CH_2)_4$-COOH
2	Caprilic acid	$C_8H_{16}O_2$	CH_3-$(CH_2)_6$-COOH
3	Capric acid	$C_{10}H_{20}O_2$	CH_3-$(CH_2)_8$-COOH
4	Lauric acid	$C_{12}H_{24}O_2$	CH_3-$(CH_2)_{10}$-COOH
5	Myristic acid	$C_{14}H_{28}O_2$	CH_3-$(CH_2)_{12}$-COOH
6	Palmitic acid	$C_{16}H_{32}O_2$	CH_3-$(CH_2)_{14}$-COOH
7	Stearic acid	$C_{18}H_{36}O_2$	CH_3-$(CH_2)_{16}$-COOH
8	Arachidic acid	$C_{20}H_{40}O_2$	CH_3-$(CH_2)_{18}$-COOH
9	Behenic acid	$C_{22}H_{44}O_2$	CH_3-$(CH_2)_{20}$-COOH

Table 1.3: Unsaturated fatty acids present in various vegetable oils

S. No.	**Fatty acid type**	**Molecular formula**	**Structure**
1	Oleic acid	$C_{18}H_{34}O_2$	CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOH
2	Linoleic acid	$C_{18}H_{32}O_2$	CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH
3	Linolenic acid	$C_{18}H_{30}O_2$	CH_3CH_2CH=$CHCH_2CH$=$CHCH_2CH$=CH-$(CH_2)_7$-COOH
4	Palmitoleic acid	$C_{16}H_{30}O_2$	$CH_3(CH_2)_5$-CH=CH-$(CH_2)_7$-COOH

Few fatty acid chemical structures for vegetable oils are shown in Fig. 1.5.

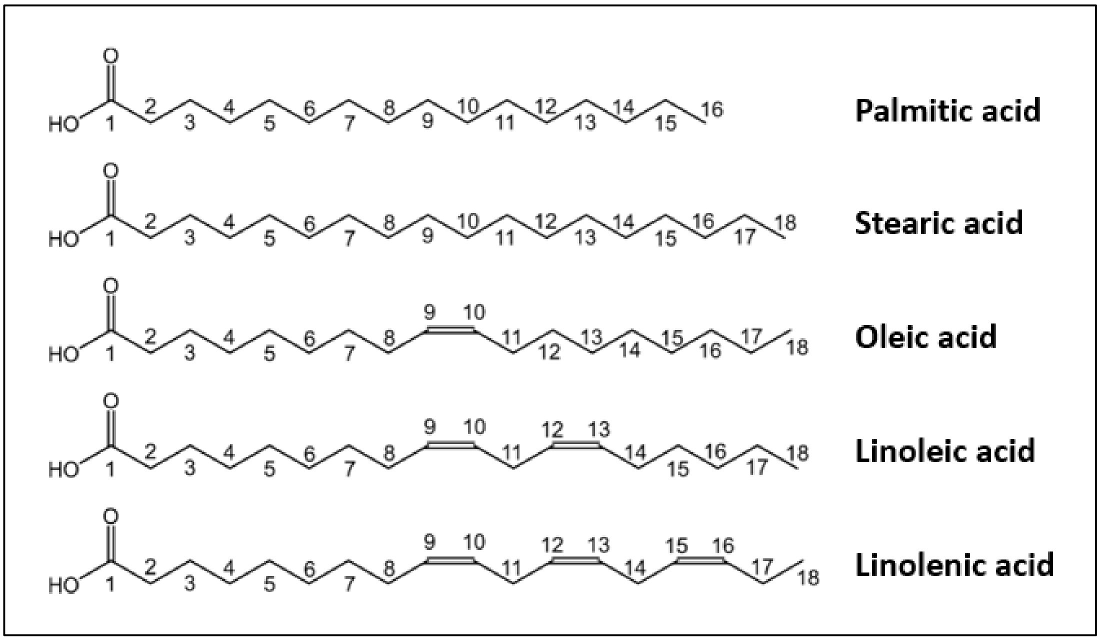

Fig. 1.5: Fatty acids chemical structures of vegetable oils

(With permission from M. E. D. Pietro, A. Mannu and, A. Mele, Processes, 8, 410, 2020)

All vegetable oils contain C_{18} saturated and unsaturated acids. Coconut and palm oil have lauric, myristic and palmitic acids[33].

Oil is a viscous organic liquid, and it is available as fatty, mineral and silicone based on their chemical composition. As per ASTM D1566, process oil is "Hydrocarbon oil derived from petroleum or other sources, used as an extender or process aid". Rubber plasticizers also known as rubber process oil are used in rubber compounds for many years. Process oils or aids are used in rubber formulation due to high viscosity of rubber compounds. They lower the processing temperature and increase the flow properties. They act on rubber by swelling effect. They improve flexibility and processability of rubber compounds by penetrating polymer matrix and establishing polar attractive forces between their chain segments. They also increase softness, elongation and low temperature flexibility, decease glass transition temperature (Tg), and compound cost. Primary plasticizers assist Brownian motion of polymer chains and reduce the compound viscosity. They can be used in large quantity. Secondary plasticizers act as lubricants between polymer chains and improve the compound flow. They cannot be used in large quantity. Solubility parameter is very important for primary plasticizers as they solubilize the rubber[34].

Rubber is very important materials, which is required for of manufacturing everyday use products. However, it cannot be used alone due to many limitations, so it is reinforced by various fillers like carbon black and silica. Fillers provide strength and stiffness to the rubber compounds. However, excellent interaction between rubber and filler is required to achieve the target properties. Carbon black is used as important filler in rubber industry due to its unique nature of reinforcement in rubber compound as compared to other fillers. This is due to presence of active polar groups like phenol, carboxyl, quinone, and lactone. Carbon has more interaction with polar rubber than hydrocarbon rubbers due to presence of these polar groups. For hydrocarbon rubbers like natural rubber (NR, SBR and PBR, carbon interact through double bond of rubbers main chain. Vegetable oil can act as coupling agent between general purpose rubber and carbon black. Due to colloidal properties of carbon black like high surface activity and high structure formation, rubber compound mixing process is very difficult. Process aids or oils help in improving interaction between rubber and carbon black and carbon black dispersion by increasing the compatibility between them. Plasticizers also help in addressing dispersion related issue faced for few rubber ingredients. They should not affect the mechanical or dynamic mechanical properties of the rubber vulcanizate.

Process aids are required in rubber compounding due to following reasons:

- To assist mechanical breakdown of rubber compounds,
- Reduce uncured compound viscosity,
- Permit incorporation of fillers,
- Reduce internal friction and improves flow of rubber compounds in mixing, calendaring and extrusion,
- Saves energy during processing of rubber, and
- Reduce durometer or modulus.

Processing aid enhances interaction between rubber filler by boosting their compatibly. They can be divided in different categories as:

- **Hydrocarbons:** Improve filler incorporation, filler dispersion and compound flow. Examples are petroleum oil and resins and waxes.
- **Fatty acid derivatives:** Improve filler incorporation, filler dispersion, compound homogenization, compound flow and compound release properties. Examples are fatty acids, fatty acid esters, fatty alcohols, metal soap and fatty acid amides.
- **Synthetics resin:** Improve tack. Examples are phenolic resins.
- **Low molecular weight polymers:** Improve filler incorporation, filler dispersion and compound flow properties. Examples are liquid rubbers and norbornene.
- **Organo-thiocompounds:** Peptizing and reclaiming agents to reduce rubber Mooney viscosity and compound cost.

Processing aids provide easy processing during mixing, milling, extrusion and calendaring by providing lubrication between rubber molecules. Rubber industries also use various types of petroleum oils extended synthetic rubber, where a higher dosage of process oil addition is not possible practically as it leads to slippage during mixing. The oil must have a certain degree of miscibility for the rubber. For a rubber containing a significant proportion of aromatic groups, such as SBR, a highly aromatic oil is usually employed. polycyclic aromatic hydrocarbon are organic compounds having two or more fused aromatic rings. They react with atmospheric ozone, nitrogen oxide and sulfur dioxide and generate carcinogenic components like diones, nitro & dinitro PAH and sulfonic acid, respectively. As per International Agency for Research in Cancer (IARC), number of PAH compounds are carcinogenic to human health including lung cancer. In 1994, KEMI report discussed the presence of polycyclic aromatic hydrocarbon content in petroleum oils. Commercially available OE-SBR's with highly aromatic oil contains about 70-85 weight percent total aromatics and 10-15 weight percent (Polyaromatic hydrocarbon)/ (Polycyclic aromatics).

Aromatic oil has good compatibility with commonly used natural and synthetic rubbers like SBR and polybutadiene rubber, however, they are toxic and carcinogenic due to high PCA content. According to REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) legislation (European Union regulation 1907/2006), an oil containing less than 3% by weight of PCAs (measured by IP-346) is suitable as extenders for rubber compounds. In 2010, BLIC workgroup has proposed Mild Extraction Solvate (MES), Treated Distillate Aromatic Extract (TDAE) and naphthenic oil as an alternative with low PAH content[27,36,37]. Petroleum oils are having long chain hydrocarbon, which are harmful to the environment. Use of process oil containing PAHs like benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbFA), benzo(j)fluoranthene (BjFA), benzo(k)fluoranthene (BkFA), and dibenzo(a, h)anthracene (DBAhA) were restricted by Commission Regulation (EC) No. 552/2009[38,39].

1.3.1 Petroleum Oil as Extender (Free)

Petroleum based plasticizers are made from crude petroleum and they are effective, controlled quality, low cost and easy to use in rubber processing. They are used for general purpose rubbers like NR, SBR and PBR. These plasticizers can be classified as aromatic, naphthenic and paraffinic oils. This classification is based on carbon structure present in these oils like aromatic, naphthenic and paraffinic carbon. Table 1.4

Table 1.4: Carbon structure of various petroleum oils

S. No.	Type	C_A (%)	C_N (%)	C_P (%)
1	Aromatic oil	35-50	20-40	20-35
2	Naphthenic oil	10-30	30-45	35-45
3	Paraffinic oil	0-10	20-35	60-75

C_A:- Aromatic content, C_N:- Naphthenic content, C_P:- Paraffinic content

The carbon structure of various petroleum oils are presented in. Excessive oil or wrong selection of process oil may lead to blooming issues, which may result in poor mechanical properties and mold fouling problems[40,41]. Tire compound contains 40 to 60% rubber (NR or SR), 20 to 35% filler (Carbon black or silica) and 15 to 20% mineral oil (extender oils or process aids). Petroleum oils release aromatic hydrocarbons during automobile tire production, use and recycling and it can cause some adverse effects on human health and environment. Petroleum oils contains high proportion of polycyclic aromatic (PCA) molecules, which are carcinogenic in nature and are not considered environment friendly. Tire particles are generated and distributed in the environment on its use, so awareness is required about its effect on human health and our environment.

Big particles are deposited on the road itself, however, wind may transport these particles to other areas. Sources of environmental pollution by PAH throughout their lifecycle are waste tires stock, pyrolysis of waste tires and recycled tire materials[42]. SBR extended with high aromatic oils (due to lower price) exhibit poor tire rolling resistance (RR) as glass transition temperature (T_g) is higher. On the other hand, number of properties such as abrasion resistance (AR) and RR have been improved by using non-carcinogenic low aromatic oils like mild and high viscosity naphthenic oils, Treated Distillate Aromatic Extract (TDAE) and Mildly Extracted Solvate (MES). This study was performed in low and high oil extended tire formulations. TDAE and MES was found to be more compatible with general purpose rubbers[43]. SBR compatible eco-oils with negligible quantity of aromatic compounds would provide good AR and RR properties in tires.

Refractive index is the ratio of velocity of the light in vacuum to medium[44]. It is more than one for fluid materials. It is used to measure thermophysical properties of petroleum fluids. It also helps in estimation of presence of aromatic content in petroleum oils. Higher refractive index means more aromatic content in oil samples.

1.3.2 Vegetable Oils as Extender (Free)

Many factors are considered while choosing a process oil by rubber industry like price, production capacity, compatibility with rubber, and chemical reactivity. In tire industry, vegetable oils were incorporated in formulations due to high content of toxic content in petroleum derived oils. Investigation on vegetable oils were started in 2008, due to their low PAH content. Vegetable oils could be an alternate to process oils commercially available as mineral oils. These oils are sustainable, environmentally friendly, and non-toxic raw materials. Vegetable oils are extracted from various types of fruits, seeds, grains, and nuts. They are liquid at room temperature. The raw vegetable oil undergoes a refining process to remove the impurities, which affect the color and smell.

Vegetable oil production has increased globally, and it has reached to around 200 million metric tons for 10 major vegetable oils. These oils are soybean, palm, sunflower, rapeseed, palm kernel, peanut, coconut, cottonseed, and olive oils. However, soybean, palm and rapeseed are oils produced at large scale worldwide and have less price as compared to other oils due to their commercial applications. It is used in some large-scale industries like soaps, lubricants, biofuels, paints, etc. Crude vegetable oil contains around 95% triacyl glycerides along with free fatty acids, monoacylglycerides and diacylglycerides[45]. Vegetable oils contain unsaturated fatty acids, which may affect the cure characteristics and mechanical properties of filled compounds as these free acids took part in vulcanization.

Most of the vegetable origin oils are rich in oleic and linoleic acids, such as sesame, rapeseed, sunflower, soybean and peanut oils. Linseed oil is most unsaturated vegetable oil with presence of oleic, linoleic, and linolenic acids. Coconut oil is most saturated vegetable oil, which contains very less oleic and linoleic acids. It contains mainly palmitic, stearic, lauric and myristic acids. Palm oil has both saturated and unsaturated carbon chains due to presence of palmitic acid and oleic acid. The fatty acid composition for various vegetable origin oils are summarized in Table 1.5.

Table 1.5: Fatty acid composition (%) for various vegetable oils

Oil source	**Palmatic acid (16:0)**	**Stearic acid (18:0)**	**Oleic acid (18:1)**	**Linoleic acid (18:2)**	**Linolenic acid (18:3)**	**Unsaturation / Saturation ratio**
Number of unsaturated bonds	**0**	**0**	**1**	**2**	**3**	
Castor*	2.6	1.5	4.7	8.4	--	23.2
Palmolein**	37.0-42.4	3.0-6.0	40.0-45.0	8.0-11.3	--	1.2
Groundnut	7.5-11.0	2.0-3.0	48.0-71.1	18.2-40.0	--	7.5
Soybean	6.0-12.0	3.0-5.2	20.2-27.3	48.5-63.7	5.0-8.2	6.2
Mustard	9.6-9.7	5.9-6.5	40.8-41.5	40.9-40.9	--	5.2
Coconut***	0.0-11.0	1.0-3.0	5.0-8.0	0.0-1.6	--	0.1
Sunflower	6.1-7.0	1.9-5.3	18.7-28.0	62.2-68.6	0.2-1.9	11.0

Cottonseed	18.0-26.0	2.0-5.0	15.0-41.0	38.0-58.0	0.0-1.0	2.9
Linseed	4.0-5.0	2.0-4.0	19.1-22.0	12.0-18.0	52.0-56.6	12.0
Rubberseed	7.9-9.3	8.4-9.0	25.4-28.9	40.5-41.1	13.5-15.3	4.8

Castor* has 82.8% ricinoleicacid(18:1:OH)

Palmolein** has 1% myristic acid (14:0)

Coconut*** has 13.0-19.9% myristic acid (14:0), 8.1% caprylic acid (8:0), 5.5% Capric acid (10:0) and 44.0-52.0% lauric acid (12:0)

Ratio of unsaturated to saturated acid content is very high for castor oil and it is very low for coconut oil. Palm oil has this ratio slightly higher with respect to coconut oil. Groundnut, soybean and mustard oils have the moderate ratio[46-52].

Dasgupta et al.[35,53-55] have evaluated 10 vegetable and 6 petroleum-based oils in various tire rubber compounds. They have used formulations like 100% NR based bias truck tire tread cap, NR/PBR blend based bias truck tire tread cap, NR/PBR blend based rib truck tire tread cap, solution system /NR/PBR blend based passenger car radial tire tread cap and 100% SBR based tire tread compounds. They found few vegetable oils are showing better processing, polymer-filler interaction, filler dispersion, mechanical, fatigue and tire performance properties like mileage, etc.

Few researchers have also worked on using palm oil, soybean oil and sunflower oil as alternative processing aid in place of aromatic oil in carbon black-filled natural rubber (NR) based recipe. They found that vegetable oils can be used as processing aid and activator without adversely affecting vulcanizate properties. Palm oil has shown best heat resistance ability. Soybean oil can be used as so-activator based on its cure characteristics and mechanical properties[56]. Compounds prepared with vegetable oil and vulcanized vegetable oil displayed improvement in flow behavior, plasticization action, low temperature flexibility and ozone resistance. Linseed and peanut oils can replace stearic acid activator in accelerated sulfur vulcanization system[57].

Mohamed et al.[58] has we used sunflower and soybean oil as an alternate processing oil for greener tire tread compound development in NR/PBR/SSBR based recipe. Comparable cure time and rheometric torque were observed for all compounds. Vegetable oils have shown better processing safety measured through scorch safety time and lower crosslink density than mineral oil. Soybean oil has shown better tear strength and fuel saving, whereas sunflower oil has shown better tensile strength and abrasion resistance. Dynamic mechanical properties were found to be comparable for all compounds. sunflower and soybean crude vegetable oils were analysed in SBR based compounds with respect to high aromatic oil. Improvement in processability, fatigue life and compatibility with slight reduction in rolling resistance was observed for vegetable oils[59].

Goodyear tire has produced the tire with use of soybean oil in place of conventional petroleum oil in tread compound. It reduced the petroleum oil by 60% in overall tire[60]. Goodyear tire has increased the soybean oil consumption to 73% in 2020 with respect to 2019. Company has replaced petroleum derived oils with soybean oil. With use of soybean oil, rubber compound is pliable in changing temperatures. Company has commercialized this technology in 2017's Assurance Weather Ready consumer tire line, the Eagle Enforcer all weather in 2018, the Eagle Exhilarate in 2019 and the Assurance Comfort Drive in 2020. Goodyear will replace all petroleum oils with vegetable oils by 2040[61]. Tea oil, palm oil and coconut oil were investigated in silica-filled NR based compound with respect to heavy and light naphthenic oils. Vegetable oil-based compounds have shown higher thermal stability, greater mixing efficiency, improved silica dispersion and greater plasticization effects[62].

Abbas and Ong[63] have checked effect of crude palm oil as replacement of naphthenic oil in the natural rubber (Standard Malaysian Rubber, SMR20) based recipe. Due to presence of unsaturated fatty acids in crude palm oil, plasticization effect was seen as reduction of minimum and maximum torque of rubber compound. It also resulted in higher curing time, lower tensile strength, and elongation at break. However, improvement in tear strength was observed for experimental compound. Comparative study of mechanical and thermal degradation characteristics was done to check the effect of coconut and castor oil with respect to naphthenic oil in NR based compound. Marginal reduction in cure time, improvement in tensile strength, tear strength, resilience and abrasion were observed for coconut oil-based compound. Crosslink density was found comparable and degradation temperature was slightly increased (better thermal stability). Optimum loading of coconut oil was found between 4 to 8 parts per hundred rubbers (phr) range. Marginal reduction in cure time (may be due to presence of fatty acids), improvement in tear strength and modulus were observed for castor oil-based compound. Other mechanical properties were found comparable and degradation temperature was slightly increased (better thermal stability). Optimum loading of castor oil was found between 2 to 4 phr range[64,65].

Castor and other vegetable oils like Cashew Nutshell Liquid (CNSL), etc. were evaluated against naphthenic oil in carbon black filled NR/PBR blend based recipe. Effect of vegetable oils was studied for physical, mechanical, and adhesion properties. All the vegetable oils have shown improvement in tensile strength, modulus, elongation at break, hardness, abrasion, tear, and adhesion strength as compared to paraffinic oil. Unsaturated oils have improved mechanical and physical properties as compared to saturated oils[66]. Agro-byproduct cashew nutshell liquid has cardanol (m-pentadecenyl phenol) as main ingredient. Cardanol is obtained by distillation of cashew nutshell liquid. It is low cost and easily available in quantity it was evaluated against aromatic oil in High Abrasion Furnace (HAF) filled NR based recipe. mechanical properties, ageing study and rheometric study was done for these compounds. Cardanol based compound has shown improvement in tensile strength, shorten cure time and superior ageing properties as compared to aromatic oil[67].

Rubber seed oil was evaluated in NR and SBR based compounds. It has displayed multifunctional properties like improvement in mechanical properties, ageing resistance, abrasion resistance and Demattia flex properties as compared to aromatic oil. A 5 to 7 phr of rubberseed oil can be used to replace 6 phr of aromatic oil and 2 phr of stearic acid[31]. Use of rubberseed oil in SBR compounds showed improvement in mechanical properties[33]. Comparable rheological and physical properties were observed for moringa and niger oils with respect to naphthenic oil based natural rubber-silica compound and have also exhibited better filler dispersion and rolling resistance. These vegetable oils have shown better plasticization effect[40]. Niger and moringa oil in silica filled NR based compounds can replace naphthenic oil. Similarly, linseed oil can be used as green plasticizer in nano calcium carbonate filled NR compound[24]. Mechanism of possible chemical interaction between ester groups of vegetable oil and silanol group of silica filler is given in Fig. 1.6[24,40].

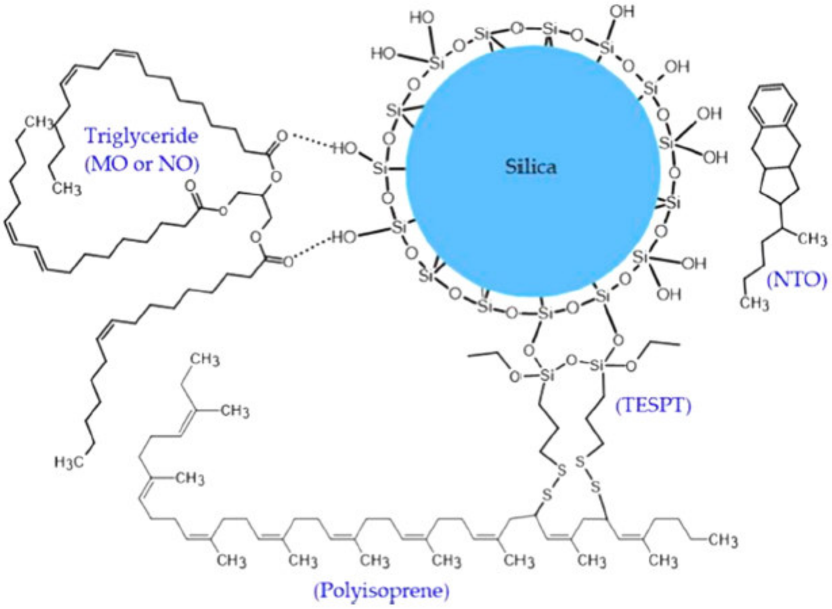

Fig. 1.6: Possible chemical interaction between ester groups of Niger oil (NO) and moringa oil (MO) and silanol groups of silica filler

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This interaction may lead to satisfactory dispersion of silica filler in NR matrix. This may further help in rolling resistance reduction for tires as compared to petroleum-based oils[24]. Moringa oleifera, gum of drumstick tree, was evaluated in SBR compound. It has shown improvement in cure rate, tack strength, and improved processing as compared to phenol formaldehyde resin[68].

Vegetable origin oils may be used as renewable resource raw materials for monomers and polymers synthesis. Variety of monomers and polymers like polyolefins, polyesters, polyethers, polyamides, epoxy and polyurethane resins can be synthesized using vegetable oils. These monomers and polymers have many industrial applications too[1].

1.3.3 Modified Vegetable Oils as Extender (Free)

Rubber industry has used vegetable origin oils for many applications like tires, automotive components, and other industrial products due to their renewable and environmentally friendly nature. They affect the properties of compounds due to their reactivity, viscosity, and glass transition temperature. They contain many functional groups so it can be treated, modified, and polymerized based on requirements. Oleic, linoleic and linolenic groups present in double bond of vegetable oils can be converted into reactive oxirane moiety through peracids or peroxides reaction. Various techniques are available to modify vegetable oils to achieve desired functionality and properties. These techniques include blending, fractionation, hydrogenation, chemical catalyzed transesterification, enzyme catalyzed transesterification, etc. Such techniques for vegetable oil modification are developed to get perfect bio-degradable oil to meet environment sustainability[41,46,48].

Transesterification modified soybean oil-based compound is prepared with use of benzyl alcohol. This materials has shown additional absorption peaks at 3020 cm^{-1} and 750 cm^{-1} due to –CH stretching vibration and C–H out-of-plane bending of aromatic. This is confirmed by NMR study also as signal of proton in aromatic ring at 7.40–7.55 ppm confirmed the presence of aromatic ring. New developed process aid was evaluated in SBR/PBR based tread compound recipe, while have comparable mechanical properties with better wet grip and lower heat buildup as compared to mineral oils like aromatic and TDAE[69]. Benzyl esters were synthesized using coconut, palm, and soybean oils by hydrolysis of vegetable oils, followed by esterification with benzyl alcohol in presence of sulfuric acid. These process aids were compared with respect to aromatic oil in natural rubber-based compound. Palm oil-based plasticizer has shown better mechanical properties with comparable mixing energy and dynamic mechanical properties[70]. Edible or non-edible oils were epoxidized to get sustainable oil as it represents a green pathway for environmentally friendly replacement for petroleum oil. It has increased the green content in rubber compound and contributed to green tire manufacturing. Experimental compound has shown improvement in tearing energy[71].

Double bonds present in soybean oil can react with active site of rubber molecular chains during the vulcanization, which makes it reactive plasticizer. This double bond was converted to norbornyl group in different ratios by reaction with dicyclopentadiene (DCP). The modified soybean oil was evaluated in carbon black filled NR based recipe with respect to untreated soybean and naphthenic oils. Gel fraction was increased, but crosslink density and bound rubber decreased for SBR/modified soybean oil vulcanizate with increased modification level. Vegetable oil-based compounds have shown lower glass transition temperature and better thermal stability as compared to naphthenic oil.

