CHAPTER – I

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.

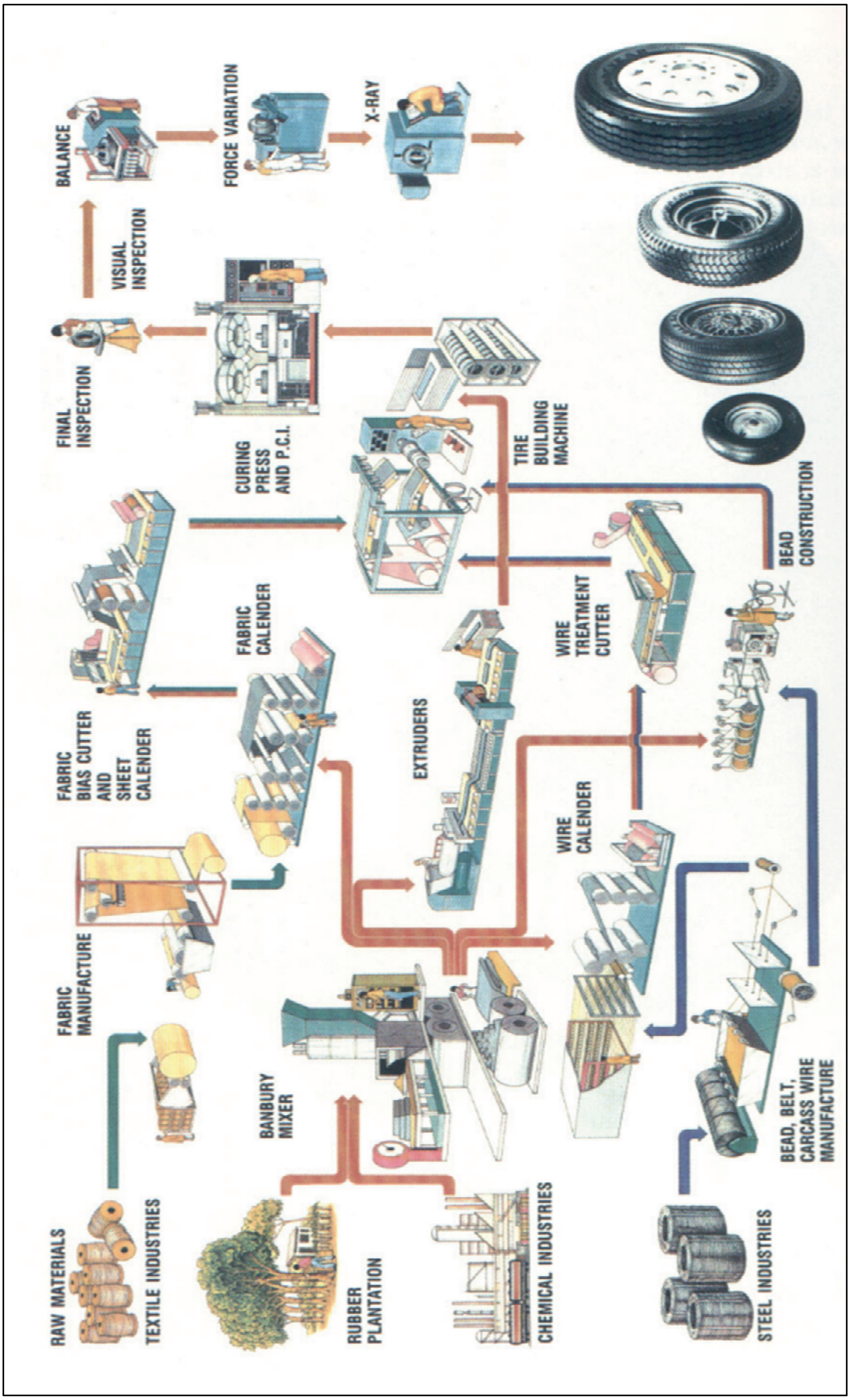

Fig. 1.1: Tire manufacturing flow diagram

(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.

