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Activation of Crumb Tires Rubber by Zinc oxide Nanoparticles to Improve the Performance of Rubber Compounds.

A Thesis

Submitted to the Council of the College of Materials Engineering / University of Babylon in Partial Fulfillment of the " Requirements for the Higher Diploma Degree in Materials Engineering / Polymer

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المجادلة: 11

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In the name of ALLAH, the Most Gracious and the Most Merciful for giving me the determination and will to complete this research work.

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Tabark

Dedication

*To whom their presence in my life prompted me to provide the best...to the path of my conciliation and the light of my success, my heaven on earth (my mother and my father)

* To my strength when I am weak... To those who were the best help and support for me (my dear brothers)

To my shadow and my mirror...to my happiness and source of my laughter and joy (my dear friends)

* To those whom I see as a light illuminating my heart... To those who made me look at life with the spirit of an innocent child, at the fragrance of winds, the butterflies of orchards, and the fruits of life, my beautiful princesses (Girls sister)

* To my uncle and role model, the martyr Prof. Dr. Eng. Jamil Habib

Al-Ammari

Tabark

Supervisor Certification

I certify that this thesis entitled " Activation of crumb Rubber by zinc oxide nanoparticles to improve the Performance of rubber Compounds" by (Tabark Alaa Abdulkadhim) was prepared under my supervision at the Department of polymer and petrochemical industries at the University of Babylon, in partial fulfillment of Requirements for the Higher Diploma Degree in Materials Engineering / Polymer

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Date: / /

Abstract

In this work, the reuse of tire crumbs has been studied as a filler and used many amounts of zinc oxide particles as activator in natural rubber / styrene butadiene rubber (NR/SBR) compounds for production of rubber resist the antibacterial , which used in handles grips for a wheelchair or a patient's wheel bed . Five samples were made including, Micro ZnO (5 P h r)/ Crumb(A), Micro ZnO (5 P h r)/ HAF-N.330 (B), Nano ZnO (1 P h r)/ Crumb(C), Nano ZnO (2 P h r)/ Crumb(D), and Nano ZnO (3 P h r)/ Crumb (E). Crumbs tires are a cheap and help to increase the degradation of rubber compounds with increases wettability by reducing the contact angle with water Several investigations were performed such as curing properties, crosslink density, and surface morphology as Scanning Electron Microscope (SEM) images and water contact angles, mechanical properties(Strength of tensile, Hardness, and compression set). Results prove that , rubber compounds sample (B) had highest tensile stress was 14.82 Mpa , modulus of elasticity was 4.184 Mpa , and elongation at break 325.83 % as a result of high torque 67.78 (Ib-In) and crosslink density was (0.57 mol/ cm^3) with goodness dispersion of HAF-N.330 particles in rubber matrix. Beside had a strong bonds appearance in Fourier Transform Infrared (FTIR) test, while a weak bonds appearance at rubber compound sample (A) which had tensile stress 2.01Mpa, modulus of elasticity was 2.03 Mpa , and elongation at break 90.83 % as a result of high torque 52.77 (Ib-In) and crosslink density was (0.436 mol/ cm^3) with low dispersion of crumb rubber in rubber matrix and apparent the avoids and micro cracks dependent on SEM images .According to the results above , the rubber compound (A) lead to high activity against S. aureus and E. coli and had inhibition zone was 2 cm against S. aureus and 1 cm for E. coli.

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List of Abbreviations

ABS	Acrylonitrile Butadiene Styrene
APS	Average Particle Size
BR	Polybutadiene Rubber
CRI	Cure Rate Index
CuO	Copper Oxide
ECC	Engineered Cementitious Composites
EDX	Energy-Dispersive X-Ray
FTIR	Fourier-Transform Infrared Spectroscopy
GTR	DE-Vulcanization Of Ground Tire Rubber
KBR	Potassium Bromide
MgO	Magnesium Oxide
NaOH	Sodium Hydroxide
NPs	Nurse Practitioners
NR	Natural Rubber
NRLF	Natural Rubber Latex Foam
ROS	Reactive Oxygen Species
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
TC	Cure Time
TDAE	Treated Distillate Aromatic Extract
TEM	Transmission Electron Microscopy
TiO2	Titanium Dioxide
TMTD	Tetramethylthiuram Disulfide
TS	Scorch Time
TSR	Technically Specified Rubber
XRD	X-Ray Diffraction
ZnO	Zinc Oxide

Chapter one
Introduction

1.1 Introduction

The annual increase in the automotive industry in the world is a natural result of the increase in the number of old tires, because they are non-biodegradable materials, they cause the problem of environmental pollution [1, 2].

Tire crumbs or tire powder is the new description of recycling old tires without changing their physical specifications and turning them into raw materials of economic benefit after tire cutting and separation of the fabric or steel, then reducing crumb particles to appropriate limits (40-80 mesh) ,these Dimensions are suitable for extrusion or calendaring operations[3].

On the other hand, rubber crumbs without surface treatment leads to a weak adhesion between its particles and the matrix [4,5], so some researchers worked several treatments and using different alkaline solutions, including sodium hydroxide, to treat the surface of the rubber crumbs and form polar groups that contribute to increasing the interaction with the matrix material [6,7].

Most tire rubber consists of a mixture of natural rubber and styrene butadiene rubber in order to achieve good specifications in terms of thermal stability and abrasion resistance [8].

Therefore using the crumb tires rubber as a filler had good compatibility with blend of the NR and SBR [9].

The quantity, shape and size of rubber granules lead to the formation of rubber compounds with good specifications [10], and making the surface properties composites rubber more hydrophilicity by reduced the contact angle between the rubber composite and water [11 . Moreover, tire crumbs are used as a filler with thermoplastics or original rubber [12], and it is also used to improve the specifications of asphalt [13], and concrete [14].

Due to the transfer of sulfur from the NR / SBR composite to the rubber granules as a result of adding tire crumbs as a filler, the maximum torque is reduced, while the transfer of vulcanization accelerators from rubber granules to fresh rubber leads to a decrease in the vulcanization time [10].

In practice, the use of tire crumbs with NR/ SBR leads to a reduction in mechanical properties, so rubber products can be used in the manufacture of materials that are not subjected to great mechanical stress, such as floor tiles and other flooring materials, windshield wipers, and washing machines [15].

Zinc oxide enhances the kinetics of the sulfur polymerization reaction, and reducing the content of ZnO in the rubber matrix leads to an increase in the efficiency of ZnO for improvement the interaction between its particles, accelerators and sulfur [16].

These properties are achieved when the particle size decreases and the surface area of ZnO increases [17]. Metal oxides such as (TiO2, MgO, CuO, and ZnO) have a good ability to reduce the growth of bacteria or fungi on elastomer materials. Zinc oxide is one of the most important of these oxides, especially nanoparticles of ZnO; the mechanism to reduce bacterial growth is the production of hydrogen peroxide (H_2O_2) of the photocatalytic generation [18, 19].

Recent studies have shown that the vulcanization of SBR with tire rubber crumbs with presence of moss worms (Tenebrio Monitor Linnaeus larvae) causes desulfurization and increases biodegradation [20], because of the transformation of the three-dimensional network into small parts of cross-links [21].

1.2 Aims of Work

Preparation and study the effect of tire crumb rubber as a filler and zinc oxide with many amounts were added to NR:SBR compounds for using in antibacterial handles grips of wheelchair or a patient's wheel bed.

Chapter Tow

The Theoretical Part and Literature Review

2.1 The Theoretical Part

2.1.1 Introduction

Destroys more than 200 million tires annually, and the quantity is expected to increase, thus posing a great threat to humans and the environment. They are a source of pollution and a waste of natural resources. The danger of these tires also comes as their components are difficult to decompose naturally and are flammable, and their danger increases when they come into contact with acidic materials, as they secrete some chemicals that are absorbed into the ground, leading to groundwater pollution, so different mechanisms have been found to get rid of these Waste by using it in engineering applications to reduce the percentage of damaged tires and benefit from them economically and environmentally. The second section includes literature review.

2.1.2 Rubber Compounds

A compound is a combination of basic polymer(s), fillers, and additional ingredients that results in a rubber material. More specifically, a "compound" is a particular combination of components designed to boost performance in a certain service. The polymer type is the fundamental component of compound design.

The compounder may incorporate strengthening substances into the elastomer, such as carbon black, colored pigments, curing or vulcanizing agents, activators, plasticizers, accelerators, anti-oxidants, or additives for ant radiation. Such combinations can number in the hundreds.

The filler is spread in several sizes, since the final size of the minutes in the mixture cannot be acquired. In reality, the diffusion may not be complete and some agglomerates may stay in the blend, making the actual size of the booster minutes bigger. On the other side, elevated shear strength grows during mixing, and some cluster cracking can also happen, and the actual size of the strengthened minutes is generated less than anticipated on the basis of the filler characteristics.

As a result, the filler is referred to as a particle, which relates to either minutes or clusters. Clearly, the diffusion of the particle size filler to the rubber dough is very susceptible. (X-ray) or neutron diffraction [22] assays were conducted to describe the diffusion of the particles in the rubber dough, but these techniques are very restricted owing to the elevated concentration of the filler and are very near to the coefficient of reflection of the rubber diffraction.

Another technique for defining the size of the particle is to extract the filler from the dough by thermal decomposition or catalyst, this action impacts the size of the particle owing to the possibility of recombination. In particular, the techniques used to characterize the spread of filtrate in the foundation material continue to develop.

2.1.2.1 Natural rubber

Early (natural rubber) is produced from rubber trees in the form latex, which is a by-product of agriculture that primarily belongs to the spurge family Euphorbiaceae [23]. Only a small number of the over 2000 plant species that produce natural rubber are important industrially. The first position is held by a tree known as Hevea brasiliensis that is native to the tropical rain forest [24,25].

This species is widely utilized because it thrives in cultivation and can generate more latex with careful management of tree wounds. Other plants that have been used to make natural rubber for commercial purposes include the funtumia, the gutta-percha, the rubber fig, the vine rubber, and the Panama rubber tree (Castilla elastica) [24]. Examples of rubber-bearing species include Taraxacum species, "such as “Taraxacum” officinale and "Taraxacum kok-saghyz, which were developed by Russian scientists, and guayule Parthenium argentatum, which was grown by "American" scientists due to its hypoallergenic features [23,24]. These rubber sources needed additional processing, and some were challenging to extract, making them ineffective in the rubber business.