Modification has led to faster curing characteristics of rubber compound. So, vulcanizate has shown lower modulus and higher elongation at break in comparison to naphthenic oil. Dynamic mechanical properties indicated the improvement in traction with increase in rolling resistance for modified soybean oil. Low level modification with adjustment in cure dosage has shown improvement in modulus, ensile strength and abrasion properties as compared to naphthenic oil[10].

Soybean oil was modified using sulfur to reduce double bond quantity in this oil. This was done to reduce negative effect of double bonds on crosslink density and mechanical properties. Tire tread compound durability was improved with use of modified soybean oil to great extent. Modified soybean oil prepared with 6% sulfur content has exhibited the best processing properties. It has also shown comparable Mooney viscosity, Payne effect and mechanical properties with respect to aromatic oil. Ageing resistance and wear resistance were found to be better for experimental compounds[72]. Diene-modified soybean oil was evaluated in SBR-carbon black filled recipe and it not only improved wet traction but also increased rolling resistance[41]. Use of soybean oil as a replacement of petroleum oil resulted in reduction in properties. So, derivatization of high molecular weight soybean oil was investigated in carbon black filled SBR based recipe. Modified soybean has improved the mechanical properties. This was due to higher crosslink density because of higher unsaturation per molecule. Experimental compounds have also shown lower rolling resistance as compared to soybean oil[73].

Process oil type affect the NR properties significantly. Various dosage of modified soybean oil were investigated in NR silica-based recipe and properties were compared with naphthenic oil-based compound. It was found to have lower reversion, which may be due to higher thermal stability for soybean oil-based compound. Soybean oil also affect the silica dispersion level as found in Atomic Force Microscopy (AFM) study[74]. Soybean and modified soybean oils were evaluated in carbon black and silica-filled SBR-based recipe with respect to naphthenic oil. Vegetable oil-based compounds have lower crosslink density and improved thermal stability. With small adjustment in recipe, modified soybean oil-based compound has better wet traction, lower rolling resistance and better abrasion for both silica and carbon black-filled recipe as compared to naphthenic oil.[75].

Modified soybean oil was compared against treated residual aromatic extract (TRAE) oil in NR/SSBR/PBR based passenger car radial tread compound and NR/PBR based tire sidewall compound. This study was performed to promote green mobility due to price fluctuation and health issues on using petroleum oils. Comparable filler dispersion, physical properties and abrasion resistance were found for all the compounds[4]. Soybean oil was investigated in NR based tread compound recipe in their natural state and chemically modified from by epoxy ring introduction. Vegetable oil was used in place of aromatic oil and stearic acid. Rheological properties, crosslinking degree and mechanical properties were found to be comparable with respect to aromatic oil. Epoxidized soybean oil-based compound has better filler dispersion and deterioration in mechanical properties[76].

Vegetable oils were epoxidized by in formation using peracetic acid technique. Epoxidation was confirmed by NMR studies. Natural rubber-based compounds prepared with epoxidized palm, sunflower and soybean oils displayed better processing properties with respect to polymer-filler interactions and carbon black dispersions as compared to aromatic process aid and activators. Experimental compound has best heat stability. Epoxidized sunflower oil can be used as an accelerator, when used with sulfenamide accelerator to improve reversion. Epoxidized palm oil can be used as activator in rubber compound as it improved cure characteristics and physical properties[77]. Palm oil can be epoxidized using performic acid also to achieve more than 85% of epoxidized palm oil[78]. Flanigan et al.[79] have evaluated low saturated soybean oil (in 10 phr level) with respect to Treated Distillate Aromatic Extract (TDAE) oil in 80/20 SSBR/NR based tire compound recipe. Vegetable oil-based compounds exhibited good tire performance in wet and winter condition with slight deterioration in rolling resistance. They have also noticed well balanced properties with use of palm oil with inferior dry handling.

Carbon black filled NR/SBR based compounds are very important combination for production of high-performance tires. Epoxidized palm oil could be used an alternate to aromatic oil and polymerized soybean oil could replace naphthenic oil in carbon-filled NR/SBR based compound. Silica is used in green tire due to fuel saving because of lower rolling resistance[24]. Polymerized soybean oils of different molecular weights are synthesized by cationic polymerization technique. Due to presence of double bond in vegetable oils, they depressants viscosity and take part in curing reaction. Polymerized soybean oil has provided better thermal stability without affecting much mechanical and dynamic mechanical properties in NR/SBR based compound with respect to petroleum oils. This is due to better compatibility of this oil with NR and SBR. These modified soybean oils were used in EPDM based recipe as compared to paraffinic oil. They have good compatibility with EPDM rubber but decreased the crosslink density due to presence of double bonds. As a result, mechanical properties dropped[34,80].

Soybean oil can be replaced partially or completely from naphthenic oil in rubber compounds. Polymerized soybean oil can be used as plasticizer for natural rubber/styrene butadiene rubber-based compounds without affecting much mechanical and dynamic mechanical properties[81]. Many researchers[4,34,72,82-84] have worked with use of vegetable origin oils in compound after various modifications. Castor, palm, and fried palm oils were evaluated in 90/10 NR/SBR blend and carbon black based solid tire compound with respect to petroleum oils like white oil and minarax oil. Comparable tensile strength, modulus, density, abrasion, compression set, and ozone resistance were observed for compounds prepared with petroleum and vegetable oils. These vegetable oils are potential alternative plasticizers to naphthenic/petroleum-based oils[82].

Various general-purpose rubber-based compounds prepared with epoxidized palm oil have comparable rheological and mechanical properties and better abrasion resistance with respect to DAE oil due to improved filler dispersion and polymer filler interaction[83,84]. Silica-filled natural rubber-based compounds prepared with epoxidized and amine modified epoxidized palm oil have less filler-filler interaction with respect to TDAE oil. Amine modified epoxidized palm oil-based compound exhibited higher crosslink density, better mechanical properties and lower tan δ @60°C. Increase in epoxide content resulted in improvement in cure rate, tensile properties and tan δ @60°C[85,86].

Song[87] has evaluated palm-based hybrid oil in comparison to palm oil in rubber compound with respect to physical and chemical properties. Hybrid oils were prepared by using methyl ester, palm monoglyceride and dammar with pam oil. Hybrid oil-based compounds improved mechanical properties like tensile strength, elongation at break, modulus and toughness, which may be due to better filler dispersion. Experimental compounds have outstanding improvement in heat build-up, abrasion and rebound properties. Purified palm oil and NR were used in recipe to develop earth-friendly tire in place of SBR and petroleum oil. Minimum 75% by weight based on total tire weight was taken for non-petroleum-based materials. High speed durability, rolling resistance coefficient, breaking test, and evaluation test on real automobile like grip, rigidity and riding comfort characteristics were performed. Eco tire has met all the performance requirements[88].

Nynas has developed, Nytex Bio 6200, a bio-based tire oil. Tires (205/55 R16) were made using bio-based and TDAE oil for comparative study. Both tires have comparable wet grip index, rolling resistance coefficient, snow breaking distance, and ice breaking distance. This indicates that bio-based plasticizer can be used in tire without compromising the tire performances[89]. Epoxidized jatropha oil was evaluated as plasticizer in poly(lactic acid) with different dosage level. It improved the flexibility and elongation at break of the compound. This also improved the heat stability of the compound[90]. Two modified bio-based plasticizers epoxidized esters of glycerol formal from soybean and canola oils were evaluated with respect to treated distillate aromatic extract (TDAE) oil in acrylonitrile butadiene rubber (NBR) based compounds to address health risk issue due to use of conventional additives. Bio-based plasticizers displayed improvement in mechanical and thermal properties[91]. Soybean oil was co-vulcanized with bis-(3-(triethoxysilyl)-propyl) tetrasulfide (TESPT) using sulfur accelerator curing system to synthesize silanized plasticizer. It improved filler dispersion in styrene butadiene rubber (SBR)/silica-based compound. As a result, it also improved tensile strength, modulus and hardness[92]. Modified soybean based plasticiser can replace petroleum based plasticisers in EPDM compounds with minimal impact on properties. These plasticisers increase the crosslink density[93]. Carbon–carbon double bond modification in bio-based oils can improve both the processability and mechanical properties of rubber composites[94].

In future, vegetable oil plasticizers may lead advancement in filled rubber compounds in more sustainable manner. However, there will be some basic challenges for commercialization in industrial products, which needs to overcome such as[24]:

- Attention to important fillers other than carbon black like silica and calcium carbonate.

- Alternate vegetable oil source to be identified with lower price to control overall compound cost. This is required to compete with low cost petroleum oils.
- Performance of vegetable oils are deteriorating at high loading due to reaction between their double bond and vulcanizing agents. So, more research is required to overcome this issue like vegetable oils modifications, etc.
- Vegetable oils are tested at lab scale only. So, commercialization at production/manufacturing level is required to validate the findings.

1.4 RUBBERS

Rubbers can be classified as general purpose and special purpose rubber based on their application. Natural rubber, styrene butadiene rubber, and polybutadiene rubber are classified as general-purpose rubber as these rubbers have fast cure rate with low-cost vulcanizing agent and their vulcanizates have good wear and tear properties. However, due to unsaturation, they have poor resistance to oxidation, heat, and ozone. Also, they have poor resistance to swelling due to their non-polar nature. Special purpose rubbers have specific properties like Isoprene isobutylene rubber (IIR) has low air and gas permeability, Ethylene propylene diene rubber (EPDM) has good weather resistance and set property, Acrylonitrile butadiene rubber (NBR) has oil resistance, Chloroprene rubber (CR) has fire resistance, Silicone rubber (Q) has good biocompatibility and low temperature flexibility, Fluoro elastomer (FKM) has very high heat and oil resistance, and so on. These rubbers are costly as compared to general purpose rubbers.

Environmentally friendly polymers are manufactured using raw materials from renewable resources like corn, etc. They are either biodegradable or bio-based polymers. Due to dependency of polymers on fossil fuel and sustainability issue, these polymers are area of currently research. Their lifecycle reduces the carbon dioxide emissions and human carbon footprint on the environment. Biopolymer is important materials to address sustainability problem however, it showed deterioration in properties, which can be improved using reinforcing filler like lignocellulosic[95,96].

1.5 OIL EXTENDED RUBBERS

Around 25 to 50% petroleum oil emulsions are incorporated in latex as process aid. These oils increase low temperature flexibility and resilience of the rubber. It also reduces the cost of rubber due to low price of petroleum oils. Oil extended rubbers show improvement in processing with almost similar mechanical properties as compared to dry mixing of rubber and oil. Considering the green chemistry movement, vegetable oils can be used for extension of these rubbers[97]. Rubber industries also use various types of petroleum oils extended synthetic rubber, where a higher dosage of process oil addition is not possible practically as it leads to slippage during mixing. Natural rubber or high molecular weight synthetic rubbers are generally extended with oil. The purpose behind oil extension of a high molecular weight synthetic elastomer is to improve quality of compound mixing and subsequent processing with existing rubber processing equipment like extruder/calendar etc., in addition to improved life and product performance.

Petroleum oils like distillate aromatic extract (DAE), residual aromatic extract (RAE), treated distillate aromatic extract (TDAE), naphthenic oil, etc. are generally used for extension of synthetic rubber with typically 37.5 phr level. The SBR is a popular choice for oil extension as its latex is produced with higher molecular weight polymer chains (approx. 9 lakhs Dalton). It shows good mechanical properties in spite of addition of high oil dosage, due to high molecular weight latex.

Also, Mooney viscosity of oil extended SBR matches with dry grade SBR as in the former case, a slightly higher molecular weight grade is used. Rubber is extended with oil because free oil cannot be used to higher dosage level in rubber compound recipe. Higher dosage level leads to slippage of rubber compound during mixing and hence, poor filler dispersion. In the case of oil extension with rubber, this issue is resolved because extender oil is bound with rubber and avoid slippage action during mixing. Additionally, it affects the hardness and modulus significantly less in comparison to addition of free oil. Apart from processing ease, use of higher oil dosage in rubber compound helps in reducing compound cost. But one must see the ageing properties of the vulcanizate because higher oil dosage adversely affects the mechanical properties retention after ageing. If free oil is used in higher dosage, then it may also lead to leaching out of oil on surface of rubber compounds after mixing as well as curing. This will deteriorate green tack of rubber compound and surface gloss of vulcanizate. If the process oil is added less than 10 parts phr in rubber compound, it is termed as process aid. Otherwise, it is termed as an extender. Commercially available oil extended rubbers are synthetic rubbers mainly[98].

First emulsion styrene butadiene rubber (SBR) was produced in Germany and USA during Second World war. It was known as BuNa-S rubber, where Bu stands for butadiene monomer, S stands for styrene monomer and Na stands for sodium. Styrene and butadiene monomers were polymerized in presence of sodium. Oil extended SBR started commercial production in 1950 in United States based on various petroleum oils. Later, during 1955-1960, SBR was produced through anionic solution polymerization technique using alkyl lithium catalyst. Rubbers could be produced with various microstructures using solution polymerization technique. Currently, it is largest produced synthetic rubber (more than half of total synthetic rubber production and almost equal to NR production).

Emulsion SBR is World's oldest synthetic rubber, and it is copolymer of styrene and butadiene monomer (1:3 ratio) and contains approx. 23.5% of styrene. Water is used as dispersant medium, mixed fatty acid soaps are used emulsifier, organic peroxide is used as initiator, mercapton is used as chain transfer agent, hydroxylamine is used as shortstop, phenol is used as stabilizer and sulfuric acid is used as coagulant. Polymerization temperature is maintained between 5 to 10°C. Flow diagram of OE SBR manufacturing is shown in Fig. 1.7.

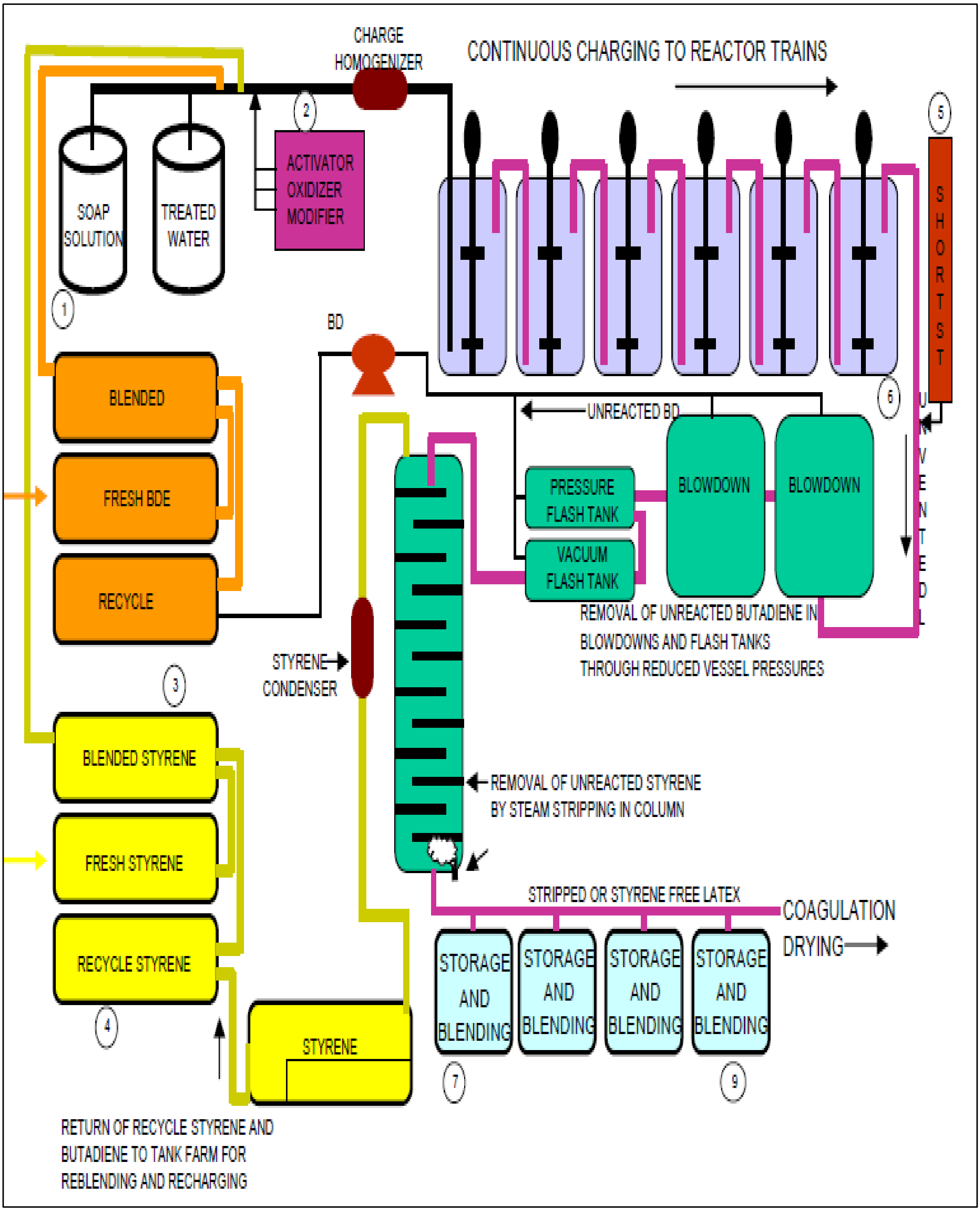


Fig. 1.7: Flow diagram of oil-extended styrene butadiene rubber (OE-SBR) (https://www.slideshare.net/kareemtharaa/styrene-butadiene-rubber-42686736)

First, styrene and butadiene monomers are polymerized in presence of an emulsifier, an initiator, a modifier, and water. Initiator generates the free radical required to initiate polymerization reaction. Polymerization reaction takes place inside the "micelles" (Fig. 1.8).

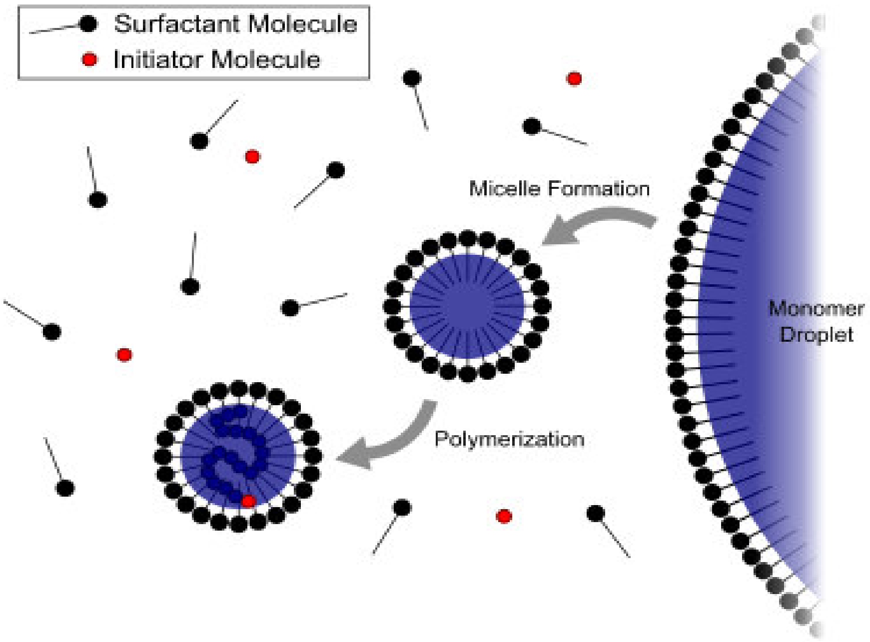


Fig. 1.8: Polymerization reaction inside "micelles"
(en.wikipedia.org/wiki/emulsion polymerization)

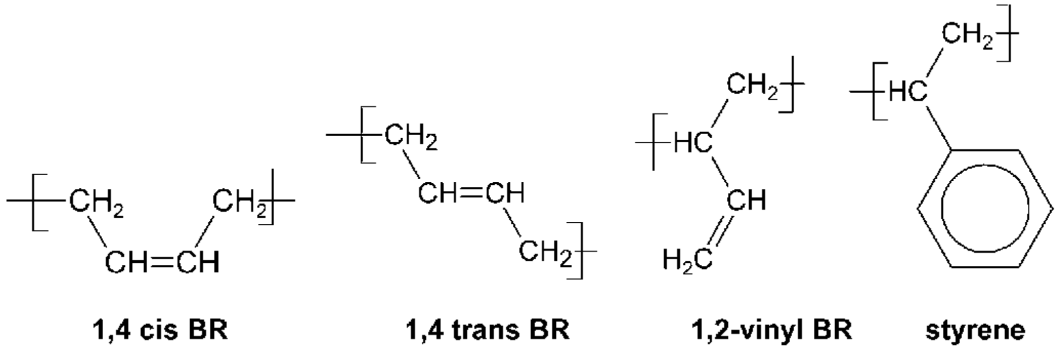
Molecular weight of polymer is controlled by using chain transfer agent, which terminates the growing polymer chain and initiates the new chain. Short stop is added after getting the desired conversion (approx. 60 to 70%) to stop the polymerization reaction. It blocks further polymerization by rapid reaction with free radicals. Unreacted monomers are stripped out from the latex and purified for reuse. Latex is stabilized by adding stabilizer (around 1% level) and coagulated using sulfuric acid. In case of oil extended SBR, desired level and type of extender oil is added. Coagulated crumbs are floated to shaker screens, where catalyst, emulsifier and other soluble materials are removed by washing with water. Crumbs are dewatered by passing through dewatering extruder and hammer mill. Then it is sent to dryer to control the moisture content in final SBR. Then it is baled and packed in polyethylene wrapping film and packed for transportation.

Composition of various SBR in Table 1.6.

Table 1.6: Composition of various SBR produced commercially

S. No.	SBR grade	Bound styrene (%)	Oil (phr)	Oil type
1	SBR1502	22.5 – 24.5	--	--
2	SBR1712	22.5 – 24.5	37.5	DAE
3	SBR1723	22.5 – 24.5	37.5	TDAE
4	SBR1783	22.5 – 24.5	37.5	RAE
5	SBR1778	22.5 – 24.5	37.5	Naphthenic
6	SBR1721	39.0 – 41.0	37.5	DAE
7	SBR1739	39.0 – 41.0	37.5	TDAE
8	SBR1789	39.0 – 41.0	37.5	RAE

The SBR has two variety, dry and oil grade. Dry grade like SBR1502 does not contain oil whereas oil grades like SBR1712, SBR1723, SBR1783, SBR1778, SBR1721, SBR1739 and SBR1789 contain 37.5 phr oil. This nomenclature is given by International Institute of Synthetic Rubber Producers (IISRP) based on oil type and styrene content. Generally, two types of SBR are available based on styrene content, 23.5% is normal styrene and 40% is high styrene grades of SBR. The structure of SBR is shown in Fig. 1.9.



1,4 cis BR 1,4 trans BR 1,2-vinyl BR styrene

Fig. 1.9: Microstructure of styrene butadiene rubber (SBR)
(With permission from F. Vimlin, C. Dussap, and, N. Coste, Appl. Spectroscopy, 60, 6, 2006)

It has cis-1,4, trans-1,4 and vinyl-1,2 structure of butadiene part. This structure is fixed for emulsion SBR like around 10% cis content, 72% trans content and 18% vinyl content. Trans content provides traction properties and cis content provides the abrasion resistance in the rubber vulcanizates. It is mainly used for passenger car radial (PCR) tire tread compound. The structure can be varied for solution polymerized SBR based on requirement. Various applications of emulsion SBR are given in Fig. 1.10.

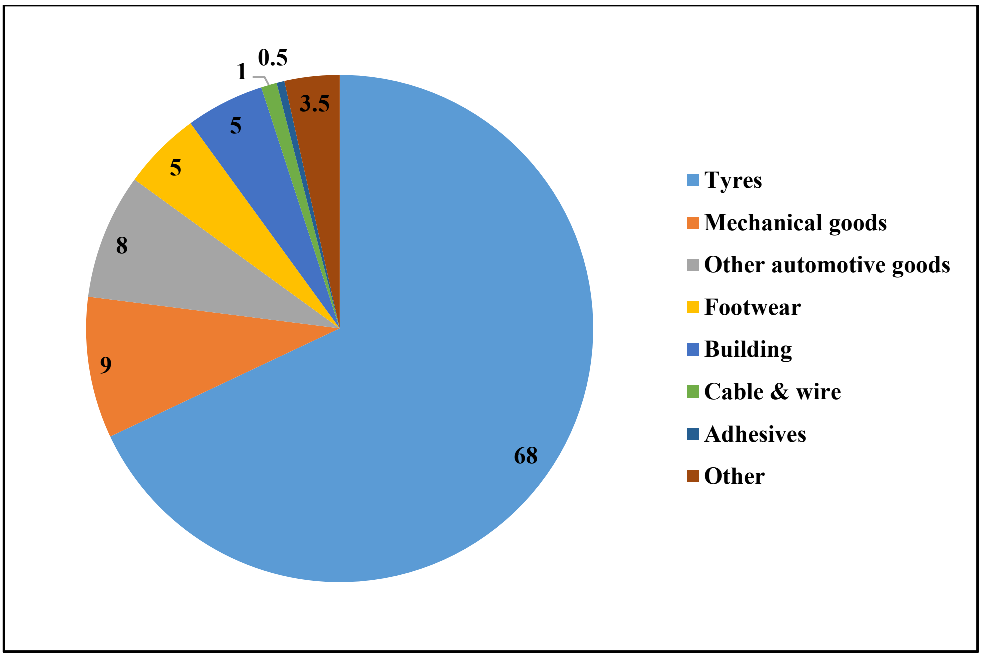


Fig. 1.10: Applications of emulsion SBR

(wiki.zeroemissions.at/index.php?title=fil:main applications of ESBR.jpg)

More than half production is used for tire manufacturing. It can used as replacement of NR based on price trends.

