



A review on reinforcing rubber goods for different valuable applications

Doaa E. El Nashar* and Aman I. Khalaf



CrossMark

Polymers and Pigments Department, National Research Centre, 33 Elbehouth st., Dokki, Giza 12622, Egypt

Abstract

Over the past few decades, filler techniques for elastomers have been the subject of in depth research. Numerous tests have been conducted over this time to determine how an elastomer is reinforced when fillers are added. Enhanced strength, modulus, abrasion resistance, and dynamic mechanical properties are among the characteristics of these reinforced materials. Separating the contributing impacts and describing how they operate have both been done using a variety of approaches. Most of these procedures examine the interactions between the fillers and rubbers in terms of their properties and structures. These processes have developed into three main areas: interactions between elastomers and fillers, filler structure, and hydrodynamic reinforcement. Fillers with an average particle size between 1 and 100 nanometers are referred to as nanofillers. Nanofillers are performance enhancers, as opposed to conventional non-active fillers, which are primarily employed to cut costs. To enhance the physical and other features, they can be employed in small quantities (5–10%). In the polymer matrix, nanoparticles (40 nm in diameter) can create an extremely fine, uniformly distributed network. Carbon nanotubes, carbon nanofibers, graphite platelets, and other fillers under investigation, including synthetic clays and natural fibers, are good valuable nanofillers. Although carbon nanotubes are more expensive than frequently available nanoclay fillers, they have high electrical and thermal conductivity qualities.

Key words: Filler, elastomer, nanofiller, Application

1. Introduction

Fillers are particles that are added to polymeric materials (such as rubber, plastics, composites, and concrete) to improve certain qualities or reduce the need for more expensive binder materials. Almost all elements that have been added in sufficient quantities to lower the amount of rubber needed are commonly given rubber fillers.

They are referred to as reinforcing fillers while simultaneously strengthening the rubber [1]. Fillers are therefore utilized to enhance the performance-related characteristics of rubber and other polymeric materials. Rubber is created by crosslinking a weak and flexible amorphous elastomer. Rubbers'

resistance to fracture and stiffness can be increased by reinforcing them with fillers or hard domains [2]. Enhancing mechanical qualities including elongation, tensile strength, and resistance to rip, abrasion, and friction, among others, reinforced fillers extend the product's useful life. The most significant reinforcing filler type include carbon black, precipitated silica, fumed silica, calcium silicate, aluminum silicate, activated calcium carbonate, hard clays, and zinc oxide, among others.

The other kinds of fillers, known as inert fillers, don't impart these qualities; instead, they aid in processing, cut costs, and alter attributes like elongation, stiffness, and hardness, but not tensile strength, rip strength, or abrasion resistance [1]. Non-reinforcing fillers include soft clay, white barite, talc, brown asphalt, pulverized coal dust, powdered vulcanized rubber (crumb), etc.

*Corresponding author e-mail: doaaelnashar@yahoo.com; (D. E. El Nashar)

Received 7 Nov 2022; revised 27 Nov 2022; accepted 23 Dec 2022

DOI: [10.21608/EJCHEM.2022.173291.7164](https://doi.org/10.21608/EJCHEM.2022.173291.7164)

©2023 National Information and Documentation Center (NIDOC)

2-Importance of fillers

Fillers rank among the ingredients used most frequently in the production of rubber goods among all other compounding ingredients.

The main justifications for including the fillers are:

1. To decrease the price value of the final rubber material
2. To improve the processing of the base polymer (rubber)
3. To modify and improve the properties of the (rubber) base polymer

The impact of fillers on the end product's characteristics, including density, hardness, tensile strength, impact strength, chemical resistance, heat distortion temperature, processability, and even the final product look [3]. A wide range of cost and benefit alternatives are available for the rubber compound due to the hundreds of commercial fillers that are available. These fillers give performance options from low reinforcement to high reinforcement.

3- Classifications of fillers

Fillers commonly categorized as being utilized in rubber composites that include [1, 3-5]

I. Black fillers

Rubber's black filler is carbon black. Carbon black is basically carbon atoms in their elemental state. Principal types of reinforced black carbon are made by the furnace process. Carbon black is mostly used with rubber to strengthen it. Rubber compounded with carbon black has better abrasion, fatigue, and modulus resistance. etc.

There are different types of carbon black as:

- 1- Pure black
- 2- Acetylene black
- 3- Black lamp
- 4- Thermo black
- 5- Black furnace

The furnace process produces the main forms of reinforcing carbon blacks. For primary function of furnace-type carbon black in plastics is to transfer reinforcements during vulcanization. There are about 30 grades of carbon blacks in use. Table (1) shows the properties of some grades of carbon blacks as examples.

I. Nonblack fillers

Nonblack fillers have an assortment of biological and inorganic materials with different particle sizes and shapes. It comes in a wide range of diameters, ranging from approximately 0.015 to 10 microns.

- **The inorganic materials**

The majority of the non-black fillers employed were either naturally occurring or manufactured by products such as iron oxide, magnesium carbonate, clay, whiting, barytes, mica, asbestos, blanc-fixe, kieselguhr, and zinc oxide. They were employed in rubber to improve durability, increase hardness, and boost cost efficiency. The elastomer industry also uses titanium oxide, aluminum oxide, and aluminum hydrate as significant non-black fillers. The development of calcium carbonate, calcium silicate, hydrated silica, and fumed silica was prompted by the demand for more reinforcing non-black filler in numerous rubber applications. They were distinguished by extremely small particle sizes, which were comparable to reinforcing carbon black and smaller than the natural products.

- **The organic materials**

There are some organic nonblack fillers such as wood flour and cork, glue, crumb rubber, high styrene resins, and phenolic resins. So we can say that fillers should be very fine, uniform and should not be contaminated with manganese, copper, and moisture. Metallic contaminants cause early deterioration of rubber, and the presence of moisture, apart from other effects, makes the product porous during vulcanization. Usually, fillers are ground, screened, and dried before use [5].

4-Property-affecting factors for fillers

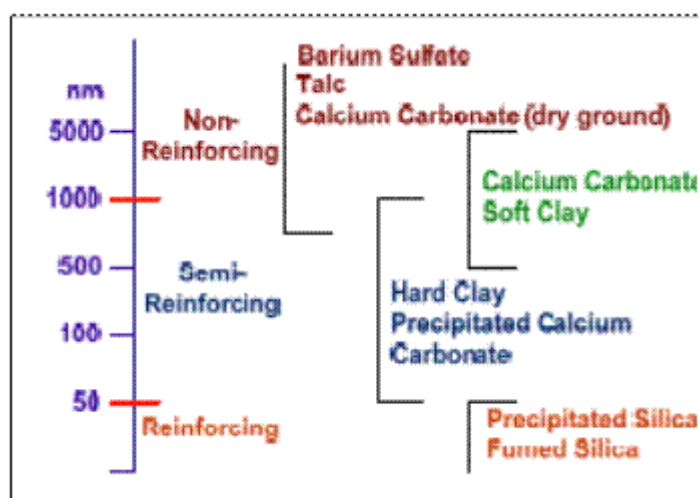
Particle shape, particle size, surface activity, and surface area are the qualities used to gauge filler's ability to perform a certain function in a rubber compound [1-3]. The activity of the surface depended on the compatibility of the specific elastomer with filler and the capability for adhering rubber to the filler. Functional fillers applied stress is transferred from the elastomer matrix to the dense, rigid mineral. These particles will effectively prevent the spread of stress through the matrix if they have a platy or fibrous form.

Additionally, as the matrix mostly adheres to the mineral particles, air gaps show spots with zero strength. If the matrix adheres to the mineral's surface due to chemical bonding, compound strength can be increased [6-8].

Local tension is introduced when the size of the filler particles greatly exceeds the spacing between the polymer chains. This may contribute to the chain elastomer rupturing during stretching or flexing. In general, fillings bigger than 10,000 nanometers are avoided since they might shorten rather than lengthen or increase performance. However, fillers with particles between 1,000 and 10,000 nanometers in diameter are mostly utilized as diluents and typically

Table (1): The properties of some grades of carbon black

Grades of carbon blacks	Properties and Application
1. SAF (super Abrasion Furnace)	Very small particle size (20-25nm) black gives maximum strength and resist the abrasion. Used in premium grade tread rubber, tank treads and severe service belting and mechanical goods.
2. ISAF (Intermediate Super Abrasion Furnace)	Small particle size (24-33 nm) black imparting high tensile strength and abrasion resistance. Used in treads, heavy duty belts and mechanical goods, in abrasion resistant application.
3. HAF (High Abrasion Furnace)	Small particle size (28-36 nm) black gives good abrasion resistance and tensile strength. Most widely used particularly in tire treads, tread rubber, industrial belting and mechanical goods.
4. FEF (Fast Extruding Furnace)	Medium particle size (39-55 nm) black gives moderate abrasion resistance and improved processing, giving smooth calendaring and extrusion properties. Used in tire body stocks, sidewalls, inner tubes and calendared and extruded products. Gives good heat conductivity.
5. SRF (Semi Reinforcing Furnace)	Substantial particle size (70-96 nm) black giving moderate reinforcement and very economical to use, because the possibility of high loadings. Gives very good resilience. Used in cycle tire, tyre beads, breaker plies mechanical molded and extruded goods.
1. FT (Fine Thermal)	Large particle size (180-200 nm) black giving reinforcement to rubber, used in very high loadings. Used in mechanical goods, matting, footwear, special chloroprene and nitrile rubber compounds.
2. 5. MT (Medium Thermal)	Largest sized (250-350 nm) black, giving the least reinforcement to rubber. Used in very high loading. Used in mechanical goods, footwear, special chloroprene, and nitrile rubber compounds.

a- Size of particles**Fig. (1): Classification of particle size**

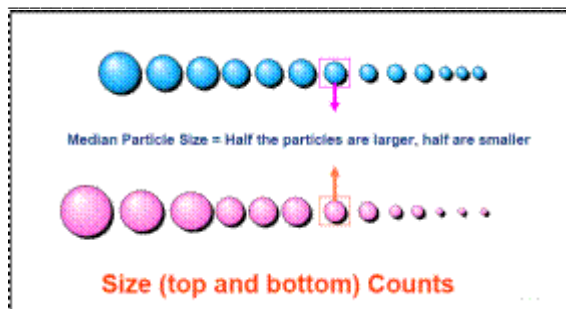


Fig.(2): Schematic representation of particle size of nonblack fillers

have little to no impact on the characteristics of rubber. Semi-reinforcing fillers have a size range of 100–1000 nanometers. As shown in Figure (1), true reinforcing fillers with a size of 10 nm to 100 nm can greatly improve the characteristics of rubber. Unreinforced and semi-reinforced fillings typically have average-sized particles, with half being larger and half being smaller. As previously mentioned, this may not accurately depict the particle size distribution.

Most of the time, measured as the actual dimensions or size as indicated in Figure (2), the size particle of the mineral filler is given as the mean or average size. There is little variation in calcium carbonate, whether it is round or block-shaped. Most automated particle meters simulate the behavior of round particles with a given diameter for sheet minerals like talc, mica, and clay as well as needle-like minerals like wollastonite. A clay plate with a reported equivalent spherical diameter of 200 nm, for instance, might actually be 1 nm thick and 600 nm wide.

b-Shape of particles

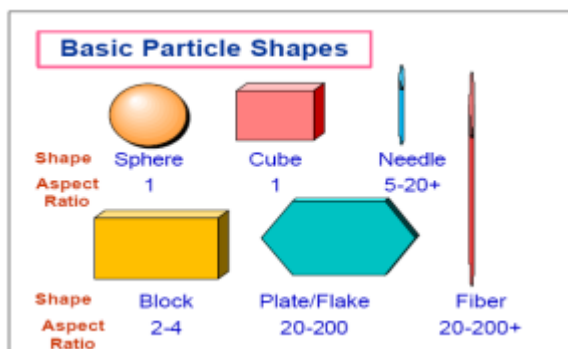


Fig.(3): Schematic representation of particle shape of fillers

The particle shape of most metal fillings can be compared to a cube, ball, plate, block, fiber, or needle. Some fillers are made up of a variety of

shapes. The shape of the particle for plurality mineral filler can be as a cube, sphere, plate, block, fiber or needle. Some filling materials contain an admixture of shapes; these types are shown in Figure (3). Aspect ratios are further characterized for plates, needles, and fiber like mineral particles. For shaped fillers made of fiber and needle, the length to diameter ratio is known as the aspect ratio. Clay and kaolin are platy minerals that have a ratio between their faces and the diameter of a circle with an area equal to their thickness. Fillings are roughly isometric cubic, full, or round, which is considered a low aspect ratio. In this text, low means the aspect ratio is less than about 5:1. Circular, fibrous, and platy fillers with a needle-like form have a high aspect ratio. For silica and carbon that have precipitated, the aspect ratio is not used. The functional precipitated silica and carbon black filler "particles" are bundles or chains with varying degrees of branching, even though the elementary particles of these fillers are essentially spherical. These fills' anisotropy is defined in terms of their "structure," which encompasses their general form, size, and density. The potential for reinforcement increases with the height of the building.

c- Particle surface area

If the filler is to contribute to the strengthening of the rubber filler compound, it must be in close contact with the elastomer chains. High surface area fillers have a greater area of contact, which increases their capacity to strengthen rubber links. The shapes of the particles are also crucial. In comparison to spherical particles with an equivalent average diameter, flat-shaped particles have more surfaces obtained for rubber interaction. Particles with a planar shape, like clay, that align with the rubber chains during mixing or processing. As a result, it helps to improve the form of particles other than those that are spherical and have the same average particle size as calcium carbonate. Less than clay particles are carbon black chains, precipitated silica, and bundles. As a result, when in contact with the polymer, you gain a higher surface area per unit weight. With rubber grade, carbon black fluctuates from 6 to 250 m²/g. Precipitated silica has a strength of roughly 125 to 200 m²/g, compared to 20 to 25 m²/g for ordinary hard clay.

d- The behavior of particles' surfaces

Even though filler has a high aspect ratio, a large surface area, and a small particle size, if its surface activity is low, it will still perform poorly at accelerating progression. The physical and chemical

properties of the filler surface with respect to those of the elastomer are used to compute the specific activity of the filler surface per cm^2 of the filler elastomer interface. The function of polar fillers is greatest in polar elastomers; fillers that are nonpolar are best suited to work with them. This general chemical compatibility is the possibility of contact between the active sites on the surfaces of fillers and elastomers. For instance, the carbon black particles contain carboxylate, lactone, quinone, and other organic functional groups that enhance the high affinity of the rubber to the filler. The surface activity is related to numerous chemical groups on the surface of the filler materials. These active spots could interact chemically with the chains of elastomers due to the close proximity of carbon black and elastomers. In essence, the carbon black particle forms a crosslink. Nonblack fillers typically have reduced surface activity and elastomer affinity. Some surface treatments can compensate for this to a greater or lesser extent [9, 10].