The inclusion of non-rubber substances has a significant impact on the unique and specific chemical and physical characteristics that natural rubber demonstrates [26]. Table(2.1) demonstrates the natural rubber's composition. Due to its chemical features, which typically give it a latex look, this polymer is made up of cis-1,4-polyisoprene, which has the chemical formula C5H8 and a high molecular weight [24,26].

Because each repeating unit of "polyisoprene" has a double bond, it can be generated synthetically as synthetic natural rubber and is also vulcanization-prone. By improving the components of raw rubber by adding sulfur to latex, natural rubber loses its thermoplastic elastomer properties and becomes a thermoset [27]. In-depth examinations of natural rubber's physical characteristics reveal that it primarily "exhibits elasticity due to its high stretch ratio and resilience trait. This happens because numerous intricate polyisoprene" molecular chains crumpled under load, producing practically linear chains [28]. They returned to their original positions as soon as the burden was lifted. Instead, because rubber incorporates characteristics of both solid and liquid materials, its viscoelastic properties are also highlighted [29]. Natural rubber is a renewable resource since it is an agricultural product, and it is "the only biomass that strain crystallizes spontaneously at low temperatures or when it is stretched, decreasing its elasticity value" [24].

When vulcanization is advised, rubber reduces the degree of freedom by generating disulfide connections between chains, which causes the chains to swiftly tighten. The rubber becomes harder and less extensible as the elastic force increases. [30]. It should be emphasized that rather than the polymer itself, modifiers, fillers like carbon black, factice, whiting and many others have a substantial impact on the final qualities of a rubber item.

Table (2.1): Composition of natural rubber [31].

Component	Percentage by weight
Rubber Hydrocarbon	93.7
Lipids	3.4
Proteins	2.2
Carbohydrates	0.4
Ash	0.2
Others	0.1

The use of various raw rubber products has been slightly expanded thanks to natural rubber processing. Latex will be gathered into cups once the rubber tree has been tapped in order to stop it from flowing into other parts of the tree. Two main techniques are used when working with "rubber field latex: the first involves ammoniating (adding a large amount of concentrated ammonia) to preserve the latex before it is patterned into soft solid slabs of rubber", and the second involves either keeping the latex of cups for a set amount at time until it coagulates naturally or using formic or acetic acid to hasten the process of turning it into "cup lump" [32]. The higher-grade forms of coagulated latex Processing can then result in the creation of products like "block rubber, ribbed smoked sheet, pale creep, and air-dried sheet". [31] TSR10 and TSR20 grade rubbers are produced using naturally coagulated cup lump. [25["In recent years, Asia has been the main supplier of natural rubber", with the three biggest producers being Thailand, Indonesia, and Malaysia. A little over a million tons of rubber are produced annually, with the majority going toward synthetic rubber products and up to 40% being used, roughly, for natural rubber products [33]. Instead of employing solely raw rubber, modern science and technology have created "new liquid natural rubber, sheet creep variations of natural rubber, or other modified forms" to see the possibilities.

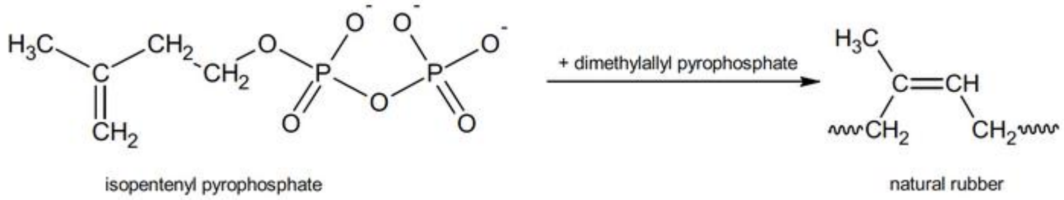


Figure (2.1): Biochemical production of natural rubber

2.1.2.2 Styrene butadiene rubber

Styrene butadiene rubber is a widely used synthetic rubber. It is one of the earliest rubber products to achieve industrial production as a substitute for natural rubber (NR). Natural rubber, consisting of mostly cis-1,4-polyisoprene and a small percentage of other ingredients, is a rubber latex that is collected from the rubber tree mainly grown in the jungles in Brazil [34]. Although NR has many unique "physical and chemical properties after vulcanization, its price rose rapidly due to its limited supply and huge use during the Second World War. Around that time, synthetic rubber was prepared by polymerizing the monomers, styrene and butadiene to meet the demand of rubber, later to be known as SBR. SBR was first prepared about 1929 in tries to overcome the insufficiencies of free-radical emulsion polymerized polybutadiene, but failed in commercial use [35]. When a German company generated free radicals for cold emulsion polymerization of SBR at low temperature in Second World War [36], SBR overtook NR and became the most significant synthetic rubber in the market. In the middle of 1950s, K. Ziegler and G. Natta introduced an anionic polymerization process to produce solution SBR (SSBR) that allowed tailoring of the polymer and promised high yield [36].

In addition, treated distillate aromatic extract (TDAE) oil was added in SBR to improve the processing ability. Nowadays, SBR has become one of the most important synthetic rubbers with a wide range of applications around the world, especially in tire industry owing to its excellent abrasion resistance and stability. Reinforcement fillers are used to improve the mechanical properties of SBR vulcanizes and the most traditional and commonly used reinforcement filler in industry has been carbon black.

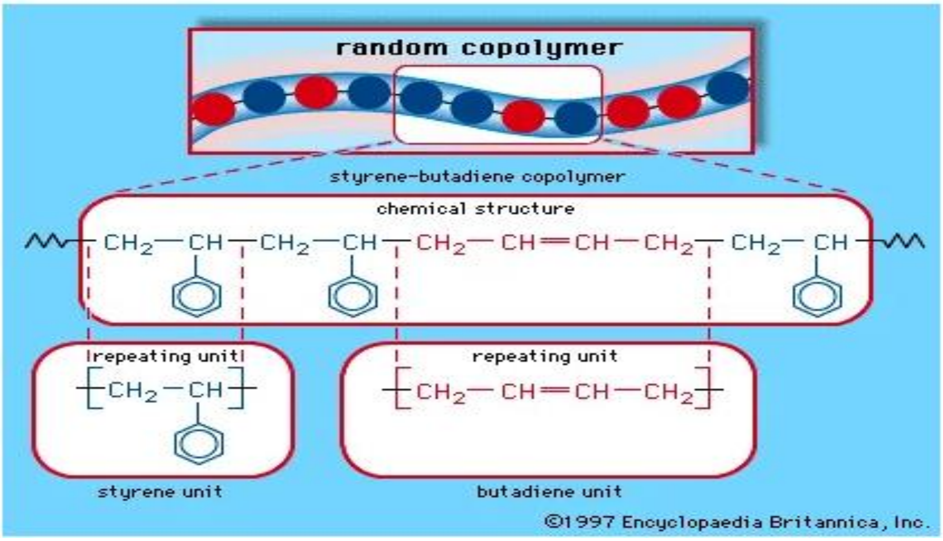


Figure (2.2): shows the chemical structure of styrene – butadiene rubber after polymerization.

2.1.2.3 Zinc Oxide Nanoparticles

Nanotechnology is concerned with the nanometre-level control, modification, structures,and fabrication of materials, and devices. It assists in comprehending the physics, chemistry, biology, and technology that underpin nanometre-scale phenomena [37]. ZnO nanoparticles are ZnO particles having a diameter of less than 100 nm. They might be solid, liquid (chemical), or gaseous in nature. Chemical techniques include mechanochemical processes, precipitation processes, precipitation in the presence of a surfactant, sol-gel methods, solvo-thermal, and emulsion, hydrothermal and micro-emulsion methods [38].

One of the most important and effective methods in terms of reliability and cost is the chemical method, as it is environmentally friendly and has high flexibility in controlling the shape and size of the manufactured nanoparticles, which have a high surface area to volume ratio. The nano size of the particle is not sufficient in terms of good applied results due to its agglomeration, so development of the particle surface is carried out or the particle is attached to polymer particles such as Triton-X 100 or PEG, which leads to obtaining unique magnetic and structural properties in addition to the physical and chemical properties [39].

For this reason, the above characteristics are directly responsible for the expansion of nanoparticle applications, especially in the biological and medical fields. On the other hand, zinc oxide particles are very important in cancer treatment, biosensing, and drug delivery.

These particles act as biomimics and act as biomaterials in tissue engineering. Zinc oxide nanoparticles are made in the form of nanowires, nanotubes, nanobelts, as well as other complex formations [40].

2.1.2.4 Crumb Rubber

Rubber from old automobile and truck tires is recycled to make CR. Tire cord (fluff) and steel are removed throughout the recycling process, leaving just tire elastic with a granular consistency. The size of the particles is further reduced by continued handling using a granulator or cracker mill, maybe under the guidance of cryogenics or by mechanical means.

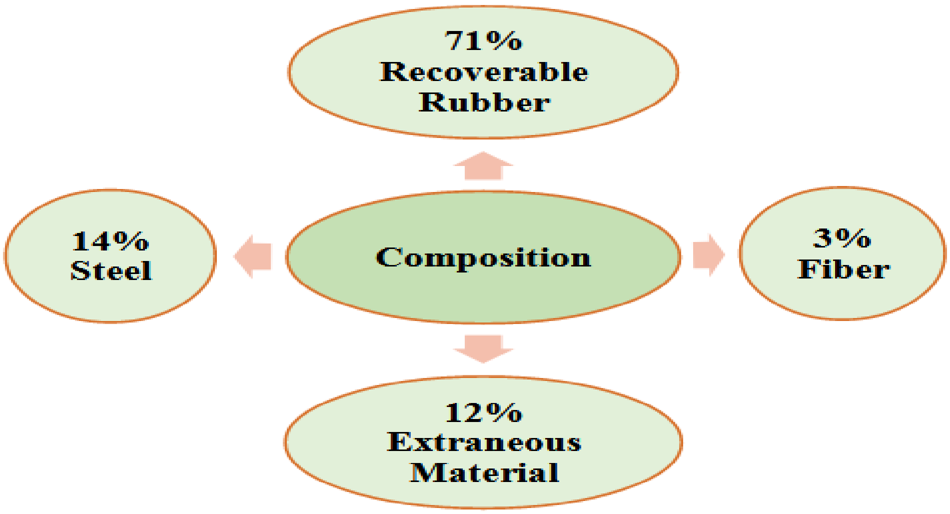


Figure (2.3): Composition of materials in rubber tire.