1.6 VEGITABLE OILS AS EXTENSION TO RUBBERS

The NR can also be extended with process oil. Oil extension of NR in latex stage was done using vegetable origin oils like palm, coconut and castor oils and improvement in processing, tensile strength and wear resistance was observed by Kondo[99]. The NR extension with coconut kernel/soybean oil nanoemulsion as renewable vegetable oil source was done for film application. Nanoemulsion of vegetable oils was prepared by blending vegetable oil, Tween 80 and water through phase inversion temperature method. This nanoemulsion was added to NR latex. They found that tensile strength could be improved by increasing the vulcanization temperature to 120°C[98]. An interesting study revealed that the sequence of materials addition during extension of natural rubber with vegetable oils like coconut and soybean in the form of microemulsion has shown effects on the vulcanizate properties. Ingredients blending sequence affected crosslink density and tensile properties. Compounding of vegetable oils nanoemulsion with premature NR latex has promoted easier penetration and dispersion of curatives. This led to improvement in crosslink density and tensile properties[100].

SSBR was extended with a new sustainable biooil (Bioextensoil 2021) and petroleum oils like TDAE, RAE, and naphthenic oils. Biooil extended SSBR was evaluated in a carbon black and silica filled SSBR/PBR blend based tire tread formulations with respect to mineral based SSBRs. Biooil extended SSBR has shown better abrasion resistance due to high plasticization capacity and better filler dispersion as compared to mineral oil. It has also shown lower Payne effect value[6]. Various researchers have used vegetable oils for extension of solution and emulsion SBRs for environmental sustainability, processing, and performance improvement[101-107].The SSBR was extended with soybean, sunflower, canola, corn, coconut, cottonseed, olive, palm, peanut and safflower oils and improvement in abrasion resistance and tear strength with comparable physical properties was observed as compared to SSBR extended with naphthenic oil[101]. Emulsion polymerized SBR latex was extended with modified (Mixture of triglycerides containing oligomeric structures esterified with ethanol) vegetable oils[102]. Functionalized emulsion polymerized SBR latex was extended with (soybean oil) as such and modified (epoxidized soybean oil)[103]. High glass transition temperature SSBR was extended with triglyceride vegetable oils like sunflower, rapeseed, canola, palm, and soybean oil in place of petroleum oils. It was evaluated in tire compound with use of traction resin[104,106]. The SSBR latex was extended with soybean, sunflower, and canola oil[105].

High glass transition temperature SSBR was extended with triglyceride vegetable oils like sunflower, rapeseed, canola, palm, and soybean oils in place of petroleum oils. It was evaluated in shoe outsole compound[107].Coconut oil with less than 0.05% free fatty acid content was used for extension of PBR rubber. Improvement in mechanical properties was observed for these new PBR grade when it was blended with other rubbers like NR or SBR, which may be due to reduction in Payne effect[108].

Palm and soybean vegetable oil based microemulsions were prepared and incorporated in NR latex. Few studies have revealed that addition of oil to elastomer resulted in lowering of modulus and tensile strength due to plasticizing effect of oil droplets in the latex. Mechanical properties of NR latex film are further decreased with increasing oil dosage. This can be improved as curing temperature and duration was increased[97,109]. Cardanol grafted natural rubber-based carbon black filed compound has shown better crosslink density, bound rubber, lower filler-filler interaction and carbon black dispersion than aromatic oil plasticized NR[110].

Currently emulsion polymerized styrene butadiene rubber (E-SBR) is extended with various petroleum based mineral oils like Distillate Aromatic Extract (DAE), Treated Distillate Aromatic Extract (TDAE), Residual Aromatic Extract (RAE) and naphthenic oils. It is obvious that introduction of vegetable oil should result in almost zero polycyclic aromatic content (PCA) content and therefore, there are environmentally friendly, renewable, and sustainable.

Passenger car is considered as lightweight automobile and it runs at very high speed. It requires good traction and high abrasion resistance at high speed, which can be achieved by using styrene butadiene rubber in blend with polybutadiene rubber. Among various parameters of PCR, tire tread performance, dry and wet traction, rolling resistance and mileage, are important as they conform the safety requirement, fuel economy and durability. These three parameters are called magic triangle properties because it is very difficult to improve all the three parameters at a time. If one improves rolling resistance and mileage, then there will be compromise on traction properties and vice-versa.

The quality of motorcycle has undergone revolutionary change over last decade worldwide. Technological upgradation, customer demand and road infrastructure has contributed to this revolution. These necessitated higher performance of motorcycle tires as tires being interface between powerful engines and the road. In this application also, magic triangle properties are very important. In general, Oil-extended Styrene Butadiene Rubber (OE-SBR) with high styrene provides better traction and abrasion with little deterioration in rolling resistance properties.

In the present work styrene butadiene rubber latex (normal and high styrene content) was extended with various vegetable oils. Oil-extended rubbers prepared with normal styrene content latex were evaluated in American Society for Testing and Materials (ASTM) standard recipes and passenger car radial (PCR) tire tread compound formulation. Oil-extended rubbers prepared with high styrene content latex were evaluated in motorcycle tire tread compound formulation. Detailed characterization of the compounds was done with respect to processing, stress-strain, performance properties and dynamic mechanical properties.

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CHAPTER – II

EXPERIMENTAL

CONTENTS

2.1 MATERIALS

Materials used in the present investigation are given in Table 2.1.

Table 2.1: Materials and specifications

Materials	Specification
Styrene butadiene rubber latex (23.5% Styrene content)	Reliance Ind. Ltd., India
Styrene butadiene rubber latex (40 % Styrene content)	Reliance Ind. Ltd., India
Sulfuric acid	Labort Fine Chem Pvt. Ltd., India
Styrenated phenol (SP) antioxidant	National Chemical, India
Polybutadiene rubber Cisamer 01	Reliance Ind. Ltd., India
Polybutadiene rubber, Neodymium catalyst (Synteca 44)	Synthos S. A., Poland
Industrial reference carbon black, IRB#9 (Standard Carbon Black)	Balentine Enterprises Inc., USA (Manufactured by Orion Engineered Carbon)
Carbon black N220	PCBL, India
N330 carbon black	PCBL, India
Zinc oxide pure	SD Fine-Chem Ltd., India
Stearic acid LR Grade	SD Fine-Chem Ltd., India
Zinc oxide	Silox India Pvt. Ltd., India
Stearic acid	Godrej, India
Antiozonant MC wax	Gujarat Paraffins, India
Antioxidant TMQ	NOCIL, India
Antioxidant 6PPD	NOCIL, India
Sulfur powder (98% extra pure)	LobaChemie Pvt. Ltd., India

Soluble sulfur	Jain Chemicals, India
Accelerator TBBS, N-ter-butyl-2-benzothiazole sulfenamide (97% pure)	Alfa Aeser by Thermo Fisher Scientific, India
Accelerator TBBS	Yaso Industries, India
Accelerator DPG	Yaso Industries, India
Accelerator CBS	NOCIL, India

2.2 PHYSICO-CHEMICAL CHARACTERIZATION OF OILS

The oils were characterized for flash point (ASTM D92), pour point (ASTM D97), kinematic viscosity (ASTM D445), refractive index (ASTM D1218) by Abbemat 300 Refractometer from Anton Paar and Fourier Transformed Infrared Spectroscopy (FTIR) Spectrum Two (ASTM D2702) Perkin Elmer was used for surface groups study.

2.2.1 Metal Content of Oils by ICP-OES

The oil samples were also characterized for metal contents using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) Optima 4300 DV from M/s Perkin Elmer using Charge-coupled device (CCD) detector. Oil sample (5-10 g) was taken in a platinum crucible, then sulfuric acid (3-4 mL) was added for digestion of oils to remove organic content by heating these samples on hot plate. Then the sample was heated @ 850°C for one h. The ash was diluted with demineralized water to make solution (4% w/w). This solution was tested using ICP-OES instrument to measure 25 metals at a time. Standard solution was run to get standard peak value for various metals. Metal content for experimental samples was calculated by software based on relative intensity of various peaks with respect to standard solution for different metals. This equipment can measure the metal content with accuracy level of 0.5 ppm. Transition metals are like poison to rubber compound as they drastically reduce the stress-strain properties after ageing in aerobic, anaerobic, oil and outdoor conditions[1]. Presence of these metals in high concentration affect the hot air ageing stress-strain properties adversely and as a result, service life of the product.

2.2.2 Measurement of Different Structural Groups in oils

Nuclear Magnetic Resonance (NMR) Spectrometer (Advance III^{TM} HD 400 from M/s Bruker, Switzerland) liquid was used for phase NMR to check various structural groups like aliphatic, olefinic and aromatic (Mono, di and poly). It was calculated as the distribution of proton present in different structural group in percentage.

2.3 E-SBR LATEX PREPARATION AND ITS CHARACTERIZATION

SBR latex was prepared using emulsion polymerization of styrene and butadiene monomer in 1:3 weight ratio for normal styrene content and 3:4 weight ratio for high styrene content rubbers. Free radical polymerization technique was used and reaction temperature was maintained between 0° to 20°C. Organic peroxide was used as initiator, rosin/fatty acid was used as emulsifier, mercaptan as chain modifier to control molecular weight, water was used as emulsifying media and hydroxylamine was used as short stop to achieve desired level of conversion.

SBR latex was characterized for solid content by acid coagulation and drying step. Then, further characterizations were made like Mooney viscosity using MV2000E from Alpha Technologies (ASTM D1646) and bound styrene content through refractive index by Abbemat 300 Refractometer from Anton Paar (ASTM D5775), Degradation study using Thermo Gravimetry Analyzer, TGA-Q50 from TA Instrument (ASTM D6370), Glass transition temperature using differential scanning calorimetry, DSC-Q20 from TA Instrument (ASTM E794), Gel permeation chromatography study for molecular weight and its distribution using GPC1260 Infinity from Agilent Technologies, etc. were determined.

2.4 SBR EXTENSION WITH OILS AT LABORATORY SCALE

SBR latex was extended with various oils and details are presented in Table 2.2.

Table 2.2: Various oil and their suppliers

S. No.	Source of oils	Name of oils	Supplier
1	**Petroleum**	Panoil C 160A, Distillate Aromatic Extract (DAE) oil	Panama Petrochem Ltd., India
2		Panoil 2500, Treated Distillate Aromatic Extract (TDAE) oil	Panama Petrochem Ltd., India
3		Elasto Supreme H, Residual Aromatic Extract (RAE) oil	Hindustan Petroleum Corporation Ltd., India
4		RPO, Naphthenic oil	Apar Industries Ltd., India
1	**Vegetable**	NO_2 (RQ, DECAS oil)	Jayant Agro-Organics Ltd., India
2		NO_6 (RBD Palmolein oil)	Satguru Oils Pvt. Ltd., India
3		NO_7 (Ground nut)	Local market
4		NO_8 (Soybean)	
5		NO_9 (Mustard)	
6		NO_10 (Coconut)	

Oil emulsion was prepared using oil and fatty soap in 1:1 ratio and heated with continuous stirring (250-350 rpm, 60°-90°C). Measured amount of this oil emulsion was mixed with SBR latex with continuous stirring at high speed (700-1200 rpm). The latex was then coagulated with sulfuric acid and salt mixture. Latex crumbs are separated from water and washed with demineralised water properly to remove acid. These rubber crumbs are dried in air oven and moisture removal was ensured to less than 0.5%. Dried rubber crumbs are passed on two roll mill to prepare proper sheet for further characterization.

2.5 PHYSICO-CHEMICAL CHARACTERIZATION OF OE-SBR'S

Total extractables (ASTM D5774) were measured using acetone and bound styrene content was measured using Abbemat 300 Refractometer Anton Paar (ASTM D5775).

OE-SBRs were characterized for density using bulk density Tester model RD3000 from M/s MonTech, Germany (ASTM D297), Mooney viscosity using MV2000E (ASTM D1646), moisture content using Halogen Moisture Analyzer, degradation study using Thermo Gravimetry Analyzer, TGA-Q50 and glass transition temperature (Tg) using Differential Scanning Calorimetry, DSC-Q20 were determined.

2.6 COMPOUND MIXING AND CHARACTERIZATION

2.6.1 ASTM Compound Mixing (Master batch)

Compound characterization was performed following ASTM for oil extended rubbers. Master batch mixing of rubber compound was carried out using a two-wing rotor laboratory Miniature Internal Mixer (MIM) of 350 mL capacity from Thermo Fisher Scientific. The formulation (as per ASTM D3185-2B) used for compound evaluation is given in Table 2.3.

Table 2.3: ASTM rubber compound recipe for master batch

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (23.5% styrene)	137.5
Carbon, IRB#9	68.75
Zinc oxide	3
Stearic acid	1

Master batch mixing was done setting the temperature control unit (TCU) at 70°C and rotor speed at 60 rpm for 6 min. The master batches were sheeted out in a laboratory two-roll mill for 6 passes at 2 mm nip gap and 2 passes at 0.8 mm nip gap. The dump temperature, mixing energy, maximum torque and final torque were measured for all the master batches.

2.6.2 PCR Tire Tread Compound Mixing

Master and final batch mixing of PCR tire tread compound was carried out using a two-wing rotor laboratory Miniature internal mixer (350 cc) from Thermo Fisher Scientific. The formulation used for compound evaluation are shown in Table 2.4.

Table 2.4: PCR tire tread compound recipe

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (23.5% styrene)	96.25
Polybutadiene rubber Cisamer 01	30
Carbon black N220	70
Respective process oil	10
Zinc oxide	2.5
Stearic acid	1
Antiozonant MC wax	2
Antioxidant TMQ	1
Antioxidant 6PPD	1.5
Soluble sulfur	2
Accelerator TBBS	1.2
Accelerator DPG	0.2

Master batch mixing was done setting the Temperature Control Unit (TCU) at 90°C and rotor speed at 60 rpm for 5 min. Final batch mixing was done setting the TCU at 60°C and rotor speed at 30 rpm for 3 min. The master and final batches were sheeted out in a laboratory two-roll mill using standard procedure.

2.6.3 ASTM Compound Mixing (With curatives adjustment)

Mixing was carried out using a two-wing rotor laboratory Miniature internal mixer, MIM (350 cc) from M/s Thermo Fisher Scientific. Single stage mixing was done setting the Temperature Control Unit (TCU) at 60°C and rotor speed at 60 rpm for 9 min. The mixed batches were sheeted out in a laboratory two-roll mill using standard procedure. The formulations used for compound evaluation are given in Table 2.5.

Table 2.5: ASTM compound recipe (phr)

Ingredients	Naphthenic	NO_2	NO_6	NO_7	NO_8	NO_9	NO_10
OE-SBR (23.5% Styrene)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)	137.5 (100 SBR & 37.5 oil)
Carbon, IRB#9	68.75	68.75	68.75	68.75	68.75	68.75	68.75
Zinc oxide	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1
Soluble sulfur	1.75	2.19	1.75	2.10	2.01	2.01	1.75
Accelerator TBBS	1.38	1.73	1.38	1.66	1.59	1.59	1.38

Curatives were adjusted for vegetable oil extended E-SBR based formulations to achieve the close modulus with respected to naphthenic oil extended E-SBR formulation.

2.6.4 ASTM Gum Compound Mixing (High styrene content rubbers)

Mixing was carried out using a two-wing rotor laboratory Miniature internal mixer, MIM (350 cc) from Thermo Fisher Scientific. The formulation used for compound evaluation are tabulated in Table 2.6.

Table 2.6: ASTM gum compound recipe

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (40 % styrene)	137.5 (100 rubber)
Zinc oxide	3
Stearic acid	1
Soluble sulfur	1.75
Accelerator TBBS	1.38

Single stage mixing was done setting the Temperature Control Unit (TCU) at 60°C and rotor speed at 60 rpm for 9 min. The mixed batches were sheeted out in a laboratory two-roll mill using standard procedure.

2.6.5 Motorcycle Tire Tread Compound Mixing

Master and final batch mixing was carried out using MIM. The formulation used for compound evaluation are given in Table 2.7.

Table 2.7: Motorcycle tire tread compound recipe

Ingredients	Parts per hundred rubber (phr)
Oil extended styrene butadiene rubber (40 % styrene)	89.375 (65 rubber)
Polybutadiene rubber, Neodymium catalyst	35
N330 carbon black	70
Respective process oil	3
Zinc oxide	4
Stearic acid	2
Antiozonant MC wax	1
Antioxidant TQ	1
Antioxidant 6PPD	1
Soluble sulfur	1.7
Accelerator CBS	1.2

Master batch mixing was done setting the Temperature Control Unit (TCU) at 90°C and rotor speed at 60 rpm for 5 min. Final batch mixing was done setting the TCU at 60°C and rotor speed at 30 rpm for 3 min. The master and final batches were sheeted out in a laboratory two-roll mill using standard procedure. Density of all the above mixed final batch filled compounds was checked using Compressed Volume Densimeter from Montec (ASTM D297).

2.7 CHARACTERIZATIONS OF UNCURED RUBBER COMPOUND

Bound rubber content was done by chemical method for master batch rubber compounds. Final compounds were characterized for processing parameters like Mooney viscosity (ASTM D1646), processing behaviour, filler dispersion and activation energy for flow (ASTM D6204). Cure characteristics (ASTM D5289) was evaluated by

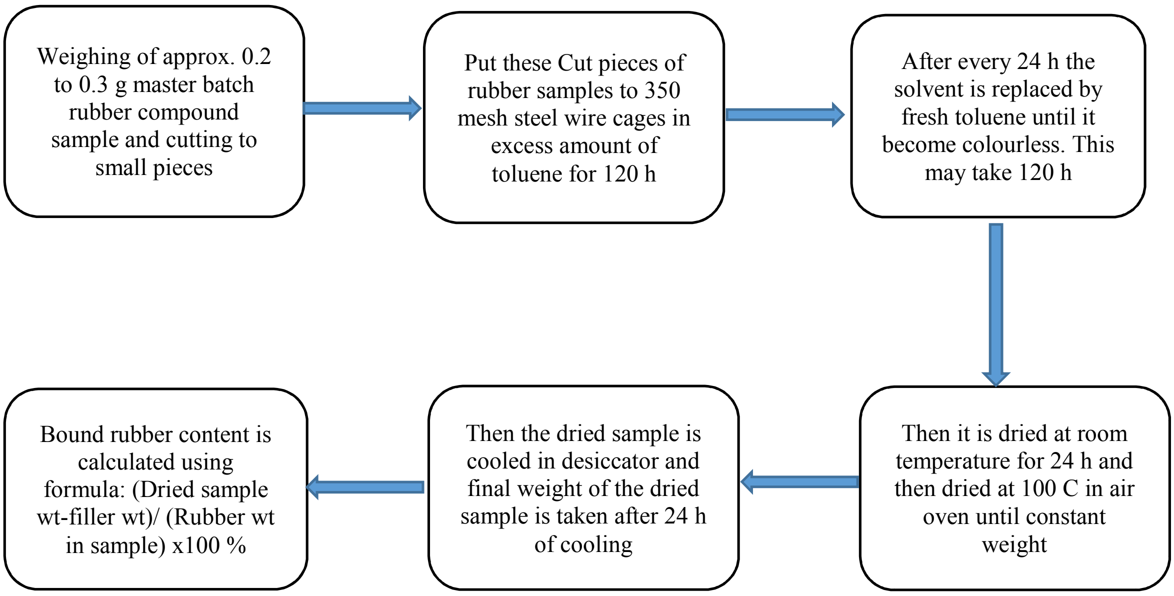
MDR2000 from M/s Alpha Technologies, USA at 160°C for 30 min for PCR, ASTM (curatives adjustment), motorcycle tire tread and ASTM gum compounds. Frequency sweep, strain sweep and temperature sweep tests were performed using RPA2000 from M/s Alpha Technologies, USA. RPA test conditions are reported in Table 2.8.

Table 2.8: RPA test conditions for various tests

Parameter	**Temperature (°C)**	**Strain (%)**	**Frequency (Hz)**
Flow behavior study (Power law index)			
Frequency sweep (compounded rubber)	100	14	0.05, 0.1, 0.2, 0.4, 0.9, 1.8, 3.7, 7.6, 15.6, 30, 31, 32
Filler dispersion			
Strain sweep (compounded rubber)	70	0.5, 1, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, 5, 1, 0.5	0.2
Activation energy study by Arrhenius equation			
Temperature sweep (Shear rate, 5.03 sec^{-1}) for compounded rubber	70, 80, 90, 100, 110, 120, 130	100	0.8
After cure (@160°C for tC90) properties by RPA			
Dynamic properties	40 and 70	5	10
Filler-filler interaction study (Payne effect) by strain sweep	70	0.5, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20, 25, 30, 40, 50	10

2.7.1 Bound Rubber Content Test

It is carried out master batch (without curatives) rubber compound to check polymer-filler interaction[2-4].



Weighing of approx. 0.2 to 0.3 g master batch rubber compound sample and cutting to small pieces

Put these Cut pieces of rubber samples to 350 mesh steel wire cages in excess amount of toluene for 120 h

After every 24 h the solvent is replaced by fresh toluene until it become colourless. This may take 120 h

Then it is dried at room temperature for 24 h and then dried at 100 C in air oven until constant weight

Then the dried sample is cooled in desiccator and final weight of the dried sample is taken after 24 h of cooling

Bound rubber content is calculated using formula: (Dried sample wt-filler wt)/ (Rubber wt in sample) x100 %

Around 0.2 to 0.3 g of sample was accurately weighed and cut to small pieces. It is then put to 350 mesh steel wire cages in excess amount of toluene for 120 h. After every 24 h, the solvent was changed until it became colourless. It is dried at room temperature for 24 h and then dried at 100°C in air oven until constant weight. It is then cooled in desiccator and final weight taken after 24 h. The bound rubber content (%) is calculated using the below equation (2.1).

$$\text{Bound rubber content (\%)} = \{(W_d - W_f)/\, W_o\} \times 100 \qquad \ldots (2.1)$$

Where,

W_d = Final weight of the dried sample in g,

W_f = Weight of the filler in the sample in g,

W_o = Weight of the rubber in the sample in g

When green rubber compound was exposed to toluene, some part of rubber was not extracted and it is known as bound rubber. Higher bound rubber content value indicates more polymer-filler interaction. This is desirable to achieve better mechanical and failure properties due to higher reinforcement.

2.7.2 Mooney Viscosity

Mooney viscosity of rubber compounds was checked as ML(1+4)@100°C using Mooney Viscometer (MV2000E) from M/s Alpha Technologies, USA.

2.7.3 Frequency Sweep Test

The flow behaviour of rubber compound measured as power law index in frequency sweep test[5] as per Newton's power law. Power law index (n) close to zero or relative lower value means plastic nature of rubber compound and hence, better shear thinning (Flow behaviour) of rubber compound.

2.7.4 Strain Sweep Test

In strain sweep test, the temperature and frequency remained constant and strain changes, the filler networking or agglomeration of filler particles, which is controlled mainly by filler-filler interactions in a rubber compound. It was quantified from the strain dependence of the elastic modulus G'. Elastic modulus G' is expressed as MPa unit. The filler network was gradually destroyed on increasing the strain (at strains well below 100%). This resulted in a decrease in elastic modulus G' with strain amplitude. Payne effect was measured as difference between elastic modulus (G') at low and high strain and it indicated filler-filler interaction. It was measured for filled rubber compound only. Higher Payne effect means more filler-filler interaction, which is not desired in rubber compound. Generally, high filler loading compounds and silica filler-based compounds show high Payne effect value[5]. Strain sweep test was performed in reverse direction also, which means strain reached to highest level and then decreases with same trend. Elastic modulus G' was recorded in reverse sweep test also. Filler dispersion was calculated as retention of G' at low strain in reverse sweep to forward strain sweep.

2.7.5 Temperature Sweep Test

Activation energy of the rubber compound can be measured using temperature sweep test in RPA in which frequency and strain (shear rate) remained constant and temperature rises. Complex viscosity (η*) was measured at interval of 10°C. Normally test starts at 70°C and ends at 130°C. Activation energy can be calculated using the Arrhenius-Eyring formula[5]. Higher activation energy value means rubber compound need high energy for compound flow, which indicated poor processing.

2.7.6 Scanning Electron Microscopy (SEM) Study

Scanning Electron Microscope, Nova NanoSEM 650 from M/s FEI Co. was used to check carbon black dispersion. Images of master batch rubber compounds were captured at 40000X magnification.

2.8 CHARACTERIZATIONS OF CURED RUBBER COMPOUND

Uncured rubber compounds were vulcanized for various tests using compression molding press (LP3000) from M/s MonTech, Germany. Tensile slabs were molded at 160°C for tC90 + 2 min and other specimen were molded at 160°C for tC90 + 5 min as per ASTM D3182. Cured specimen were tested for parameters like stress-strain properties (ASTM D412) by UTM (Z005) from M/s Zwick, Germany, hardness (ASTM D2240) by Shore A Durometer from M/s Gibitre, Italy, Heat Build Up (HBU) by Goodrich Flexometer (EKT-2002GF) from M/s Ektrontec, Taiwan (ASTM D623) following chamber temperature as 50°C, test time 20 min and 7 Kg load, Abrasion loss (ASTM D5963) using DIN Abrasion tester from M/s Zwick, Germany with 10 N load on specimen and Akron angle abrasion tester GT7012-A from M/s Gotech Testing Machines Inc., Taiwan with 20° slip angle for 4000 cycles, Heat Build Up (HBU) by Goodrich Flexometer EKT-2002GF from M/s Ektrontec, Taiwan (ASTM D623) following chamber temperature as 50°C, test time 30 min and 7 Kg load, Rebound @30° and 70°C (ISO4662-2) using Rebound Resilience tester (2108RR-T) from M/s Ektrontec, Taiwan and glass transition temperature Tg using Differential Scanning Calorimetry (DSC-Q20) and Volume resistivity (ASTM D257) using High Resistance Meter (model 6517B) and Resistivity test fixture (model 8009) from M/s Keithley (A Tektronix company), US. Dynamic properties and Payne effect (ASTM D6601) were performed using RPA (test conditions are given in Table 2.8). Dynamic mechanical properties of cured rubber specimen were measured using DMA1000+ from M/s Metravib, France (ASTM D5992).