Regarding the mechanical properties of the elastomer with fillers, the surface activity of filler particles is significantly more important.

5-The differences between properties of rubbers loaded with carbon black and mineral fillers

Some fillers have specific effects on certain properties of rubber and these [3, 11] effects tabulated in Table (2).

Table (2): The main difference properties for rubbers loaded with carbon black and mineral fillers

Carbon black	Mineral fillers
Improve abrasion resistance.	Improve heat resistance (whiting)
Improve tear resistance.	Improve tear resistance (silica)
Increase modulus and tensile strength.	Increase modulus
Increase hardness.	Increase hardness
Improve ozone resistance.	Reduce gas permeability (mica)
Improve weathering resistance.	Improve flame resistance
Reduce swell in oils.	Improve properties at high temperatures.
Improve processability.	Improve electrical properties (resistivity)

The following succinct statement can be used to summarize the general filler influence of features on the rubber properties of rubber [3, 12]:

1) Reduction in particle size (increasing surface area) has: higher Mooney viscosity, abrasion resistance, strength testing, hysteresis and resist of tear; less flexibility.

2) Higher abrasion resistance, modulus (at elongation >300%), chemical adsorption or reactivity, and hysteresis are all results of the surface activity increase (including surface treatment) (except treated clay by silane).

3) Higher Mooney viscosity, hysteresis, and modulus (at elongation 300%), longer incorporation time, reduced robustness, and extrusion shrinkage are all effects of increasing aspect ratio.

7- Rubber filler interactions

Filler dispersion in rubber is obtained[1, 8, and 13], three types of interactions which affect

- (1) Relative motion, elastic recovery, and rubber molecule interaction are viscoelastic qualities.
- (2) The interaction of filler and rubber particles.
- (3) Interaction of the individual filler particles.

(1) Interactions between rubber molecules

The mobility of a macromolecule, its chemical make-up, the regularity of its segments, and the existence of transient or stable crosslinks, entanglements, and loose ends in the vulcanizate all play major roles in how they interact with one another. The relative segmental mobility of the rubber barely changes when fillers are included. The interaction of rubber molecules with the majority of active fillers causes a small increase in temperature.

(2) Interaction of fillers with elastomers

The most important interaction is that between the base polymer and filler; during the processing mill, part of the rubber is attached to reinforcing fillers so that it cannot be extracted with regular solvents of rubber. This insoluble rubber is named rubber black gel or bound rubber. Rubber that is bound can be used to gauge the surface activity of the white or black filler. On the other hand, bound rubber as such does not contribute appreciably to the crosslink density of the final vulcanizate. However, it is believed that the interaction between rubber and filler leads to bound rubber, which is used to gauge the filler's surface activity ($S_0 = 3/\rho \cdot R$, where S_0 is the specific surface area defined as a function of the carbon black's specific gravity ρ and R is the particle radius) i.e. Additionally, it was believed that a chemical process led to the creation of bound rubber.

Previously, it was believed that only adsorption effects specifically, Van der Waals forces process brought on by interactions between the rubber and functional groups or aromatic hydrogen found on the surface of carbon black and chemisorption's could produce bound rubber.

(3) Filler-filler interactions

In the instance of carbon black, this disregard is brought on by the outdated idea that the black's fundamental unit is an approximately spherical particle, and that the surface area and behavior of the particle in rubber depend on its size (based on photos of channel and thermal blacks).

Larger aggregates are created when the original particles, which are typically spherical, are fused together, according to universal consensus. These aggregates, especially at modest deformations, may include a few to several hundred, or possibly a thousand, of the black vulcanizates deformational characteristics [14].

Silica and carbon black (CB) were the two main reinforcing fillers used by Rattanasom et al. [15] to strengthen rubbers. Because each filler has advantages of its own, the application of CB/silica mixes should improve the dynamic and mechanical properties of natural rubber (NR) vulcanizates. In terms of tensile strength, rip strength, fracture growth resistance, abrasion resistance, heat accumulation resistance, and rolling resistance, they found that vulcanizates with 20 and 30 percent silica in the hybrid filler have improved overall mechanical properties. Moustafa and his coworkers [16] investigated the effects of ageing on the mechanical properties of styrene butadiene rubber (SBR) and nitrile butadiene rubber (NBR) compounds. The results demonstrate that when the ageing temperature increases, the compressive strength of both forms of vulcanizates diminishes because chain scission produces a high oxidation process and ageing results in an increase in hardness as temperature rises.

To reduce the environmental damage caused by ash buildup from burning agricultural wastes and to reduce costs without sacrificing the mechanical properties of rubber vulcanizates, cellulose fibers derived from bagasse waste were used as reinforcing fillers in rubber composites. The impacts of natural ground bagasse powder (GBP) and carbon black (CB) reinforcing fillers were studied in relation to the mechanical and physical properties of styrene butadiene rubber (SBR) composites.

The grinding machine generated GBP with an mm to 180 mm wide grain size distribution. 2.5phr of maleic anhydride was used to improve the interfacial

adhesion between SBR and agricultural waste fillers (i.e. bagasse). Investigations were conducted into the rubber vulcanizates physico-mechanical properties, including their degree of swelling, elongation at break, and modulus at 100% elongation, resilience, and hardness (Shore A). [17].

The potential for using limestone dust waste (LDW) as filler in natural rubber was examined by Sae-oui et al. [18]. (NR). The effects of various commercial fillers, including LDW reinforcement, light-precipitated calcium carbonate (PCC), and nanoprecipitated calcium carbonate (NPCC), were compared. According to the findings, while the addition of LDW had no effect on the compound's ability to be processed, it had a negative effect on the bulk of the vulcanizates mechanical properties, including its tear strength, tensile strength, and abrasion resistance. The three fillers could be used to organize the degree of reinforcement as the following order: LDW > NPCC > PCC.

Due to their low specific surface area and insufficient reinforcement capacity, PCC and LDW can both be classified as nonreinforcing fillers, whereas NPCC, whose specific surface area is relatively high, can be classified as semi reinforcing filler for rubber due to its relatively high specific surface area. On the mechanical and rheological properties of ternary rubber nanocomposites consisting of natural rubber (NR), styrene-butadiene rubber (SBR), and nitrile butadiene rubber (NBR), the effect of carbon black (CB) filler loading was investigated. A melt mixing procedure was used to create four separate samples with different filler loadings: S2 (15 phr), S3 (30 phr), S4 (45 phr), and S5 (60 phr). Researchers studied the properties of ternary rubber nanocomposites, including their tensile strength, stress at 100%, 200%, and 300% elongations, elongation at break percentage, rip strength, compression set, compression stress, and crosslink density. The findings demonstrated that the scorch time, cure time, cure rate index, swelling coefficient, elongation at break%, and filler rubber interaction decreased with increasing CB loading. A rise in the minimum torque, maximum torque, tensile strength, stress at 100%, 200%, and 300% elongations, elongation at break%, tear strength, compression set, compression stress, and crosslink density is also shown by the data. S4 represented the greater tensile strength values for these samples (loaded with 45-phr CB). Consequently, it had a higher stiffness than the other content ratio. Additionally, S4's tensile strength increased by 233.58%. These results showed that filler loading at the appropriate level can improve compatibility

between CB and NBR/SBR/NR. These results were confirmed by a micrograph created using a scanning electron microscope [19].

The mechanical and electrical properties of SBR/NBR blends in various amounts were studied by Reffae et al. [20]. It is found that mechanical properties have improved, such as tensile and elongation at yield and rupture. We tested the electrical and mechanical characteristics of SBR, NBR, and a 50/50 blend of SBR/NBR loaded with various concentrations of high abrasion furnace black (HAF).

The electrical conductivity of carbon black filled composites increased from pure polymer to pure carbon through the alteration of the different composites. Up to a particular concentration of HAF (30 phr for both SBR and NBR, and 20 phr for SBR/NBR blends), the conductivities of the composites are almost equal to those of pure materials. The formation of conductivity chains increases as a result of the network aggregation of the carbon black particles. Tensile and elongation tests at yield and rupture were used to assess the mechanical properties, and they show an increase at the same concentration of HAF as observed in the case of the electrical testing. These findings offer good applicability to both mechanical and electrical research through the creation of networks.

The filling effect of silica on the mechanical and dielectric properties of various compositions of EPDM/NBR mix (ethylene propylene diene/acrylonitrile butadiene rubber) was studied by Eid and El-Nashar [21]. In order to prevent phase separation, 10 phr of polyvinyl chloride (PVC) was added to the mixture. The research found that the 25/75 NBR/EPDM blend has the most promising properties. This mixture was chosen to investigate the different qualities while containing silica in increasing concentrations up to 90 phr. This experiment revealed that when loaded with 50–60 phr of silica, the NBR/EPDM blend exhibited the best mechanical and electrical properties.

Some researchers investigated the effects of mixing two secondary fillers into silica-based natural rubber compositions at a ratio of 45/10 phr, such as N134 carbon black and organic nanofiller. Based on the procedure generally used for silica-filled NR systems, the rubber vulcanizates were produced using a variety of mixing temperatures. According to the results of Mooney viscosity, cure behavior, the Payne effect, and mechanical properties, silica is hydrophobic. Additionally, the organoclay's modifier, an organic ammonium derivative, has a significant impact on the coupling reaction of the silane coupling

agent with elastomers and silica. This has an effect on the scorch safety and rate of cure. When carbon black was employed as an additional filler, these tendencies were not present in the compounds. They offer inferior filler dispersion than the pure silica filled material because of the improperly high mixing temperature and the significant specific surface area of the carbon black used. The dynamic characteristics demonstrated that using organoclay as a secondary filler has the ability to boost wet traction and rolling resistance of a tire tread, in contrast to the combination of carbon black and silica filled NR.

It is not possible to combine blends of styrene butadiene rubber (SBR) and nitrile butadiene rubber (NBR). Fillers may be used as compatibilizers, claim Perez et al. [23]. To describe the NBR/SBR blends reinforced with mesoporous silica and precipitated silica, researchers looked at mechanical performance, changes in heat capacity at each glass transition temperature, and miscibility by rubber binding. In order to increase the dispersion of silica surfaces, NBR is used more frequently. For blends reinforced with mesoporous silica, whose high surface area and ordered porous structure allow a better polymer + filler interaction, larger rubber + filler as well as NBR / SBR interphases are formed. When broken, the reinforced blends are stronger than the individual reinforced polymers. Mesoporous silica-reinforced blends are researched for their greatest performance.

Polymer blends like acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber have had montmorillonite clay added in a variety of ratios by Essawy, El-Nashar [24]. SEM, differential scanning calorimetry, and physico mechanical properties were utilized to investigate the filler's reinforcing and compatibilizing properties. With the addition of filler to all blend compositions, the strain at yield and rupture is also increased, while toluene swelling resistance is boosted. In comparison to filled blends, the stress at yield was greater. According to SEM pictures, the filler is located near the interface of the mixtures. The DSC of the filled blends reveals variations in the glass transition temperatures T_g because of the enhanced strength at the interface.

Carbon black (CB) and silica co-filled rubber composite were widely used for tire tread and other rubber products because of the benefits of binary fillers, which include superior abrasion resistance, low hysteresis, and reinforcement. A considerable lot of study has been done on the interaction between filler rubber in order to achieve the greatest performances. To investigate the impact of modification on the properties of rubber composite, a modified CB and silica co-filled rubber composite

was created utilizing the multifunctional silane coupling agent 2-aminoethyl-2-(3-triethoxysilylpropyl) aminoethyl disulfide (ATD). This modification enhanced the interaction of the filler rubber and filler dispersion. For the modified composites, especially with low ATD dosage, the state of cure, hardness, tensile strength before and after ageing, stress at 300% elongation, tear strength, abrasion resistance, rebound resilience, compression set, temperature rise, and the value of the dynamic loss coefficient ranging from 20°C to 80°C were all significantly improved. With this alteration, silica and CB co-filled rubber composites can be created with superior mechanical and dynamic mechanical properties [25].

Gallate ester of castor oil (GECO), a castor oil-based multipurpose additive for rubber composites, was created by esterifying castor oil (CO) and gallic acid. Thermogravimetric analysis and Fourier transform infrared spectroscopy (FTIR) were used to characterise GECO (TGA). The high abrasion furnace (HAF), carbon black filled natural rubber (NR) composites at varied ratios (1, 2, and 4 phr), GECO were utilised to assess their effect on the curing, mechanical, swelling, and ageing properties of the resulting composites. The use of GECO significantly improved the antiaging properties of the resulting composites and successfully sped up the curing process. The mechanical and swelling properties of the finished composite were found to be improved by adding 1 phr of GECO; however, after this concentration was reached, a slight drop in the properties was seen. Scanning electron microscopy (SEM) results show that the application of 1 phr of GECO increased the dispersion of HAF in the NR matrix, which enhanced the HAF reinforcement [26].

In Sattayanurak et al. [27] examination of silica-reinforced natural rubber (NR) tire tread compositions, organoclay (OC) was utilized as supplementary filler. By adjusting the mixer temperature setting at a silica/OC ratio of 45/10 phr, temperatures of approximately 120, 140, 150, and 160 °C can be reached. Mooney viscosity, a smaller mixing torque, and the Payne effect are produced as a result of a better salinization reaction brought on by the higher temperature. It was found that mixing was best at a temperature of about 150 °C. Indicators for ice traction and wet skid resistance of tire treads constructed from silica filled NR compounds, which ranged in OC loadings from 0 to 36 wt% relative to total filler quantity, were elevated at 20 and 0 °C by increasing OC loadings while decreasing compound viscosities and Payne effect. The findings indicated that, in comparison to a system filled entirely with

pure silica, using this hybrid filler might give tires of lower rolling resistance, better wet grip, and greater wear resistance. 9 wt% of the total filler content is the ideal loading of OC. Better Payne effect, cure rate index, and tan delta values at 20 and 60 °C are produced as a result, which are indicators of DIN (German Institute of Standardization) rolling resistance and abrasion resistance.

El-Nashar et al. [28] examined the effects of Na, Ca, and kaolin fillers on the macrostructure and microstructure of acrylonitrile butadiene rubber, ethylene propylene diene rubber, and their blend (50/50), using electrical, mechanical, and positron annihilation lifetime spectroscopy techniques. It was found that filler content increased the real component of permittivity, dielectric loss, and crosslinking density.

The blend with greater filler has a lower equilibrium swelling of up to 21.50 weight percent in comparison to blends without fillers, that is observed in the blend's higher crosslinking density. The mechanical examination demonstrated a noticeably higher tensile strength and elongation at break with the addition of up to 21.50 wt% of filler.