Table (2.2): Physical properties of crumb rubber

Property	Range
Specific gravity	0.51 – 1.2
Bulk density	524 – 1273 kg/m^3

Tire crumb rubber particles are characterized by a good ability to absorb water and a lower density than carbon black. In addition, crumb rubber is a non-polar material and is characterized by its hatred of water and traps air in its surface.

Table (2.3): Explain the chemical properties of crumb rubber waste

Chemical Properties	Percentage [%]
SBR	48.0
Carbon black	47.0
Extender oil	1.9
Stearic acid 0.5	0.5
Accelerator 0.7	0.7
Sulphur 0.8	0.8
Zinc oxide 1.1	1.1

Crumb rubber has a number of thermomechanical and physicochemical properties. Crumb rubber is made by shredding scrap tyres, thus it is a particle material free of fiber and steel. High quality tire crumb granules are available commercially with a granular size of about 0.2 mm, or approximately 80 mesh, and are packed in bags weighing 50 pounds. The granular size of tire crumbs, which is called rubber asphalt, ranges from 2.0 mm to 0.5 mm, i.e. 10 mesh to 40 mesh, because tire crumbs are light in weight and non-toxic, as they are used for long periods. They are also used in sound insulation applications, i.e. noise reduction [41]. Because the tire crumb particles represent a loose state, that is, they are not like the solid materials or the original rubber sheets. Therefore, intercalating the tire crumb particles with rubber compounds or recycling them gives an opportunity to manufacture rubber sheets that contain a high percentage of air voids. Which enhances the porosity of new rubber compounds and gives them a high ability to absorb sound compared to rubber compounds that do not contain in their composition rubber crumb particles, and at the same time, environmental pollution is reduced by tires.

2.1.2.4.1 Use of Rubber Crumbs in Rubber Compounds.

It is known worldwide that the production of tires constitutes more than 65% of the total rubber products. Therefore, tire waste constitutes a great burden and a threat to environmental pollution due to the non-decomposition of these wastes. Therefore, tire recycling is considered one of the important factors in the disposal of these wastes, as tire crumbs enter with ease. Determined with the components of the original compounds after conducting the treatment processes for them without interfering with the specifications of quality and performance for the pleasure of the compounds. The best percentage of some tire crumbs is 5-15%) of the total components of the rubber compound. Mixing processes have several advantages, including:

1 -Through the vulcanization process, hatching can be improved

2 -Improved template editing

3 -The use of tire crumbs leads to a decrease in processing time and an increase in manufacturing efficiency.

4 -Improved corrosion resistance in some applications

Based on all these features, tire crumb can be used as a filler in the new rubber compound.

2.1.2.4.2 Waste-Tire Recycling Industry

In 2022, there will be 3.2 billion tires sold worldwide [42]. In 2019, the USA received around 223 million replacement passenger tires [43]. The process of collecting used tires and placing them in illegal places leads to the collection of mosquitoes, flies and rodents, which enhances environmental pollution. [44]. The 2019 Scrap Tire Management Report was released by the U.S. Tire Manufacturers Association on 14th oct. With the increasing production of rubber products, but still the largest production of tires in the world and in the United States, which constitutes a new increase in the annual rate of scrap tires. According to the study, roughly 76% of used tires were recycled in 2019 and used to make fuel, mulch for landscaping, rubber-modified asphalt, and automotive items. Compared to 2013, when scrap tire recycling peaked, its value is lower at 96% [45]. The rubber compounds that produce tires consist of (45-47%) original rubber, (21.5-22%) filling materials such as carbon black, (12-25%) metallic materials, (0-10%) textiles, (1-2%) Zinc oxide, (1%) ripening materials such as sulfur, and (5-7.5%) other additives [46]. Since tires cannot be crushed to reduce the amount of room they take up for disposal, landfills need a large amount of space. Prior to disposal, shredding discarded tires is one way to lessen the amount of space they take up in landfills; but, because of the high operational expenses, this method is not practicable. Sending things to landfills is a missed opportunity for a circular economy and getting more use out of garbage. There are some ways to turn this large stream of rubber trash into energy or new polymer products. [47]. Brown of Watson Brown HSM Ltd. (London, UK) [48] the following information for global estimates related to the life cycle of the rubber manufacturing [49]. The rubber waste prepared to be used in new projects or new products, for example, consists of 5-23%, 25-60% is used for energy recovery purposes, 20-30% for recycling purposes and for economic development, especially in South Africa, where 177,385 tons of waste were used in 2014 tires that were in the landfill [50].

Figure (2.4): Life cycle of a tire.

2.1.3 Manufacturing and Application

Manufacturing of crumb rubber:

Crumb rubber is made by combining or using a number of size reduction processes. The two main processing categories for these technologies are mechanical "grinding" and cryogenic reduction.

Mechanical Grinding:

The most used the technique is mechanical grinding. The rubber is mechanically broken down into small particles using a variety of grinding methods, including granulators and cracker mills. A magnetic separator removes the steel components (sieve shakers and conventional separators, such as centrifugal, air classification, density, etc. are also used). Air classifiers or other separation tools are used to separate the fiber components. These technologies are well-known and efficient in producing crumb rubber (changing particle size, grades, and quality, for example). Few workers are needed to run and service the system, and it is easy to maintain. Most replacement components are simple to find and install. The main disadvantage relates to cost.

Cryogenic: The process of crushing rubber waste under very low temperatures is one of the successful operations to obtain small particles of rubber waste easily after separating the fabrics or metal wires from the rubber. It is better than the mechanical grinding mechanism, but this process is somewhat expensive because of the use of liquid nitrogen in the process and the amount the energy spent for the purpose of freezing it.

Crumb rubber applications:

Rubber crumbs have been incorporated into rubber and plastic materials such as:

1- Floor pedals

2- Mudguards for cars

3- Carpet filling

4- Adhesives

There are three main advantages of using rubber pellets in the manufacture of rubber and plastic products.

1- They are used as fillers to reduce costs.

2- Adding functions or modifying the characteristics of the final products.

3- An environmentally beneficial product as a result of recycling and reducing waste.

2.1.3.1 Rubber manufacturing

Large quantities of natural rubber are used in the production of high-quality rubber products. When it comes to properties, cost, and process, compounding rubber with additives is unmatched. This method was developed to produce rubber products in the automotive sector, such as tires and rubber materials used in the manufacture of engines, conveyor belts, and products that require the expenditure of mechanical energy. [23]. Large quantities of natural rubber are used in the production of high-quality rubber products. When it comes to qualities, cost, and technique, compounding rubber with additives is unmatched. This approach was developed for rubber to manufacture end products like tyres, belting, engines, and other mechanical items [23,28,51].

In addition to vulcanization, rubber compounding by incorporation of additives, fillers, and small amounts of oils aids in enhancing the modulus and strength of rubber compounds while lowering processing costs [23]. Since the Second World War, vulcanized rubber has experienced high demand, which has reduced its supply.

The commercial value of rubber increased after the advent of synthetic polymers and became a major market force [23]. After the advent of synthetic rubber, rubber products entered the fields of manufacturing marine equipment such as conveyor belts and rubber insulators for the purpose of sound and vibration insulation, as these polymers are considered as a result of the polymerization of a variety of petroleum-based precursors [52]. Silicone rubber, butyl rubber, nitrile rubber, chloroprene rubber, foam rubber, and styrene butadiene rubber are a few examples of synthetic rubber that are produced [52].

The primary goal of a synthetic rubber company's introduction of polybutadiene rubber (BR) chemical production in Malaysia is to increase the usage of the material in tires and other industrial rubber products. [53].

Modifying natural rubber immediately after it is harvested from the tree is another chemical method for creating rubber applications. This is due to the fact that natural rubber cannot be polymerized by itself to produce preferred pendent groups, unlike synthetic rubber, because it has a fixed structure of cis-polyisoprene [31].

Numerous functional groups have been used to prepare modified rubber, each with a unique cross-section [54]. Hydrogenated NR, chlorinated NR, hydrohalogenated NR, cyclized NR, epoxidized NR, resin-modified NR, etc. are all examples of modified NR [31,55]. To avoid wastage, some of these modifications were later replaced by alternative materials, which resulted in a decrease in production volume [56].

2.1.3.2 Applications of Rubber Compounds:

1- Tires: One of the important applications of rubber compounds is the tire industry, which consists of 100% of natural rubber or what is called radial tires, for aircraft tires, and 50% for car tires, and these designs began to appear in the year 1970.

2- Synthetic rubber is used in other applications in the automotive industry, such as the manufacture of seals and fillers, and in the manufacture of sealants for the windshield of the car.

3- Synthetic rubber is also used in the manufacture of airbags, which help people from shocks.

4- The use of synthetic rubber in the manufacture of floors for sports halls, where the rubber floors work on slip resistance, water resistance and are considered easy-to-maintain and long-term floors and are considered acceptable in terms of efficiency and economic cost.

5- Clothing: We can find some clothes such as wetsuits or cycling shorts that are made of rubber in its fibrous form.

6-Natural rubber gaskets: Gaskets are used between two or more mechanical parts, and are usually blocked leakage or to fill any type of irregular space in between.

7- Adhesives and Coatings: Rubber, in the form of latex, can be used as an adhesive or protective coating for many surfaces.

8- latex gloves: Latex gloves can be unapproved (rubber only) or backed (rubber coating and textile glove). Their primary purpose is to protect the hands while performing tasks that involve chemicals.

9- Anti-vibration: uses rubber to absorb shock and eliminate noise.

10-Other applications Rubber is used in wire wrapping, rubber tubes, belts, shoes, etc.