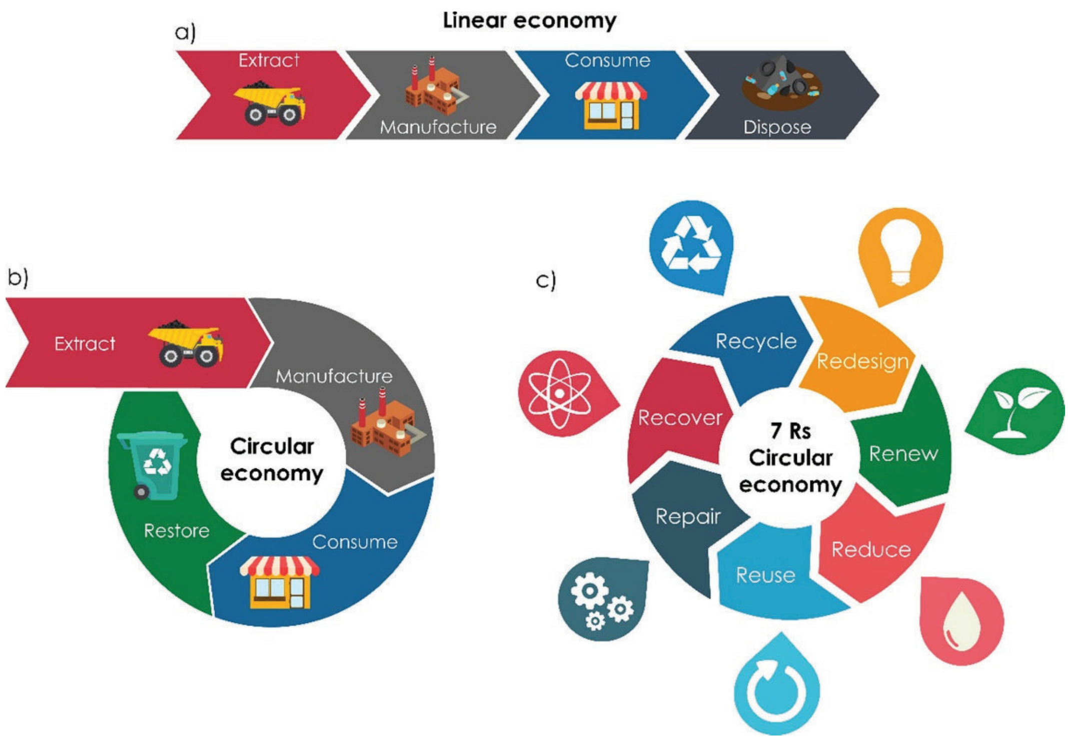

Fig. 1.2: (a) Linear economy model, (b) Circular economy model and (c) Circular economy model with 7R approach

(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

(With permission from A. Akbas, and, Y. Yuhana, Recycling, 6, 78, 2021)

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.

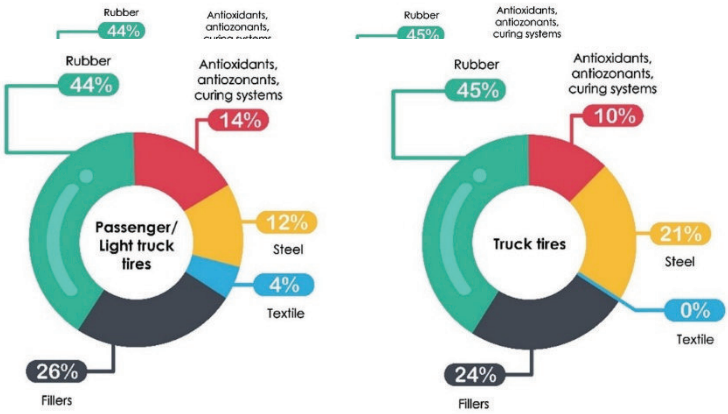

Fig. 1.4: Tire material compositions for passenger/light tires and truck tires

(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:

$$E = ED + EP + EH \quad \ldots (1.1)$$

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

$$\delta^2_T = \delta^2_D + \delta^2_P + \delta^2_H \quad \ldots (1.2)$$

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.