2.8.1 Reinforcement Index and Rubber-Filler Interaction Parameter

Reinforcement index was calculated using equation (2.2)[6-8]:

$$RI = M300/M100 \qquad \ldots (2.2)$$

where M300 is modulus of rubber compound at 300% elongation in MPa, and

M100 is modulus of rubber compound at 100% elongation in MPa.

Rubber-filler interaction parameter is the ratio of slope of stress-strain curve in relatively linear region (σ) and filler-filler networking factor (η), which is calculated as the ratio of elastic modulus at low (1%) and high (25%) strain. It was calculated using equation (2.3)[9,10]:

$$I = \sigma/\eta = [(M300\text{-}M100)/\lambda] \,/\, [G'@1\%/\ G'@25\%] \qquad \ldots (2.3)$$

where λ is strain ratio, 2 to 4 measured over an elongation range of 100% -300%

G′@1% & G′@25% are storage moduli of rubber compound at 1% and 25% strain, respectively (in MPa).

2.8.2 Crosslink Density

Specimens were kept in toluene for 48 h and Swell index was measured using ASTM D3616. It was calculated as the ratio of swollen weight to original specimen weight. Volume fraction was measured by drying the swollen specimen in oven at 100°C for 2 h. It was calculated using equation (2.4)[11,12]:

$$V_r = [(D - FT)/\rho_r]/[(D - FT)/\rho_r + A_o/\rho_s] \qquad \ldots (2.4)$$

Where, D Weight of the de-swollen specimen

F is the Weight fraction of the insoluble non-rubber ingredients,

T = Original dry weight of the specimen,

A_o = Weight of solvent absorbed; it can be calculated as (S-T),

ρ_r = Density of the respective raw rubber, and

ρ_s = Density of the solvent (0.867 for toluene).

The cross-link density X of the rubber specimen was calculated using the Flory – Rehner relationship[13-17].

$$X = (-) [\ln (1-V_r) + V_r + \chi(V_r)^2] / [2 * \rho_r * V_s * (V_r)^{1/3}] \qquad \ldots (2.5)$$

where X = Cross-link density (mol/ cm^3),

V_r = Volume fraction of the specimen,

χ = Rubber-solvent interaction parameter (0.31 for SBR-toluene),

ρ_r = Density of the respective raw rubber, and

V_s = Molar volume of solvent (106.3 for toluene).

2.8.3 Strain Sweep Test by RPA

In strain sweep test, in which temperature and frequency remained constant and strain changes, the filler networking or agglomeration of filler particles, which is controlled mainly by filler-filler interactions in a rubber compound, was quantified from the strain dependence of the elastic modulus G'. Elastic modulus G' is expressed as MPa unit. The filler network was gradually destroyed on increasing the strain (at strains well below 100%). This resulted in a decrease in elastic modulus G' with strain amplitude. Payne effect was measured as difference between elastic modulus (G') at low and high strain and it indicated filler-filler interaction. It measured for filled rubber compound only. Higher Payne effect means more filler-filler interaction, which is not desired in rubber compound. Generally, high filler loading compounds and silica filler-based compounds show high Payne effect value[18]. Strain sweep test is performed in reverse direction also, which means strain reached to highest level and then decreases with same trend. Elastic modulus G' is recorded in reverse sweep test also. Filler dispersion was calculated as retention of G’ in reverse sweep to forward strain sweep.

2.8.4 Dynamic Mechanical Properties by Dynamic Mechanical Analyzer (DMA)

Rectangular specimens (2 mm thickness, 10 mm width) were tested at 10 Hz frequency, 0.1% dynamic strain and temperature scan from -80° to +80°C. Elastic modulus, E′ and loss factor, tan δ were measured at 0°, 30° and 60°C temperatures. Dynamic Tg was calculated as the temperature value at peak tan δ for PCR tire tread compounds.

Rectangular specimens (2 mm thickness, 10 mm width) were tested at 10 Hz frequency, 1 % dynamic and 2 % static strain. Elastic modulus, E′ and loss factor, tan δ were measured at 0°, 30° and 60°C temperature, respectively for ASTM compound (curatives adjustment) and motorcycle tire tread compounds.

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CHAPTER – III

RESULTS

CONTENTS

3.1 PHYSICO-CHEMICAL CHARACTERIZATION OF PETROLEUM AND VEGETABLE ORIGIN OILS

Test results for physico-chemical properties for oils are reported shown in Tables 3.1-3.3.

Table 3.1: Physico-chemical properties of oils

Parameter / Samples	Flash point (°C)	Pour point (°C)	Kinematic viscosity @100°C (cSt)	Refractive index @20°C
DAE oil	240	21	25.5	1.5672
TDAE oil	248	24	18.2	1.5398
RAE oil	235	15	52.5	1.5449
Naphthenic oil	228	-12	13.8	1.4853
NO_2 oil	290	-35	15.3	1.4828
NO_6 oil	325	9	10.0	1.4652
NO_7 oil	>300	-5	7.9	1.4689
NO_8 oil	>300	-10	8.0	1.4738
NO_9 oil	>300	-10	9.8	1.4729
NO_10 oil	292	18	5.5	1.4556

Table 3.2: Thermogravimetry analysis (TGA) of oils

Parameter Sample	Degradation temperature (°C)	Ash content (%)	Volatile content (%)
DAE oil	376.0	0.02	0.16
TDAE oil	357.3	0.03	0.15
RAE oil	454.1	0.08	0.06
Naphthenic oil	394.9	0.00	0.16
NO_2 oil	433.0	0.06	0.12
NO_6 oil	432.9	0.04	0.03
NO_7 oil	430.1	0.10	0.01
NO_8 oil	427.0	0.13	0.02
NO_9 oil	430.1	0.08	0.31
NO_10 oil	403.9	0.02	0.06

Table 3.3: ICP-OES study of oils for metal contents

Parameter / Sample	Copper (ppm)	Iron (ppm)	Manganese (ppm)	Cobalt (ppm)	Molybdenum (ppm)
DAE oil	*	6	*	*	*
TDAE oil	*	8	*	*	*
RAE oil	*	5	*	*	*
Naphthenic oil	*	5	*	*	*
NO_2 oil	3	23	*	10	*
NO_6 oil	5	10	*	*	2
NO_7 oil	2	17	2	*	*
NO_8 oil	2	52	2	159	*
NO_9 oil	2	15	*	*	*
NO_10 oil	*	10	2	5	*

* not detected

Note: Ti, V, Cr, Zn, etc. were not detected in all these samples

Flash point more than 225°C is safer for rubber compound mixing and further processing for vegetable oil it was found greater than 290°C, which may be due to presence of triglyceride ester carbonyl groups in these oils. So, the rubbers extended with these vegetable oils are safe for processing on the shopfloor. Vegetable oils have lower pour point (< 20°C), which is good for handling them at shopfloor during oil extension stage because oils with higher pour point need heating for flow during their use. The samples NO_6 and NO_10 have shown higher pour point due to their saturated structure. Lower kinematic viscosity of oil indicated better flow ability during processing. The NO_6 to NO_10 oil samples have shown lower viscosity as compared to TDAE oil, so these oils will have less resistance for flow. Refractive index for vegetable oils was found to be comparable with naphthenic oil. The TDAE oil has shown higher refractive index, which is due to more aromatic content in this oil and it was found low for NO_6 and NO_10 samples due to low aromatic content in these oils. Aromatic content was found to be low in vegetable oils as confirmed by NMR study also.

Metal content values determined by ICP-OES were found less than 160 ppm for transition metals like copper, iron, manganese, cobalt, and for all oil samples. Titanium, vanadium, chromium and zinc were not detected in these oil samples. Presence of these metals in high concentrations affect the hot air ageing stress-strain properties adversely and in consequence, service life of the product. However, presence of these metals are found lower in vegetable oils so compound prepared with vegetable oil extended rubbers will have better ageing properties. FTIR spectra of oil samples are presented in Fig. 3.1.

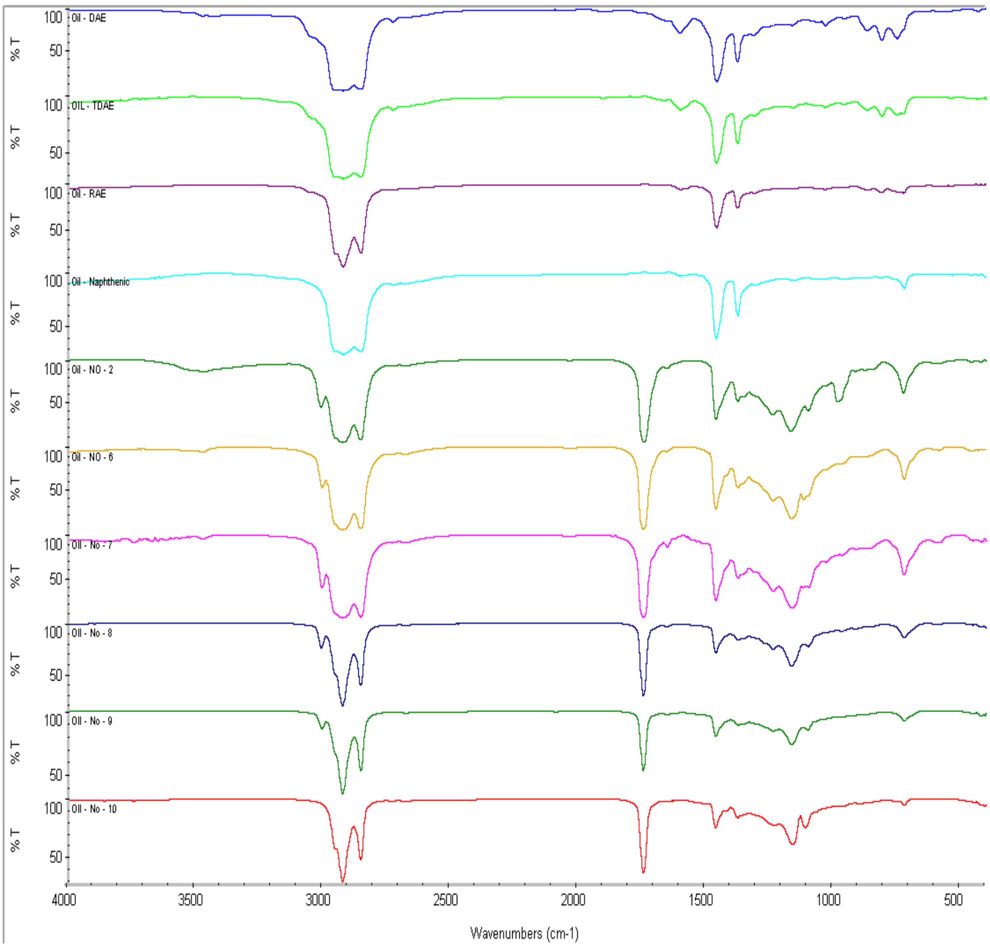

Fig. 3.1: FTIR spectra for oil samples

The DAE, TDAE, RAE and naphthenic oils show presence of weak aromatic C=C stretch (around 1600 cm^{-1}). Aliphatic CH_2 and CH_3 stretching (around 1375 and 1455 cm^{-1}) were also observed for these oils. The DAE and TDAE oils have shown peaks around 800 cm^{1} due to high aromatic content. Few additional peaks were observed for vegetable oils due to presence of additional functional groups. All vegetable oils show presence of triglyceride ester carbonyl groups (strong peak around 1745 cm^{-1}), hydrogen bonded C-O group (around 1100 and 1165 cm^{-1}) and acyl C-O group (around 1240 cm^{-1}), which may be due to presence of acidic groups. Aliphatic CH_2 group (around 725 and 1460 cm^{-1}), were also present in all vegetable oils. The C=C peak (around 1650 cm^{-1}) was missing in palm oil and coconut oil.

NMR data for oils are given in Fig. 3.2 and 3.3.

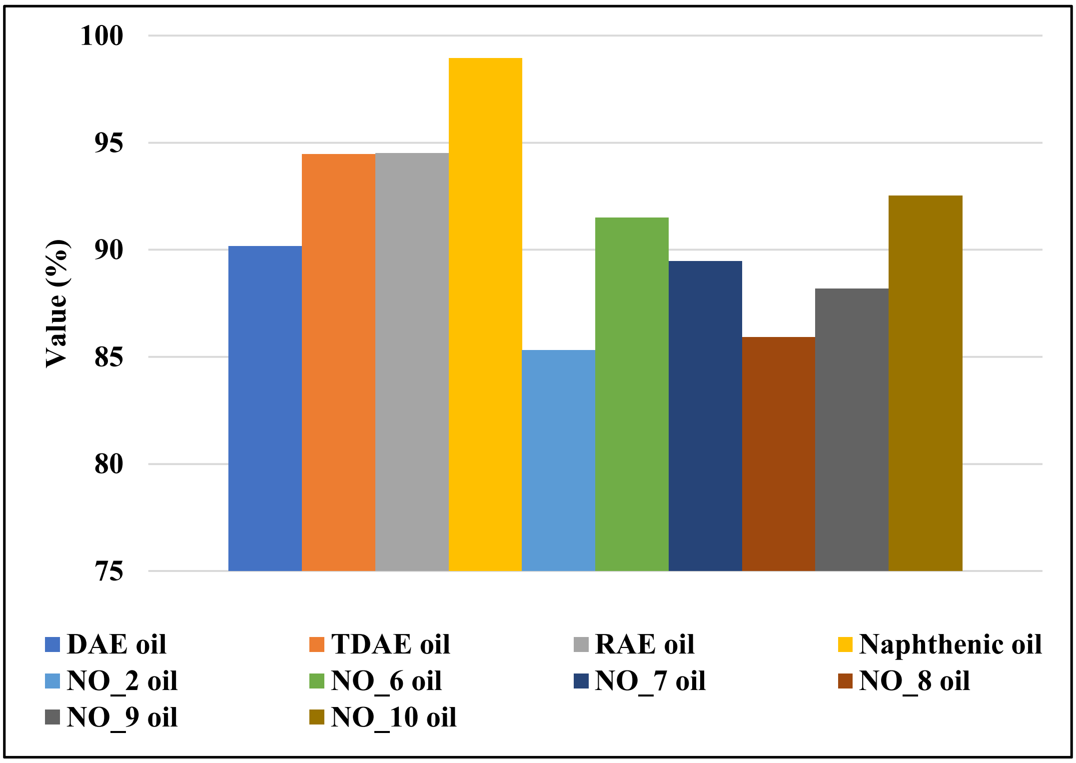

Fig. 3.2: Aliphatic proton content in detected by in oil samples

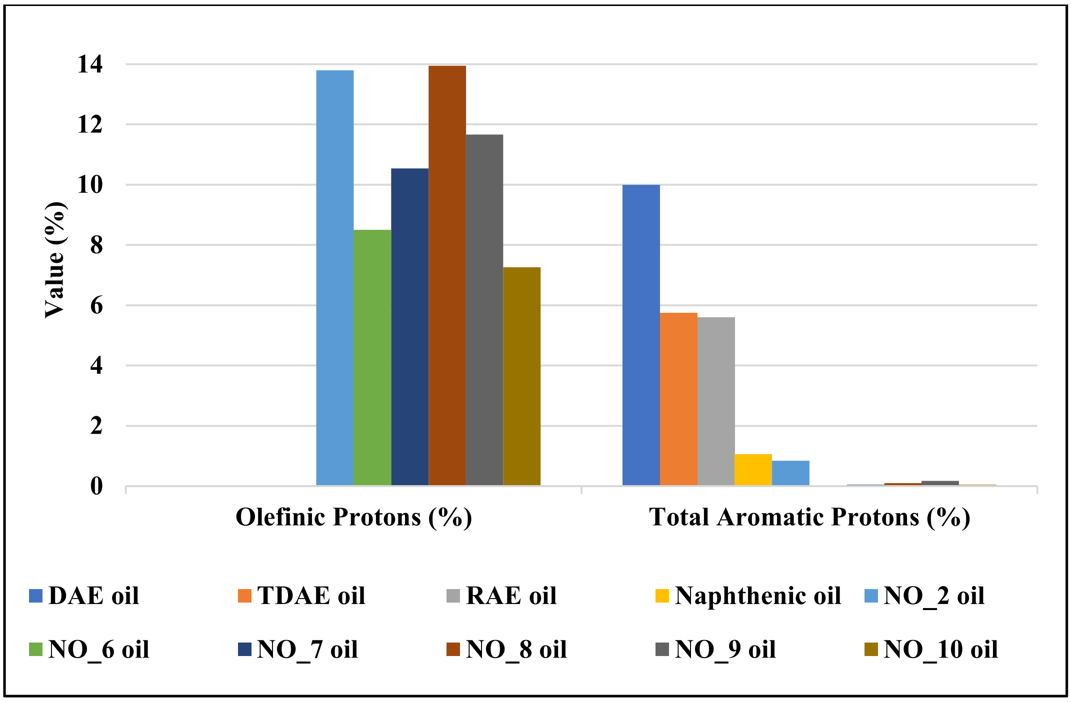

Fig. 3.3: Other structural groups detected by NMR in oil samples

All oil samples have aliphatic content more than 85% and all the vegetable oils have olefinic content more than 7%. The DAE, TDAE and RAE oils have aromatic content more than 5% (including poly aromatic content). This indicates that mineral oils have some PCA/PAH content, which may be carcinogenic for human. All vegetable oils have negligible aromatic content (< 1%). Hence, vegetable oils are safer to use in rubber industry to produce eco-friendly products.

3.2 PHYSICO-CHEMICAL CHARACTERIZATION OF STYRENE BUTADIENE RUBBER LATEX

3.2.1 Normal Styrene Content (23.5%) Latex

Test results for physico-chemical properties for styrene butadiene rubber latex is given in Table 3.4.

Table 3.4: Physico-chemical properties of styrene butadiene rubber latex (Normal styrene content)

Parameter	Value
Solid content (%)	19.9
Mooney viscosity (ML1+4) @100°C (MU)	106.2
Refractive index	1.5349
Bound styrene content (%)	23.9
Degradation temperature (°C)	465
Glass transition temperature (°C)	-53.4
Mn (g $mole^{-1}$)	1.9 lacs
Mw (g $mole^{-1}$)	8.0 lacs
Polydispersity index	4.2

Solid content of styrene butadiene rubber latex, Mooney viscosity, bound styrene content, glass transition temperature, molecular weight, molecular weight distribution and degradation, and temperature of coagulated dried latex sample were found within the specified range. This latex was used for oil extension and further study.

3.2.2 High Styrene Content (40%) Latex

Test results for physico-chemical properties of SBR latex are tabulated in Table 3.5.

Table 3.5: Physico-chemical properties of styrene butadiene rubber latex (High styrene content)

Parameter	Value
Solid content (%)	21.0
Mooney viscosity (MU)	127.7
Refractive index	1.5488
Bound styrene content (%)	39.4
Degradation temperature (°C)	405.4
Glass transition temperature (°C)	-31.8
Mn (g $mole^{-1}$)	2.0 lacs
Mw (g $mole^{-1}$)	7.7 lacs
Polydispersity index	3.8

All the properties of high styrene (40%) SBR latex sample were found within the specified range. This latex was used for oil extension and further study.

3.3 PHYSICO-CHEMICAL CHARACTERIZATION OF OIL EXTENDED STYRENE BUTADIENE RUBBERS

3.3.1 Normal Styrene Content (23.5%) SBRs

Vegetable oil-based SBRs were found to be light in color. So, these rubbers could be used for light color products. Physico-chemical properties of rubber samples are summarized in Tables 3.6 and 3.7.

Table 3.6: Physico-chemical properties of oil extended styrene butadiene rubber (Normal styrene content)

Parameter Sample	Total extractables (%)	Bound styrene content (%)	Density (g cc^{-1})	Mooney viscosity (MU)	Moisture content (%)
S23.5_TDAE	32.8	24.0	0.945	50.4	0.13
S23.5_Naphthenic	31.1	24.0	0.923	45.3	0.10
S23.5_NO_2	32.1	23.9	0.939	44.7	0.19
S23.5_NO_6	30.9	24.1	0.933	46.4	0.09
S23.5_NO_7	34.3	23.2	0.938	45.5	0.15
S23.5_NO_8	35.4	23.0	0.936	44.1	0.12
S23.5_NO_9	30.7	24.2	0.934	43.2	0.14
S23.5_NO_10	35.8	23.4	0.940	48.2	0.18

Table 3.7: Physico-chemical properties of oil extended styrene butadiene rubber (Normal styrene content)

Parameter / Sample	Degradation temperature (°C)	Ash content (%)	Tg (°C)
S23.5_TDAE	456.3	0.42	-55.4
S23.5_Naphthenic	456.3	0.28	-56.7
S23.5_NO_2	435.5	0.30	-63.0
S23.5_NO_6	455.6	0.29	-58.0
S23.5_NO_7	449.4	0.06	-58.7
S23.5_NO_8	447.1	0.18	-62.3
S23.5_NO_9	439.4	0.18	-62.5
S23.5_NO_10	456.3	0.17	-56.2

Acetone extraction for SBRs prepared with vegetable oils were found to be comparable with petroleum oil-based rubbers, which indicates that proper oil is present in these rubbers, and this may be due to good compatibility of these oils with SBR. Bound styrene content was calculated through refractive index value, which was found comparable to these extracted SBR rubber samples. This indicates comparable composition of monomer for all SBR samples.

Density of OE SBRs were found to be in line with density of respective oil sample. Mooney viscosity was found to be higher for SBR prepared with TDAE and NO_10 oil and is within the range for all rubber samples. Variation in Mooney viscosity value may affect the processing behavior of rubber during compounding, calendaring, extrusion, etc. Moisture content was found less than 0.2%, which indicates that all rubber samples were dried properly. Higher moisture content may lead to poor processing and mechanical properties of rubber compounds. Degradation temperature and ash content were found comparable for all OE SBR samples. The NO_2, NO_8 and NO_9 oil extended SBRs have lower glass transition temperature, which may improve the abrasion and rolling resistance properties of the rubber compound based on these oils.

3.3.2 High Styrene Content (40%) SBRs

Physico-chemical properties of their rubber samples are given in Tables 3.8 and 3.9.

Table 3.8: Physico-chemical properties of oil extended styrene butadiene rubber (High styrene content)

Parameter / Sample	Total extractables (%)	Bound styrene content (%)	Density (g cc^{-1})	Mooney viscosity (MU)	Moisture content (%)
S40_DAE	33.7	40.5	0.979	62.3	0.13
S40_TDAE	32.3	40.4	0.962	61.7	0.14
S40_RAE	33.2	39.7	0.971	63.6	0.17
S40_Naphthenic	33.6	39.5	0.946	52.6	0.12
S40_NO_2	32.8	40.3	0.963	40.2	0.19
S40_NO_6	34.2	40.9	0.961	50.0	0.15
S40_NO_7	33.3	41.0	0.955	52.5	0.17
S40_NO_8	34.3	40.1	0.957	52.0	0.12
S40_NO_9	32.2	39.4	0.956	54.3	0.18
S40_NO_10	31.8	40.4	0.958	56.0	0.14

Table 3.9: Physico-chemical properties of oil extended styrene butadiene rubber (High styrene content)

Parameter / Sample	Degradation temperature (°C)	Ash content (%)	Tg (°C)
S40_DAE	394.6	0.25	-33.2
S40_TDAE	391.5	0.30	-38.4
S40_RAE	379.2	0.36	-31.5
S40_Naphthenic	386.9	0.37	-39.4
S40_NO_2	405.4	0.30	-48.8
S40_NO_6	413.9	0.28	-43.3
S40_NO_7	420.1	0.27	-47.8
S40_NO_8	416.2	0.31	-56.3
S40_NO_9	423.9	0.29	-49.5
S40_NO_10	389.2	0.24	-38.3

Acetone extraction for SBRs prepared with vegetable oils were found to be comparable with petroleum oil-based rubbers, which indicates that proper oil is present in these rubbers, and this may be due to good compatibility of these oils with SBR. Bound styrene content was calculated through refractive index value, which was found comparable within the specified range for these extracted SBR rubber samples. This indicates comparable composition of monomer for all SBR samples.

Mooney viscosity was found to be lower for S40_NO_2 sample and it was within the range for other samples. Moisture content was found less than 0.2 %, which means all rubber samples were dried properly. Degradation temperature was found in the range of 380° to 420°C in TGA test for all OE-SBRs. The S40_NO_2, S40_NO_6 to S40_NO_9 samples have lower Tg, which may improve the abrasion and rolling resistance properties of the rubber compound based on these OE-SBRs.

3.4 MIXING BEHAVIOUR DURING COMPOUND PREPARATION

3.4.1 ASTM Master Batch Recipe

Various mixing parameters like mixing energy, maximum torque and dump temperature are tabulated in Table 3.10.

Table 3.10: ASTM master batch mixing behaviour

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Density (g cc^{-1})
ASTM_M_DAE	227.0	155.6	110.4	1.152
ASTM_M_TDAE	231.6	153.3	105.9	1.141
ASTM_M_RAE	235.1	155.8	113.5	1.145
ASTM_M_Naphthenic	236.3	156.6	105.5	1.126
ASTM_M_NO_2	210.6	138.1	107.8	1.135
ASTM_M_NO_6	209.6	141.6	107.3	1.130

Master rubber compound mixed using modified vegetable oils NO_2 and NO_6 based styrene butadiene rubbers exhibited around 8.5% less mixing energy, around 8.5% less mixing torque and around 11.5% less final torque. This may be due to lower Mooney viscosity of these rubber samples. Dump temperature for all the batches was found within the acceptable range. Batch weight after mixing was checked for all the mixed master batches and it was found within acceptable range. Density of all master batches were found related with the density of respective raw styrene butadiene rubber.