As a result, it was discovered through comparing different fillers that whereas Na bentonite has a better overall reinforcing effect than kaolin, Ca bentonite has a lower physical mechanical strength than kaolin. The type and quantity of the filler had a considerable impact on the free volume properties, according to the positron canceled life time measurements. In the example, as filler content rose, the free volume fraction decreased dramatically. There was a correlation between the free-volume characteristics and the mechanical and electrical qualities.

As reinforcing elements for the vulcanizates of natural rubber (NR), styrene-butadiene rubber (SBR), and their combinations, El-Nashar et al. [29] investigated the synthesis of distinctively modified micronized phosphate pigments. Carbon black and white generated phosphate pigments were used to the rubber compositions in place of the commonly used and accessible commercial reinforcing material for rubber vulcanizates. The results showed that phenyl phosphate pigments performed at a high level with different mechanical qualities, and also had a substantial impact on rheological features. For instance, for rubber mix vulcanizates loaded with 30 phr of modified phosphate pigments, carbon black, and Hisil, respectively, the tensile strength results were (20.0-23.4), 18.01 MPa, and 15.05. Modified phosphate-laden rubber has better stress and strain properties at yield and rupture than rubber loaded with carbon black and Hisil. These results suggest a

novel approach for numerous non-black rubber vulcanizate applications.

The impact of the carbon black content on curing and mechanical properties such tensile strength, elongation at break, abrasion resistance, and hardness was investigated using a blend of natural rubber (NR) and acrylonitrile butadiene rubber (NBR). It was accomplished by using a blend of 65% NR and 35% NBR loaded with varying quantities of carbon black N330. The curing findings demonstrated that the scorch and curing times decreased as the filler content increased, while the viscosity and crosslink density of rubber composites rose. The CB's inherent capacity for reinforcing was demonstrated by the improved tensile modulus and hardness of the CB filled NR/NBR blend. The tensile strength and abrasion resistance rise to 50 phr with the addition of carbon black. The subsequent inclusion of filler led to a slight reduction in these properties [30].

The traditionally sulfur-cured ethylene-propylene diene monomer rubber (EPDM) is mixed with various concentrations of high abrasion furnace black filler (HAF) and white filler (silica). The prepared samples' swelling measurements, physicochemical properties, and thermogravimetric analyses have all been studied (TGA). It included EDAX analysis. When white and black fillers were examined, it was found that the filler's absorption into the rubber matrix was one of the major elements enhancing tensile strength and swelling resistance. As the filler ratios were increased to 40/60 phr, the tested samples become tougher. This can be due to the filler being distributed more evenly and thoroughly throughout the rubber matrix. Carbon and silica are frequently used as fillers in the industry because they are affordable and have effective reinforcing characteristics. Therefore, the inclusion of precipitated silica at the extent of toxic carbon black (CB) is the first step in lowering the health risk associated with the presence of CB filled EPDM composites [31].

We contrast and compare the properties of acrylonitrile butadiene styrene (ABS) and styrene butadiene rubber (SBR). Comparisons are made between a blend of incompatible and compatible nitrile rubber (NBR), physical rheological properties, and abrasion resistance. The mixtures' resistance to abrasion is improved with the compatibilizer ABS. The results show that filled mixes containing carbon and silica outperform empty blends in terms of processing benefits. Ultrasonic and scanning electron microscope (SEM) techniques are used to analyses the collected data [32].

8 -Modified surface of the filler

The filler's surface activity has influence on the reinforcement of rubber [3, 33]. Several methods are being used to modify the filler surface.

8.1- Surface modification of carbon black

a) Heat treatment

Heat treatment in an inert atmosphere alters the physicochemical characteristics of carbon black. The chemical nature of surface is modified at a temperature below 1000°C whereas the physical nature of the surface gets modified around 1000-1500°C. A drastic change in surface energy and a change in the crystalline property are the major physical changes of heat treatment.

b) Surface grafting [29, 30]

The grafting of polymers on to carbon black are done by chain termination or chain transfer of a growing polymer radical, they were done by two methods as follows:

- 1- Grafting through copolymerization of the small molecules and this is the favorable process.
- 2- Grafting by direct reaction of carbon black surface and functionalized polymer.

c) Plasma treatment

Plasma treatment is an efficient mean to modify carbon black surface and the change is largely homogeneous throughout the entire surface. The significant changes in surface chemistry occurred on air and ammonia plasma treatment of graphitized black. When air plasma is treated, oxygen produced containing groups and ammonia plasma treatment results in nitrogen containing groups.

Surface oxidation

The process of surface oxidation of carbon blacks can be classified into two methods gas phase and liquid phase. Oxygen, ozone, air or oxides nitrogen are basically the gas phase oxidation whereas nitric acid, aqueous potassium permanganate and bromine water are the liquid phase oxidation.

8.2- Surface modification of non black fillers

This property of kaolin clay applies to all non-black, non-carbonate reinforcing or semi reinforcing fillers. The clays, silica's, and silicates' surface silica (SiO₂) groups have all hydrolyzed to silanols. Since they exhibit an acidic behavior (SiO- H⁺), these silanol groups are chemically active [3, 31–39]. The fillers with higher surface areas, which are shown in Figure (4), are more reactive because there are more silanols available.

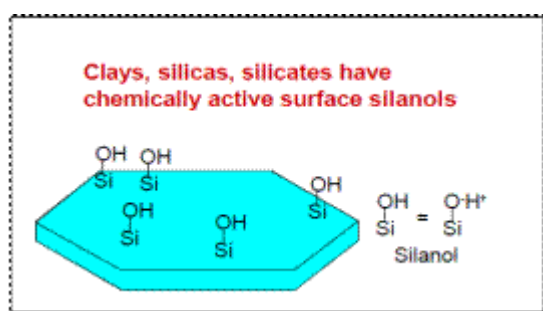


Fig.(4): The surface-area active groups of the nonblack fillers

The effective technique to alter the surface chemistry of non-black fillers is the inclusion of silane coupling agents, as shown in Figure (5). They have a functional group that will bind to the rubber during vulcanization and interact with the silanols on the surface of the filler to form a solid bond. Thus, filler-polymer bonding (crosslinking) takes place, improving the compound's modulus and tensile strength as well as other properties.

The filler's surface is modified to improve dispersion. Three silane coupling agents are often used in compounds that are sulfur-cured and filled with kaolin clay and other non-black fillers. They have mercapto, tetrasulfide, and thiocyanate functions, respectively. Each substance's sulfur-containing group reacts and binds to the polymer during vulcanization. For non-sulfur cures, epoxy silane and amino silane are widely utilized. Clay and other nonblack fillers are commonly treated on-site, not with standing the ease with which silane-pretreated clay may be obtained. In this case, the silane is added during processing to interact with the filler. The order of addition is very important when adding silane coupling agents, especially when using sulphur cures. The polymer, filler, and silane coupling agent should be well mixed for 1 to 2 minutes prior to introducing any additional elements that will hinder the interaction between the filler and the silane

Surface modification of fillers to improve polymer filler interaction has become popular during the past 10 years, and various papers have been written about it.

Yin and his colleagues [40] used methylacrylic acid (MAA) and methyl methacrylate (MMA) as additives for peroxide-cured styrene-butadiene rubber (SBR) filled with three inorganic fillers, such as MgO, Mg(OH), and BaSO₄ that had variable particle sizes and surface activities.

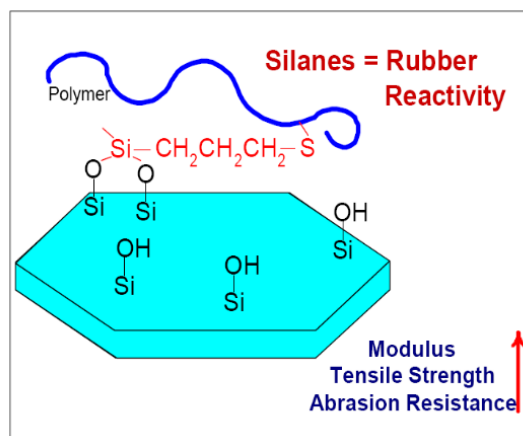


Fig.(5): Schematic representation for surface chemistry of fillers that are not black

The results showed that the mechanical properties of SBR vulcanizates produced with BaSO₄, Mg(OH)₂, or MgO can be enhanced by adding MAA. A small amount of MAA causes increases in the tensile strength, modulus, and rip strength. The mechanical properties of SBR vulcanizates are not considerably affected by MMA. The SEM micrographs show that MAA can improve the interfacial bonding between SBR and the three different filler types. Strong contact between the SBR and filler produces strong mechanical properties.

The physical, mechanical, and dielectric properties of acrylonitrile butadiene rubber (NBR) filled with various concentrations of mica and silica were researched by El-Nashsr et al. in their article published in 2011 [41]. The compound containing 25phr silica was found to have the most promising properties. Furthermore, the inclusion of mica in the NBR/silica vulcanizates marginally modifies the required characteristics. Triethoxyvinyl silane as a coupling agent improves the contact between NBR, silica, and mica because of the filler's efficient dispersion. Compared to other compositions, the NBR/silica/mica mixture (100: 25:11) exhibits better mechanical and dielectric properties. Additionally, the mix's reduced value of dielectric loss supports its employment as an insulator. SEM was used to demonstrate the preceding findings.

The effects of aluminum powder on the properties of nitrile rubber (NBR) composites and the role of the bonding agent hexamethylene tetramine-resorcinol have been examined by Vinod et al. [42]. Although the hardness Shore A of the NBR composites filled with acetylene black (ACB) and high abrasion furnace (HAF) is higher than that of the aluminum

powder filled composites, it can be increased by adding a bonding agent. Utilizing hexamethylene tetramine-resorcinol decreased equilibrium swelling, demonstrating enhanced nitrile rubber aluminium powder adhesion. Increased heat conductivity is the result of adding aluminium powder. The material was consistently cured to the increase in heat conductivity, which also reduced the extra time needed to vulcanize bulky rubber products. The mechanical and thermal conductivity of composites were increased by mixing aluminium powder with HAF in NBR.

The effects of introducing chemical blowing agents to a cellular rubber mix of natural rubber (NR) and styrene butadiene rubber (SBR) at a fixed blend ratio of 1: 1 were investigated by Wimolmala et al. [43]. They examined morphological parameters, mechanical attributes, and curing characteristics. In this experiment, the chemical blowing agents Azo dicarbonamide and Oxybis (benzene sulfonyl) hydrazide (OBSH) were used. Three different fillers—fly ash (FA) particles, precipitated silica and carbon black (CB)—were used at their optimal concentrations of 40 phr. The chemical treatment of bis (3-triethoxysilylpropyl) tetrasulphide was applied to the FA and silica particles. The results showed that the overall cure time was shortened by OBSH and ADC components. When it came to quickening the cure of NR/SBR blends, the OBSH outperformed the ADC. NR/SBR vulcanized foams with closed cell topologies were produced by ADC and OBSH agents. The blend's mechanical properties and specific density tended to decline as the amount of blowing agent increased. The CB created NR/SBR foams with smaller cells, higher mechanical **properties**, and increased cell dispersion in comparison to the precipitated silica and FA particles. The hardness and tensile modulus rose as a result of the heat ageing and weathering, but the tensile strength, elongation at break, and rip strength fell. Better elastic recovery was seen in cellular NR/SBR vulcanizates with FA than in those with CB and silica, and the blends' elastic recovery decreased as the blowing agent proportion rose. The resilience property was enhanced by the presence of gas phases.

The dual cross-linking networks were produced in a pre-made NBR matrix using covalent and sacrificial metal-ligand interactions. In comparison to pure rubber, Zn²⁺-CN coordination bonds dissipated energy to boost NBR composites tensile strength, modulus, and elongation at break. Dual cross-linking network topologies allow for simple modification of the elasticity and glass transition temperatures of NBR composites. Additionally, after being submerged in oil at 70 °C for 72 hours, NBR composites display good oil resistance qualities,

demonstrating very little swelling. What's more astonishing is that the NBR composites that were created demonstrated thermally induced shape memory behaviours with exceptional form fixing and shape-recovery ratios in both oil and air. As a result, we believe that dual cross linked NBR composites may help mechanical and shape memory applications [44].

Styrene butadiene rubber (SBR) loaded with various carbon black/silica blend loading ratios was examined by Ward and Khalf [45]. The dielectric properties were examined in the frequency range of 102 to 105 Hz as a function of the filler concentration in the mixture. Evaluating the conductivity in relation to the frequency, temperature, and filler loading of the blend, the percolation limit is determined. Thus, the change in conductivity brought on by heating and cooling cycles illustrates electrical hysteresis. The silane treatment has been put through a comparative evaluation of its effect on the preceding attributes and the interaction of the filler rubber. SEM confirmed that the silane treatment had an impact on the filler dispersion. ReaxFF molecular dynamics simulations show that nanoparticles (NP) have a range of parameters-dependent effects on the strength and dispersion of silica styrene butadiene rubber (SBR) nanocomposites.

One of the aspects considered is the type of silane coupling agent (SCA), as well as the size of the silica NP, the surface occupancy of SCA at the silica surface, and the spatial distribution of Sulphur cross links at the molecular level. Numerous metrics from various systems, including strength modulus, peak normal traction, interface energy, radius of gyration, and distance between NP, were studied to discover which factors affect NP's dispersion and strength. It was shown that the strength increased as the NP's size and volume percentage increased. The size of the NP or the type of SCA had no impact what so ever on the dispersion. A specific SCA's surface occupancy has a significant effect on the NP dispersion. Furthermore, it was shown that compared to introducing Sulphur cross links closer to the nanoparticles (NP), doing so farther away from the NP increased the tensile strength of the nanocomposite. This result implies that changing the distribution of sulphur cross links may have a significant impact on the strength of the nanocomposite [46]

Maziad et al. [47] produced various compositions of blends from natural rubber and low density polyethylene in the presence of maleic acid anhydride and dicumyl peroxide. The effects of the rice husk (RH) and the silane coupling agent, 3 aminopropyl triethoxy silane (3-APE, 1 wt% of filler content) contents on the physicommechanical properties and masswell of the tested blend were examined. To enhance hardness and young's modulus while

reducing elongation at break, tensile strength, impact strength, and mass swell, untreated RH was added to the mixture. The 3-APE-treated composite outperformed the untreated one in terms of mass swelling, tensile strength, Young's modulus, hardness, and impact strength with noticeably reduced elongation. The results showed that silane treatment improved the resistance to irradiation in comparison to untreated samples. Silanized RH (30 phr) showed greater thermal stability and crosslink density than untreated RH. Scanning electron microscopy (SEM) additionally confirmed the preceding findings. Thongsang et al. created natural rubber (NR) that was filled with an equal mixture of fly ash silica (FASi) and precipitated silica (PSi) fillers.