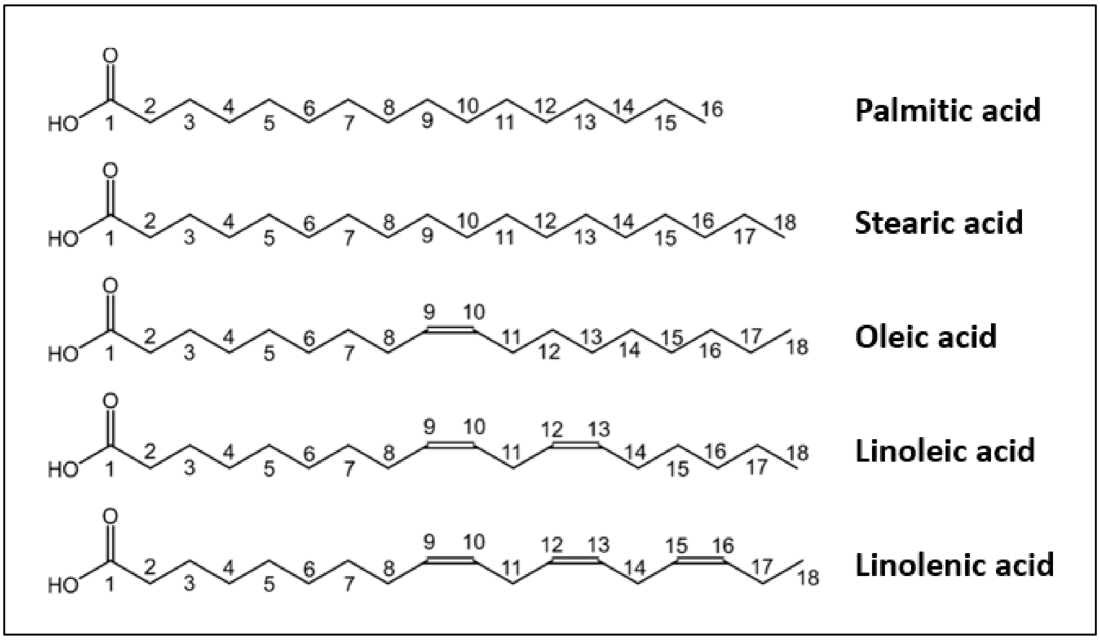

Fig. 1.5: Fatty acids chemical structures of vegetable oils

(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].

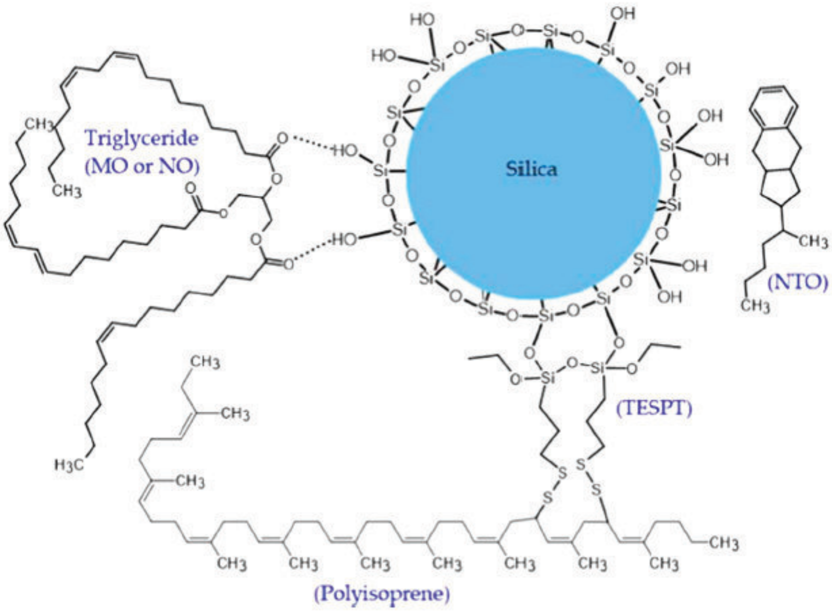

Fig. 1.6: Possible chemical interaction between ester groups of Niger oil (NO) and moringa oil (MO) and silanol groups of silica filler

(With permission from S. Boonrasri, P. Sae-Oui, A. Reungsang, and, P. Rachtanapun, polymers, 13, 1-12, 2021)

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.