3.4.2 Passenger Car Radial Tire Tread Compound Recipe

Various mixing parameters including bound rubber content and density are presented in Tables 3.11 and 3.12 for master and final batches, respectively.

Table 3.11: PCR tire tread master batch mixing and characterization

Parameter / Sample	**Mixing energy (kJ)**	**Maximum torque (N-m)**	**Dump temperature (°C)**	**Bound rubber (%)**
PCR_M_TDAE	213.2	153.6	129.5	27.2
PCR_M_Naphthenic	204.7	145.1	130.4	29.4
PCR_M_NO_2	211.7	142.8	129.7	31.9
PCR_M_NO_6	200.6	134.7	129.0	28.8
PCR_M_NO_7	198.8	141.9	129.3	30.0
PCR_M_NO_8	193.3	134.9	128.1	27.2
PCR_M_NO_9	202.7	136.4	128.7	28.5
PCR_M_NO_10	199.6	142.8	129.5	28.2

Table 3.12: PCR tire tread final batch mixing and characterization

Parameter Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Density (g cc^{-1})
PCR_F_TDAE	84.9	188.3	82.4	1.143
PCR_F_Naphthenic	75.5	160.0	84.3	1.130
PCR_F_NO_2	73.0	149.3	83.3	1.133
PCR_F_NO_6	75.3	160.0	84.6	1.126
PCR_F_NO_7	75.2	143.0	84.0	1.134
PCR_F_NO_8	73.9	141.3	83.5	1.135
PCR_F_NO_9	71.6	148.5	82.4	1.135
PCR_F_NO_10	77.8	161.0	84.5	1.137

Master and final batch compounds were mixed using NO_6 to NO_10 vegetable oil-based SBRs displayed less mixing energy as compared to TADE oil. Dump temperature was found comparable for all samples in both; master and final stage mixing. Higher bound rubber content value indicates higher polymer-filler interaction. This is desirable to achieve better mechanical and failure properties due to higher reinforcement. Bound rubber was found to be comparable for all master compounds. Density of all final batches were found in line with the density of respective raw SBRs.

3.4.3 Motorcycle Tire Tread Compound Recipe

Various mixing parameters including bound rubber content and density are given in Tables 3.13 and 3.14 for master and final batches, respectively.

Table 3.13: Motorcycle tire tread master batch mixing and characterization

Parameter / Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Bound rubber (%)
MCT_M_DAE	203.3	186.3	145.7	19.8
MCT_M_TDAE	196.5	174.3	146.1	19.2
MCT_M_RAE	200.7	178.8	146.5	21.2
MCT_M_Naphthenic	198.5	171.2	143.3	19.6
MCT_M_NO_2	178.7	166.3	137.7	18.2
MCT_M_NO_6	178.0	156.3	140.7	20.2
MCT_M_NO_7	189.4	163.2	141.8	18.1
MCT_M_NO_8	183.3	160.7	140.9	18.2
MCT_M_NO_9	185.9	153.6	142.4	18.9
MCT_M_NO_10	184.0	162.7	140.4	19.5

Table 3.14: Motorcycle tire tread final batch mixing and characterization

Parameter Sample	Mixing energy (kJ)	Maximum torque (N-m)	Dump temperature (°C)	Density (g cc^{-1})
MCT_F_DAE	59.6	116.1	114.0	1.176
MCT_F_TDAE	60.7	126.0	113.0	1.167
MCT_F_RAE	55.8	118.1	113.0	1.169
MCT_F_Naphthenic	57.4	130.2	111.0	1.152
MCT_F_NO_2	46.7	96.7	110.0	1.167
MCT_F_NO_6	50.0	103.7	111.3	1.153
MCT_F_NO_7	56.2	113.0	112.8	1.160
MCT_F_NO_8	53.7	111.4	113.4	1.162
MCT_F_NO_9	57.4	111.0	113.3	1.159
MCT_F_NO_10	53.2	115.7	112.8	1.161

Master rubber compound mixed using S40_NO_2 and S40_NO_6 show slightly less mixing energy for both; master and final stage as compared to compound prepared with petroleum oil based SBR. This may be due to lower Mooney viscosity of these rubber samples. Dump temperature was found comparable for all samples in both; master and final stage mixing. Higher bound rubber content value indicates more polymer-filler interaction. This is desirable to achieve better mechanical and failure properties due to higher reinforcement. Bound rubber was found to be comparable for all master batch compounds. Density of all final batches were found in line with the density of respective raw SBRs.

3.5 RUBBER COMPOUND PROCESSING BEHAVIOUR

3.5.1 ASTM Recipe

Test results for master compounds like Mooney viscosity, power law index, dispersion, activation energy and bound rubber are tabulated in Table 3.15.

Table 3.15: ASTM master batch compound processing properties

Parameter / Sample	Mooney viscosity (ML1+4) @ 100°C (MU)	Power law index	Bound rubber (%)	Dispersion (%)	Activation energy, Eα (kCal mol^{-1} g^{-1})
ASTM_M_DAE	62.0	0.235	18.0	81.4	1409
ASTM_M_TDAE	59.6	0.239	17.9	83.3	1363
ASTM_M_RAE	66.2	0.235	19.8	82.7	1408
ASTM_M_Naphthenic	61.7	0.235	27.0	81.2	1100
ASTM_M_NO_2	52.5	0.231	28.7	79.8	1298
ASTM_M_NO_6	56.1	0.234	27.4	83.5	1249

Compounds prepared with NO_2 and NO_6 modified vegetable oil-based styrene butadiene rubber exhibited lower (around 12%) Mooney viscosity because these raw rubbers are also having low Mooney viscosity, comparable power law index, lower (around 15%), Payne effect (Fig. 3.4) and higher (around 55%) bound rubber content due to presence of various additional groups in vegetable oils, comparable filler dispersion and lower activation energy.

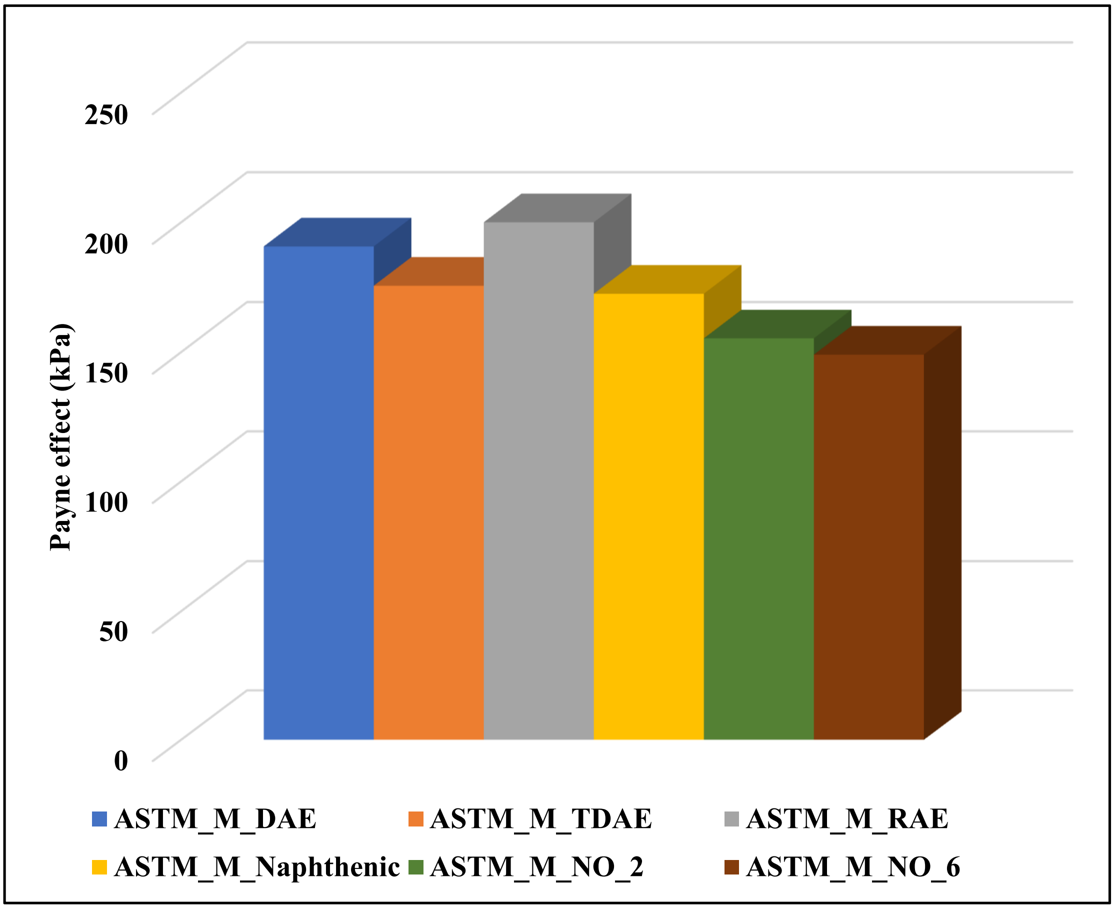

Fig. 3.4: RPA strain sweep test for ASTM master batch compound

This indicates comparable or slightly better processing properties for compounds prepared with modified vegetable oils-based styrene butadiene rubber as compared to compounds prepared with petroleum oil-based rubbers.

Carbon black dispersion was also measured through Scanning Electron Microscopy (SEM) analysis. SEM images for various rubber compound samples are presented in Fig. 3.5- 3.10.

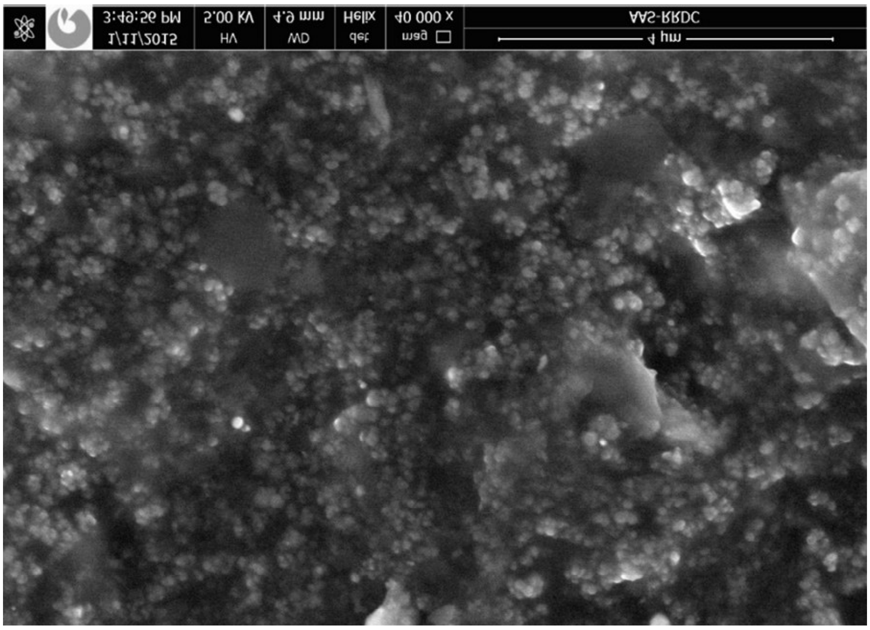

Fig. 3.5: SEM image (40000 X magnification) for DAE_ASTM master batch compound

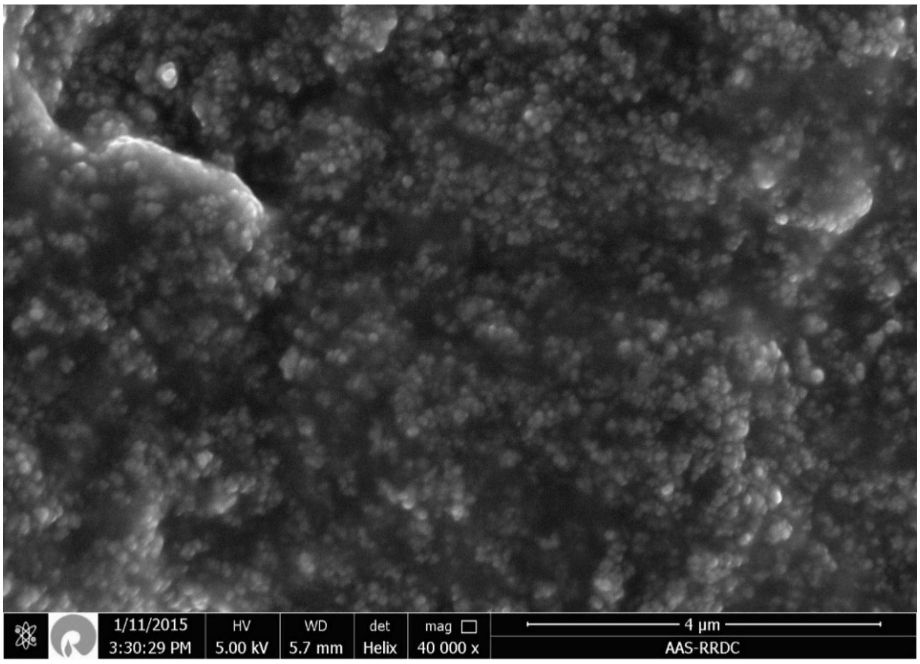

Fig. 3.6: SEM image (40000 X magnification) for TDAE_ASTM master batch compound

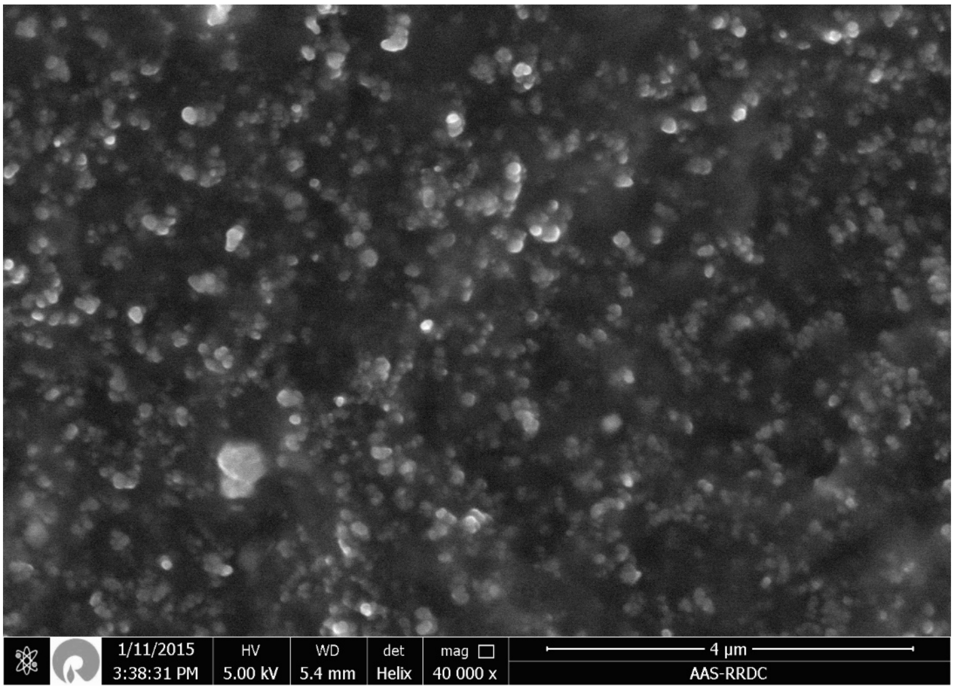

Fig. 3.7: SEM image (40000 X magnification) for RAE_ASTM master batch compound

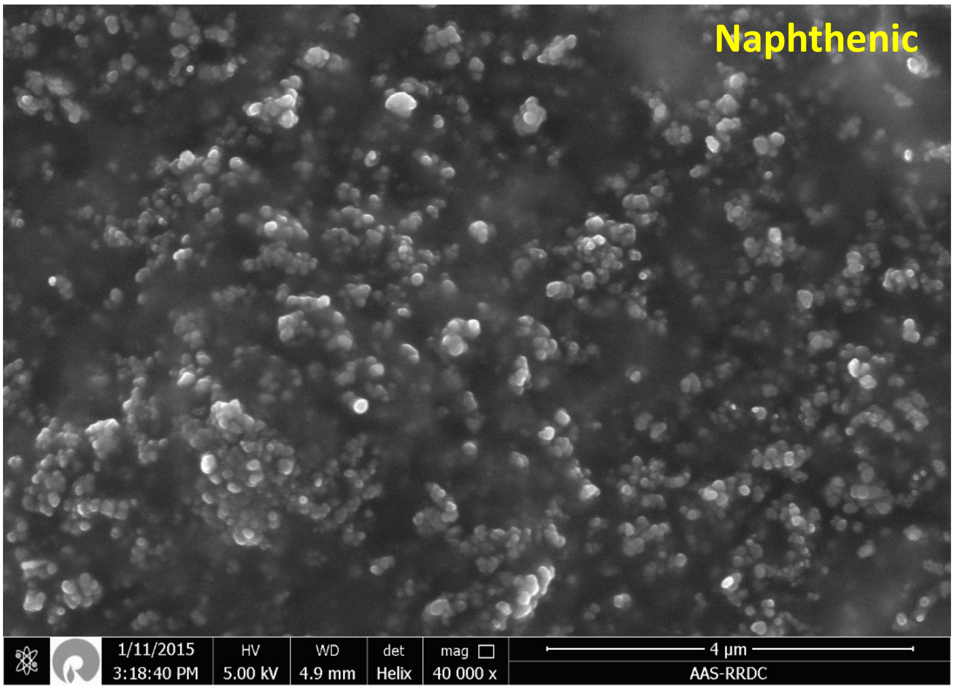

Fig. 3.8: SEM image (40000 X magnification) for Naphthenic_ ASTM master batch compound

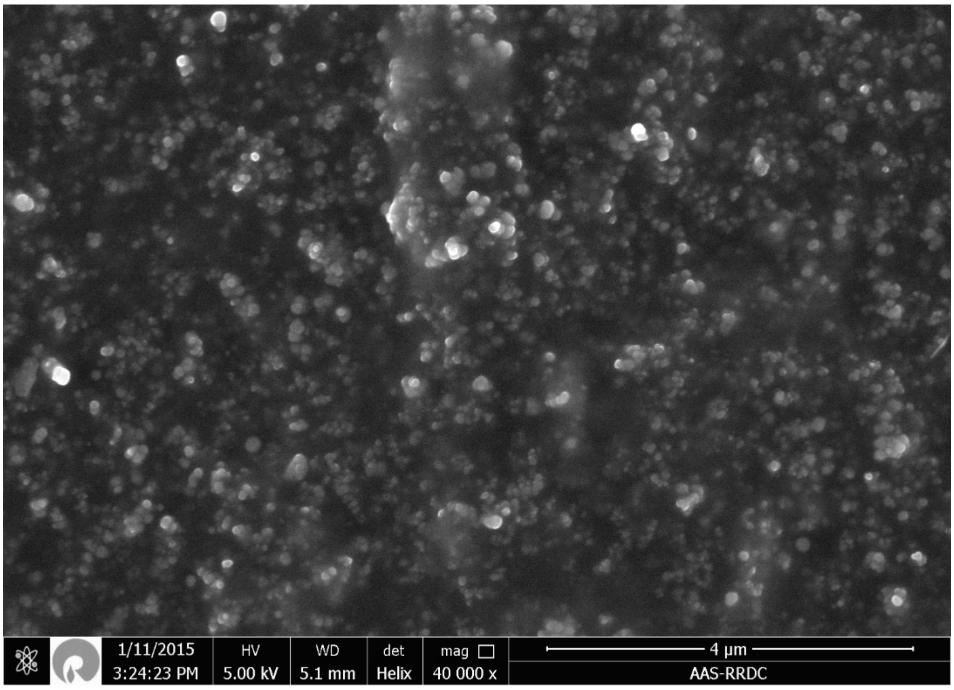

Fig. 3.9: SEM image (40000 X magnification) for NO2_ASTM master batch compound

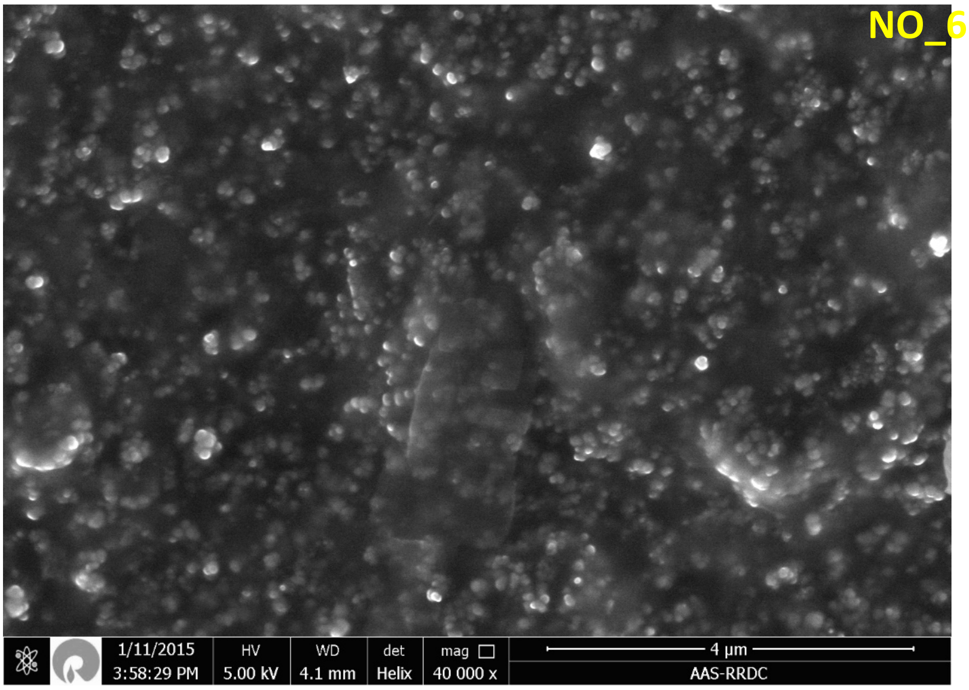

Fig. 3.10: SEM image (40000 X magnification) for NO6_ASTM master batch compound

Test results are showing comparable carbon black dispersion for all samples while analysing images captured for 10000X and 20000X magnification. However, some difference was observed while analysing the images captured at 40000X magnification. Carbon black aggregate size and inter-aggregate distance were found to be comparable for all the samples. This indicates that modified vegetable oil extended SBR based compounds have comparable properties with petroleum oil extended SBR based compounds for dispersion properties.

3.5.2 Passenger Car Radial Tire Tread Compound Recipe

Test results for final compounds like Mooney viscosity, power law index, dispersion, activation energy and rheometric properties are given in Tables 3.16 and 3.17.

Table 3.16: PCR tire tread final batch compound processing properties

Parameter / Sample	Mooney viscosity (MU)	Power law index	Filler dispersion (%)	Activation energy, Eα (kCal mol^{-1} g^{-1})
PCR_F_TDAE	55.4	0.202	53.0	3248
PCR_F_Naphthenic	56.7	0.187	67.3	2805
PCR_F_NO_2	55.8	0.180	65.4	2853
PCR_F_NO_6	54.6	0.167	61.5	2954
PCR_F_NO_7	54.7	0.189	57.0	2841
PCR_F_NO_8	54.2	0.192	63.0	2785
PCR_F_NO_9	51.9	0.190	57.7	2870
PCR_F_NO_10	57.5	0.179	64.2	2669

Table 3.17: PCR tire tread compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	tS2 (min)	tC10 (min)	tC50 (min)	tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
PCR_F_TDAE	2.44	10.30	4.32	2.64	6.44	14.99	7.86	8.1
PCR_F_Naphthenic	2.61	8.61	4.27	2.05	6.32	15.29	6.00	7.6
PCR_F_NO_2	2.56	8.27	4.20	1.93	6.10	14.82	5.71	7.8
PCR_F_NO_6	2.51	9.57	4.22	2.28	6.46	15.36	7.06	7.6
PCR_F_NO_7	2.65	8.79	4.26	2.25	6.21	14.59	6.14	8.1
PCR_F_NO_8	2.36	7.74	4.09	1.82	5.92	14.31	5.38	8.0
PCR_F_NO_9	2.46	7.70	4.15	2.08	5.90	14.13	5.24	8.3
PCR_F_NO_10	2.75	10.14	3.96	2.14	6.05	14.34	7.39	8.2

* Cure rate = 100/(tC90 -t C10)

Mooney viscosity was found comparable for all compounds. Power law index (n) close to zero or relative lower value, while means plastic nature of rubber compound and hence, better shear thinning (Flow behavior) of rubber compound. Higher activation energy value means rubber compound need high energy for compound flow, which indicates poor processing. Compounds prepared with vegetable oil-based SBRs displayed lower power law index, lower activation energy and higher filler dispersion as compared to compound prepared with TDAE oil extended SBR. This indicates better processing properties for compounds prepared with vegetable oils-based SBRs. Compounds prepared with naphthenic oil and vegetable oil based SBR show comparable processing properties. Compound prepared with NO_6 and NO_10 vegetable oil-based SBRs have comparable rheometric properties with respect to TDAE oil. Compound prepared with NO_2 and NO_7 to NO_9 vegetable oil-based SBRs exhibited less delta torque value as compared to TDAE oil. This may be due to presence of more olefinic content as indicated by NMR of these oils.

3.5.3 ASTM Compound Mixing (With curatives adjustment)

Rheometric properties are shown in Table 3.18.