The rubber fillers were either used untreated or with bis [3-triethoxysilyl propyl] tetrasulfide treatment (TESPT). Silica is chemically bound to rubber by the bifunctional organosilane TESPT, which also prevents it from interfering with the reaction mechanism of the Sulphur cure. According to the SEM results, the fly ash silica (FASi) fillers had a better particle size distribution and were bigger than the precipitated silica (PSi) particles. During mixing, the viscosities of the compounds gradually decreased, and those filled with FASi had lower viscosities than those filled with PSi. The application of the silane coupling agent treatment did not improve the dispersion of the fillers in the rubber matrix. At low temperatures, the loading and type of filler had no impact on the storage and loss moduli of the compounds, while at high temperatures, the effect was more evident [48].

Mansour et al. [49] composites were made from chemically treated wood flour and a mixture of polystyrene (PS) and styrene butadiene rubber (SBR). This procedure employs sodium hydroxide (NaOH) maleic anhydride (MAN), maleic anhydride glycidyl methacrylate, and silane coupling agent to enhance the dispersion of wood flour in the SBR/PS blend. The rheological and mechanical qualities were improved when the modified wood flour containing MAN glycidyl methacrylate was used, as opposed to the other treatments, which only slightly changed these parameters. According to the findings of the dielectric testing, the samples of wood flour treated with MAN glycidyl methacrylate and MAN had better permittivity values and lower dielectric loss values, making them suitable for use as insulating materials. The increased relaxation time and crosslinking density for such composites demonstrate that there is an increase in filler-polymer interaction rather than filler-filler interaction.

The addition of bis (3-triethoxysilylpropyl) tetrasulfide (TEPST) improves the physical,

mechanical, dielectric, and curing properties of styrene butadiene rubber (SBR) samples containing precipitated silica, according to Ward and Khalf [50]. As silane content grew, permittivity and dielectric loss values decreased; this could be because TEPST lowered the amount of very polar silanol groups. This experiment also showed that 8phr TEPST improved bonded rubber, tensile strength, and cycle fatigue life.

9- Nanomaterials

A novel type of material called nanocomposites has dispersion of the dispersed phase at nanoscales, typically 1–100 nm, within a particular matrix. Despite the fact that these materials have been in use since the turn of the century, the words "nanocomposites," "nanomaterials," and "nanofillers" are relatively new [51]. Manufacturers who incorporate nanoparticles into polymers reap three key benefits:

- 1- Less weight since the filler loading is reduced.
- 2-Low cost due to the absence of fillers.
- 3-Better properties than normal composites with very low filler loading, such as thermal, mechanical, electrical, optical, barrier, etc.

For instance, silica nanoparticles [54], carbon nanotubes [55], alumina nanoparticles [53], and organoclays [51–54] have all been used to improve polymer properties. Polymer nanocomposites are given specific properties that cannot be acquired from conventional or micro scale fillers by the introduction of low concentration nanofillers (5 wt%) [55]. Polymer nanocomposites have been produced using natural rubber (NR), epoxidized natural rubber (ENR), ethylene propylene diene monomer rubber (EPDM), and chloroprene rubber (CR), among other thermoplastics (polypropylene (PP), polyethylene terephthalate (PET), nylon 6, polymethylmethacrylate (PMMA), polycarbonate, etc.) and polymer blends [59].

By melting together acrylonitrile butadiene rubber (NBR) and organoclay (OC) in polystyrene, acrylonitrile butadiene rubber/clay nanocomposites are produced. The cationic surfactants bromododecyl hydroxyuronium and 1, 12-dibromododecyl hydroxyuronium have been used to create clay formations. Separate colloidal suspensions of each organoclay in toluene are combined with polystyrene to create two distinct types of polystyrene-organoclay composites. The created polystyrene organoclay PS-OC composites were studied and assessed using TEM, X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. The results demonstrated the formation of intercalated and

partially exfoliated polystyrene organoclay composites. For the PS-OC (6 phr) included in NBR compound as compared to unfilled NBR, the rheometric characteristics investigation shows an increase in minimum and maximum torque with an increase in cure rate index (i.e. faster cure times). When comparing NBR/PS-OC1 composites to NBR/PS-OC2 composites at the same loading ratio, this effect is more significant, demonstrating the reinforcing effect of clay on these composites' mechanical properties. Compared to compounds filled with PS-OC2, those filled with PS-OC1 have higher tensile strength, less elongation at break, and a higher Young's modulus. The rheometric characteristics analysis for the PS-OC (6 phr) added to the NBR compound in comparison to unfilled NBR reveals an increase in minimum and maximum torque with an increase in cure rate index (i.e. faster cure times and scorch). This effect is stronger when comparing NBR/PS-OC1 composites to NBR/PS-OC2 composites at the same loading ratio, illuminating the reinforcing impact of clay on the mechanical properties of these composites. Compounds filled with PS-OC1 have a greater Young's modulus, lower elongation at break, and better tensile strength than those filled with PS-OC2.

9.1- Nanoparticle preparation [61–63]

Because a layered silicate and polymer may not physically combine to create a nanocomposite, nanoparticles obtained from natural resources typically require treatment. In this work, a separation into different phases occurred. Weak thermal and mechanical qualities result from the inorganic and organic components, poor physical interaction. In contrast, the organic and inorganic phases are scattered at the nanoscale scale as a result of significant interactions between the layered silicate and the polymer nanocomposites. Nanocomposites hence have distinctive higher characteristics than traditional composites. Simply because there isn't an atomic size combination of the reactants, standard procedures cannot be used to manufacture or treat solids of nanoparticle size. In order to solve this issue, atomic scale reactant mixing is accomplished by all alternative techniques, including hydrothermal, sol-gel, chemical vapor deposition, and microwave, in gaseous, liquid, or even solid phases. Almost all of these are low temperature methods; high temperature final firing, particularly for ceramic-type items, may be necessary.

1-Thermochemical synthesis

Typically, closed vessels are used for hydrothermal reactions. The reactants are suspended or dissolved in a small volume of water before being

put to acid digestion reactors or autoclaves. Reactants those are often difficult to dissolve and precipitate under hydrothermal conditions.

2- Synthesis of Sol Gel

Sol gel synthesis is a very effective alternative method for making alloys, nanocrystalline elemental and composite powders. At considerably lower pressures and temperatures, nanocrystalline particles may be combined.

3- A complicated polymerized technique

Numerous ceramic oxides have been prepared utilising the wet chemical procedure based on the polymeric precursor of the Pechini process. The method has various benefits for processing ceramic powders, including precise control and direct stoichiometry, homogeneous molecular mixing of many components, and accuracy.

4-Deposition of chemical vapor

Chemical vapor deposition, or CVD, is the process by which a solid results from a chemical reaction that occurs in the vapor phase on a heated surface. Coatings, fibers, monolithic components, and powders can all be created with this multiethnic process.

5-Infrared synthesis

Recently, microwave sintering and ceramic, many people are interested in heating. Microwave processing has many different applications, including food processing, pharmaceuticals, and chemical processes. Dielectric characterization, microwave material interaction, novel material development, microwave equipment design, sintering, joining, and modelling are major research areas in microwave processing for ceramics. Coils and carbon nanotubes are created in a microwave chemical deposition device. It includes a microwave magnetron as well as a circulator, cavity, waveguide, and four stub tuners.

6-Processes for high-energy ball milling

For a very long time, size reduction has been performed prior to ball milling in many different sectors. High energy ball milling methods have recently been used to successfully manufacture materials with unique characteristics and microstructures. Three terms mechanical milling (MM), mechanical alloying (MA), and mechanochemical synthesis are typically employed to designate the behavior of powder particles during milling, despite the fact that other expressions describe high energy ball milling operations that have been used. High energy ball milling procedures have some intrinsic advantages over other processing methods, including scalability, exceptional

adaptability, and cost efficiency. As a result, high intensity ball milling processes are ideal for producing a huge amount of nanomaterial.

9.2- Types of nanomaterials

According to the number of diameters of the scattered particles in the nanometer range, three types of materials can be separated [64] as follows:

(1) Isodimensional nanofillers are created when the three dimensions are on the nanoscale scale.

Examples of nanoparticle fillers include silica, aluminum oxide, titanium dioxide, zinc oxide, silicon carbide, and carbon black. Spherical silica nanoparticles can be produced via in-situ solgel techniques or by polymerization that is stimulated directly from their surface.

(2) An extended structure results when the third dimension is greater and two dimensions are less than a nanometer. Examples include carbon nanotubes (CNT), carbon nanofibers, cellulose whiskers, gold or silver nanotubes, boron nitride tubes, and boron carbon nanotubes. They have undergone significant research as reinforcing nanofillers to produce materials with outstanding characteristics.

(3) In the nanoscale range, the third category of nanocomposites can be distinguished by just one dimension. Here, the filler is found in sheets with thicknesses between one and a few nanometers and lengths between hundreds and thousands of nanometers. The term "nanoplatelet based nanocomposites" can be used to group together this class of composites.

Examples of layered nanofillers include layered double hydroxides, layered graphite flakes, and layered silicates. These composites are referred to as polymer layered silicate nanocomposites (PLSNs) or polymer clay nanocomposites (PCNs) and are made of layered silicates and clays. The principal reinforcing action of the fillers is greatly influenced by their surface functional groups, aggregate structure, and average particle size. Filler is often encapsulated in a polymerized media in polymer/clay nanocomposites [65].

9.3- Nanoclay's structural makeup

This new class of material has better properties than conventional composites because it disperses at the nanoscale in a polymer matrix. Similar to the dispersion of particles in liquid, the total dispersion or exfoliation of the clay layers in the monomer or polymer may include up to three processes. The clay tactic's surface is first wetted with monomer or polymer particles. The next process is intercalation or

infiltration of the monomer or polymer, and the exfoliation of the clay layers occurs after that. The first and second phases are governed by thermodynamics, and the third step's size is determined by mechanical and reaction driving forces. As shown in Figure (6), three different types of polymer composites may emerge depending on the strength of the interfacial contacts between the polymer matrix and the silicate layers. Poor mechanical qualities are the result of the clay tactoids' original aggregated state in typical composites, which have nanolayers piled face to face without any polymer intercalation. A few molecular layers of the polymer penetrate the clay in the case of intercalated polymer clay nanocomposites. Finally, individual nanolayers are separated in a continuous polymer matrix by an average distance that depends on the clay loading in exfoliated polymer clay nanocomposites. Exfoliated nanocomposite clay content is often lower than intercalated nanocomposite clay content, as shown in in Figure (6). Due to the high degree of dispersion and large interface area between clay and polymer, exfoliation is more appealing for improving certain material properties [54, 66].

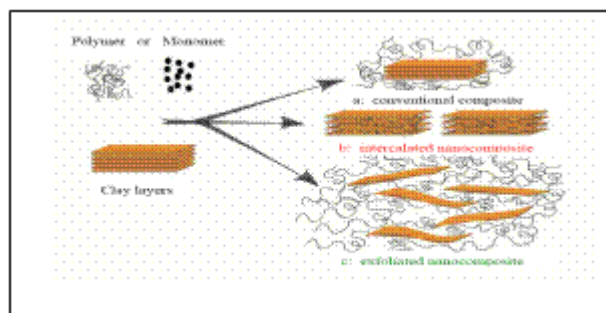


Fig. (6): Layered silicate in (a) conventional composites, (b) Intercalated nanofiller and (c) exfoliated nanofillers

The nanoparticle dispersion and adhesion at the particle-matrix interface have a significant impact on the mechanical properties of nanocomposites. Without appropriate dispersion, the mechanical properties of a nanomaterial cannot be enhanced over those of conventional composites and the mechanical qualities of a nanomaterial with poor dispersion may even deteriorate [67]. Additionally, by strengthening the connection between the matrix and the particle at the interface, one can modify the overall composite's characteristics in a manner similar to that which occurs in macrocomposites. For instance, good interface adhesion will improve the resistance to fatigue, delamination, interlaminar shear strength, and corrosion.

9.4- preparing nanocomposites

For the production of layered silicate nanocomposites, a significant breakdown of the clay's layered structure and thorough dispersion of the resulting platelets throughout the polymer matrix are required. Strong interfacial interaction between the clay and polymer matrix to generate the required shear forces for processing. Three common methods are used to incorporate nanofillers into polymers to produce nanomaterials [68].

1) In-situ polymerization: During this process polymerization phase, Nanofillers are immediately introduced to the liquid monomer. It is a very practical processing method that makes it possible to create composites offering great miscibility with practically any type of polymer and high nanoparticle loading. The production of thermally unstable and soluble polymers that cannot be processed through melt or solution requires the use of this approach in particular. Radiation, heat, or an appropriate initiator can all be used to drive the polymerization reaction.

2) The solution technique, which involves incorporating nanofillers into a polymer solution using solvents including toluene, chloroform, and acetonitrile, integrates the polymer and filler molecules. Because using solvents is not environmentally friendly, the two methods for making nanomaterials that are most frequently used are melting processing and in-situ polymerization.

3) When a polymer is processed using an extruder, an injection molded, or another processing tool, the process is known as melt compounding, nanofillers are processed into the polymer at the same time. Shear forces are used to press the filler (clay) and polymer pellets together in order to aid exfoliation and dispersion.

10- Nanotubes of carbon

In 1991, Iijima made the discovery of carbon nanotubes (CNTs). They have distinctive physical properties, a number of techniques, such as chemical vapor deposition, arc discharge, and laser ablation; can be used to create CNTs. Despite conflicting claims in the literature about the precise characteristics of CNTs, certain findings have revealed extremely high elastic moduli and strengths [69]. In addition to their exceptional mechanical qualities, they also have great electrical and thermal qualities. They are thermally stable in a vacuum up to 2800 °C. They have dielectric current carrying capacities that are roughly 1000 times greater than copper wires and thermal conductivities that are roughly twice as high as diamond.

Consider a carbon nanotube as a sheet of graphene that has been rolled up into a tube. Concentric single-

walled carbonnanotubes (SWCNTs), which make up multi walled carbon nanotubes (MWCNTs), can have one or more walls (SWCNTs). The schematic for CNTs is shown in Figure (7).

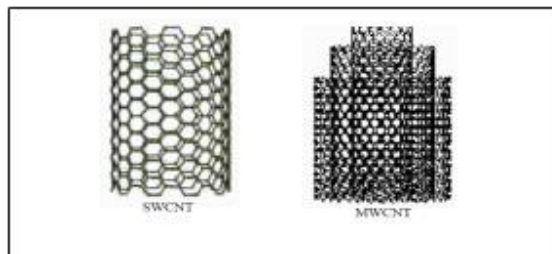


Fig. (7): Schematic of carbon nanotubes

It has been demonstrated that the helicity and diameter of carbon nanotubes significantly affect their electrical conductivity [68].