2.1.3.2.1 Engineering Applications

A-The application of crumb rubber in civil engineering can be categorized into three types such as**:**

1-Crumb rubber in concrete

2-Masonry bricks

3-Engineered cementitious composites (ECC)[57].

B- Application of activated recycled rubber from used tyros in oil spill cleanup [58].

2.1.3.2.2 Antimicrobial studies in rubber nanocomposites

Polymeric materials offer a wide range of uses in both everyday life and industry. Rubber materials having the greatest elasticity are widely used in real-world applications [59]. However, the limited mechanical strength and other features of plain rubber make it inefficient for practical purposes. One of the finest solutions for this problem is the incorporation of different nanofillers into rubber matrices, which results in an improvement in existing.

Zinc oxide nanoparticles have aroused the interest of many researchers because they are low in cost and low in toxicity and are used in many medical and biological fields, as they are considered to be good antioxidants, bacterial activity, diabetes, and in the field of delivery and bio imaging. [60,61]. We detailed the most recent advances in the usage of

ZnO here. Nurse Practitioners (NPs) in biomedicine. ZnO NPs are less common.

2,2 Lectures Preview

Ismail et al., (2002),[62] studied the mechanical properties such as tensile strength, polymer behavior, chemical solvent direction (swelling) and curing properties of natural rubber compounds containing reconstituted rubber powder at concentrations between 0 and 50 phr. On the other hand, the minimum torque increases with the increase in viscosity with the improvement of resistance to swelling and elongation at break with the increase in the amount of recycled rubber powder.

Yehia et al., (2004),[63] studied the treatment of recycled rubber waste and converting it into a plastic mass using Brabender premixer in different conditions and in the presence of reclaiming agents, and then mixed with amounts of natural rubber and styrene butadiene rubber with different loading ratios. The results of the two researches showed that the behavior of the rheological properties is similar to the behavior of NR and SBR rubber, and that increasing the amount of reconstituted rubber leads to a decrease in the mechanical specifications, especially the tensile strength and elongation at break, and the addition ratio 10-30% does not affect the physical properties of rubber compounds.

Ganjali et al., (2009),[64] For the sulphur vulcanization of the NR/SBR blend, various different activator systems incorporating zinc oxide, zinc stearate, calcium oxide, thiodiglycol metal complexes, and nano-zinc oxide were utilized. The systems were chosen for their improved metal ion release during the vulcanization process, increased dispersion in the rubber matrix, and lower zinc content. The results showed that reducing the loading percentage of zinc oxide from 4 to 2 phr does not lead to damage to the physical properties of the preparations, and zinc stearate can be added with zinc oxide to improve the tensile properties. The results of using calcium oxide were poor. Zinc complex of thiodiglycol is more widely dispersed in rubber matrix and has better ability to release zinc ions.

Zhan & Xiong (2013),[65] reviewed of existing ZnO nanoparticle biological uses, including biological imaging, drug release, and biosensing, along with the benefits and drawbacks of these applications. In addition, the relative toxicity of ZnO nanoparticles vs other types of common nanoparticles is reviewed. The results showed that many biological, medical and biological applications, including aerial imaging applications and drug transport, were incorporated into rubber compounds in the presence of zinc oxide nanocrystals, because they have high stability, high dispersibility, and high biocompatibility, specially the medical tests.

Fadiel et al. (2014),[66] attempted to create a lightweight, low thermal conductivity composite construction material out of used tires in an effort to discover a workable, environmentally friendly solution to the issue of discarded tires. In order to accomplish this, an experimental program was designed to look into how the quantity and size of crumb rubber affected the thermal characteristics of mortar. Twelve distinct combinations of the rubberized mortar were created using four levels of crumb rubber addition: 10, 20, 30, and 40%, as well as three sizes of crumb rubber (30, 10_20, and a combination of both sizes). Thermal conductivity of the samples was measured using a specially built heat transfer measurement instrument. Results were utilized to calculate the right quantity of crumb rubber to add in order to produce the least amount of thermal conductivity, which immediately improved the thermal resistance of concrete mixtures. The thermal characteristics of the specimens under investigation were discovered to be influenced by the size and quantity of crumb rubber.

Rathnayake et al. (2014),[67] discussed the creation and evaluation of natural rubber latex foam with ZnO nanoparticles (NRLF). In contrast to the NRLF control sample, which was generated without the addition of any

ZnO particles, ZnO nanoparticles were added as the main gelling agent by replacing the micronized ZnO particles. Transmission electron microscopy (TEM) micrograph analysis was used to assess the aqueous dispersion of nano-ZnO while X-ray diffraction (XRD) was used to assess ZnO Nano powder. Energy-dispersive X-ray (EDX), X-ray diffractometer (XRD), and scanning electron microscopy (SEM) analyses were used to assess the modified NRLF materials.

Bedi & Kaur (2015),[68] presented review about the uses of zinc oxide nanoparticles are further described in the current review. It has been discovered that nanoparticles (NPs) are utilised in a variety of industries due to their unique features. Zinc oxide nanoparticles are the most significant of all metal nanoparticles since they are employed in a variety of applications, including biomedicine, gas sensors, drug delivery systems, biosensors, cosmetics, agriculture, and others. According to recent studies, nanoparticles are employed in waste water management, textile production, and cancer treatment as well as in agriculture, water purification, and cosmetics to fight bacterial infections.

Mohammadi & Khabbaz (2015),[69] assessed the effectiveness of rubberized concrete made with rubber that has been treated with sodium hydroxide (NaOH). The authors used ten series of concrete specimens with various rubber contents and water cement ratios were created. Concrete samples were put through mechanical tests both before and after hardening. The most promising time for treating crumb rubber, which produced favorable fresh and hardened concrete qualities, was found to be 24 hours. The compressive and flexural strengths of rubberized concrete prepared using the 24-hour NaOH treated technique were both (25 & 5) % higher than those of rubberized concrete prepared using untreated rubber.

Mohammed et al., (2018),[70] studied the effect of nano-zinc oxide on the mechanical properties, especially the tensile strength of natural rubber compounds, and for several load ratios, and compared these results to the presence of ordinary zinc oxide at 1.8 phr, as the results showed an increase in tensile strength values of 38.31% at 300% elongation. .

Chukwu et al., (2019),[71] examined how the mechanical properties of natural rubber composite are affected by the activator level of zinc oxide. It has been observed that during the compounding process and the recovery of burnt compounds, technicians frequently apply more zinc oxide than the dosage specified in the formulation receipt. Zinc oxide was added to natural rubber at concentrations of 0, 2, 3, 4, 5, 6, 7, and 10 parts per hundred rubber (100phr). The results showed that the tensile strength, elongation at break, modulus, hardness and pressure group reached their maximum values at 5.0 phr with increasing ZnO content, after which there was a gradual decrease in the same parameters due to rebound. A known quantity of 5.0 phr is advised for the sake of hardness and improved tensile characteristics.

Nuzaimah et al., (2020),[72] examined the best NaOH concentration for treating rubber crumbs to increase the adherence of the rubber filler to the polymer matrix in rubber polyester composites. Rubber bits from used rubber gloves were combined with an unsaturated polyester matrix to create the composite. Volumetric ratios from 7% to 10% of sodium hydroxide solution were used, which had a great role in treating cooled rubber waste such as gloves, because it also has the ability to reduce the angle of contact with the surface by about 27°.

A higher NaOH concentration deeply etched the rubber, intensifying the process and producing a rougher surface with more microcracks. This gave the polyester a wider surface area to cover, firmly keeping the rubber in place. Additionally, it produced more functional groups, which raised the surface energy of the rubber and eliminated the hydrophobic layer. These elements improved the interfacial adhesion between rubber and polyester.

A higher peak intensity in the FTIR measurement of rubber that had been exposed to a higher NaOH concentration indicated that more polar groups had been produced on the rubber surface. The polyester matrix's polar groups were connected to by additional polar groups, which improved the adherence of the rubber filler to the matrix.

Krainoi et al., (2021),[73] prepared a nano-zinc oxide (ZnO np)-filled natural rubber (NR) film that is hygienic using latex techniques. In addition of, the calcium carbonate ($CaCO_3$) was coated on ZnOnp in the ratios of 90:10 and 60:40. (ZnOnp-Ca10 and ZnOnp-Ca40). The unique anti-microbial activity of the resulting NR film materials, along with their mechanical and thermo-mechanical properties, were carefully examined. Results indicate that an essential factor in improving the characteristics of NR films is the ZnO dispersion's nature. When ZnOnp-Ca10 was added to the films, the properties of NR were discovered to be improved, but unmodified ZnOnp caused a decrease in NR properties. The findings are in good agreement with both qualitative and quantitative analyses of gram-negative E. coli anti-microbial research.

Morera et al., (2021),[74] described how to change the surface of GTR by combining a cryo-grinding procedure with a chemical treatment. Up to a particle size of 100 to 150 μm was attained, various cryo-grinding methods were investigated. Analysis of chemical modifications using various acids led to the best alteration using sulfuric acid (H_2SO_4). A styrene-butadiene rubber (SBR) matrix was enhanced with modified GTR. With increases in tensile strength and elongation at break of 115% and 761%, respectively, the addition of 10 phr of this filler produced a composite with superior mechanical performance. These outcomes support using recovered tire waste as a sustainable filler in rubber composites.