Table 3.18: ASTM compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	Scorch safety time, tS2 (min)	tC10 (min)	tC50 (min)	Optimum cure time, tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
ASTM Naphthenic	2.50	11.83	4.53	2.81	6.28	13.00	9.33	9.8
ASTM_NO_2	1.95	11.94	4.16	3.42	5.57	10.43	9.99	14.3
ASTM_NO_6	1.94	11.77	4.95	3.29	6.93	13.98	9.83	9.4
ASTM_NO_7	2.56	12.54	3.60	2.32	4.97	10.01	9.98	13.0
ASTM_NO_8	2.66	11.91	3.59	2.26	4.97	10.47	9.25	12.2
ASTM_NO_9	2.41	11.87	3.50	2.17	4.95	10.30	9.46	12.3
ASTM_NO_10	2.07	12.26	4.02	2.78	5.97	12.38	10.19	10.4

*Cure rate = 100/(tC90 - tC10)

Compounds prepared with vegetable oil-based SBRs have comparable delta torque value with respect to naphthenic oil. Lower delta torque and modulus were observed for compounds based on few vegetable oils (like NO_2, NO_7, NO_8 and NO_9) extended SBRs, when similar dosage of curatives was used. This is due to presence of more olefinic content in these vegetable oils. For better comparison of rubber or any other ingredients in standard recipe, it is better to match compound torque/modulus first by adjusting filler, oil and curatives dosage. So, higher dosage (15 to 25%) of curatives (sulfur and accelerator) was used for compounds prepared with vegetable oil-based SBRs (except NO_6 and NO_10) to achieve similar delta torque value. These compounds show higher cure rate index due to use of higher curatives. The NO_6 and NO_10 vegetable oil extended SBRs do not need additional curatives due to relatively higher saturation with respect to other vegetable oils.

Vegetable oils contain unsaturated fatty acids, which may affect the cure characteristics and mechanical properties of filled compounds as these free acids took part in vulcanization. Most of the vegetable origin oils are rich in oleic and linoleic acids such as sesame, rapeseed, sunflower, soybean and peanut oils, linseed oil is most unsaturated vegetable oil with presence of oleic, linoleic, and linolenic acids Coconut oil is most saturated vegetable oil, which contains very less oleic and linoleic acids. It contains mainly palmitic, stearic, lauric and myristic acids. Palm oil has both; saturated and unsaturated carbon chains due to presence of palmitic acid and oleic acid. Ratio of unsaturated to saturated acid content is very high for castor oil and it is very low for coconut oil. Palm oil has this ratio slightly higher with respect to coconut oil. Groundnut, soybean and mustard oil has the moderate ratio[1-7].

3.5.4 ASTM Gum Compound Recipe (High styrene only)

Test results for rheometric properties are given in Table 3.19.

Table 3.19: ASTM gum compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	tS2 (min)	tC10 (min)	tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
Gum_DAE	0.79	4.68	15.62	11.07	23.28	3.89	8.2
Gum_TDAE	0.78	5.19	14.00	10.83	25.85	4.41	6.7
Gum_RAE	0.81	4.60	18.36	12.75	27.57	3.79	6.7
Gum_Naphthenic	0.67	4.35	21.36	14.68	31.63	3.68	5.9
Gum_NO_2	0.19	2.12	8.67	4.82	17.00	1.93	8.2
Gum_NO_6	0.64	4.00	21.30	13.54	30.54	3.36	5.9
Gum_NO_7	0.46	3.29	23.04	11.12	29.05	2.83	5.6
Gum_NO_8	0.24	2.36	8.43	4.88	19.65	2.12	6.8
Gum_NO_9	0.51	3.28	18.34	8.42	22.72	2.77	7.0
Gum_NO_10	0.56	4.44	18.91	12.80	29.33	3.88	6.0

* Cure rate = 100/ (tC90 - tC10)

Compounds prepared with S40_NO_6 and S40_NO_10 have shown rheometric properties almost comparable with naphthenic oil. Compounds prepared with S40_NO_2 and S40_NO_7 to S40_NO_9 have less delta torque value, which may be due to presence of more olefinic content as a indicated by NMR of these oils.

3.5.5 Motorcycle Tire Tread Compound Recipe

Test results for final batch uncured compounds are presented in Tables 3.20 to 3.21.

Table 3.20: Motorcycle tire tread final batch compound processing properties

Parameter / Sample	Mooney viscosity (MU)	Power law index	Activation energy, Eα (kCal mol^{-1} g^{-1})
MCT_F_DAE	70	0.187	2444
MCT_F_TDAE	67	0.194	2434
MCT_F_RAE	66	0.191	2550
MCT_F Naphthenic	60	0.190	2419
MCT_F_NO_2	53	0.198	2596
MCT_F_NO_6	57	0.194	2273
MCT_F_NO_7	64	0.188	2349
MCT_F_NO_8	63	0.185	2201
MCT_F_NO_9	65	0.187	2301
MCT_F_NO_10	64	0.185	2257

Table 3.21: Motorcycle tire tread compound rheometric properties

Parameter / Sample	Min TQ (dNm)	Max TQ (dNm)	tS2 (min)	tC10 (min)	tC90 (min)	Delta TQ (dNm)	Cure rate* (sec^{-1})
MCT_F_DAE	2.70	13.31	5.08	4.27	10.81	10.61	15.3
MCT_F_TDAE	2.56	13.46	5.45	4.51	12.07	10.90	13.2
MCT_F_RAE	2.55	12.87	5.59	4.67	11.79	10.32	14.0
MCT_F Naphthenic	2.35	12.37	5.23	4.20	11.50	10.02	13.7
MCT_F_NO_2	2.08	9.67	4.76	3.70	10.69	7.59	14.3
MCT_F_NO_6	2.31	11.37	5.09	3.89	10.41	9.06	15.3
MCT_F_NO_7	2.61	10.73	4.80	3.52	10.82	8.12	13.7
MCT_F_NO_8	2.51	10.67	4.76	3.48	10.54	8.16	14.2
MCT_F_NO_9	2.53	11.04	4.74	3.49	10.75	8.51	13.8
MCT_F_NO_10	2.56	13.19	4.67	3.70	11.18	10.63	13.4

* Cure rate = 100/ (tC90 - tC10)

All the compounds have shown Mooney viscosity in line with respective raw OE-SBRs Mooney viscosity. Power law index (n) close to zero or relative lower value means plastic nature of rubber compound and hence, better shear thinning (Flow behaviour) of rubber compound. Power law index was found to be comparable for all compounds. Higher activation energy means rubber compound need high energy for compound flow, which indicates poor processing. Compounds based on S40_NO_6 to S40_NO_10 have shown lower activation energy as compared to compound prepared with petroleum oil extended SBR. This may be due to absence of aromatic content in these vegetable oils. Refractive index[8] and nuclear magnetic resonance (NMR) data indicates the presence of aromatic content in oil samples. Rheometric properties for motorcycle tire tread compounds were found in line with gum compounds.

3.6 VULCANIZATE PROPERTIES

3.6.1 Passenger Car Radial Tire Tread Compound Recipe

Test results for stress-strain including hardness are in Table 3.22.

Table 3.22: PCR tire tread compound stress-strain properties

Parameter / Sample	M100 (MPa)	M200 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)
PCR_F_TDAE	2.3	6.3	11.3	21.2	494	60
PCR_F_ Naphthenic	1.5	4.3	8.5	18.9	536	53
PCR_F_NO_2	1.7	5.0	9.3	18.9	500	53
PCR_F_NO_6	1.9	5.7	11.1	18.9	444	55
PCR_F_NO_7	1.7	4.7	9.1	18.9	521	56
PCR_F_NO_8	1.3	3.5	7.0	18.9	603	51
PCR_F_NO_9	1.4	3.8	7.4	19.1	597	53
PCR_F_NO_10	1.9	5.6	10.9	18.6	427	57

Reinforcement index and rubber-filler interaction parameter are given in Table 3.23

Table 3.23: PCR tire tread compound reinforcement index and rubber-filler interaction parameter

Parameter Sample	RI (M300/M100)	M300-M100 (MPa)	G′@1%/ G′@25%	I (MPa)
PCR_F_TDAE	4.9	9.0	2.315	1.94
PCR_F_Naphthenic	5.7	7.0	1.993	1.76
PCR_F_NO_2	5.5	7.6	1.922	1.98
PCR_F_NO_6	5.8	9.2	1.946	2.36
PCR_F_NO_7	5.4	7.4	2.015	1.84
PCR_F_NO_8	5.4	5.7	2.013	1.42
PCR_F_NO_9	5.3	6.0	1.934	1.55
PCR_F_NO_10	5.7	9.0	1.884	2.39

Swell index, Volume fraction and crosslink density and glass transition temperature are given in Table 3.24.

Table 3.24: PCR tire tread compound crosslink density and glass transition temperature

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink density X 10^4 (mol cm^{-3})	Tg (°C)
PCR_F_TDAE	2.24	0.266	1.68	-50.2
PCR_F_Naphthenic	2.37	0.248	1.45	-52.1
PCR_F_NO_2	2.41	0.242	1.38	-57.3
PCR_F_NO_6	2.24	0.268	1.70	-54.2
PCR_F_NO_7	2.31	0.256	1.54	-51.8
PCR_F_NO_8	2.54	0.225	1.18	-56.4
PCR_F_NO_9	2.49	0.231	1.24	-57.9
PCR_F_NO_10	2.20	0.277	1.83	-51.6

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have shown similar (within experimental error) static modulus as compared to TDAE oil. Vulcanizates prepared with vegetable oil-based SBRs have shown slightly less tensile strength and less hardness, which may be due to less crosslink density. Vulcanizate prepared with NO_8 and NO_9 have lowest modulus and hardness due to lowest crosslink density and lowest delta torque. However, crosslink density may be increased by adjustment of curatives type and dosage level. Tg of all the vulcanizates were found to be in line with respective OE SBR.

3.6.2 ASTM Compound Mixing (With curatives adjustment)

Test results for stress-strain including hardness and reinforcement index are given in Table 3.25.

Table 3.25: ASTM compound stress-strain

Parameter / Sample	M100 (MPa)	M200 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)	RI (M300 /M100)
ASTM_Naphthenic	1.8	5.1	9.8	21.4	540	54	5.4
ASTM_NO_2	1.9	5.5	10.0	20.2	532	56	5.3
ASTM_NO_6	1.9	5.7	10.9	19.7	467	54	5.7
ASTM_NO_7	1.8	5.2	9.7	19.7	510	55	5.4
ASTM_NO_8	1.8	4.9	9.4	19.2	505	55	5.2
ASTM_NO_9	1.8	5.0	9.7	20.4	513	53	5.4
ASTM_NO_10	1.9	5.6	10.8	18.8	458	56	5.7

Swell index volume fraction and crosslink density are shown in Table 3.26.

Table 3.26: ASTM compound crosslink density

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink Density X 10^4 (mol cm^{-3})
ASTM_ Naphthenic	1.92	0.327	2.59
ASTM_NO_2	1.93	0.327	2.55
ASTM_NO_6	1.92	0.330	2.62
ASTM_NO_7	1.93	0.326	2.52
ASTM_NO_8	2.00	0.314	2.33
ASTM_NO_9	1.98	0.315	2.36
ASTM_NO_10	1.88	0.332	2.65

Vulcanizates prepared with vegetable oil based SBRs have comparable static modulus value with respect to naphthenic oil. This may be due to matching of the delta torque value for all the compounds. Tensile strength, elongation at break and hardness were found to be comparable for all compounds. Reinforcement index was found to be slightly high for NO_6 and NO_10 oil extended SBR based compounds. This may be due to relatively high rubber-filler interaction for these oil-based rubbers. Crosslink density was found slightly low for NO_8 and NO_9 and slightly high for NO_6 and NO_10 oil extended SBR based compounds. This may be due to relatively less unsaturation to saturation ratio which helps in tighter crosslinking.

3.6.3 ASTM Gum Compound Recipe (High styrene only)

Test results for stress-strain including hardness and reinforcement index are shown in Table 3.27.

Table 3.27: ASTM gum compound stress-strain properties

Parameter / Sample	M100 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)	RI (M300/ M100)
Gum_DAE	0.6	1.7	2.7	395	31	2.8
Gum_TDAE	0.7	2.2	2.3	309	36	3.1
Gum_RAE	0.6	1.6	3.2	458	32	2.7
Gum_Naphthenic	0.6	1.6	2.5	409	29	2.7
Gum_NO_2	0.3	0.6	1.1	512	19	2.0
Gum_NO_6	0.5	1.4	2.0	444	27	2.8
Gum_NO_7	0.4	1.0	2.1	512	24	2.5
Gum_NO_8	0.3	0.6	1.6	610	20	2.0
Gum_NO_9	0.5	1.1	2.2	494	22	2.2
Gum_NO_10	0.6	1.8	2.3	366	27	3.0

Swell index volume fraction and crosslink density data are shown in Table 3.28.

Table 3.28: ASTM gum compound crosslink density

Parameter / Sample	Swell index	Volume fraction, Vr	Crosslink density X 10^5 (mol cm^{-3})
Gum_DAE	4.33	0.160	5.68
Gum_ DAE	3.83	0.191	8.16
Gum_ RAE	4.38	0.161	5.82
Gum_ Naphthenic	4.47	0.162	6.05
Gum_NO_2	7.16	0.100	2.36
Gum_NO_6	5.05	0.143	4.64
Gum_NO_7	5.51	0.127	3.72
Gum_NO_8	6.77	0.101	2.44
Gum_NO_9	5.63	0.126	3.68
Gum_NO_10	4.56	0.155	5.43

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have similar (within experimental error) static modulus as compared to naphthenic oil. Higher unsaturated to saturated acid content ratio may affect the crosslink density adversely. Due to this, vulcanizate prepared with NO_2 has lowest crosslink density and lowest delta torque. This results in lowest modulus and hardness of this compound. Gum compound study was also made to check the effect of various oils (in absence of carbon black) on crosslink density.

3.6.4 Motorcycle Tire Tread Compound Recipe

Test results for stress-strain including hardness and reinforcement index are reported shown in Table 3.29

Table 3.29: Motorcycle tire tread compound stress-strain properties

Parameter Sample	M100 (MPa)	M300 (MPa)	TS (MPa)	EB (%)	Hardness (Shore A)	RI (M300 /M100)
MCT_F_DAE	2.0	10.1	20.5	530	60	5.1
MCT_F_TDAE	2.0	10.2	20.7	537	60	5.1
MCT_F_RAE	2.0	10.0	20.7	536	59	5.0
MCT_F_ Naphthenic	1.9	10.5	19.6	489	58	5.5
MCT_F_NO_2	1.3	6.3	18.9	707	52	4.9
MCT_F_NO_6	1.9	10.1	19.9	549	55	5.3
MCT_F_NO_7	1.6	8.4	18.6	568	53	5.3
MCT_F_NO_8	1.4	7.2	20.4	670	53	5.1
MCT_F_NO_9	1.6	8.4	21.4	640	54	5.3
MCT_F_NO_10	1.9	10.3	19.0	479	57	5.4

Swell index, volume fraction and crosslink density data are exhibited in Table 3.30.

Table 3.30: Motorcycle tire tread vulcanizate crosslink density

Parameter **Sample**	**Swell index**	**Volume fraction, Vr**	**Crosslink density X 10^4 (mol cm^{-3})**
MCT_F_DAE	2.43	0.234	1.29
MCT_F_TDAE	2.52	0.233	1.27
MCT_F_RAE	2.46	0.233	1.27
MCT_F_Naphthenic	2.53	0.230	1.24
MCT_F_NO_2	3.20	0.168	0.66
MCT_F_NO_6	2.64	0.209	1.01
MCT_F_NO_7	2.80	0.197	0.90
MCT_F_NO_8	3.03	0.174	0.71
MCT_F_NO_9	3.08	0.172	0.69
MCT_F_NO_10	2.70	0.213	1.05

Modulus and hardness values for motorcycle tire tread vulcanizates were found in line with gum vulcanizates. Crosslink density for motorcycle tire tread batches were found in line with crosslink density of respective gum batches.

3.7 PERFORMANCE

3.7.1 Passenger Car Radial Tire Tread Compound Recipe

Test results for heat build up, abrasion loss and rebound resilience shown in Table 3.31.

Table 3.31: PCR tire tread compound performance properties

Parameter / Sample	HBU (°C)	Abrasion (mm^3)	Rebound (%) at 30°C	Rebound (%) at 70°C
PCR_F_TDAE	18.9	97	34.9	44.5
PCR_F_ Naphthenic	22.5	98	36.4	45.9
PCR_F_NO_2	23.6	76	36.1	45.4
PCR_F_NO_6	18.5	92	36.2	46.2
PCR_F_NO_7	23.5	105	34.0	43.5
PCR_F_NO_8	27.5	92	32.3	41.9
PCR_F_NO_9	27.0	82	36.1	46.4
PCR_F_NO_10	18.2	98	37.0	46.2

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have less heat generation, which may be due to high crosslink density, high reinforcement index and high rubber-filler interaction parameter. Higher heat generation in rubber compound during dynamic application may lead to fast rubber degradation and deteriorate service life of the product. So, lower heat generation is better for product service life. The NO_2, NO_6, NO_8 and NO_9 oil extended SBR based vulcanizates have less abrasion loss as compared to vulcanizate prepared with TDAE oil extended SBR due to lower Tg value of these vulcanizates. Rebound resilience values measured at

30° and 70°C were found to be lowest for NO_8 oil extended SBR based vulcanizate. This may be due to lowest crosslink density and lowest rubber-filler interaction parameter for this compound. Other all vulcanizates have comparable rebound value.

3.7.2 ASTM Compound Mixing (With curatives adjustment)

Test results for angle abrasion loss and rebound resilience are presented shown in Fig. 3.11 and 3.12, respectively.

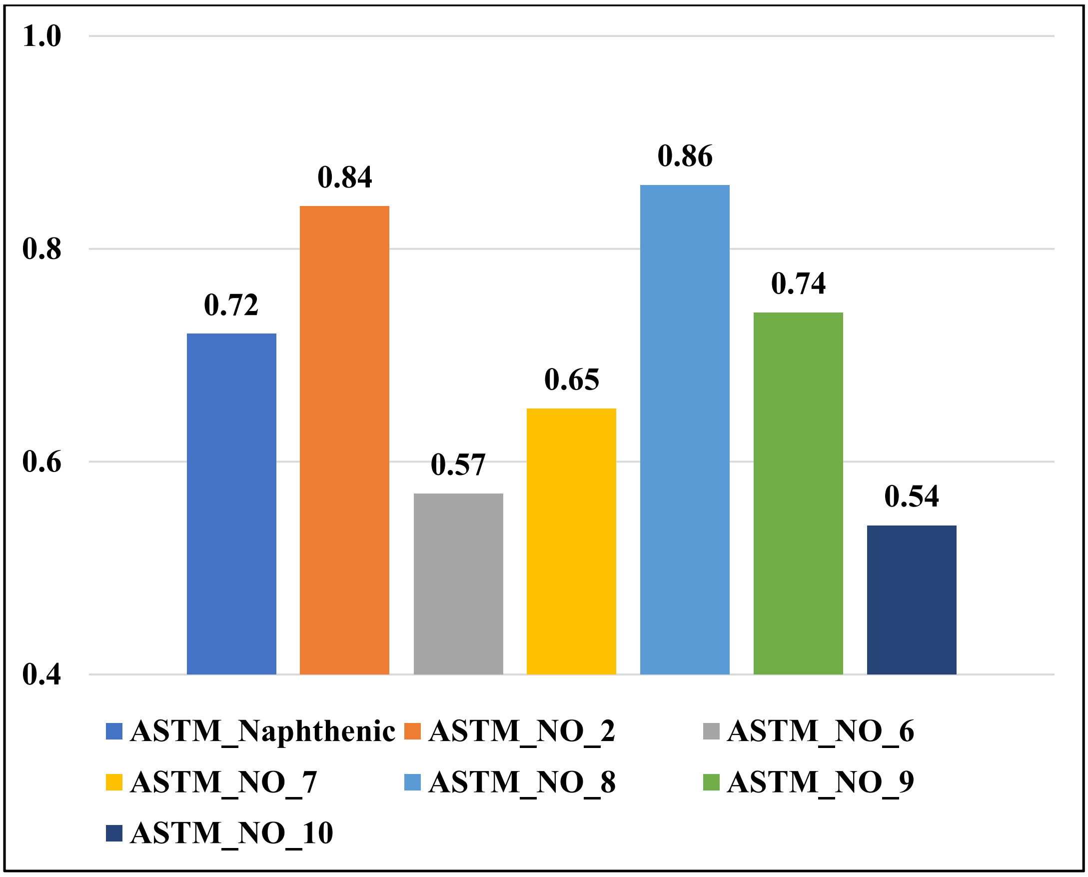

Fig. 3.11: Angle abrasion loss (g) by Akron tester (20° slip angle, 4000 cycles) for ASTM compounds

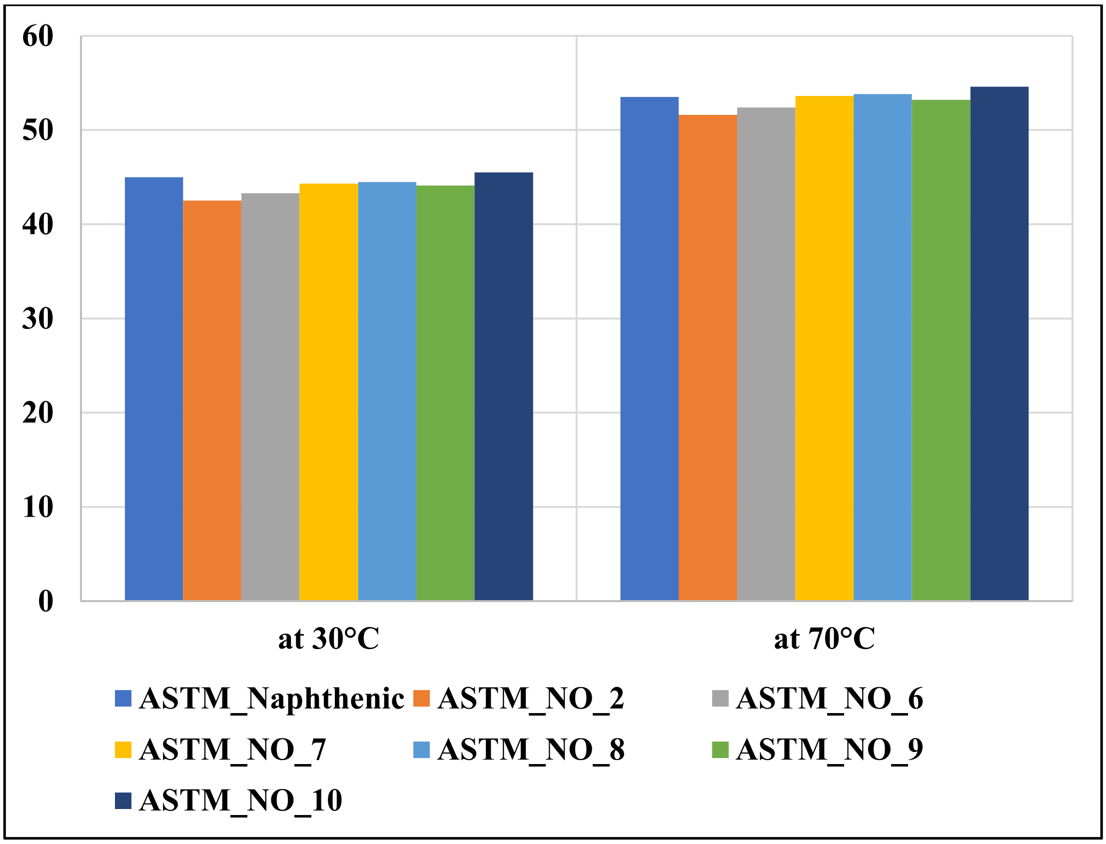

Fig. 3.12: Rebound resilience (%) for ASTM compounds

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have less abrasion loss as compared to naphthenic oil, which may be due to slightly high crosslink density, slightly high reinforcement index and high rubber-filler interaction parameter (Fig. 3.13).