CNT dispersion in rubber materials is still difficult because of the potential for CNTs' high aspect ratio and the high viscosity of rubbers to become entangled. Although CNT-reinforced rubbers have been the subject of significant research, the overall performance of these rubber nanocomposites currently falls short of expectations [70–75]. After the creation of the CNT-reinforced rubber composites using rubber suspension and the spray drying process, the performance of these powder rubber nanocomposites was enhanced [76, 77]. In order to conduct further research on the production and properties of solid rubber nanocomposites in bulk, a two-roll mill was used to assist the solvent mixing. The developed rubber composites possessed several great characteristics, and practical results were obtained.

11- Nanoparticle surface modification

To enhance the mechanical, physical, and other properties of polymer nanocomposites, all nanoparticles in the matrix must be distributed equally and chemically or physically linked to the matrix [78-80]. To achieve this, a wide range of tactics, including both physical and chemical ones, have been used, such as surface-modifying nanoparticulates, using coupling and compatibilizing agents, using grafting agents, and more. Surface treatment of fillers, which increases the interfacial contacts between the fillers and polymer matrix, is frequently the source of the development of surface functional activity on the filler surface.

12- Nanomaterial characterization and characteristics

There is a noticeable improvement when comparing the mechanical and material properties of nanocomposites to those of pure polymers. Improvements include a higher modulus, improved

strength and heat resistance, decreased gas permeability, and decreased flammability [70, 75]. These improved features are mostly due to the increased interfacial interaction between the matrix and nanofillers in nanocomposites. These qualities lead to the development of fire resistance, gas barrier, thermal stability, and degradation. Because of their superior mechanical behaviors and greater aspect ratios, nanomaterials are regarded as the top reinforcement for increasing features. Different methods can be used to characterize composites, nanofillers, and nanocomposites, including transmission electron microscopy (TEM), X-ray and neutron diffraction, dynamic infrared spectroscopy, atomic force microscopy (AFM), differential scanning calorimetry, small angle neutron scattering, tensile tests, etc. [71, 74, 76, 78].

Numerous experiments have already been conducted to reinforce rubber with various kinds of nanofillers. This section's goal is to review the research that has been published in the literature and to provide a quick summary of the experimental work that has been done on the topic so far. Kaushik et al. [81] produced blends of high styrene rubber (HSR) and natural rubber (NR) with nano silica in the presence of several types of carbon black. The impact of filler on morphological and wear parameters was studied. The type of carbon black utilised in ISAF (Intermediate Super Abrasion Furnace) has shown a substantial impact on the optimal cure time, cure rate index, and mechanical properties by reacting at the interface between the HSR and NR matrix. The fact that just one melting peak could be identified on the DSC curve for all of the samples may be due to the carbon black and matrix supporting each other's structural integrity. In samples with 30 wt% HSR and ISAF type carbon black, less swelling, a lower compression set value, and a greater maximum heat build up were noted. Blends containing 30 weight percent HSR and ISAF-type carbon black showed exceptional abrasion resistance. Polyvinyl chloride (PVC) and acrylonitrile butadiene rubber (NBR) were mixed in various ratios. The properties of PVC/NBR blends were examined using the solution casting process in relation to different concentrations of nanosized filler (copper and graphite). The results of the mechanical properties show that the elongation at break in the (PVC/NBR) blends increases with increasing NBR content, however the tensile strength values in all composites decrease as filler concentration increases. The dielectric properties of these materials were investigated using broadband ac relaxation spectroscopy at a temperature of 25 °C and a frequency range of 0.01 Hz to 10 MHz. It was discovered that, increasing the content of both fillers had an impact on the conductivity and dielectric

characteristics. The nano composite of PVC/NBR (50/50) packed with 5% copper is classified as a semiconductor-type material based on conductivity values [82].

In an effort to significantly enhance the performance of rubber materials, Sui et al. [83] attempted to create carbon nanotube (CNT) reinforced rubber composites. The natural rubber (NR)/CNT nanocomposites were made by solvent mixing on the basis of CNT pretreatment. The addition of the characteristics, mechanical properties, rolling resistance, and bound rubber content were all examined in relation to the produced compounds. The best graphene concentration for vulcanization process is 2.5 phr, demonstrated superior qualities. The Payne effect was seen in the vulcanizates sample at low strain measurements, demonstrating the impact of graphene's replacement for carbon black. The relationship between the modified graphene and the elastomer was demonstrated by the rise in bound rubber content and elongation at break for formulations with graphene replacement. Additionally, analysis of the samples using measurements from micro computed and scanning electron microscopy, it was discovered that fillers were distributed more evenly throughout the formulations. Additionally, it is discovered that the graphine compounds decreased rolling resistance indicates a reduction in hysteresis.

Heat conductivity and mechanical characteristics of a hybrid multi-walled carbon nanotube/silicon carbide (MWCNTs/SiC) reinforced thermoplastic natural rubber (TPNR) nanocomposite were studied. TPNR was produced utilising a volume ratio of 70:20:10 of polypropylene, liquid natural rubber (NR), and natural rubber (NR). The Young's modulus, tensile strength, storage, and loss moduli of the nanocomposites with a single filler of MWCNTs or SiC were higher than those of virgin TPNR. The composite's composition of 1.5 weight percent SiC and 1.5 weight percent MWCNTs led to the greatest improvements in these properties. Additionally, the 3 wt% SiC-reinforced nanocomposite sample outperformed the pure sample and the other reinforced nanocomposite samples in terms of thermal conductivity and specific heat capacity, as determined by the laser flash method. According to these findings, SiC and MWCNTs make excellent percolated networks of hybrid reinforcement fillers to achieve the best thermal and mechanical properties in the TPNR matrix [89].

Lianshi et al [90] used latex CR231 as the raw rubber material, polymeric resin as the coating resin, and high abrasion furnace black (HAF, grade N330) [P (CR231/HAF)] as the reinforcing filler to manufacture nonsulfur modified powdered

polychloroprene rubber. The effects of coating resin and dispersing agent content on carbon black's contact staining and dispersion characteristics in [P (CR231/HAF)] were examined. The results showed that the level of carbon black contact can be successfully decreased by coating resins and dispersing agents. By combining the dispersing agent and HAF at a ratio of 0.12 or 0.1, one can create 10 phr coating resin and [P (CR231/HAF)] without contact staining. [P(CR231/HAF)] particles include free carbon black bits both on the outside and interior. According to investigations of the surface energy spectrum and scanning electron microscopy. Contact staining can be successfully removed.

Zhang and his colleagues [91] selected a novel nanomagnesium hydroxide powder and three different types of micro-Mg (OH)₂ with varying particle sizes as fillers and combined them with ethylene propylene diene monomer rubber (EPDM) to create a group of composites using a conventional rubber processing method. The results showed that the mechanical properties of the composites were enhanced by reduced particle size. The nanocomposites were substantially stronger than the microcomposites, supporting the need for nanoreinforcement in rubber reinforcement. In comparison to microcomposites, nanocomposites showed improved fire resistance.

Surface modification of the particles occasionally significantly improved the mechanical properties of nanocomposites; however, neither the mechanical properties of microcomposites nor the fire resistance or flame retardance of nanocomposites were impacted. The nitroglycerin and triacetin barrier properties of layered silicate reinforced (EPDM/CR) nano rubbers were investigated as rocket propellant inhibitors.

Melt compounding was used in the formulation and manufacture of EPDM/CR nanorubbers with intercalated structures. Triacetin permeability and nitroglycerin absorption were observed to decrease with increasing layered silicate concentration. The stacked silicates further increased the flame retardancies of the nano rubbers by resulting in carbonaceous chars reinforced with silicates. The consumption of rocket propellant may be avoided by using layered silicate reinforced EPDM/CR nano rubbers [92].

Epoxidized natural rubber-alumina nanoparticle composites were made by Noraiham et al. [93]. For consistent 10 phr filler loading, the compounding melt features an internal mixer. The computed optimal values of the tested variables with the highest impact strength, with predicted impact strength of 208.88 J/m, were determined to be rotor speed of 60

rpm and mixing period of 6 min. The actual impact strength was found to be just 3.33% off from the predicted value of 215.84 J/m.

Rugmini and Menon [94] modified china clay (kaolin) by using sodium salt of rubber seed oil (SRSO). According to XRD examination, the spacing between kaolin platelets in the unmodified and SRSO-modified samples rose from 7.15 to 14. FTIR spectroscopy suggests that the organic component of (RSO) may have been grafted onto the clay surface. According to DTA of the SRSO, the modified kaolin SRSO was more firmly bonded in a constraint environment within the kaolin lamellae. In comparison to mixture comprising unmodified kaolin, it was found that a natural rubber (NR) mixture containing 10 phr of modified kaolin. Using SRSO cured faster. The potential of the substance as organ modified nanofiller was shown by the greatly improved tensile strength, tensile modulus, and elongation at break of NR vulcanizates containing modified kaolin.

Yehia et al. [95] created nanocomposite materials from rubber and natural montmorillonite clay (MMT) via a cation exchange method involving MMT's Na⁺ ions and the rubber's ammonium cations from amine-terminated butadiene acrylonitrile. The clay layers are structured as nanosized layers, and the d-spacing clusters are significantly larger, according to the TEM and SEM data. As uniformly as feasible, the produced rubber MMT material was added to the matrices of NBR, SBR, and NR as a reinforcing agent in concentrations up to 12 phr (10%). CBS/S vulcanized the rubber that had been synthesized. The rubber vulcanizates' physical and mechanical characteristics were estimated. It was found that in natural and synthetic rubber vulcanizates, the 4 phr rubber MMT nanocomposites are comparable to 40 phr of carbon black (HAF).

Four different rubber types, including styrene butadiene rubber (SBR), natural rubber (NR), butadiene rubber (BR), and ethylene-propylene diene methylene, were combined with one type of nanokaolin (NK) powder. This powder has measurements of 300-500 nm in average diameter, 20-50 nm in average thickness, and 32 m²/g specific surface area (EPDM). To evaluate the effects, comparisons between the effects of reinforcing and precipitated silica were made (PS). The results showed that NK might considerably enhance the vulcanizing procedure by reducing the cross-linked rubbers optimal cure time (t₉₀) and increasing their setting up time (t₁₀). This promotes manufacturing output and operational safety. The rubber composites that contain nanokaolin exhibit good mechanical,

elastomeric, and thermal stability properties. The modulus and rip strength of the rubber/NK composites are inferior to those of materials containing precipitated silica, but their tensile strengths are equivalent to those of rubber/PS composites. The NK sheets are equally dispersed throughout the rubber matrix and are placed in parallel, according to microstructural analysis. The excellent processability, thermal stability, and mechanical characteristics of these rubber composites are a result of the strong interfacial contacts between the rubber chains and NK [96].

Organophilic kaolinitic black shale was produced by combining natural kaolinitic black shale with cetyl trimethyl ammonium bromide (CTAB C16) as a surfactant. It was described using transmission electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. Utilising the acrylic acid modifying agent, the organophilic kaolinitic black shale can be more evenly distributed throughout the rubber matrix. The ethylene propylene diene monomer received additions of modified organophilic kaolinitic black shale in various ratios. Exfoliated nanocomposites were found in the modified organophilic kaolinitic black shale's dispersion, which was confirmed by SEM and X-ray diffraction studies. After being filled with kaolinitic black shale, the elastomeric material was investigated utilising thermal gravimetric analysis and its physicomechanical properties. The nanocomposites showed appreciable improvement in terms of Young's modulus, tensile strength, elongation at break, and hardness. The use of modified organophilic kaolinitic black shale was also found to boost thermal stability [97].

The creation of nanocomposites using the materials ethylene-propylene terpolymer rubber (EPDM), chlorobutyl rubber (IIR-C1), and organically modified montmorillonite (OMMT) was looked into. A mixture of 0, 3, and 6 phr (part per 100 parts of rubber) OMMT were done. They were combined properly for 11 minutes at a high temperature in a Plastic Corder Brabender internal mixer after being received by melt intercalation. On a laboratory mill, the curing components were embedded for five minutes at a friction ratio of 1:1.1 and a temperature range of 70 to 100 °C. Rubber specimens were created by compressing rubber samples using a hydraulic press at 300 KN of pressure and 165 °C. The Monsanto rheometer was used to determine the cure time, which decreases with increasing amounts of OMMT in the mixtures. It was demonstrated that mixes containing OMMT also have superior physico-mechanical properties. Rubber

space application seals could be made with these types of nanocomposites [98].

Zhou et al. explored silicon nitride (Si_3N_4) reinforced vinyl end-blocked polymethylsiloxane either alone or in conjunction with silicone carbide whisker (SiCw). When compared to fillers that only used one particle size, silicone rubber that contained 50 vol% hybrid Si_3N_4 particles of various sizes at an ideal weight ratio displayed the highest thermal conductivity, according to the findings [99]. In addition, when combined with SiCw at a weight ratio of 9:1, hybrid Si_3N_4 and SiCw presented composites with higher thermal conductivity due to filler structure in hybrid fillers, as well. The surface modification of the hybrid fillers with 3-methacryloyloxy-propyltrimethoxysilane lowered coefficient of thermal expansion (CTE) and improved heat conductivity of the composites. Since the sizes and dispersion of filler particles have a significant impact on the packing fraction, hybrid fillers with various sizes at a preferred weight ratio may improve the packing volume fraction of filler in the matrix. This is due to the fact that smaller particles can easily occupy spaces than the larger particles cannot in the continuous matrices as shown in Figure (8).

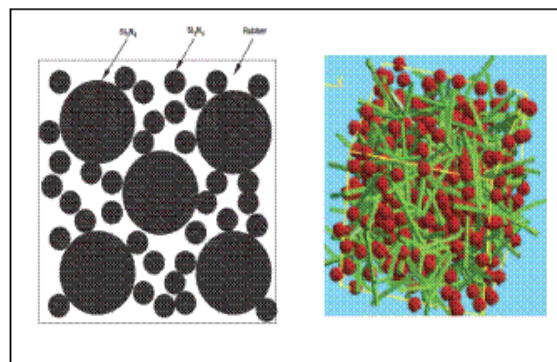


Fig. (8): Model for packing particles of varying sizes

Rubber mixtures have been searching for qualities that fall between two rubber matrices. On the other hand, polymer clay nanocomposites' low gas permeability and remarkable mechanical properties have attracted the attention of several researchers, and experimental results are provided in a substantial amount of patents and papers. Only 10% of clay particles with a diameter less than one nanometer are present in polymer-clay nanocomposites, a novel type of mineral-field polymer. In this study, organically modified vermiculite clay (VMT) by quaternary alkylammonium in varied amounts (3, 6, 9 and 12 phr) as the filler and polybutadiene rubber (BR) and

ethylene propylene diene monomer rubber (EPDM) as the matrix were combined to create new nanocomposite materials. The rubber nanocomposite sheets were further characterised using a variety of analytical techniques, including the X-ray diffractometer (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and study of the mechanical properties [100].