Chapter Three

Experimental Part

3.1 Introduction:

This chapter describes the experimental work, especially the selection of materials, properties of materials, crumb rubber, Nano-zinc oxide, sample preparation methods, and the test methods used (rheological properties test), (Evaluation of the Crosslink Density test, including swelling test), (surface morphology tests, including: SEM test and FTIR test), (mechanical tests include: tensile test, hardness test, and Compression Set test), (density test) and finally (an anti-bacterial test)

3.2 Materials

3.2.1 Zinc oxide micro particles

Physicochemical Information	
Density	5.68 g/cm3 (22 °C)
Melting Point	1975 °C
pH value	6.72 (H_2O) (slurry)
Bulk density	200 - 700 kg/m3
Solubility	0.0016 g/l insoluble

(CAS #: 1314-13-2)

Table(3.1): Specifications of Zinc Oxide Micro Particles

3.2.2 Emulsified Styrene Butadiene Rubber (e-SBR)

Emulsified Styrene Butadiene Rubber Chemical Properties	
density	1.04 g/mL at 25 °C
refractive index	1.57
solubility	solvents with solubility parameters between 7.7 and 9.4: soluble
form	slab/chunk
Stability	Stable. Combustible. Incompatible with strong oxidizing agents.
IARC	3 (Vol. 19, Sup 7) 1987

CAS(9003-55-8)

Table(3.2): Specifications of Emulsified Styrene Butadiene Rubber (e-SBR**)**

3.2.3 Zinc oxide Nano powder

Purity	(98%)
granular size	80 nm

CAS No(1314-13-2)

Table(3.3): Specifications of Zinc oxide Nano powder

3.2.4 Natural Rubber

Density	0.913 g/cm
Molecular Formula	C5H8;CH2=C(CH3)CH=CH2;C5H8
decomposition	at 270 degrees
solubility	Insoluble in polar acetone and ethanol
Melting Point	-184 °F

CAS No(9006-04-6)

Table(3.4): Specifications of Natural Rubber

3.2.5 Crumb Rubber

Chemical name	**concentration**
Reprocessed Rubber	55-60
Naphthenic /Aromatic Extender oil	6-8
Carbon Black	20-25
Zinc Oxide	2
Sulfur	1

CAS NO(1314-13-2)

Table (3.5): Specifications of Crumb Rubber

3.3 Preparation of Compound Specimens

To achieve a better performance of anti-bacterial by the rubber samples and reducing the hydrophobic nature of the rubber surface, must be achieved some steps.

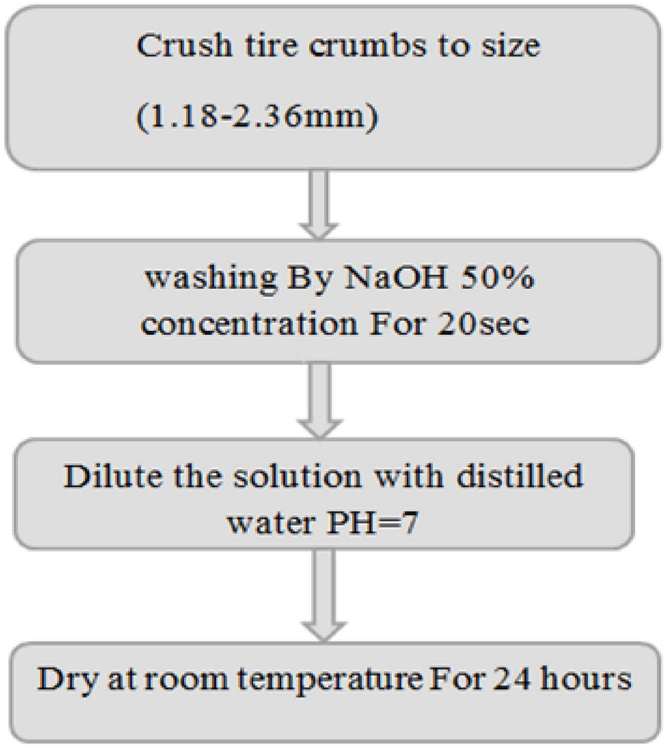
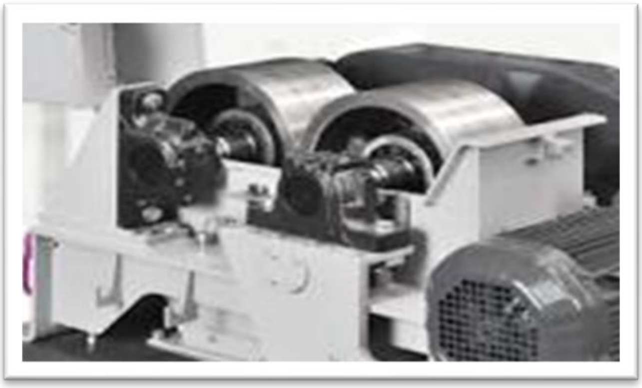
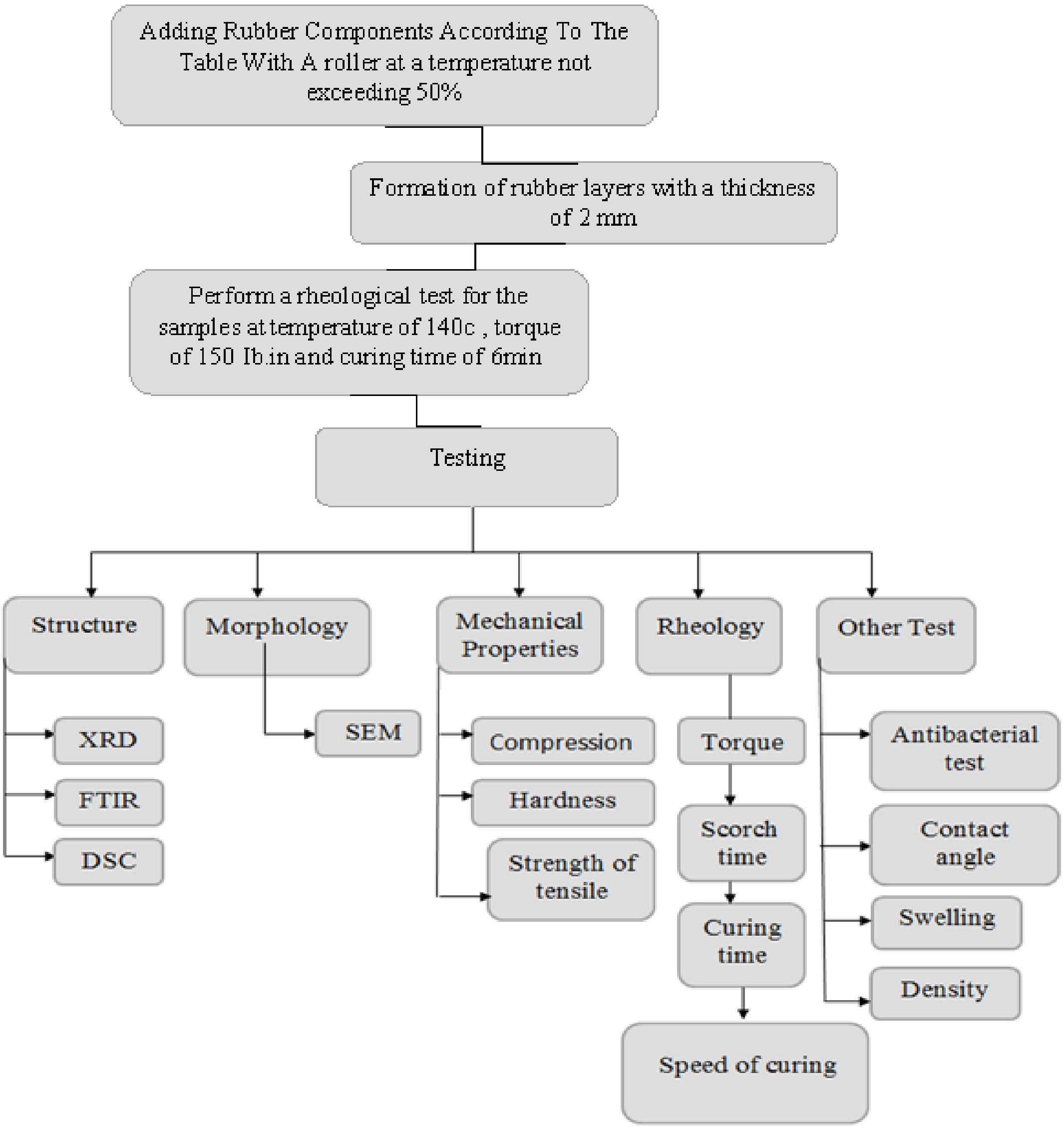


Figure (3.1): Steps of preparation Tire crumb

1. The performance of granular size tire crumbs (1.18-2.36 mm) was developed by washing appropriate amounts of tire crumbs with a saturated solution of concentrated sodium hydroxide at 20 °C for a period of 20 minutes [75]
2. The solution is diluted with distilled water until it reaches the 7 pH
3. Filtered and dried the tire crumbs.
4. Allowing the formula basic compounds of rubber shown in Table 3.6, using a 6-inch double-roller mill Bridge, UK (as seen in Figure 3.2) with a coefficient of friction of 1.1 and a speed of 20 rpm rotation, the master batch of NR/SBR was prepared. The process of preparing the rubber compounds was done at a temperature of about (50°C) based on ASTMD (15-627) to produce a uniform rubber sheet with a thickness of 2 mm.



Figure(3.2): Double-Roller mill Bridge, UK**.**



Figure(3.3): Steps Of Preparation Rubber Compounds

Table(3.6) Quantities of chemicals in Parts per hundred Rubber Added to the laboratory Mill.

No.	Ingredients	Micro-ZnO (P h r)		Nano ZnO (P h r)		
		A	B	C	D	E
1	NR: SBR (50:50)	100	100	100	100	100
2	Zinc Oxide	5	5	1	2	3
3	Stearic acid	2	2	2	2	2
4	Grump powder	50	-	50	50	50
5	Processing oil	8	8	8	8	8
6	Carbon black (HAF-N.330)	20	60	20	20	20
7	C.B.S (Accelerator)	2	2	2	2	2
8	T.M.T.D (Accelerator)	1	1	1	1	1
9	Sulfur	3	3	3	3	3
10	Total	191	181	187	188	189
11	Density (gm/cm^3)	1.1	1.14	1.06	1.07	1.08

P h r: Parts per hundred rubber; A: Micro ZnO (5 Phr)/ Crumb; B: Micro ZnO (5 Phr)/ HAF-N.330; C: Nano ZnO (1 Phr)/ Crumb; D: Nano ZnO (2 Phr)/ Crumb; and E: Nano ZnO (3 Phr)/ Crumb; High abrasion furnace (HAF) carbon black (N-330).