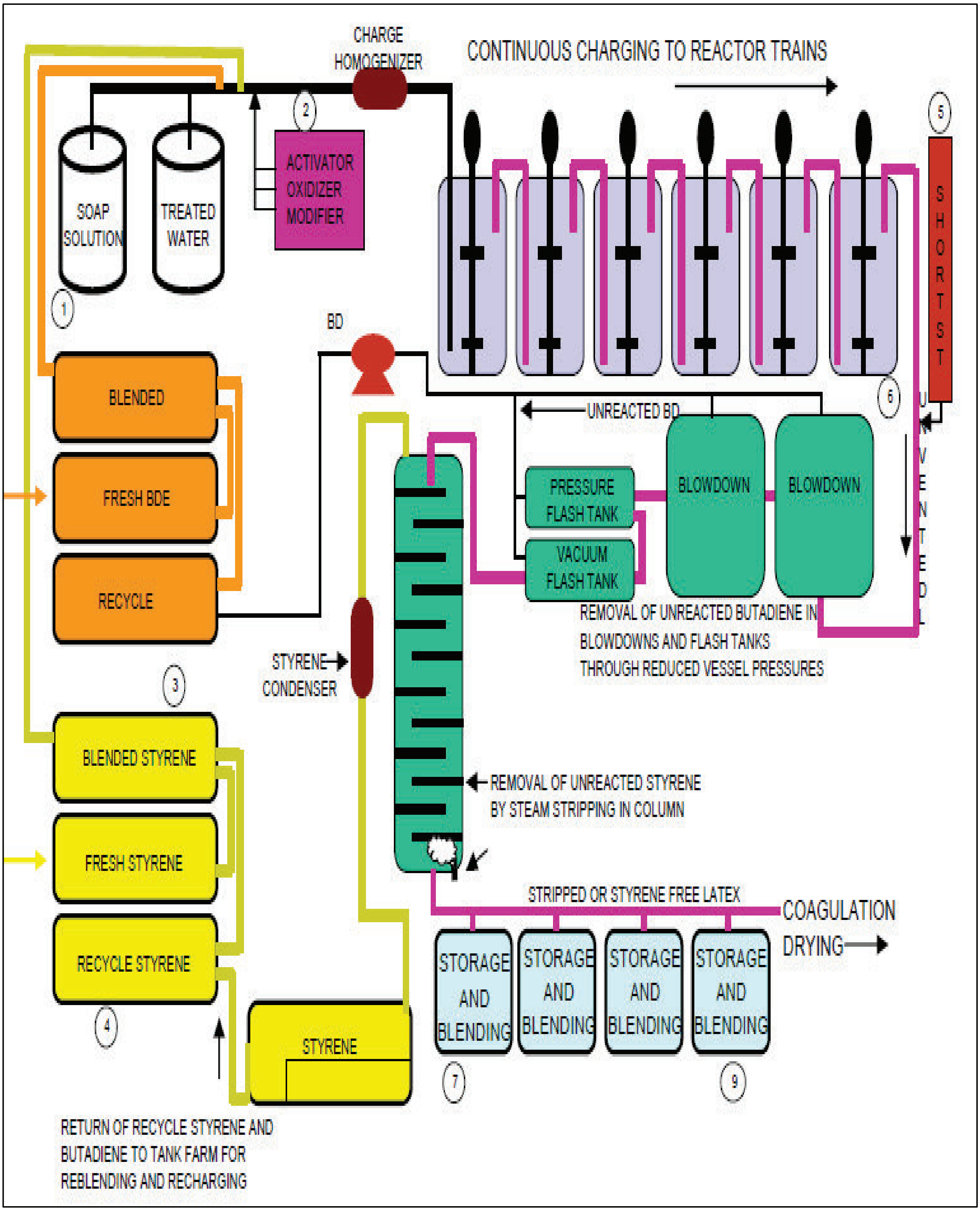

Fig. 1.7: Flow diagram of oil-extended styrene butadiene rubber (OE-SBR)

(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).