Four quaternary monomers of ammonium salt were synthesised from N, N-dimethylaminoethyl methacrylate and polymerized to produce cationic polymers. The generated monomers and polymers were characterised using proton nuclear magnetic resonance (^1H NMR) spectroscopy and Fourier transform infrared (FTIR). The generated polymers' molecular weights were determined using gel permeation chromatography. The solution intercalation method was used to make the polymer/clay nanocomposites. Then, high-resolution transmission electron microscopy, X-ray diffraction, FTIR, energy dispersive X-ray, and thermogravimetric analyses were used to analyse them. These investigations proved that the nanocomposites of polymer and clay have an intercalated structure. Researchers investigated the effects of temperature and frequency on the dielectric properties of the polymer/clay nanocomposites. [101].

Poly(N, N-dimethylaminoethyl methacrylate)/clay nanocomposites were made utilising an in-situ bulk polymerization process. N,N-dimethylaminoethyl methacrylate (DMAEMA) was alkylated with hexyl bromide to produce quaternary ammonium salt using the organomodification of the clay technique. Bulk polymerization procedures were used to form the nanocomposites after the organoclay was dispersed in the DMAEMA monomer at concentrations of 1, 3, and 5 wt%. The created nanocomposites were characterised by Fourier transforms infrared, X-ray diffraction (XRD), high-resolution transmission electron microscopy, and thermogravimetric studies. According to the XRD measurements, the polymer/clay nanocomposites have an exfoliated structure. Additionally, research was conducted on the mechanical, optical, and dielectric properties. The percentage of transparent produced polymer (PDMAEMA) film fell to 80% for PDMAEMA/clay (5 wt%). The optical bandgap of the films was measured, and they showed a permissible indirect transition. The dielectric properties of polymers and polymer nanocomposites have been discussed [102].

Using the solution intercalation method with low and high molecular weight poly(diallyldimethylammonium chloride, or PDADMAC), at ratios of 0.5, 1, and 2 times the clay's CEC, the cation exchange capacity (CEC) of sodium bentonite clay was altered. The created hybrids were characterised using X-ray diffraction, Fourier transform infrared spectroscopy, high-resolution transmission electron microscopy, differential scanning calorimetry, and thermogravimetric studies. PDADMAC/clay nanocomposites' intercalated structure was made clear by the investigation's findings. Additionally, the outcomes showed that the nanocomposite containing high molecular weight PDADMAC at a concentration one time the CEC of the clay had the greatest thermal stability among the produced nanocomposites and the most intercalated structure. Calculating and disputing the values of the real (1) and imaginary (2) sections of relative permittivity were necessary for the study of the room temperature dielectric properties as a function of frequency. Higher values of ϵ_1 and ϵ_2 are obtained by using PDADMAC with a high molecular weight. As polymer concentration is increased, the values of ϵ_1 and ϵ_2 are influenced toward lower values [103].

Optically, dielectrically, and mechanically, cast films made of poly methyl methacrylate (PMMA) filled with $\text{Mg}_{1-x}\text{Cu}_x\text{O}$, $0.05x\text{Cu}_x\text{O}$, and 0.2mm thick were studied. The structures of the produced powder and films were investigated using X-ray diffraction (XRD). The observed pattern reveals a cubic phase structure in the $\text{Mg}_{1-x}\text{Cu}_x\text{O}$ powder and films. Fourier transform infrared (FTIR) spectra were used to confirm the inclusion of $\text{Mg}_{0.9}\text{Cu}_{0.1}\text{O}$ nanoparticles into the PMMA. The morphology of the nanocomposite films was examined using field emission scanning electron microscopy (FESEM). In the PMMA matrix, it was possible to produce specific clusters and an excellent dispersion of $\text{Mg}_{1-x}\text{Cu}_x\text{O}$ nanoparticles. The optical properties of the produced nanocomposite films were evaluated using UV-Vis technology. The absorption coefficient, optical energy band gap, extinction coefficient, and refractive index of the cast films were calculated. The results revealed an increase in the absorption coefficient, extinction coefficient, and refractive index as well as a decrease in the optical energy band gap as the amount of Cu in the PMMA matrix increased. The mechanical properties have gotten better. The micro hardness increases as the Cu content increases before dropping up to $x = 0.15$ wt%. The tensile strength was measured and raised from 23.87 to 43.30 MPa when the Cu content was increased till $x = 0.10$. After that, it got smaller. Finally, whereas dielectric loss (ϵ'') and permittivity

(ϵ') decreased with frequency but remained almost constant at higher frequency ranges. When the Cu content rose. In order to appreciate the conduction process in the nanocomposite films that were presented, the AC conductivity was also measured. As the Cu concentration in the PMMA matrix rose, the anticipated dc conductivity rose as well [104].

In samples of nitrile butadiene rubber, cobalt-zinc (Co-Zn) ferrite nanoparticles ($\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, where $x = 0, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, \text{ and } 1$) were added (NBR). The structure and morphology of Co-Zn ferrite nanoparticles were examined using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction, and transmission electron microscopy, while the structure of Co-Zn nanoferrite filled NBR composites was examined using FTIR spectroscopy and scanning electron microscopy. The influence of ferrite content on cure parameters, mechanical properties, and hardness showed improvements of up to $x = 0.8$. The dielectric characteristics of ferrite were enhanced [105].

High temperature vulcanised silicone rubber samples containing $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles were made using a normal conventional rubber mixer. The compounds were dry blended using two roll mixing mills (outside diameter 470 mm, working distance 300 mm, speed of slow roll 24 rpm and fraction ratio of 1:1.4). The structure and morphology of Co-Zn ferrite were studied using X-ray diffraction and transmission electron microscopy (TEM). The homogeneity of silicone rubber loaded with Co-Zn nanoferrite was evaluated using SEM (SEM). On rheological and physical-mechanical characteristics, such as tensile strength, elongation at break, and Young's modulus, measurements of the impacts of ferrite concentration were made. These parameters were improved by increasing the ferrite load to 8 phr. Every composite sample's hardness increased. The samples' electric resistivity declined until they were loaded with 8 phr of ferrite before increasing with greater ferrite loads, but their magnetization increased quickly at high ferrite concentrations. Discussion and interpretation of these results took into account the morphology and numerous interactions between the phase of ferrite and rubber matrix. Comparisons between the acquired results and those in the literature [106] revealed that the values of the measured qualities in this inquiry were superior.

Applications

- The way to stop radiation leakage, gaskets built of electrically conductive rubber

composites have garnered a lot of interest. By adding conductive filler to a rubber matrix, conductivity can be increased. The insertion of conductive fillers into polymer matrix to produce conductive materials is the most cost-effective method of producing conductive materials. The system's conductivity is increased by the inclusion of metal in the form of powder, flake, and fibre in a rubber matrix. Conductive fillers such as conductive carbon black, polyaniline, boron carbide, nickel fibre, and ferrite particles were mentioned. Concurrent fillers, on the other hand, are utilised to give sticky electrical conductivity [107].

- The best thermal interface materials need to have high thermal conductivity and a low coefficient of thermal expansion. The material must also be flexible enough to bend when lightly contacted by all uneven mat surface areas. In order to solve the thermal management issue, it is believed that rubbers filled with thermal conductivity filler are a beneficial solution. To produce high performance thermal conductive, it has been primarily desired to include strong thermal conductivity ceramic fillers into rubbers due to the elastomeric thermal pad's poor thermal conductivity [108].
- Recently, conductivity and tensile strength have improved due to the application of coupling agents. This is because coupling agents encouraged particle wetting and dispersion within rubber, which reduced interfacial thermal barriers [109,110].
- The best fillers for tire tread compounds have high interactions between rubber and fillers and low interactions between fillers and fillers. Higher abrasion resistance is guaranteed by the former and reduced hysteresis or rolling resistance is required by the latter. A new class of filler material called "carbon-silica dual phase (CSD)" has been commercialized under the name "ECOBBLACK" and promises to provide the best balance of these qualities based on this goal. The novel filler is made of finely distributed silica phase in the carbon phase rather than the customary 90–99% elemental carbon found in traditional carbon black. The main properties of the novel material are a high polymer-filler interaction and a low filler-filler interaction, according to Sattayanurak et al. [111].

- Silica is often used as reinforcement in today's fuel-efficient tires because it produces superior wet traction and lower rolling resistance than carbon black-filled alternatives. The addition of hybrid fillers, also known as secondary fillers, to silica reinforced tread compounds has the potential to greatly improve tire performance. Two secondary fillers were added to silica-based natural rubber compounds in the current study at a silica/secondary filler ratio of 45/10 phr. These fillers included carbon black N134 and organoclay nanofiller. In accordance with the standard mixing procedure for silica-filled on NR systems, the compounds were created utilizing a variety of mixing temperatures. The silane coupling agent's silica hydrophobation and coupling reaction with silica and rubber were shown to be significantly influenced by the organoclay's modifier, an organic ammonium derivative, the Payne effect, Mooney viscosity, cure behavior, and mechanical properties results. When carbon black was employed as additional filler, these tendencies were not present in the compounds. The poorer performance of the filler dispersion as compared to the pure silica-filled material is due to the large specific surface area of the carbon black and the excessively high mixing temperature. Dynamic properties revealed that the addition of carbon black to silica-filled NR had no impact on the properties, however the application of organoclay as secondary filler was able to increase rolling resistance and wet traction of a tire tread [112,113].
- Nowadays, a variety of uses for nanomaterials are common, including the production of household items, electrical equipment, building materials, automobile parts, and aerospace products. A mixture of more than one material is required to produce a material that is superior to monolithic materials in challenging applications, which was partially the result of the availability of contemporary technology and the necessity for higher performance [114–119].
- Even rubber/clay nanocomposites have been created and show improved characteristics [52, 86, 89]. These novel materials have much better thermal, mechanical, electrical, and optical properties. The stiffness and strength, dimensional stability, flame retardancy, solvent and UV resistance, and reduced gas permeability [120].
- Recent research in the field of nanocomposites reveals that the current emphasis is on thermoset and thermoplastic rubbers as well as thermoplastic/rubber mixes. For commercial production, direct polymerization processes would be required, and melt compounding is the most promising in this regard. Making organoclay and spreading it in the rubber phase at the same time is already being attempted. Additionally, it is planned to create novel organophilic silicates that are "suited" for elastomers. The employment of coupling agents and organoclays simultaneously, such as titanates, silanes, etc. Linking the silicate surface through a reaction with the latter's hydroxyl groups is a promising way to transform clays. To further enhance the dispersion of the organoclay during melt processing, concentrated master batches from commercial clay products would be necessary. Overall, the use of nanoclay as a reinforcing component in rubber matrices presents a great opportunity for the development of novel rubber products. In order to develop materials with superior mechanical, thermal, and electrical properties, organoclays can also be mixed with other nanofillers, such as carbon nanotubes and quantum dots [121,122].
- Recently years, carbon nanotubes (CNTs), which are produced by rolling graphite sheets, have grown in popularity. CNTs have mechanical, electrical, and thermal properties. CNTs are expected to provide a stronger reinforcement effect than other nano-fillers when utilised as ideal reinforcing fillers in polymer composites because of their inherent superior features. As a result, CNTs have seen significant improvements in mechanical and electrical conductivity when used with various types of polymers [123–126].

CONCLUSIONS

It is obvious that the only locations at which black and white fillers exist in nanoobject form are either short-lived intermediates during synthesis or polymer-bound tiny aggregates. This is based on the production and utilisation of these materials. It is not physically nor chemically possible to obtain individual nano-object shapes during the lifespan of a rubber product due to the strength of the bonding forces between the individual particles in an aggregate and between the polymer and filler in

rubber compounds. As a result, nanoobject forms of carbon black or amorphous precipitated silica used as fillers to reinforce rubber pose no risk to humans or the environment.

It is not anticipated that exposure to carbon black and precipitated amorphous silica, in the forms employed in the tyre business will have a negative impact on health based on the current estimates of their toxicity. The effects of various materials, especially amorphous silica, can be different from the material's nanoscale forms (e.g. mesoporous silica). The forms utilised in the tyre industry have only ever been available as nanostructured materials since they have always been supplied as aggregates and agglomerates.

As a result, the potential consequences of these materials' nanofoms have already been covered in all prior risk assessments on their use in the rubber and tyre industries. Additional control of amorphous silica and carbon black based on their designation as nanostructure materials is unnecessary given their physical properties and what is known about their toxicity. Any future development and introduction of novel nanomaterials by the tyre industry, as well as any potential effects on human health, safety, and the environment, will be evaluated in line with all applicable chemical substance rules. To ensure safe use, the requirement for risk management measures will be assessed with the relevant authorities and, if necessary, applied throughout the sector.

References

- 1- Blow, C. M.; Hepburn, C. "Rubber technology and manufacturing" second edition, Published for the plastics and rubber institute by Butterworth Scientific London, Ch. 6, p.202, 1982.
- 2- Byers, J. T. "Rubber Technology", third edition, J. E. Mark, B. Erman and F. R. Eirich Eds., Elsevier Academic Press, San Diego Ch. 3, p. 51, 2005.
- 3- Coran, A. Y. "Science and Technology of Rubber" third edition, edited by J. E. Mark, B. Erman, F. R. Eirich, Academic Press, San Diego, Ch. 8, p. 339, 2005.
- 4-Hamed, G. R. "Engineering with Rubber ": How to Design Rubber Components, second edition, A. N. Gent, editor, Hanser Gardner Publications, Inc., Cincinnati, p. 11, 2001.
- 5-Blows, S.; "Handbook of rubber technology" New Delhi Galgotia, Publication LTD, New Delhi 1998
- 6-Encyclopedia of polymer science and engineering, Interscience publication, John Wiley and sons, New York V. 14, 1985.
- 7-Kohls, D. J.; Beaucage, G., "Rational design of reinforced rubber" Solid State and Materials Science **6**, 183, 2002
- 8- Boonstra, B. B., "Role of particulate fillers in elastomer Reinforcement" review, Polymer, 20, 691, 1979.
- 9- Yehia, A. A.; Ismail, M. N.; Hefiny, Y. A.; Abd El Bary, E. M.; Mull, M. A. "Effect of chemically modified of waste rubber powder as filler in natural rubber vulcanizates" J. Appl. Polym. Sci. 93, 30, 2004.
- 10-Zhao, J. Y.; Bi, X. L.; Zhou, L. "Application of silica modified by silane coupling agent in SR" J. of Qingdao Uni. Sci. Tech. 25, 160, 2004.
- 11- Ismail M. N.; Khalaf A. I. "Styrene–Butadiene Rubber/Graphite Powder Composites Rheometrical, Physicomechanical, and Morphological Properties" J. Appl. Polym. Sci. 120, 298, 2011.
- 12- Jingjie, H.; Xiliang, Z.; Weihong, G.; Chifei, W. "Effect of modified carbon black on the filler-elastomer interaction and dynamic mechanical properties of SBR vulcanizates" J. Appl. Polym. Sci. 100, 3707, 2006.
- 13-Tae Y. K.; Sung Y.; Won, S. H. K.; and Ur Ryong Cho "Study on the Change of Physical Properties with Silica Contents in Solution Styrene-Butadiene Rubber (SSBR)/Silica Composites" Elastomers and Composites, 52 (1) 17, 2017.
- 14- Qu L.L.; Yu G.Z.; Xie X.M.; Wang L.L.; Li J.; Zhao Q.S. "Effect of silane coupling agent on filler and rubber interaction of silica reinforced solution styrene butadiene rubber" Polym Compos.34(10):1575,2013.
- 15-Rattanasom, N.; Saowapark, T.; Deeprasertkul, C. "Reinforcement of natural rubber with silica/carbon black hybrid filler" Polymer Testing 26, 369-377, 2007.
- 16- Mostafa, A.; Abouel-Kasem, A.; Bayoumi, M. R.; El-Sebaie, M. G. "The influence of CB loading on thermal aging resistance of SBR and NBR rubber compound under different aging temperature" Materials and Design 30, 791, 2009.
- 17- Khalaf E.S.A.; Farag H. and Abdel-Bary E.M. "Some studies on the effect of bagasse concentration on the mechanical and physical properties of SBR composites" Polymers and Polymer Composites 28(8–9) 663, 2020.
- 18- Sae-oui, P. A.A.; Sirisinha, C.; Thaptong, P. "Utilization of limestone dust waste as filler in natural rubber" Journal of Material Cycles and Waste Management 11, 166, 2009.
- 19- Abdelsalam A.A.; Araby S.; El-Sabbagh S. H.; Abdelmoneim A. and Hassan M. A. "Effect of carbon black loading on mechanical and rheological properties of natural rubber/styrenebutadiene rubber/nitrile butadiene rubber blends" Journal of Thermoplastic Composite Materials 34(4) 490, 2021.
- 20- Reffaee, A. S. A.; El Nashar, D. E.; Abd-El-Messieh, S. L.; Abd-El Nour, K. N. "Electrical and