3.4 Characterizations

3.4.1 Rheological Properties

According to ASTM D2705, the components' cure time (TC), scorch time (TS), maximum torque (MH), and curing speed ratio or cure rate index (CRI) were measured by an MV-ODR-PROPERTIES Rheometer from Micro Vision Enterprises in India (as seen in Figure 3.4). The results of the aforementioned ripening properties were achieved and are displayed in Table 2 in accordance with curing settings such as curing temperature at 140°C, cure time at 6 minutes, and torque at 150 (pounds inch). Based on the ISO 6502-2:2018 test standard at 140°C and 10 MPa and the optimum curing time (TC90), which is 90% of the total cure time (TC). For the aim of maturing NR/SBR compounds, an XLB-D 350x350 electrically heated press (Huzhou, East Machinery, China) was used..

Figure (3.4): Rheological properties device

3.4.2 Evaluation of the Crosslink Density

Toluene is used as a solvent for NR/SBR blends to determine the volume fraction(V_r) and crosslink density (V) of rubber compounds by immersing a weighting sample of curing rubber with 1 cm * 1 cm for 24 hours at room temperature (25 °C), then weighting the sample after removing the solvent on its surface. dried using samples were an oven at (60°C for 24) weight and hours again (as seen in Figure 3.5).

A: The following relationship determines the volume fraction of rubber in the sample used

$$V_r = \frac{\frac{W_{dry}}{\rho}}{\frac{W_{dry}}{\rho} + \frac{W_{solvent}}{\rho s}} \quad (1)$$

Where W_{dry} is a weight of dry rubber sample, ρ is a density of the dry rubber sample,

$W_{solvent}$ is a weights of solvent in the swollen sample, ρs is a density of the solvent [76].

B: The density of crosslinks per unit volume (mol/cm3) of rubber compounds is determined by the following relationship

$$V = \frac{\ln[\,(1 - V_r) + V_r + X * V_r^2]}{V_0(\,V_r^{1/3} - \frac{V_r}{2})} \quad (2)$$

Where V (mol/cm3) denotes the crosslink density of rubber compounds as a function of volume.

The volume proportion of rubber in a swollen sample is represented by Vr .

The molar volume of the solvent is represented by Vo; for toluene, it is Vo equals 106.7 cm3/mol.χ represents the reaction coefficient of the Flory-Huggins rubber compound with the solvent (0.39 for the average sulfur-bonded NR/SBR-toluene pair) [77].

Figure (3.5): Immersion swelling samples in toluene

3.4.3.1 Scanning Electron Microscopy(SEM)

A scanning electron microscope (SEM) (VEGA 3 TESCAN) which has a 20 µm, 1.0 Kx image magnification power at a voltage high of (10 kV) was used to detect scattered tire crumbs or HAF-N.330 particles in the NR/SBR matrix (as seen in Figure 3.6).

Figure (3.6): SEM Device

3.4.3.2 Contact Angle Test:

A water contact angle system was used to test the wettability of the NR/SBR compounds by using "SL200B Optical Dynamic / Static Contact Angle Meter (as seen in Figure 3.7)

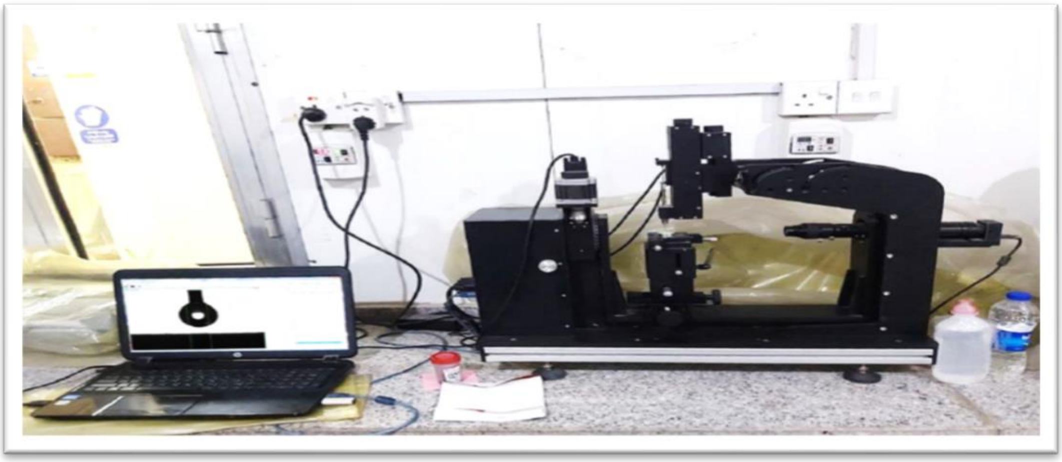


Figure (3.7): Contact Angle Meter(SL200B Optical) device

3.4.4 Fourier Transform Infrared (FTIR) Analysis

Using IR Affinity-1 from SHIMADZU, Japan, with a 4000-400 cm^{-1} scanning range, the resolution is 16 cm^{-1} and there are 15 scans (as seen in Figure 3.8). Using the KBr, 3 mg of the resulting sample were combined with potassium bromide in a ratio of 1:100 to form the compound NR/SBR, which was used to determine the chemical bonding between the fragments or particles of HAF-N.330 and NR/SBR.

Figure (3.8): FTIR Device

3.4.5 Mechanic of Properties

3.4.5.1 Strength of Tensile

Using a Wallace die cutter, dumbbell specimens 2 mm thick were cut from the molded layers and tested for tensile strength using a TIME Electronic Universal Testing Machine WDW-5E (Time Group Inc., China) in accordance with ASTM D 412. (as seen in Figure 3.9 B). Five samples were utilized in the tests for each case, and the velocity test's parameters were adjusted to 500 mm/min at 25 °C. The modulus of elasticity of NR/SBR compound samples calculated by used the Hook's low from the relation of stress- strain curves, the stress of a material is proportional to the applied pressure within the elastic limit of that material , the slope of this relation is equal to the modulus of elasticity according to following equation [78] :

$$\sigma = E.\varepsilon \tag{3}$$

Where: σ represented the shear stress (Mpa), E is the shear modulus (modulus of elasticity (Mpa)), and ε is the shear deformation (strain).

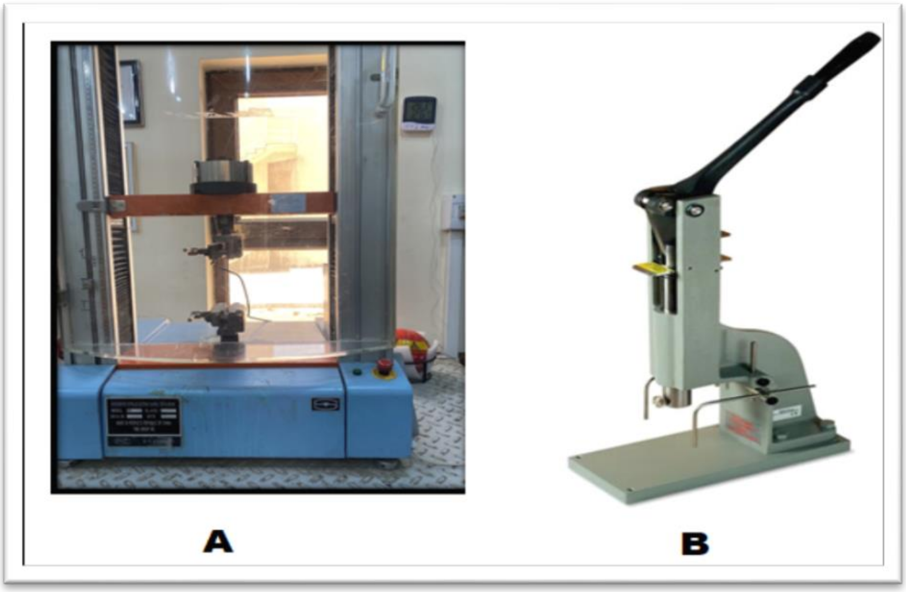


Figure (3.9): (A) Universal Testing Machine, (B) Wallace die cutter.

3.4.5.2 Hardness Test:

The hardness test of the samples was carried out using a test method according to ASTM D2240-02 and using a Shore Meter Hardness Tester A TH200 (Beijing Time Technology Ltd.) by recording five readings in different spaces at room temperature for each sample (as seen in figure 3.10).

Figure (3.10): Hardness Measuring Device

3.4.6 Density test

A high-precision density tester (GP-1205; Matsu Hako) with a range of 0.001-120 g and an accuracy of 0.0001 g/cm3 was used to measure the density of the samples (as seen in Figure 3.11).

Figure (3.11): Specific Gravity Device

3.4.7 Compression Set

The ability of an elastic material to maintain elastic properties after the compression stress is removed is determined by the compression set test. The testing of samples (12.5±0.5 mm * 29±0.5 mm) take place according to ASTM D395 (constant deflection) under the following procedures:

There are several steps for determining the compression set for rubber compounds, as follows:

1. Determining the thickness of the sample before testing.

2. Put the spacers inside the testing device with a thickness equal to 25% of the thickness of the sample before the testing and then put the samples in the testing device and then the samples is compressed to the spacers thickness (as seen in figure 3.12)

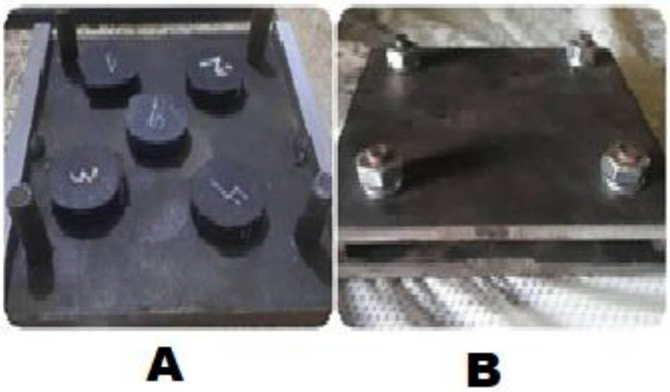
3. Leave the samples pressed inside the device for two hours, after that placed “oven at a temperature” of (70) °C use to collecting a period of 22 hours

4. Take out the sample with the collector from the oven and leave for 30 minutes, then measure the final thickness or the recovery thickness of the sample. The compression set percentage determined using the following equation [79]:

$$CS\ (\%) = \frac{Hi - Hf}{Hi - Hr} * 100 \qquad (4)$$

Elastic Recovery (ER) = 100- CS (%)

Where: Hi: initial height (mm), Hr: recovered height (mm), and Hs: Spacer height (25 % from the initial height)



Figuer (3.12): (A) Samples in the molad before testing, (B) samples in the compression set mold after compression

3.4.8 Anti-microbial properties

Antimicrobial test is carried out using rubber compounds of NR/SBR blends according to the following steps:

First: the middle of Luria Broth was pre-shrunk, and one gram-negative “Escherichia coli (E.coli) bacteria and gram-positive Staphylococcus aureus (S. aureus) bacteria” were inoculated under sterile conditions. They were then incubate at (37) °C for 12 h in a Mechanic of shaker. “Next, 100 µl of a 10^8 cfu /ml “of bacteria suspended on agar were spread plates.