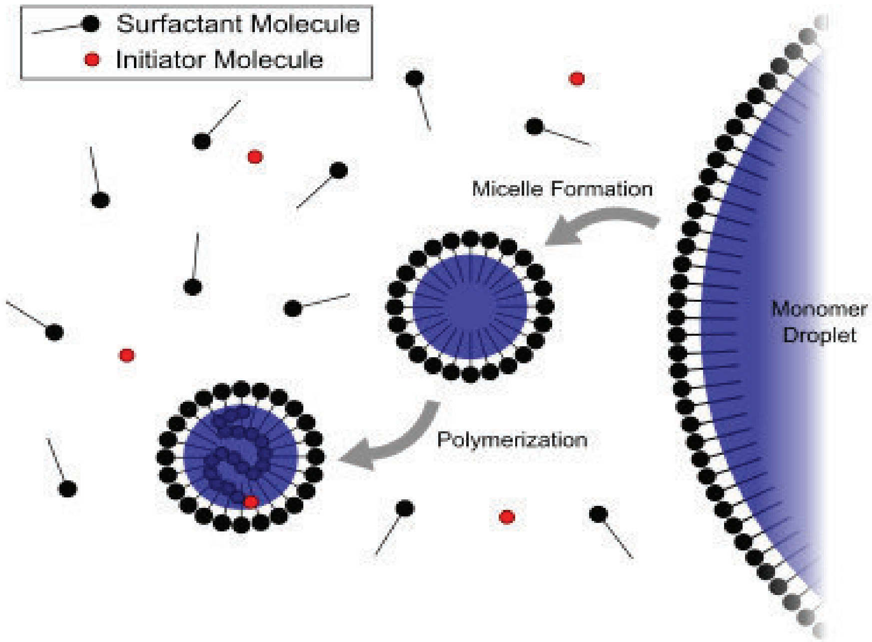

Fig. 1.8: Polymerization reaction inside "micelles"
(en.wikipedia.org/wiki/emulsion polymerization)

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.

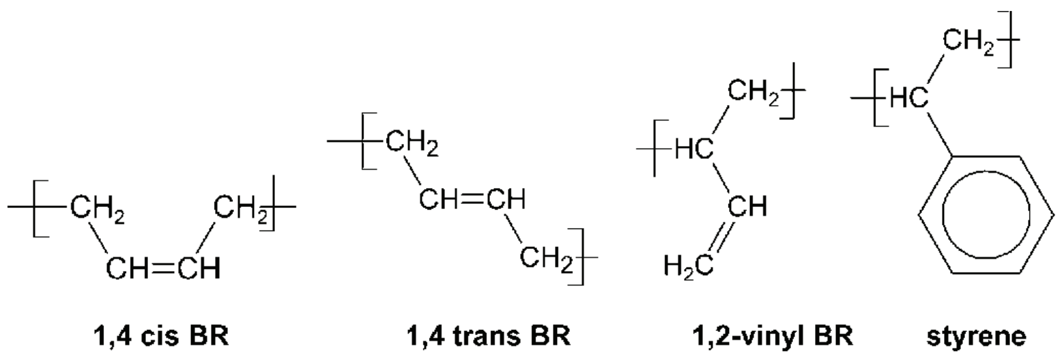

Fig. 1.9: Microstructure of styrene butadiene rubber (SBR)
(With permission from F. Vimlin, C. Dussap, and, N. Coste, Appl. Spectroscopy, 60, 6, 2006)

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.

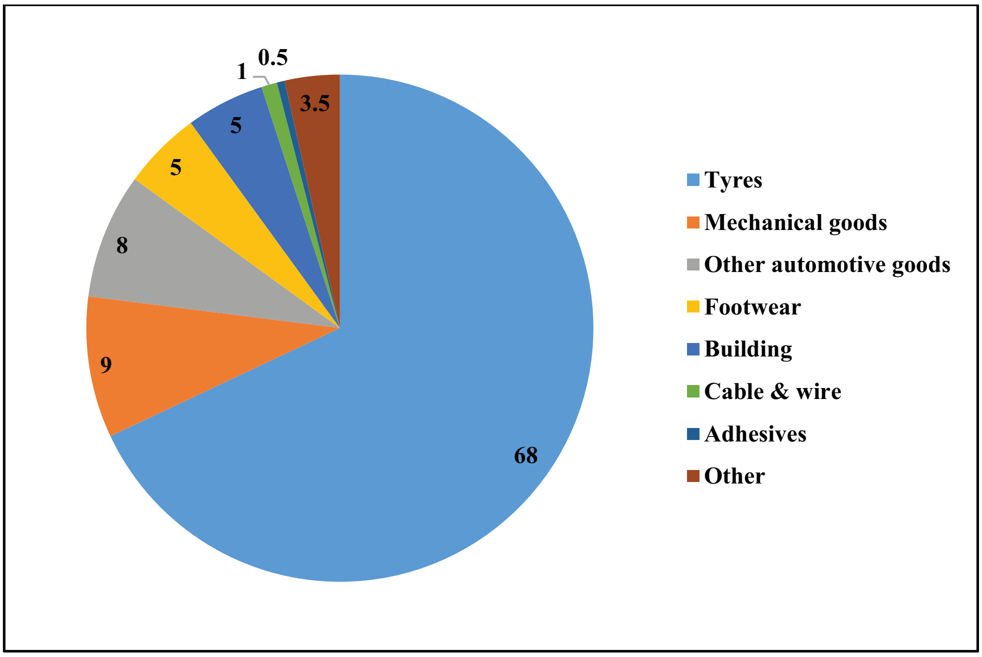

Fig. 1.10: Applications of emulsion SBR

(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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