- mechanical properties of some butadiene rubber composites in the vicinity of the percolation threshold" *Polymer-Plastics Technology and Engineering* 46, 591, 2007.
- 21- Eid, M. A. M.; El-Nashar, D. E. "Filling effect of silica on electrical and mechanical properties of EPDM/NBR blends" *Polymer-Plastics Technology and Engineering* 45, 675, 2006.
- 22- Sattayanurak S., J. W. M.; Sahakaro K.; Kaewsaku W.; Dierkes W. K; and A. Blume, "Silica-Reinforced Natural Rubber: Synergistic Effects by Addition of Small Amounts of Secondary Fillers to Silica-Reinforced Natural Rubber Tire Tread Compounds" *Hindawi Advances in Materials Science and Engineering* ID 5891051, 1,2019.
- 23- Perez, L. D.; Sierra, L.; Lopez, B. L. "Effect of the filler characteristics on the miscibility of styrene-butadiene rubber and nitrile-butadiene rubber blends" *Polymer Engineering and Science* 48, 1986, 2008.
- 24- Essawy, H.; El-Nashar, D. E. "The use of montmorillonite as a reinforcing compatibilizing filler for NBR, SBR rubber blend" *Polymer Testing* 23, 803, 2004
- 25- Wang, X.; Wu, L.; Yu, H.; Xiao, T.; Li, H. and Yang, J. "Analysis of effect of modification of silica and carbon black co-filled rubber composite on mechanical properties" *e-Polymers* 21, 279, 2021
- 26- Kandil, H.; Samy, M.; El-Nashar, D. E.; "Gallate ester of castor oil as a multifunctional additive in HAF carbon black-filled natural rubber composites" *J Vinyl Addit Technol, J Vinyl Addit Technol* 28,331, 2022.
- 27- Sattayanurak S.; Sahakaro K. ; Kaewsaku W.; Dierkes W. K.; Reuvekamp L. A. E. M.; Blume A. and Noordermeer J. W. M. "Enhancing performance of silica-reinforced natural rubber tire tread compounds by applying organoclay as secondary filler" *Rubber Chemistry and Technology* 94 (1) 121, 2021.
- 28- El-Nashar, D. E.; Gomaa, E.; Abd-El-Messieh, S. L. "Study of electrical, mechanical, and nanoscale free-volume properties of NBR and EPDM Rubber reinforced by bentonite or kaolin" *Journal of Polymer Science: Part B: Polymer Physics* 47, 1825, 2009.
- 29- El-Nashar, D. E.; Youssef. E. A. M.; Abd El-Ghaffar, M. A. "Modified phosphate pigments as high performance reinforcing materials for rubber vulcanizates" *Materials and Design* 31(3) 1350, 2010.
- 30- Boukfessa H.; Bezzazi B. "The effect of carbon black on the curing and mechanical properties of natural rubber/ acrylonitrile- butadiene rubber composites" *J. of Applied Research and Technology* 19 194, 2021.
- 31- Ateia E. E.; El-Nashar D. E.; Takla E.; Mahmoud M. Abd Alla; "Developing Ethylene-Propylene-Diene blends for Industrial Applications" *Eur. Chem. Bull.* 6(6), 258, 2017.
- 32- Ateia E. E.; El-Nashar D. E.; Hassan H. H. and Abd El-Aziz A. K. "A comparative study of the cure characteristics, mechanical properties and abrasion resistance of silica and carbon black filled NBR/SBR Blends" *Egypt. J. Chem.* 60 (5)769, 2017
- 33- Christopher G. Robertson 1 and Ned J. Hardman "Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite" *Polymers* 13, 538, 2021.
- 34-Najam M.;M. Hussain; Ali1 Z.; Maafa I. M.; Akhter P.; Majeed K.;Ashfaq A.; and Shehzad N. "Influence of silica materials on synthesis of elastomer nanocomposites: A review" *J. of Elastomers & Plastics*, 52(8) 747.2020.
- 35- Rothon, R. N. "Mineral fillers in thermoplastics: filler manufacture and characterization" *Advances in polymer science, Review, Advances in Polymer Science* 139, 67, 1999.
- 36- Parent, J. S.; Mrkoc. M. L.; Hennigar, S. L., "Silica agglomeration and elastomer reinforcement influence of surface modifications" *Plast. Rub. Compos.* 32, 114, 2003
- 37- Han, J. J.; He, X. L.; Guo, W. H.; Wu, C. F., "Effects of filler-rubber interaction on dynamic mechanical properties and reinforcement of NR vulcanisates" *Plastics, Rubber and Composites*36,154, 2007.
- 38- Hui, R.; Yixin, Q.; Suhe, Z. S. "Reinforcement of styrene-butadiene rubber with silica modified by silane coupling agents" *Chinese J. Chem. Eng.* 14, 93, 2006.
- 39- Jacob, M.;Francis, B.;Varughese, K. T.; Thomas, S. "The effect of silane coupling agents on the viscoelastic properties of rubber biocomposites" *Macromol. Mater. Eng.* 291, 1119, 2006.
- 40- Yin, D.;Zhang, Y.;Peng, Z.; Zhang, Y., "Effect of fillers and additives on the properties of SBR vulcanizates" *J. Appl. Polym. Sci.*88, 775, 2003.
- 41- El-Nashar, D. E.; Ward, A. A.; Abd-El-Messieh, S. L., "Physico-mechanical and dielectric properties of nitrile rubber filled with silica and mica" *KGK Kautschuk Gummi Kunststoff*, 434, September 2009.
- 42- Vinod, V. S.; Varghese, S.; Kuriakose , B. "Aluminum powder filled nitrile rubber composites" *J. Appl. Polym. Sci.*91, 3156, 2004.
- 43- Wimolmala, E.; Khongnual, K.; Sombatsompop, N. "Mechanical and morphological properties of cellular NR/ SBR vulcanizates under thermal and weathering ageing mechanical and morphological properties of cellular NR/ SBR vulcanizates under yhermal and weathering ageing" *J. Appl. Polym. Sci.*114, 2816, 2009.
- 44- Zhang J.; Wang C.; Zao W.; Feng H.; Hou Y. "High-Performance Nitrile Butadiene Rubber Composites with Good Mechanical Properties,

- Tunable Elasticity, and Robust Shape Memory Behaviors" *Industrial & Engineering Chemistry Research* **59** (36) 15936, 2020.
- 45- Ward, A. A.; Khalf, A. I. "Electrical and mechanical properties of SBR filled with carbon black-silica blends" *Kautschuk Gummi Kunststoff*, **60** (11) 623, 2007.
- 46- Joseph E.; Swaminathan N.; "Investigation of mechanical properties and dispersion in silica/Styrene Butadiene Rubber (SBR) nanocomposites: A ReaxFF molecular dynamics study, *Computational Materials Science* **200**, 110751, 2021.
- 47- Maziad, N. A.; El-Nashar, D. E.; Sadek, E. M., "The effects of a silane coupling agent on properties of rice husk-filled maleic acid anhydride compatibilized natural rubber/low-density polyethylene blend" *J. Mater. Sci.* **44**, 2665, 2009.
- 48- Thongsang, S.; Sombatsompop, N.; Ansarifar, A. "Effect of fly ash silica and precipitated silica fillers on the viscosity, cure, and viscoelastic properties of natural rubber" *Polym. Adv. Technol.* **19**, 1296, 2008.
- 49- Mansour, S. H.; El-Nashar, D. E.; Abd-El-Messieh, S. L. "Effect of chemical treatment of wood flour on the properties of styrene butadiene rubber/polystyrene composites" *J. Appl. Polym. Sci.* **102**, 5861, 2006.
- 50- Ward, A. A.; Khalf, A. I. "Influence of TESPT on the physico-mechanical and dielectric properties of silica filled SBR composites" *KGK Kautschuk Gummi Kunststoffe*, **62**(12), 650, 2009.
- 51- Sengupta, R.; Chakraborty, S.; Bandyopadhyay, S.; Dasgupta, S.; Mukhopadhyay, R.; Auddy, K.; Deuri, A. S. "A Short review on rubber/clay nanocomposites with emphasis on mechanical properties" *Polymer Engineering and Science*, Technical report, 1956, 2007.
- 52- Khalaf, A.I.; Yehia, A.A. ; Temraz, M.M.G. "A Short Review on Hybrid Clay/ Rubber Nanocomposites" *Kautschuk Gummi Kunststoffe* **69**(6), **22**, 2016.
- 53- Khalaf A.I. and Hegazy M.A. "Synthesis and characterization of cationic surfactants in the preparation of organobentonite and study their effectiveness on the properties of styrene-butadiene rubber/bentonite composites" *High Performance Polymers* **25** (2), 115, 2013.
- 54-Khalaf, A.I.; Hegazy M.A. and El. Nashar D. E. "Synthesis and characterization of cationic gemini surfactant modified Na-bentonite and its applications for rubber nanocomposites" *polymer composites*, **38**(2) 396, 2017.
- 55- Georgea N.; Venugopal B.; Johna H.; Mathiazhag A. and Joseph R., "Nanosilica decorated multiwalled carbon nanotubes (CS hybrids) in natural rubber latex" *Polymer* **161**, 170, 2019.
- 56- Pacheco S.; Tapia J.; Medina M.; Rodriguez R. "Cadmium ions adsorption in simulated wastewater using structured alumina-silica nanoparticles" *Journal of Non-Crystalline Solids* **352** (52-54) 5475, 2006
- 57- Liu C.-l.; Zheng S.-l.; Ma S.-h.; Luo Y.; Ding J.; Xiao-hui , Zhang Y. " A novel process to enrich alumina and prepare silica nanoparticles from high-alumina fly ash " *Fuel Processing Technology* **173**, 40, 2018.
- 58- López-Manchado, M. A.; Valentín, J. L.; Carretero, J.; Barroso, F. Arroyo, M. "Rubber network in elastomer nanocomposites " *Euro. Poly. J.* **43**, 4143, 2007.
- 59- Sadek E.M.; El-Nashar D.E. and Ahmed S.M. "Influence of modifying agents of organoclay on the properties of nanocomposites based on acrylonitrile butadiene rubber" *Egyptian Journal of Petroleum*, **27** (4) 1177, 2018.
- 60- Ajayan, P. M.; Schadler, L. S. Braun, P. V. "Nanocomposite science and technology" Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
- 61- William G., E.; Aldo B., A.; Jinwen, Z., "Polymer nanocomposites: Synthesis and natural fillers" *A Review, Maderas. Cienciay Tecnologia* **7**, 159, 2005.
- 62- Sharma, P.; Maio, W.; Giri, A.; Raghunathan, S., " Nanomaterials of nanoscience and nanotechnology. Copyright by Marcle Dekker, 2004.
- 63- Biswas, M.; Sinha, R. S. "Recent progress in synthesis and evaluation of polymer-montmorillonite nanocomposites" *Adv. Polym.* **155**, 167, 2001.
- 64- Khan I.; Saeed K.; Khan Id. " Review Nanoparticles: Properties, applications and toxicities " *Arabian Journal of Chemistry* **12**, (7) 908, 2019.
- 65- Pedro H.C.C.; Satyanarayana K.G.; Wypych F. " Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities: Exfoliation of organophilic montmorillonite nanolayers in polystyrene" *Materials Research*, **12**(1) 1, 2009.
- 66- Carrado K. "Polymer-clay nanocomposites" in *Advanced Polymeric Materials*, Shonaike, G. and Advani, S. (eds), CRC Press, Boca Raton, 349, 2003.
- 67- Kharwar P.K. and Verma R.K. " Carbon Nano Tube in polymer nanocomposites " *Materials Today: Proceedings*, **18**, 4067, 2019.
- 68- Mark, J. E. "Ceramic-reinforced polymers and polymer-modified ceramics" *Polym. Eng. Sci.* **36**, 2905, 1996.
- 69- Thostenson, E.T.; Ren, Z.; Chou, T. W. "Advances in the science and technology of carbon nanotubes and their composites" *a review Composites Science and Technology* **61**, 1899, 2001