Second: Cut a model with a diameter of 6 mm from mature rubber and sterilize it with 70% ethanol

Third: The samples placed on agar plates, incubated aerobically (37) °C for 24 hours in the incubator (as seen in the figure 3.13), and calculate the inhibition rings of S. aureus and E. coli in cm [80].

Figure (3.13): Bacterial Test Samples

Chapter Four

Results and Discussions

4. Results and Discussion

4.1 Introduction

This section discusses the results of the samples that were prepared in the previous section, which include five samples with different percentages of zinc oxide in nano and micro sizes on the (mechanical, rheological, surface morphology, antibacterial and Crosslink density) to produce handles for a wheelchair or a wheelchair for the patient.

4.2 Curing Properties

After completion of the addition of chemicals whose quantities are shown in Table 3.1 by dual-roll mill, the samples are left for 24 hours. The curing possessions of the many constituents are then tested at a temperature of 140°C, a curing time of 6 minutes, and a torque of 150 (pounds inch).

The results displayed that the drying properties such as the difference between maximum and minimum torque (ΔH= MH-ML) and the curing rate index (CRI) decreased when increased the amounts of ZnO nanoparticle with the presence of tire crumbs.

While improving these properties with present micro particles of ZnO and absence the crumb tires. On the other hand, we note that the cure time (t_{c90}) and scorch time The number of zinc oxide nanoparticles in the tire crumbs increases together with (ts_2). In addition, the findings show that the absence of tire crumb reduced the cure and scorch times. As a result, an increase in the curing rate index (CRI) causes an increase in cure speed since, according to the following relation [81], it is inversely proportional to the difference between (T_{C90}) and (T_{S2}) CRI = 100/T_{C90}-T_{S2} (5)The aforementioned findings showed little interaction between tire crumbs and NR/SBR chains, notably at 5 phr for ZnO microparticles [81]:

$$CRI = 100 / Tc_{90} - T_{S2} \qquad (5)$$

The above results indicated a low interaction between the tires crumb and the NR/SBR chains, especially at 5 phr for micro particles of ZnO, on the contrary, a good homogeneity and dispersion at absence the crumb in the polymeric matrix, which are presented in figure 4.1 and table 4.1. The increase in ΔH indicates an increase in the density of the crosslinks, while the scorch time indicates the possibility of processing the rubber mixture, also the filler with high viscosity gives less scorch time and this is what happened in the absence of tire crumbs [82].

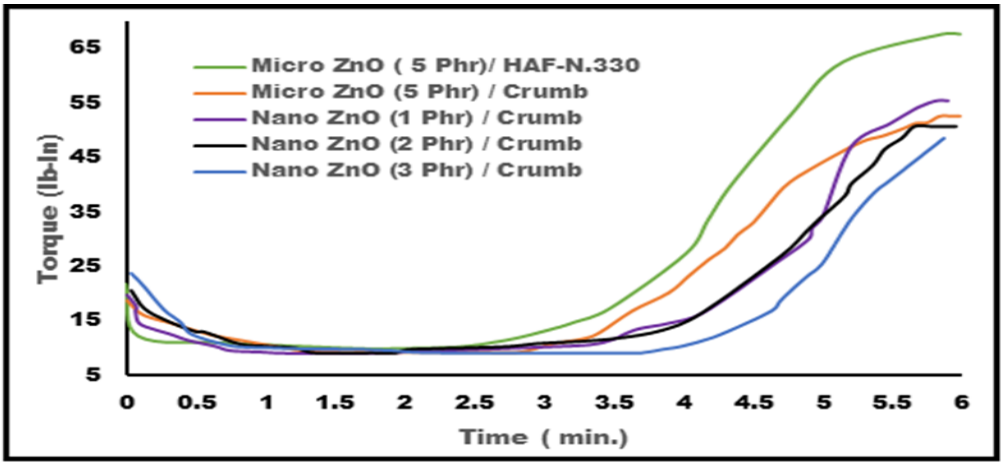


Figure (4. 1): shows the Torque- time curves at 140 °C , 6 minutes , and 150 Ib-In for NR/SBR compounds as, Micro ZnO (5 Phr)/ HAF-N.330, Micro ZnO (5 Phr)/ Crumb Nano ZnO (1 Phr)/ Crumb, Nano ZnO (2 Phr)/ Crumb, and Nano ZnO (3 Phr)/ Crumb.

Table (4.1): *Density and curing properties of the rubber sample films created at 140°C, 6 minutes, and 150 Ib. In*

NR/SBR Samples	MI (Ib.in)	ML (Ib.in)	MH (Ib.in)	t_{s2} (min)	t_{s5} (min)	t_{C50} (min)	t_{C90} (min)	ΔH (Ib.in)	CRI (min^{-1})
A	18.8	9.23	52.77	3.63	3.92	4.45	5.83	43.04	45.45
B	21.78	9.95	67.78	3.37	3.94	4.65	5.05	57.83	61.35
C	19.79	9.11	55.43	3.49	4.12	4.7	5.2	46.32	58.47
D	20.63	9.11	50.92	3.84	4.05	4.85	5.74	41.82	52.35
E	23.78	9.10	48.67	3.84	4.02	5.43	5.86	39.57	49.5

A: Micro ZnO (5 Phr) / Crumb; B: Micro ZnO (5 Phr) / HAF-N.330; C: Nano ZnO (1 Phr) / Crumb; D: Nano ZnO (2 Phr) / Crumb; E: Nano ZnO (3 Phr) / Crumb; MI: Initial torque; ML: minimum torque; MH: Maximum torque; $t_{S2:}$ Scorch time; ts5; 50 % cure time; $_{tc90}$: 90% cure time; ΔH: difference between maximum and minimum torque; CRI: cure rate index

4.3 Crosslink Density

Crosslinks are among the characteristics that limit the movement of polymer chains and the increase in the density of these bonds makes the polymeric chains cannot dissipate the heat resulting from deformation through molecular movement, and thus the elongation becomes low with increases the tensile strength. Equation 1 and Equation 2 were relied upon in calculating the rubber volume fraction and the density of cross-links after using the toluene as a solvent for the rubber samples. Figure 4.2 represents the relationship between the volume fraction of rubber samples (Micro ZnO (5 Phr)/ Crumb, Micro ZnO (5 Phr)/ HAF-N.330, Nano ZnO (1 Phr)/ Crumb, Nano ZnO (2 Phr)/ Crumb, and Nano ZnO (3 Phr)/ Crumb) and the density of crosslinks formed. The results indicate that the volume fraction and crosslink density increase with a decrease in the amount of zinc oxide nanoparticles from 3 Phr to 1 Phr with the presence of tire crumbs [83] , while they improve clearly in the absence of tire crumbs. These results depend on the properties of curing such as difference between maximum and minimum torque (ΔH) and the curing rate index (CRI). Therefore, the difference between the maximum torque (MH) and minimum torque (ML) is an approximate parameter of the crosslink density of the rubber compounds after vulcanization [84].

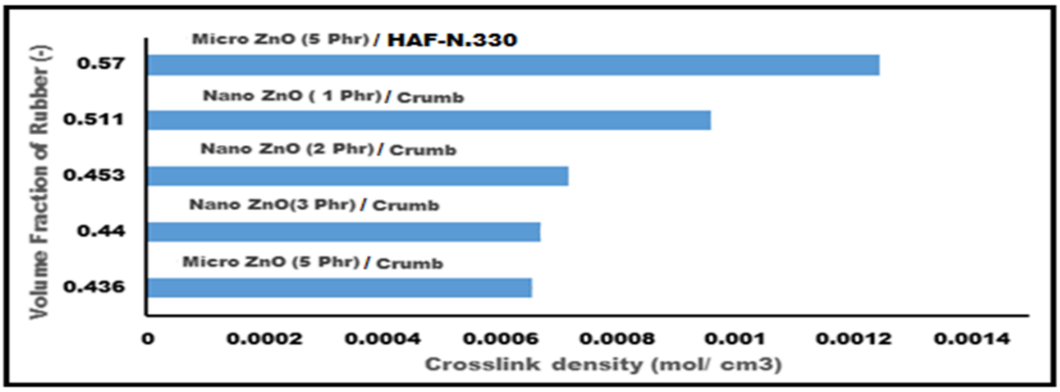


Figure (4.2): shows the relation between the crosslink density (mol/ cm3) and rubber volume fraction (-) for many NR/ SBR compounds

4.4 Surface Properties

Scanning electron micrographs of the NR/SBR compounds such as Micro ZnO (5 P h r) / crumbs and Micro ZnO (5 P h r) / HAF-N.330, also Nano ZnO (1 P h r and 3 P h r) / crumbs. These compounds contain high loading levels of granular of tire crumbs (50 P h r) and quantities of Micro and Nano particles of zinc oxide in addition to quantities of carbon black (HAF-N.330) as showed in Table (3.1).

The analyzing the electron micrographs show that the heterogeneity on the rubber surface when 5 Phr of micro particles of zinc oxide is used with quantities of tire crumbs and the appearance of agglomeration on the surface of rubber as shown in Figure 4.3A. While the rubber surface is more homogeneous and there are no aggregates on it when the tire crumbs are absent and the amount of tire crumbs is replaced with quantities of Carbon black (HAF-N.330). Carbon black -N.330 has a very high surface area compared to the granular and the surface area of the tire crumbs, these results make the rubber surface more homogeneous (Figure 4.3B). "On the other hand", we note that the surface of the (rubber) is more homogeneous and uniform distribution of the filler materials on the rubber surface with presence of tire crumbs when using zinc oxide nanoparticles with an amount of 1 P h r. While a little agglomeration of zinc oxide and crumbs when using 3 P h r of zinc oxide nanoparticles Figure 4.3(C, D). The results of SEM prove that the homogeneity of the rubber surface depends on the particle size of the filler materials and their surface area [85].