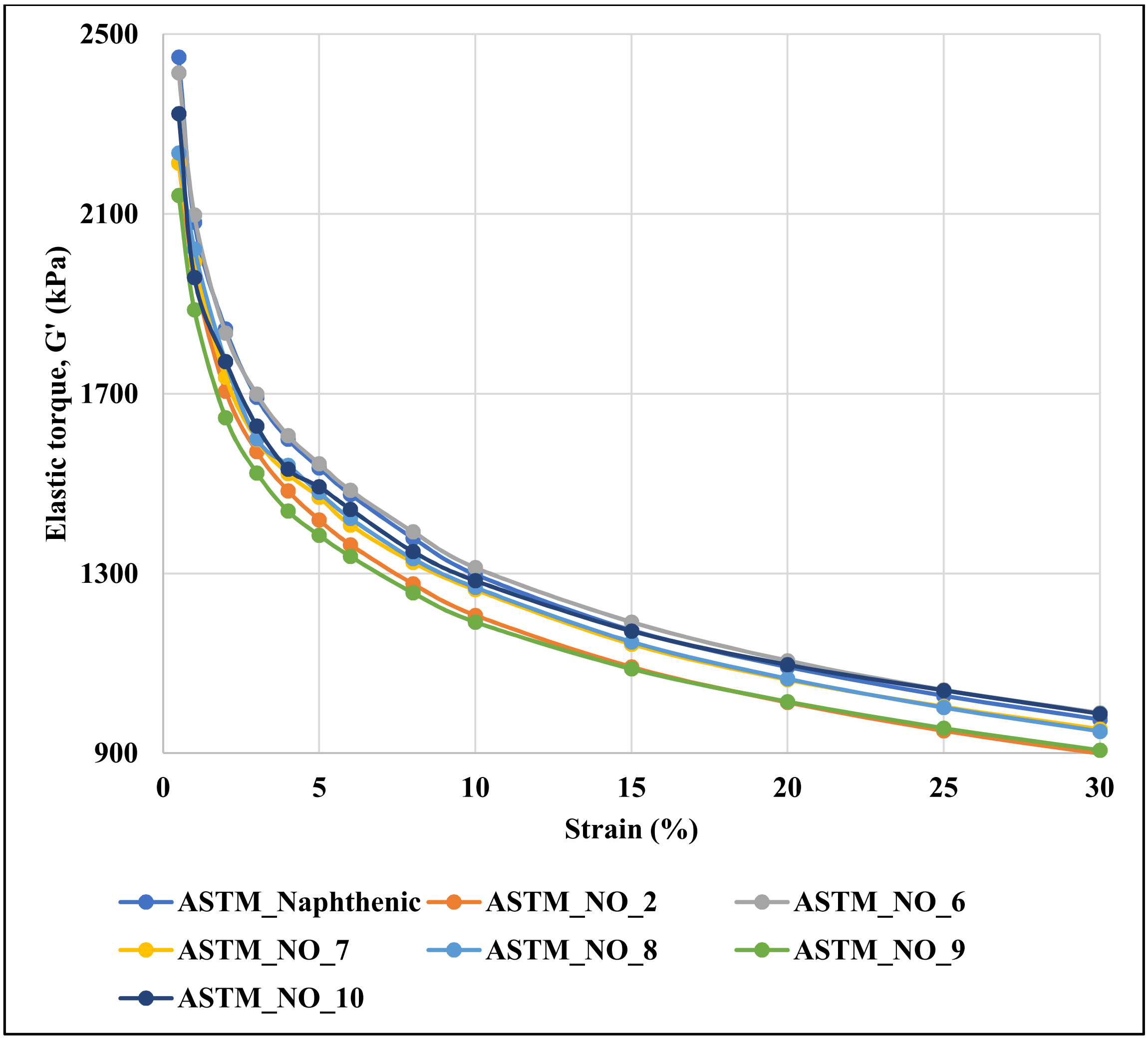

Fig. 3.13: Strain sweep test by RPA for final batch ASTM compounds @70°C (after cure)

These rubbers may be used for motorcycle tire application due to less abrasion loss in angle abrader because motorcycle tire needs frequent turns while in use. Rebound resilience values measured at 30° and 70°C were found to be comparable for all the compounds. This is due to matching of modulus of all rubber compounds. This indicated that all rubbers have almost similar elastic and viscus components, which may result in comparable traction and rolling resistance.

3.7.3 Motorcycle Tire Tread Compound Recipe

Test results for DIN and Akron abrasion loss, heat build-up (HBU) and rebound resilience @30° and 70°C are given in Table 3.32.

Table 3.32: Motorcycle tire tread compound performance properties

Parameter	**DIN abrasion (mm^3)**	**Akron abrasion (mm^3)**	**Heat build up (°C)**		**Rebound resilience (%)**	
			Surface	**Centre**	**@30°C**	**@70°C**
MCT_F_DAE	72	334	32.0	110	34.0	43.0
MCT_F_TDAE	70	291	29.3	107	35.7	46.2
MCT_F_RAE	73	288	27.1	101	34.9	45.1
MCT_F_ Naphthenic	67	565	25.5	99	36.0	47.1
MCT_F_NO_2	72	716	49.1	133	35.9	47.2
MCT_F_NO_6	68	313	32.0	106	38.2	46.5
MCT_F_NO_7	74	528	42.2	116	37.6	47.2
MCT_F_NO_8	72	669	47.2	120	37.8	47.1
MCT_F_NO_9	68	648	36.3	109	38.0	47.1
MCT_F_NO_10	70	266	33.6	104	37.8	46.8

DIN abrasion was found to be comparable for all compounds. However, Akron test at high severity condition displayed different observation. Vulcanizates prepared with all vegetable oils extended SBR (expect S40_NO_6 and S40_NO_10) have high abrasion loss and high heat generation. This may be due to low crosslink density of these compounds. Rebound resilience was found comparable for all compounds. Tg results are shown in Fig. 3.14.

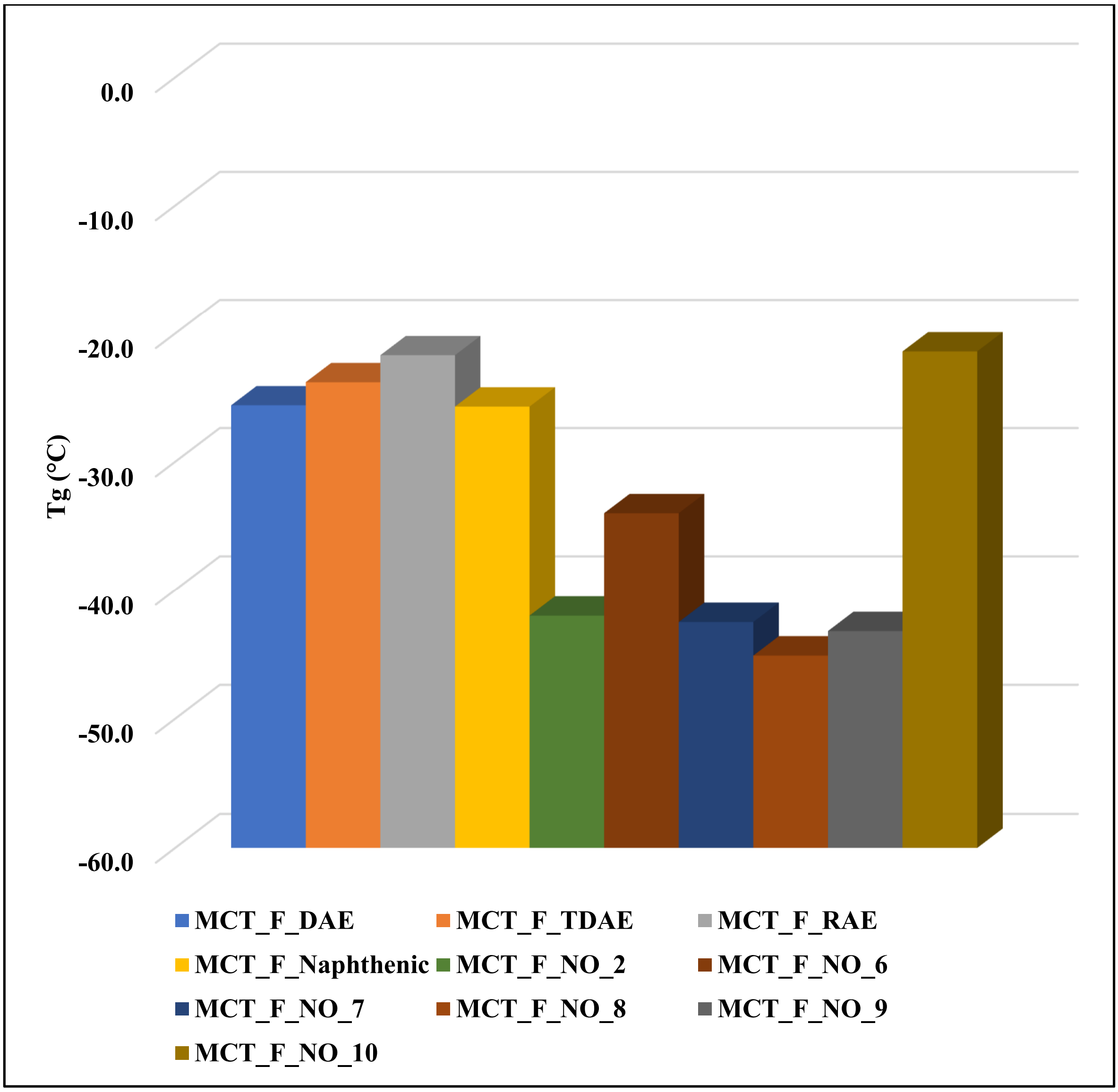

Fig. 3.14: Glass transition temperature (Tg) for motorcycle tire tread compounds

Tg of all the vulcanizates were found in line with raw rubber Tg. All vegetable oil extended SBR based vulcanizates except (S40_NO_10) have lower Tg. Despite low Tg value, vulcanizates prepared with S40_NO_2, S40_NO_7, S40_NO_8 and S40_NO_9 have high abrasion loss due to less crosslink density. Carbon dispersion was checked for cure specimen using volume resistivity measurement. Lower resistivity indicates better carbon black dispersion in rubber matrix. Test results are reported in Fig. 3.15.

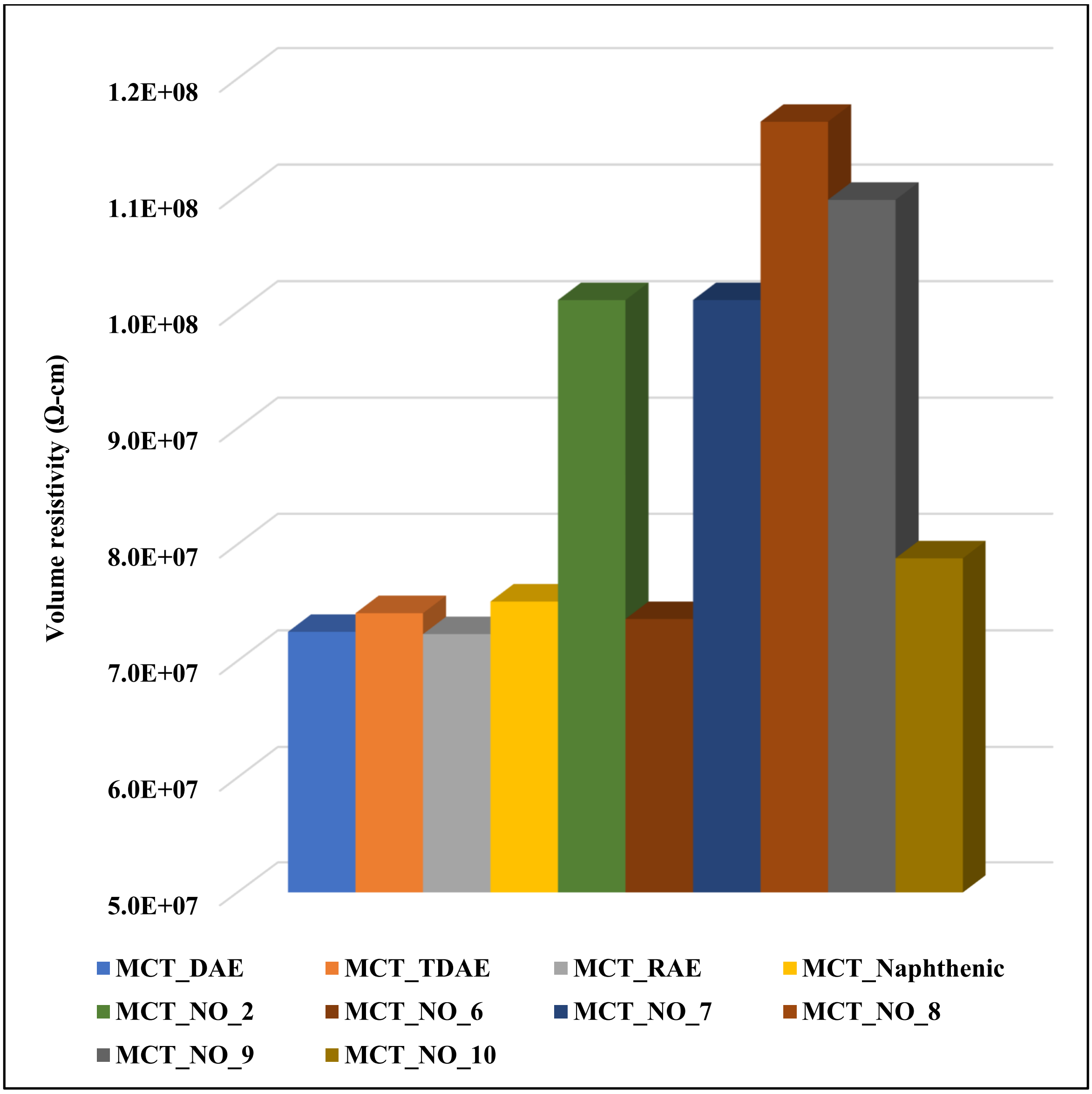

Fig. 3.15: Volume resistivity for motorcycle tire tread compound

Volume resistivity for compounds prepared with S40_NO_6 and S40_NO_10 was found comparable with petroleum oil. Poor carbon black dispersion for vulcanizates prepared with vegetable oils extended SBR (expect S40_NO_6 and S40_NO_10) may be due to for deterioration in various properties like high abrasion loss, high heat generation and lower modulus.

3.8 DYNAMIC PROPERTIES AND FILLER-FILLER NETWORK STUDY BY RPA

3.8.1 Passenger Car Radial Tire Tread Compound Recipe

Dynamic properties are presented in Table 3.33.

Table 3.33: PCR tire tread compound dynamic properties by RPA

Parameter / **Sample**	**G′@40°C (kPa)**	**G′@70°C (kPa)**	**Tan δ@ 40°C**	**Tan δ@ 70°C**
PCR_F_TDAE	2127	1540	0.28	0.23
PCR_F_ Naphthenic	1941	1330	0.25	0.20
PCR_F_NO_2	1846	1268	0.24	0.20
PCR_F_NO_6	1988	1403	0.24	0.19
PCR_F_NO_7	1963	1366	0.24	0.20
PCR_F_NO_8	1811	1180	0.27	0.22
PCR_F_NO_9	1757	1191	0.25	0.21
PCR_F_NO_10	2032	1482	0.23	0.17

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have comparable elastic modulus as compared to TDAE oil. Payne effect (after cure) is given in Fig. 3.16.

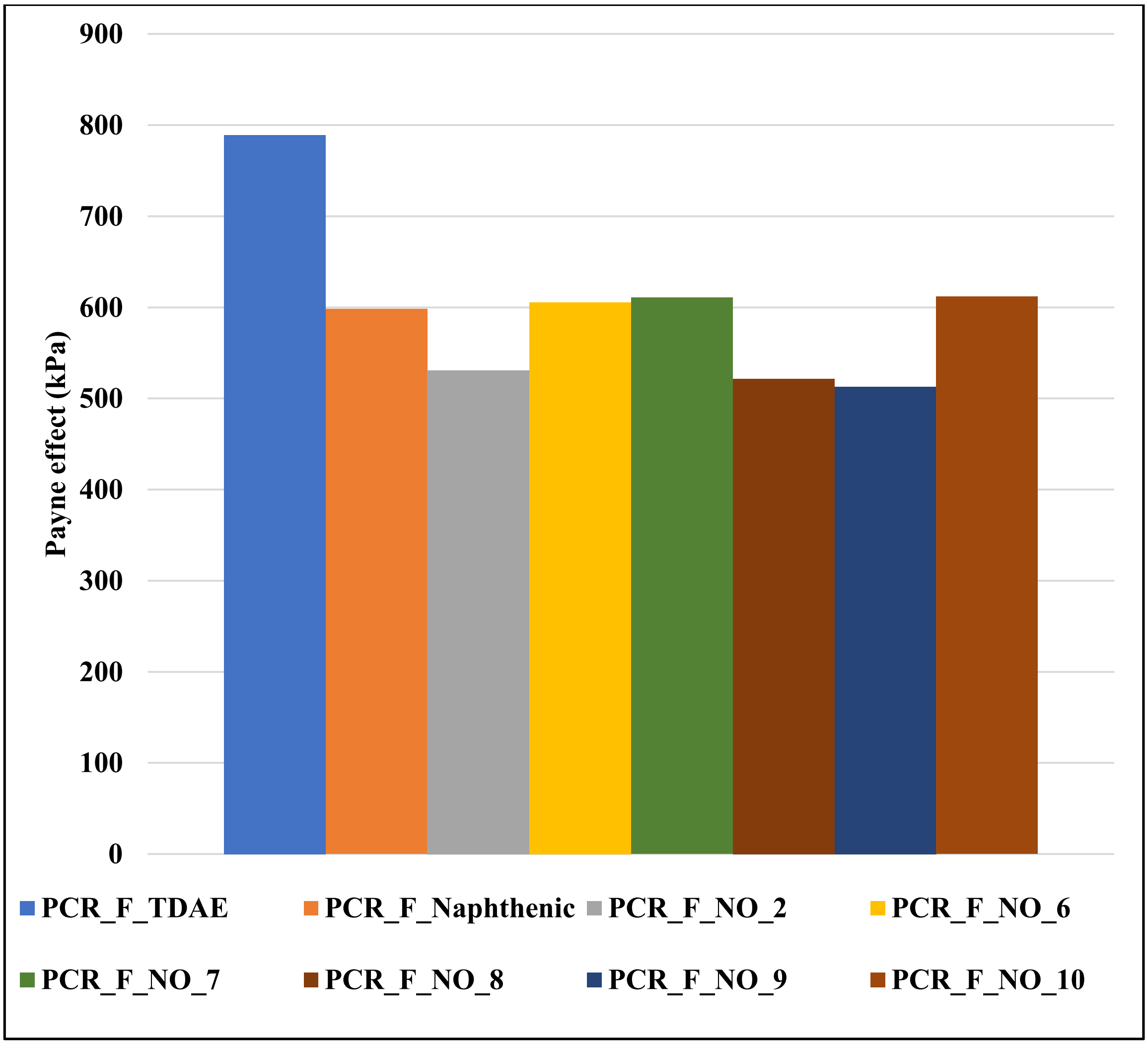

Fig. 3.16: RPA strain sweep test for final batch compound @70°C (after cure) for PCR tire tread compounds

Higher Payne effect means more filler-filler interaction. Generally high filler loading compounds and silica filler-based compounds show high Payne effect value[9]. Compounds prepared with vegetable oil-based SBRs have shown lower Payne effect (due to high polymer-filler interaction) as compared to TDAE oil

3.8.2 ASTM Compound Mixing (With curatives adjustment)

Dynamic properties and Payne effect are reported in Table 3.34.

Table 3.34: ASTM compound dynamic properties by RPA

Parameter Sample	G′@40°C (kPa)	G′@70°C (kPa)	Tan δ@ 40°C	Tan δ@ 70°C	Payne effect, ΔG□ (kPa)
ASTM_Naphthenic	1986	1522	0.24	0.19	1107
ASTM_NO_2	1998	1423	0.26	0.22	1065
ASTM_NO_6	2167	1546	0.23	0.19	980
ASTM_NO_7	2083	1469	0.24	0.21	1039
ASTM_NO_8	2098	1470	0.24	0.21	1073
ASTM_NO_9	1970	1387	0.25	0.21	1008
ASTM_NO_10	2110	1483	0.23	0.18	971

All the compounds have comparable dynamic properties. Elastic torque, G’ vs strain (after cure) in strain sweep test is shown in Fig. 3.17.

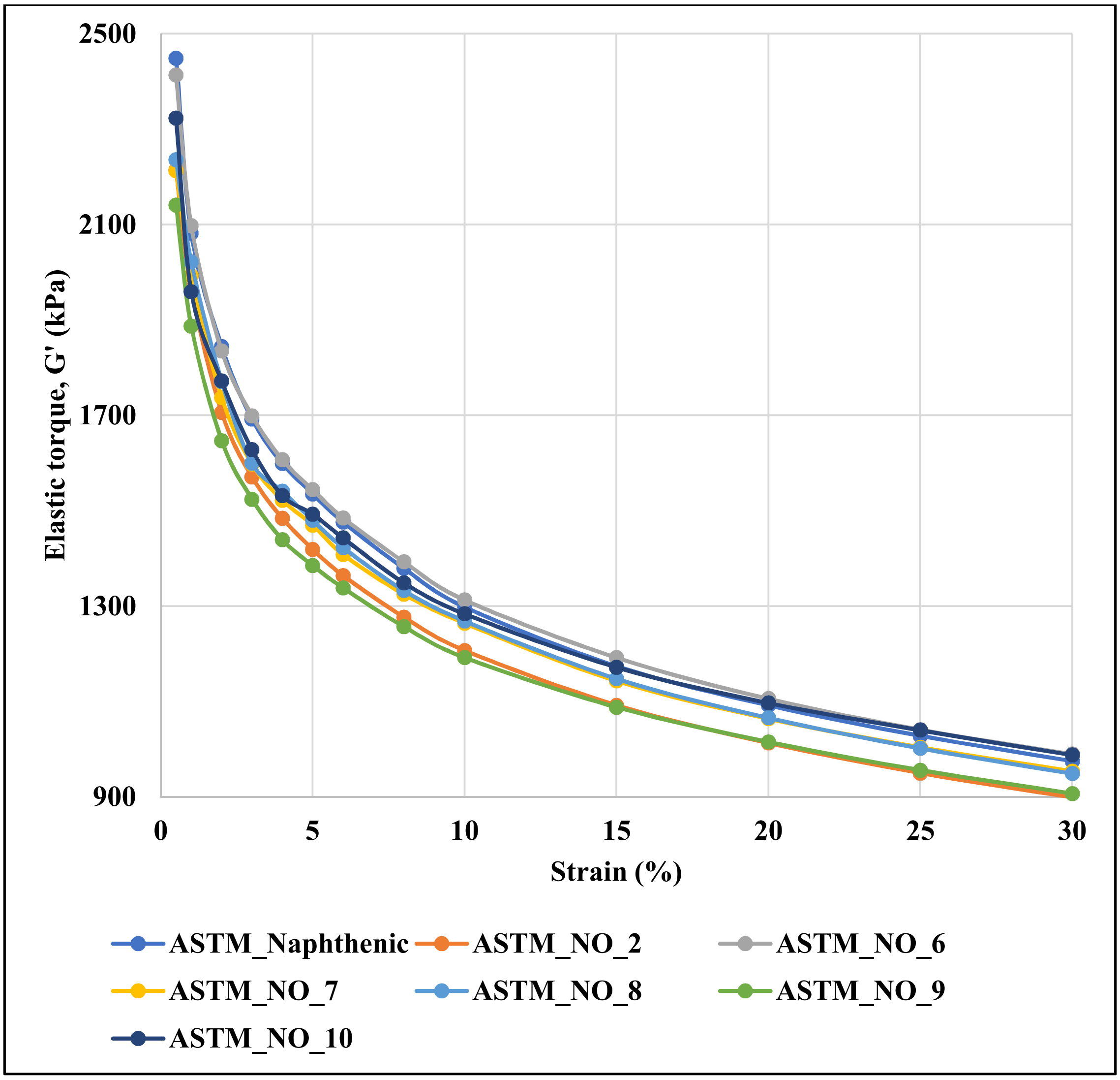

Fig. 3.17: Strain sweep test by RPA for final batch ASTM compounds @70°C (after cure)

Higher Payne effect means more filler-filler interaction. Compounds prepared with NO_6 and NO_10 vegetable oil-based SBRs have lower Payne effect (due to high rubber-filler interaction) as compared to naphthenic oil. High polymer-filler interaction helps in improvement of various mechanical and dynamic-mechanical properties. This rubber-filler interaction was improved due to presence of additional functional groups in the vegetable oils.

Motorcycle Tire Tread Compound Recipe

Dynamic properties are tabulated in Table 3.35.

Table 3.35: Motorcycle tire tread compound dynamic properties by RPA

Parameter / Sample	G′@40°C (kPa)	Tan δ @40°C	G′@70°C (kPa)	Tan δ @70°C
MCT_F_DAE	2754	0.34	1968	0.29
MCT_F_TDAE	2620	0.31	1873	0.27
MCT_F_RAE	2563	0.32	1828	0.27
MCT_F_Naphthenic	2410	0.29	1725	0.25
MCT_F_NO_2	2127	0.34	1378	0.33
MCT_F_NO_6	2383	0.31	1705	0.29
MCT_F_NO_7	1820	0.29	1291	0.28
MCT_F_NO_8	2113	0.31	1402	0.31
MCT_F_NO_9	2115	0.31	1441	0.30
MCT_F_NO_10	2395	0.28	1735	0.25

Compounds prepared with S40_NO_6 and S40_NO_10 have comparable dynamic modulus @ 40° and 70°C with naphthenic oil. This may be due to comparable maximum torque of these rubber compounds. Payne effect is presented in Fig. 3.18.