- 70- Gao J.; He Y.; Gong X. ; "Effect of electric field induced alignment and dispersion of functionalized carbon nanotubes on properties of natural rubber" *Results in Physics* 9, 493, 2018
- 71- Bokobza L. " Multiwall carbon nanotube-filled natural rubber: Electrical and mechanical properties" *eXPRESS Polymer Letters* 6 (3) 213, 2012.
- 72- Ata S.; Mizuno, T.; Nishizawa A.; Subramaniam C.; Futaba D.N.; Hata K. "Influence of matching solubility parameter of polymer matrix and CNT on electrical conductivity of CNT/rubber composite" *Sci Rep* 4 7232, 2014.
- 73- Kang I. ; Abdul Khaleque Md. ; Yoo Y.; Yoon P.J. ; Kim S.-Y.; Lim K.T. " Preparation and properties of ethylene propylene diene rubber/multi walled carbon nanotube composites for strain sensitive materials " *Composites Part A: Applied Science and Manufacturing*, Vo 42 (6) 623, 2011.
- 74- Bokobza L. " Natural Rubber Nanocomposites: A Review " *Nanomaterials*, 9(1), 12, 2019.
- 75- Zhou, X. W.; Zhu, Y. F.; Liang, J. "Preparation and properties of powder styrene-butadiene rubber composites filled with carbon black and carbon nanotubes" *Mater. Res. Bull.*, 42, 456, 2007.
- 76- Wang, J. D.; Zhu, Y.F.; Zhou, X.W.; Sui, G.; Liang, J., " Preparation and mechanical properties of natural rubber powder modified by carbon nanotubes" *J. Appl. Polym. Sci.*, 100: 4697, 2006.
- 77- Zhou, X. W.; Zhu, Y. F.; Gong, Q. M.; Liang, J. "Preparation and properties of the powder SBR composites filled with CNTs by spray drying process" *Mater. Lett.*, 60, 3769, 2006
- 78- Lokteva I.; Radychev N.; Witt F.; Borchert H.; Parisi J. and Joanna Kolny-Olesiak "Surface Treatment of CdSe Nanoparticles for Application in Hybrid Solar Cells: The Effect of Multiple Ligand Exchange with Pyridine r". . *Phys. Chem. C* 114 (29) 12784, 2010
- 79- Shang S.; Marcus L.G.; Yuen C.-W. "Improvement of carbon nanotubes dispersion by chitosan salt and its application in silicone rubber " *Composites Science and Technology*, 86 (24)129, 2013.
- 80- Jin, F-L.; Rhee, K-Y.; Park, S-J., "Surface treatment of montmorillonite on thermal stabilities of bisphenol-A diglycidyl dimethacrylate nanocomposites" *Mater. Eng., A* 435, 429, 2006.
- 81- Kaushik, P.; Rajasekar, R.; Dong Jin, K.; Zhen Xiu, Z.; Samir, K. P.; Chapal, K. D.; Jin, K. K. "Effect of fillers on natural rubber/high styrene rubber blends with nano silica: Morphology and wear" *Materials and Design*, 31, 677, 2010.
- 82- Ward A.A.; Khalaf A.I.; Ismail M.N.; Tawfik S.Y.; Mansour S.H. "Graphite and Copper Nanoparticles in PVC/NBR Composites" *KGK* 1-2, 36, 2013.
- 83- Sui, G.; Zhong, W. H.; Yang, X. P.; Yu, Y. H. ; Zhao, S. H. "Preparation and properties of natural rubber composites reinforced with pretreated carbon nanotubes" *Polym. Adv. Technol.*, 19, 1543, 2008.
- 84- Qilei, W.; Fengyu, Y.; Qian, Y.; Junhui, C.; Hongyan, G. "Study on mechanical properties of nano-Fe₃O₄ reinforced nitrile butadiene rubber" *Materials and Design* , 31 , 1023, 2010.
- 85- Mishra S.; Shimpi, N. G.; Patil, U. D. "Effect of nano CaCO₃ on thermal properties of styrene butadiene rubber (SBR)" *J. Polym Res.*, 14, 449, 2007.
- 86- Bandeira C.F.; Pereira A.C.; Botelho E.C. and Costa M.L." Benzoxazine resin and their nanostructured composites cure kinetic by DSC " *Journal of Materials Research* , 28 (22) 3094, 2013.
- 87- Srivastava S.K. and Mishra Y.K." Nanocarbon Reinforced Rubber Nanocomposites: Detailed Insights about Mechanical, Dynamical Mechanical Properties, Payne, and Mullin Effects " *Nanomaterials (Basel)*. 8(11) 945, 2018
- 88- Rajan K.P.; Gopanna A.; Theravalappil R.; Abdelghani E.A.M.; Thomas S.P. "Partial replacement of carbon black with graphene in natural rubber/butadiene rubber based tire compound: Investigation of critical properties " *Journal of Polymer Research*, 29, 76, 2022.
- 89- Tarawneh M.A.; Chen R.S.; Ahmad S.H.; Al-Tarawni M.A.M.; Sarairoh " Hybridization of a thermoplastic natural rubber composite with multi-walled carbon nanotubes/silicon carbide nanoparticles and the effects on morphological, thermal, and mechanical properties " *polymer composites*, E695, 2019.
- 90- Lianshi, W.; Yaling, L.; Anqiang, Z."Dispersion of carbon black in high-abrasion furnace black filled nonsulfur modified powdered polychloroprene rubber" *J. Appl. Polym. Sci.*, 101, 192, 2006.
- 91- Zhang, Q.; Tian, M.; Wu, Y.; Lin, G.; Zhang, L. "Effect of particle size on the properties of Mg(OH)₂-filled rubber composites" *J. Appl. Polym. Sci.*, 94, 2341, 2004.
- 92- Das, A.; Jurk, R.; Stöckelhu, K. W.; Heinrich, G., " Barrier Properties of Layered-Silicate Reinforced Ethylenepropylenediene Monomer/Chloroprene Rubber Nanorubbers " *Nanomaterials (Basel)* 8(5): 314, 2018.
- 93- Noraiham, M.; Andanastuti, M.; Mariyam, J. G.; Dahlan, H. M.; Che, H.A. "Epoxidized natural rubber-alumina nanoparticle composites: optimization of mixer parameters via response surface methodology" *J. Appl. Polym. Sci.*, 115, 183, 2010
- 94- Rugmini, S.; Menon, A. R. R., "Organomodified kaolin as a reinforcing filler for natural rubber" *J. Appl. Polym. Sci.*, 107, 3476, 2008.

- 95- Yehia, A. A.; Akelah, A. M.; Rehab, A.; El-Sabbagh, S. H.; El-Nashar, D. E.; Koriem, A. A. "Preparation and characterization of polymer-clay nanocomposites for specific applications" *KGK Kautschuk Gummi Kunststoff*, 580, November 2009 . 91-
- 96- QinFu, L.; Yude, Z.; Hongliang, X. "Properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica" *Applied Clay Science*, 42, 232, 2008
- 97- El-Nashar D. E.; Khalaf A.I. ; Temraz M.G. "Preparation and characterization of black shale-reinforced ethylene propylene diene monomer nanocomposites" 1- Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems, 227(2), 67,2013.
- 98- Stelescu M.D.; Manaila E.; Pelin G.; Georgescu M.; Sonmez M. "Advanced Materials Based on Ethylene-Propylene- Diene Terpolymers and Organically Modified Montmorillonite, " World Academy of Science, Engineering and Technology International Journal of Chemical and Materials Engineering, 14(1) 26, 2020
- 99- Zhou, W.; Wang, C.; An, Q.; Ou, H. "Thermal properties of heat conductive silicone rubber filled with hybrid fillers" *Journal of Composite Materials*, 42, 173, 2008.
- 100- El-Nemr K. F.; Ali M.A.M.; Hassan M.M.; Hamed, H. E. "Synergistic effect of vermiculite clay and ionizing irradiation on the physical and mechanical properties of polybutadiene rubber/ethylene propylene diene monomer nanocomposite" *Radiochimica Acta* 107(3) 221, 2019.
- 101- Assem Y.; Khalaf A.I.; Zidan T.A.; Rabia A.M.; Yehia A.A "Synthesis and characterization of hybride clay/ poly (N, N-dimethylaminoethyl methacrylate) nanocomposites" *polymer composites* 37 (10) 2950, 2016.
- 102- Khalaf A.I.; Assem Y.; Yehia A.A. Rabia A.M.; Zidan T.A.; "Optical, dielectric and mechanical properties of exfoliated poly(N,N-dimethylaminoethyl methacrylate)/clay nanocomposites prepared via in-situ bulk polymerization" *polymer composites* 39(8) 2603, 2018
- 103- Assem Y.; Khalaf A.I.; Rabia A.M.; Yehia A.A; Zidan T.A. "Poly (diallyldimethylammonium chloride)/clay nanocomposites: effect of molecular weight and concentration of polymer on the structural, thermal and dielectric properties" *Polymer Bulletin* 74 (8) 3015, 2017.
- 104- Abomostafa H.; Gad S.A.; Khalaf A.I. "Improving the Optical, Mechanical and Dielectric Properties of PMMA:Mg1-xCuxO Based Polymer Nanocomposites" *Journal of Inorganic and Organometallic Polymers and Materials* 28, 2759, 2018.
- 105- Sattar A.A.; El-Nashar D.E.; Agami W.R. and Aly M. A. "Mechanical and dielectric properties of cobalt-zinc nanoferrite/nitrile butadiene rubber composites" *Journal of Thermoplastic Composite Materials*, 31(1), 3, (2018).
- 106- El-Nashar D.E.; Aly M.A.; Ashmawy M.A.;W.R. Agami, "Enhancing rubber loaded by Co-Zn ferrite nanoparticles as filler" *Journal of Magnetism and Magnetic Materials*, 553 169252, 2022
- 107- Jihual Z.; Fengbo1 C.; Yunfeng Z. and Mingji L. "Improving Elasticity of Conductive Silicone Rubber by Hollow Carbon Black" *Chem. Res. Chinese Universities*, 35(6), 1124, 2019.
- 108- Dai W.; Ma T.; Yan Q.; Gao J.;Tan X.; Lv L.; Hou H.; Wei Q.; Yu J.; Wu J.; Yao Y.; Du S.; Sun R.; Jiang N.; Wang Y.; Kong J.; Wong C.; Maruyama S. and Lin C.-T "Metal-Level Thermally Conductive yet Soft Graphene Thermal Interface Materials" *Acs nano* , 13(10) 11561, 2019.
- 109- Shiva M. and Lakhi M. "Studying the effects of silica/alumina and silica/boehmite binary filler on the mechanical properties and the non-isothermal curing time of carbon black filled tyre tread composite" *Composites Part B* 175 , 107124, 2019.
- 110- Chen L.; Jia Z.; Tang Y.; Wu L.; Luo Y.; Jia D. "Novel functional silica nanoparticles for rubber vulcanization and reinforcement" *Composites Science and Technology* 144, 11, 2017
- 111- Sattayanurak S. ; Sahakaro K. Kaewsakul W.; Dierkes W. K.; Reuvekamp L. A.E.M.; Blume A.; Noordermeer J.W.M. "Synergistic effect by high specific surface area carbon black as secondary filler in silica reinforced natural rubber tire tread compounds" *Polymer Testing* 81, 106173, 2019
- 112- Mazumder A.; Chanda J.; Bhattacharyya S.; Dasgupta S.; Mukhopadhyay R.; Anil K. Bhowmick "Improved tire tread compounds using functionalized styrene butadiene rubber-silica filler/hybrid filler systems" *J Appl Polym Sci*. 138, e51236, 2021.
- 113- Sattayanurak S.; Noordermeer J.W.M.; Sahakaro K.; Kaewsakul W.; Dierkes W.K.; and Blume A. "Silica-Reinforced Natural Rubber: Synergistic Effects by Addition of Small Amounts of Secondary Fillers to Silica-Reinforced Natural Rubber Tire Tread Compounds" *Advances in Materials Science and Engineering*, ID 5891051, 2019.
- 114- Mathew J.; Joy J.; George S.G. "Review Potential applications of nanotechnology in transportation: A review" *Journal of King Saud University – Science* 31, (4), 586, 2019
- 115- Jeevanandam J.; Barhoum A.; Chan Y.S.; Dufresne A.; and Danqua M.K. "Review on

- nanoparticles and nanostructured materials: history, sources, toxicity and regulations" *Beilstein J Nanotechnol*, 9, 074, 2018.
- 116- Abbas M., Lucas B.; John V. ; Smith, H.K.; John M.; Arul A.; Suksun H.; Aeslina AK. "Nanoparticles in Construction Materials and Other Applications, and Implications of Nanoparticle Use". *Materials (Basel)*. 2019 Oct; 12(19): 3052
- 117- Ji-Hyeon Song, Soo-Hong Min, Seung-Gi Kim, Younggyun Cho.; Sung-Hoon Ahn "Multi-functionalization Strategies Using Nanomaterials: A Review and Case Study in Sensing Applications", , *International Journal of Precision Engineering and Manufacturing-Green Technology* 9 323, 2022.
- 118- Khalaf A.I.; Helaly F. M.; El Sawy S. "Improvement properties of EPDM rubber using hybrid chitin/clay filler for industrial products", *Egypt.J.Chem.* 63(1) 129, 2020.
- 119- Reffae A.S.; El-Nashar D.E.; Yaseen A.A.; Abd-El-Messieh S.L. "Sunflower Seed Husk As Green Agro-waste Filler For EPDM Rubber" *Egypt.J.Chem.*, 64 (10) 5853, 2021.
- 120- Das P.; Manna S.; Behera A.K.; Shee M.; Basak P.; Sharma A.K. "Current synthesis and characterization techniques for clay-based polymer nano-composites and its biomedical applications: A review" *Environmental Research* 212, Part E, 113534, 2022.
- 121- Saeb M. R.; Sniewsk P.W.; Susik A.; Zedler Ł.; Vahabi H.; Colom X.; Cañavate J.; Tercjak A. and Formela K. "GTR/Thermoplastics Blends: How Do Interfacial Interactions Govern Processing and Physico-Mechanical Properties? " *Materials*, 15, 841, 2022.
- 122- Fazli A. and Rodrigue D. "Waste Rubber Recycling: A Review on the Evolution and Properties of Thermoplastic Elastomers" *Materials (Basel)* 13 (3), 782, 2020.
- 123- Elango N.; Gupta S.; Jiun Y.L. and Golshahr A. "The Effect of High Loaded Multiwall Carbon Nanotubes in Natural Rubber and Their Nonlinear Material Constants" *Journal of Nanomaterials*, Article ID 6193961, 15, 2017.
- 124- Moonlek B.; Wimolmala E.; Markpin T.; mbatsompop N.S.; Saenboonruang K.m. "Enhancing electromagnetic interference shielding effectiveness for radiation vulcanized natural rubber latex composites containing multiwalled carbon nanotubes and silk textile" *Polymer Composites*, 41, 3996, 2020.
- 125- Yang B.; Wang S.; Li Y.; Liming T.; Enqiu H.; S.Song "Molecular dynamics simulations of mechanical properties of swollen nitrile rubber composites by incorporating carbon nanotubes" *Polymer Composites*, 41, 3160, 2020.
- 126- Guo H. Ji P.; Halász I. Z. ; Piriti D. Z. ;, Bárány T.; Xu Z.; Zheng L.; Zhang L.; Liu L. and Wen S. "Enhanced Fatigue and Durability Properties of Natural Rubber Composites Reinforced with Carbon Nanotubes and Graphene Oxide" *Materials* 13, 5746, 2020.