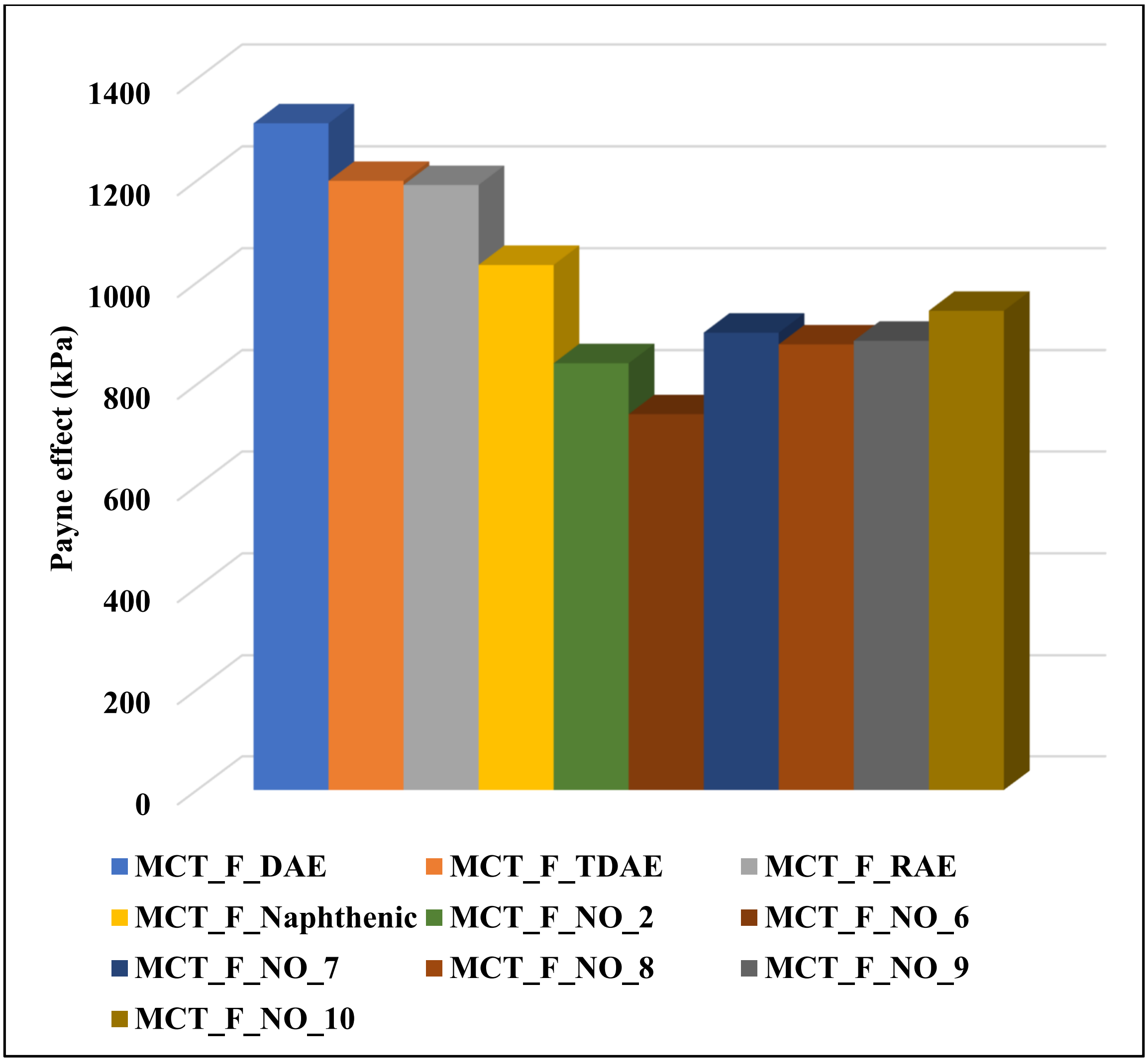

Fig. 3.18: RPA strain sweep test for final batch compound @70°C (after cure) for motorcycle tire tread compounds

Higher Payne effect means more filler-filler interaction[9]. Compounds based on vegetable oil extended SBR have lower Payne effect as compared to petroleum oil. Lower filler-filler interaction for these compounds may be due to presence of few additional functional groups in vegetable oils like triglyceride, ester, carbonyl, hydrogen bonded C-O, and acyl C-O. These groups may form bonds with surface groups present on carbon black, which resulted in more polymer-filler interaction and less filler-filler interaction.

3.9 DYNAMIC PROPERTIES BY DMA

3.9.1 Passenger Car Radial Tire Tread Compound Recipe

Test results for elastic modulus and tan δ are given in Table 3.36 and presented in Fig. 3.19.

Table 3.36: PCR tire tread compound dynamic properties measured by DMA

Parameters / **Sample**	**E′@0°C (MPa)**	**E′@30°C (MPa)**	**E′@60°C (MPa)**	**Tan δ @0°C**	**Tan δ @30°C**	**Tan δ @60°C**	**Tg (°C)**
PCR_F_TDAE	58.0	27.0	17.2	0.28	0.17	0.15	-24.7
PCR_F_Naphthenic	62.9	21.4	14.1	0.19	0.18	0.17	-31.3
PCR_F_NO_2	38.7	19.5	13.0	0.21	0.18	0.16	-36.2
PCR_F_NO_6	98.9	37.5	17.1	0.26	0.18	0.15	-30.2
PCR_F_NO_7	35.9	19.2	13.0	0.19	0.19	0.19	-30.4
PCR_F_NO_8	35.0	18.4	11.3	0.22	0.20	0.20	-35.9
PCR_F_NO_9	33.7	18.4	12.0	0.20	0.17	0.17	-35.8
PCR_F_NO_10	96.9	36.8	14.4	0.23	0.18	0.14	-25.9

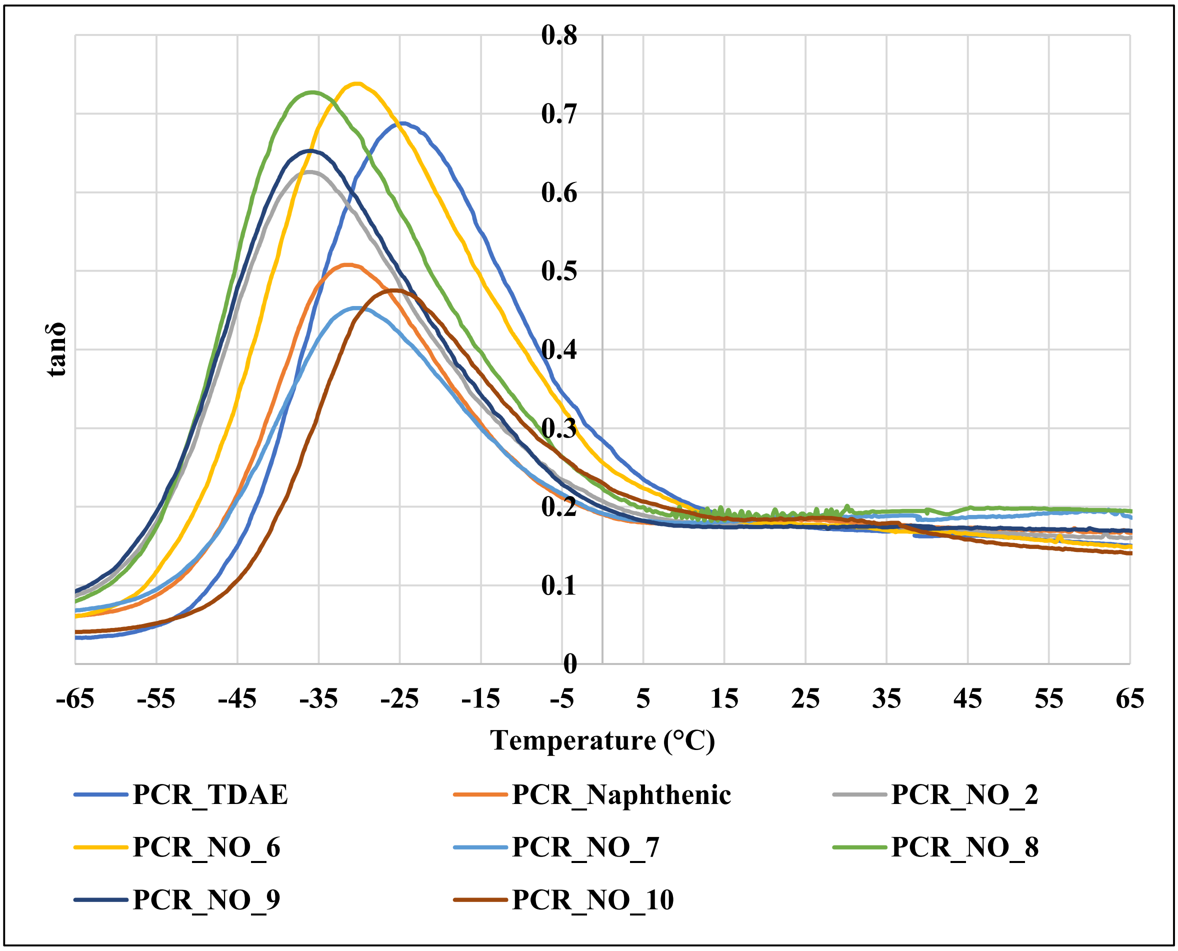

Fig. 3.19: DMA temperature sweep test for PCR tire tread compounds

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBR's have higher elastic modulus, which may be due to high rubber-filler interaction parameter.

Lower tan δ values is desired @ 60°C, which correlates with rolling resistance. Higher tan δ values are desired at 0° and 30°C, which correlate with wet and dry traction, respectively. Vulcanizates prepared with NO_6 and NO_10 vegetable oils extended SBRs have comparable tan δ value at 0°, 30° and 60°C as compared to TDAE oil. This indicates comparable performance for these vulcanizates like dry & wet tractions and rolling resistance. Vulcanizates prepared with NO_7 and NO_8 vegetable oil extended SBRs have slightly higher tan δ value at 30°, which indicates better dry traction for these vulcanizates. Dynamic Tg of all the vulcanizates were found in line with Tg of respective OE SBRs.

3.9.2 ASTM Compound Mixing (With curatives adjustment)

Rubber compounds are visco-elastic in nature. Hence, they release energy in the form of heat under deformation. This heat dissipation affects the tire traction and rolling resistance. It is very important to balance fuel economy and safety of cars. These requirements are related with rolling resistance and traction of tread compounds with respect to tire. The Tanδ is the ratio of viscous and elastic component of rubber compound. Lower tan δ values is desired @ 60°C, which correlates with rolling resistance. Higher tan δ values are desired at 0° and 30°C, which correlate with wet and dry traction, respectively. Due to this contradictory requirement, it is very difficult to achieve improvement in both: rolling resistance and traction at the same time[10,11].

Test results for elastic modulus and tan δ are presented in Fig. 3.20 and 3.21, respectively.

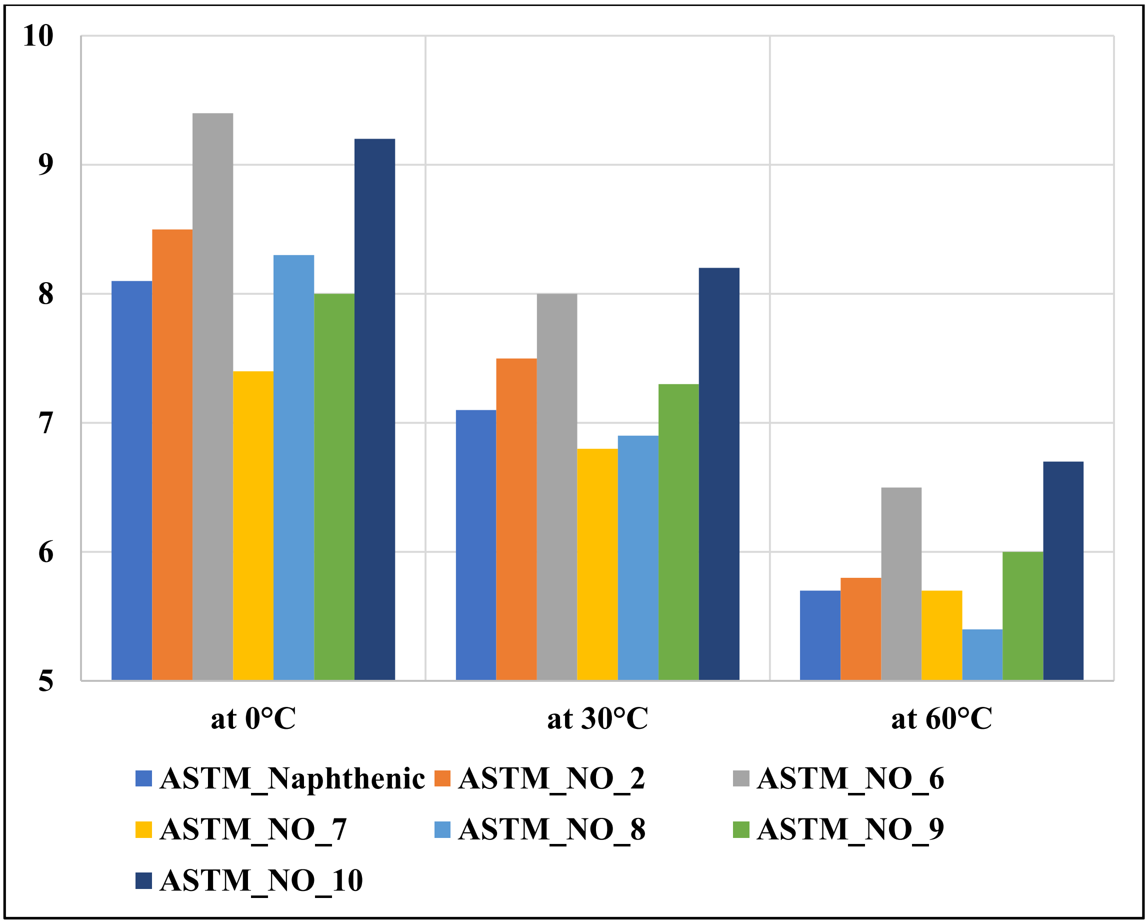

Fig. 3.20: Elastic modulus, E′ (MPa) measured by DMA for ASTM compounds

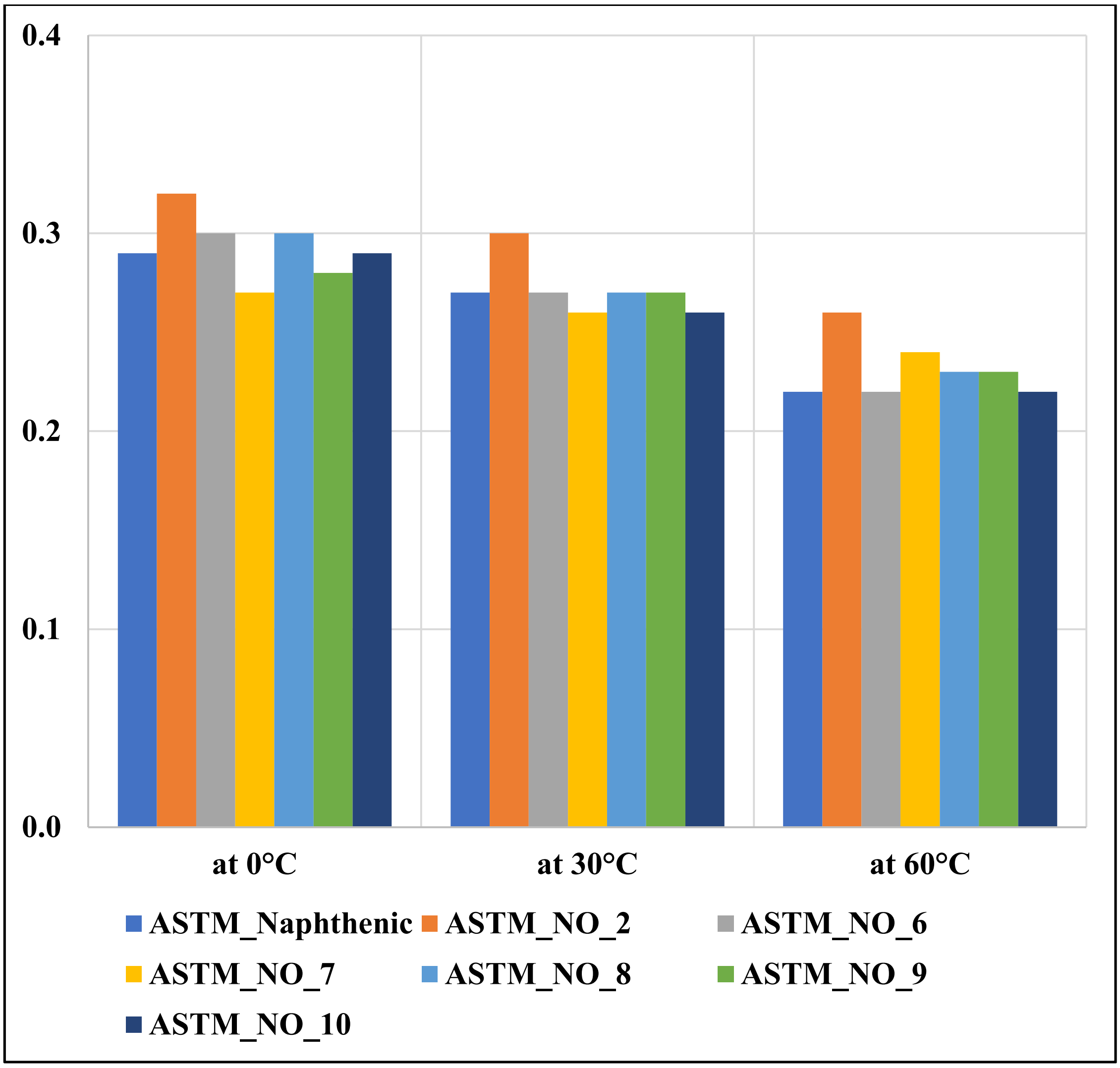

Fig. 3.21: Loss factor, tan δ for ASTM compounds

Vulcanizates prepared with NO_6 and NO_10 vegetable oil-based SBRs have slightly higher elastic modulus, which may be due to high rubber-filler interaction parameter. Vulcanizates prepared with NO_6 and NO_10 vegetable oil extended SBRs have comparable tan δ value at 0°, 30° and 60°C as compared to naphthenic oil. This indicates comparable performance for these vulcanizates like dry and wet traction and rolling resistance.

3.9.3 Motorcycle Tire Tread Compound Recipe

Test results are shown in Table 3.37.

Table 3.37: Motorcycle tire tread compound dynamic mechanical properties measured by DMA

Parameter / Sample	tan δ @0°C	tan δ @30°C	tan δ @60°C
MCT_F_DAE	0.39	0.37	0.28
MCT_F_TDAE	0.36	0.33	0.24
MCT_F_RAE	0.40	0.35	0.27
MCT_F_Naphthenic	0.35	0.32	0.23
MCT_F_NO_2	0.36	0.33	0.24
MCT_F_NO_6	0.32	0.29	0.23
MCT_F_NO_7	0.33	0.31	0.25
MCT_F_NO_8	0.34	0.31	0.25
MCT_F_NO_9	0.36	0.31	0.25
MCT_F_NO_10	0.34	0.30	0.23

Dynamic mechanical properties (tan δ) measured at 0°, 30° and 60°C indicate about wet traction, dry traction and rolling resistance properties of tire, respectively. Vulcanizates prepared with S40_NO_6 and S40_NO_10 have lower tan δ @60°C as compared to vulcanizate prepared with S40_DAE. This indicates better rolling resistance for these vulcanizates. This may be due to lower filler-filler interaction in these vulcanizates.

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CHAPTER – IV

DISCUSSION

CONTENTS

4.1 ASTM MASTER BATCH RECIPE

4.2 PCR TIRE TREAD COMPOUND RECIPE

4.3 ASTM COMPOUND WITH CURATIVES ADJUSTMENT

4.4 MOTORCYCLE TIRE TREAD COMPOUND RECIPE

4.1 ASTM MASTER BATCH RECIPE

Modified vegetable oils are eco-friendly in nature and may be used for extension of styrene butadiene rubber at latex stage to produce eco-friendly rubbers. The NO_2 and NO_6, samples were found compatible with SBR latex. Compounds prepared with these oils based SBR rubbers have comparable or slightly better processing properties, which was confirmed by lower mixing energy, lower activation energy and better rubber-filler interaction in the master rubber compound based on lower Payne effect and higher bound rubber content. All the samples have comparable carbon black dispersion, which was confirmed by strain sweep test in RPA and surface topology.

4.2 PCR TIRE TREAD COMPOUND RECIPE

E-SBR could be extended with vegetable oils like other mineral oils. Selected vegetable oils with solubility parameter close to SBR were used for oil extension purpose for better compatibility. Various chemical properties were checked for these rubbers and these were found in line with properties of mineral oil extended SBR. The developed grades of SBR were highly sustainable products as these were prepared with use of vegetable oils in place of petroleum-based oils. This is because NMR study evident from aromatic content was almost absent in these vegetable origin oils.

Passenger car radial (PCR) tire tread compounds were prepared with these new grades of SBR rubbers along with mineral oil based SBR rubbers. They have better processing properties, which was confirmed by lower mixing energy by 10-15%, lower power law index around 15%, higher filler dispersion around 20% and lower activation energy around 20%. Compounds prepared with NO_6 and NO_10 vegetable oil-based SBRs have better performance properties due to high reinforcement index around 15% and high rubber-filler interaction parameter around 20%. These compounds have also improvement in performance properties like abrasion resistance increased around 20% and tan δ value @60°C reduction around 15% as compared to TDAE oil extended SBR based compound. This may enhance service life of PCR tire and may also reduce fuel consumption. Vegetable origin oils may be alternative solution for extension of SBRs for use in PCR tire tread compound.

4.3 ASTM COMPOUND MIXING (With curatives adjustment)

ASTM compounds were prepared using OE-SBRs extended with naphthenic and various vegetable oils. Curatives like sulfur and accelerator dosage were adjusted to achieve similar static modulus for the oils (NO_2 and NO_7 to NO_9), which are having higher unsaturation to saturation fatty acid ratio. Curatives dosage was increased for these oil-based rubbers after taking few trials. Compounds prepared with NO_6 and NO_10 (Palmolein and coconut oils) vegetable oil-based SBRs have better performance (better abrasion resistance around 23%) properties due to high reinforcement index (around 5%) and high rubber-filler interaction parameter (around 12%). Vegetable origin oils may be alternative solution of naphthenic oil for extension of E-SBR in various tire and non-tire applications. Tire industry is encouraged to create sustainability culture, to reduce carbon footprint or circular economy by replacing tire components by sustainable products and replacing mineral oil by natural oils in last few years. These new grades of E-SBRs will be sustainable due to use of vegetable origin oils, which are having almost negligible PCA content. Also, these grades are improving the performance properties of the rubber compound and hence, these OE-SBR grades may be used in high performance applications.

4.4 MOTORCYCLE TIRE TREAD COMPOUND RECIPE

High styrene ESBR were extended with vegetable origin oils at laboratory scale. Selected vegetable origin oils with solubility parameter close to SBR were used for oil extension purpose. Various chemical properties for rubbers were checked for these rubbers and found in line with properties of mineral oil extended SBR. Rubbers developed with vegetable oils could find application in manufacturing of colored products due to their light color. These new grades of SBR are eco-friendly products as these were prepared with use of vegetable origin oils.

Motorcycle tire tread compounds prepared with vegetable oils based SBR rubbers have comparable or slightly better processing properties, which was confirmed by lower mixing energy, lower activation energy and better rubber-filler interaction in rubber compound. Compound prepared with samples S40_NO_6 and S40_NO_10 have most of the properties comparable with naphthenic oil extended SBR based compound.

Therefore, these vegetable origin oil extended SBR rubbers can be used for manufacturing of tire tread compound for high quality motorcycle.

Few vegetable oils based SBRs exhibited improvement in processing, performance and dynamic mechanical properties. These oils may be used for commercialisation to produce sustainable SBRs. Few vegetable oils based SBRs exhibited slow cure behaviour in rheometeric characterization. These oils extended SBRs based rubber compounds may be evaluated with higher dosage of curatives to adjust the cure rate and crosslink density. Research work may also be conducted with use of blend of oils in place of using single oil for extension of SBR. This may further optimise the properties of the rubber compounds.

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PUBLICATIONS

VEGETABLE OIL EXTENDED EMULSION STYRENE BUTADIENE RUBBERS FOR PASSENGER CAR RADIAL TIRE TREAD APPLICATION

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Abstract

Currently emulsion polymerized Styrene Butadiene Rubber (E-SBR) is extended with various petroleum based mineral oils like Distillate Aromatic Extract (DAE), Treated Distillate Aromatic Extract (TDAE), Residual Aromatic Extract (RAE) and Naphthenic oils. It is obvious that introduction of vegetable oil should result in almost zero Polycyclic Aromatic Content (PCA) content and therefore, are environmentally friendly, renewable, and sustainable. In the present work, vegetable oil extended Styrene Butadiene Rubber (OE-SBR) were characterized for chemical properties and found that all the properties were meeting the specification requirements of mineral oils extended grades. These rubbers were also evaluated in standard Passenger Car Radial (PCR) tire tread compound recipe for various processing, different vulcanizate and other performance properties. The developed grades with vegetable oils required less mixing energy (around 10% for master batch and 15% for final batch) and shown better flow behavior (around 15% power law index and 20% activation energy reduction), better carbon dispersion (around 20%), high reinforcement index (around 15%), better rubber-filler interaction parameter (around 20%), better abrasion resistance (around 20%) and lower tan δ value @60°C (around 15%) as compared to TDAE oil extended SBR based compound. This may help to improve life of a PCR tire and reduction in fuel consumption of the vehicle.

Keywords: Sustainability, vegetable oils, reinforcement index, rubber-filler interaction parameter, performance properties, etc

Published in: Journal of Elastomers & Plastics, **55**(8), 1251-1273. (2023)

TO EXPLORE EXTENSION OF EMULSION STYRENE BUTADIENE RUBBER WITH MODIFIED VEGETABLE OILS

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Abstract

Increasing industrialization and rapid change in market demand has led to aggressive competition impacting both business and environmental sustainability globally. In view of the new legislations, regulations and restrictions on the usage of hazardous materials, it becomes mandatory to use eco-friendly materials. In the present work, various petroleum-based and different modified vegetable oils are characterised for chemical and analytical properties. Styrene butadiene rubber (SBR) is extended with these oils at laboratory scale through emulsion polymerisation technique. Totally four number of petroleum-based oils like distillate aromatic extract (DAE), treated distillate aromatic extract (TDAE), residual aromatic extract (RAE) and naphthenic type oil and two number of modified vegetable oils, NO_2 and NO_6, are evaluated. All oils have shown compatibility with SBR latex which is confirmed by checking solvent extractables as well as oil leaching checking by visual inspection of oil extended rubber samples. These raw rubber samples are characterised for raw rubber properties as well as in ASTM-based rubber compound recipe to check their processing behaviour. Compounds prepared with both vegetable oil-based styrene butadiene rubber have shown comparable or slightly better processing properties as compared to compounds prepared with petroleum oil-based rubbers. Experimental compounds are also showing comparable carbon black dispersion and better polymer–filler interaction which may be due to the presence of various surface functional groups in vegetable oils. Microscopic pictures also confirm the comparable carbon black dispersion for all the samples.

Keywords: Sustainability, Eco-friendly materials, Vegetable oil, oil extended, styrene butadiene rubber, Compatibility, Processing properties, etc.

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