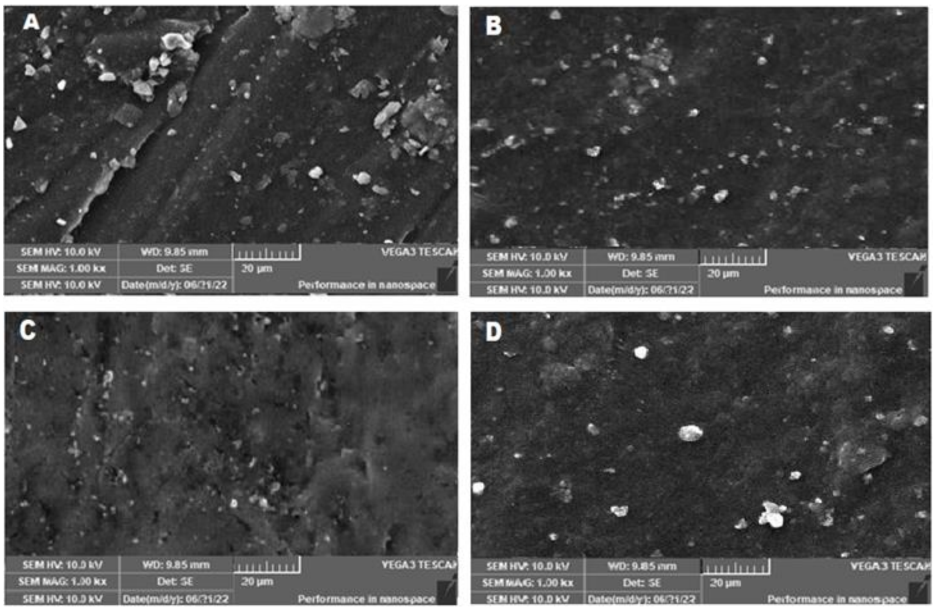


Figure (4.3): Shows the SEM micrographs for NR/SBR compounds A) Micro ZnO (5 Phr) / crumb tires, B) Micro ZnO (5 Phr) / HAF-N.330, C) Nano ZnO (1 Phr) / crumb tires, and D) Nano ZnO (3 Phr) / crumb tires.

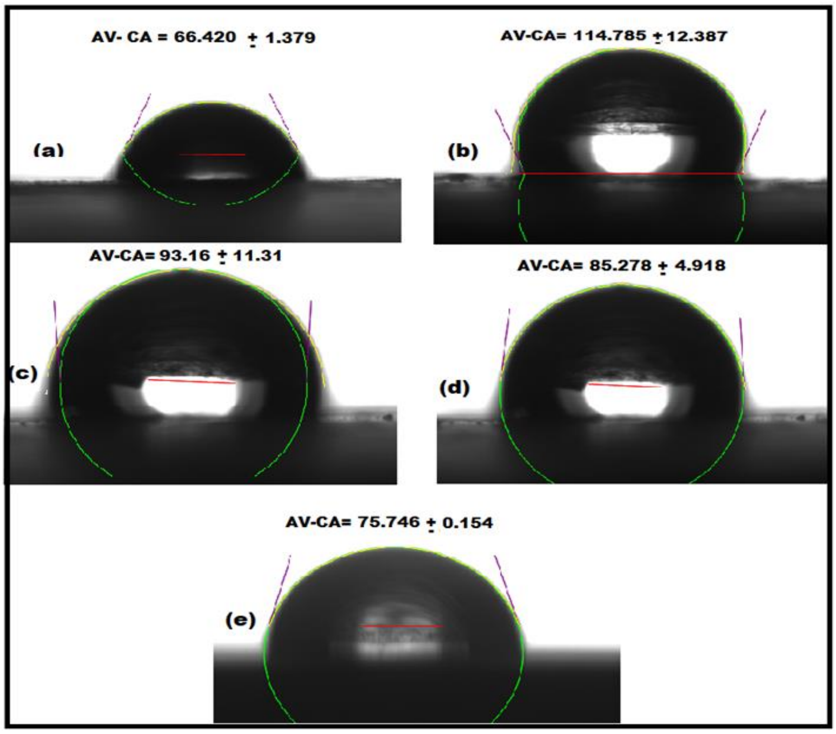


Figure (4.4): shows the average contact angles of NR/SBR compounds as (a): Micro ZnO (5 Phr)/ Crumb,(b): Micro ZnO (5 Phr)/ HAF-N.330,(c): Nano ZnO (1 Phr)/ Crumb,(d): Nano ZnO (2 Phr)/ Crumb, and(e): Nano ZnO (3 Phr)/ Crumb.

Figure 4.4 represents the contact angle of the surface of the NR/SBR compounds with water, where the tire crumbs reduce the contact angle and transform the rubber surface from hydrophobic to hydrophilic. As a result of the weakness caused by the mechanical properties and the reducing the cross-linking resulting after vulcanization of rubber compounds in addition to the weakness chemical bonds, which was discovered by FTIR testing ,also the high amount of zinc oxide leads to a decrease in the contact angle. On the other hand, we notice that the contact angle increases clearly when replacing the tire crumbs by the HAF-N.330 despite maintaining the amount of zinc oxide due to the high surface area of carbon black, which lead to high dispersion in the rubber matrix [11].

4.5 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Figures 4.5,4. 6 show the FTIR spectra Micro, Nanoparticles of zinc oxide and NR/SBR compounds were appearance in the range of (4000 to 400 cm^{-1})using the KBr method.

In this work, a peak at (470 cm^{-1})demonstrated the creation of particles that could be reduced of ZnO particles (Figure 4.6) and linked to the vibration stretching of Zn-O bonds (Figure 4.5).

The presence of C=C was established by the peak at 1627 cm^{-1}. The vibration stretching of the hydroxyl (OH) groups causes the peak between the (3000 -3600)cm^{-1}, such as 3448 cm^{-1} at micro ZnO particles and 3394 cm^{-1} at nano ZnO, to occur [86]. The peaks between 1600-1750 cm^{-1} as 1673 is due to the C=O amide I and amide II group.

The –C–H bending vibration band appears at 1440 cm^{-1} and 1381 cm^{-1} Also, the C–O stretching vibration band appears at 1111and 1018 cm^{-1}, beside the O–H bending vibration band arises at 624 and 620 cm^{-1} when used the Micro and Nano particles of ZnO respectively [87].

The surface of the tire crumbs was treated with sodium hydroxide (NaOH) for obtaining the effective functional groups, Figure 4.5 or Figure 4.6 show the FTIR spectra of treated crumb tires , peaks at 3400 cm^{-1} , which reflect O–H stretching hydroxyl group vibrations.

In addition of, we note the peaks at 2854 cm^{-1} and 2924 cm^{-1} were represented the alkyl stretch of C–H bond vibration also, peak between 660 cm^{-1} and 880 cm^{-1} which signified the presence of more C–H bond stretching connecting to C=C bonds. Beside the peaks between 1451 cm^{-1} and 1752 cm^{-1}, indicating the existence of more C=C bonds. Because the treatment of crumb by a stronger alkaline , apparent a new peak at 1430 cm^{-1} , which represent the partial degradation of crumb elements lead to changing in crumb rubber surface as formation more cracks and roughness . Peaks at 1215 cm^{-1} a quite important peak can be caused by the vibration of S=O stretching indicating the more sulphonic groups [88,89].

FTIR analysis was done for dispersion of the micro particles, nanoparticles of ZnO, and treatment crumb granules in NR/ SBR matrix. The results analysis of FTIR spectra showed the peak at 2829 cm^{-1} for compound activated by micro particles of zinc oxide and peak at 2840 cm^{-1} for compound activated by nanoparticles of zinc oxide were indicated to C–H stretching of NR and SBR. The peak at 1516 cm^{-1}, which reduction to 1451 Cm^{-1} when used the nanoparticles of zinc oxide, these peaks indicated for deformation of CH2 in plane and C-H stretching of aromatic rings of NR and SBR.

The peak at 1381 Cm^{-1}, which reduction to 1366 cm^{-1} when used the nanoparticles of zinc oxide were represented the symmetrical of CH3 and –CH2 wagging motion of NR and SBR. In addition of, the peak at 748 cm^{-1}, which reduction to 714 cm^{-1} when used the nanoparticles of zinc oxide were represented C–H out of plane deformation of vinyl and aromatic C-C stretching of SBR. According to the above results, we noted that the NR/SBR compound activated by nanoparticles of zinc oxide and present the treatment crumbs more active compared with the NR/SBR activated by micro particles of zinc oxide [90].

The peaks at 1091 cm^{-1} indicate the stretching vibrations of styrene and cis-polybutadiene units in the FTIR spectra investigation of the NR/SBR compound filled with 60 P h r of carbon black (HAF-N.330) instead of crumb rubber. The vibration peaks at 699 cm^{-1} represent the aromatic ring's CH groups' deformation and out-of-plane bending, respectively. The butadiene units' CH2 groups are stretching vibrational, as indicated by the typical peak at 3024 cm^{-1}, strong evidence for the existence of C=C bonds and the deformation vibration of (=CH) units that occur in butadiene units. In addition of, the peaks that are positioned at 1666 and 1433 cm^{-1} [91,92] (C-S-C, C-S), and (S-S bonds), respectively, induce significant peaks in the 700-600 cm^{-1}region.

Because the C-S bond stability is stronger than the S-S bond stability, the C-S vibration occurs at a higher of frequency than the S-S vibration. While polysulphide vibration bands often form at 733 cm^{-1}, monosulphide connections exist at frequencies higher than 700. Additionally, the range 700-600 cm^{-1} represents vibration peaks that are clearly discernible at 699 cm^{-1} , the clearly (bending vibration band)(C=C-H) at 950 cm^{-1} [93,94]. This finding demonstrates that NR/SBR filled with crumb has lower bonding than compounds filled with carbon black.

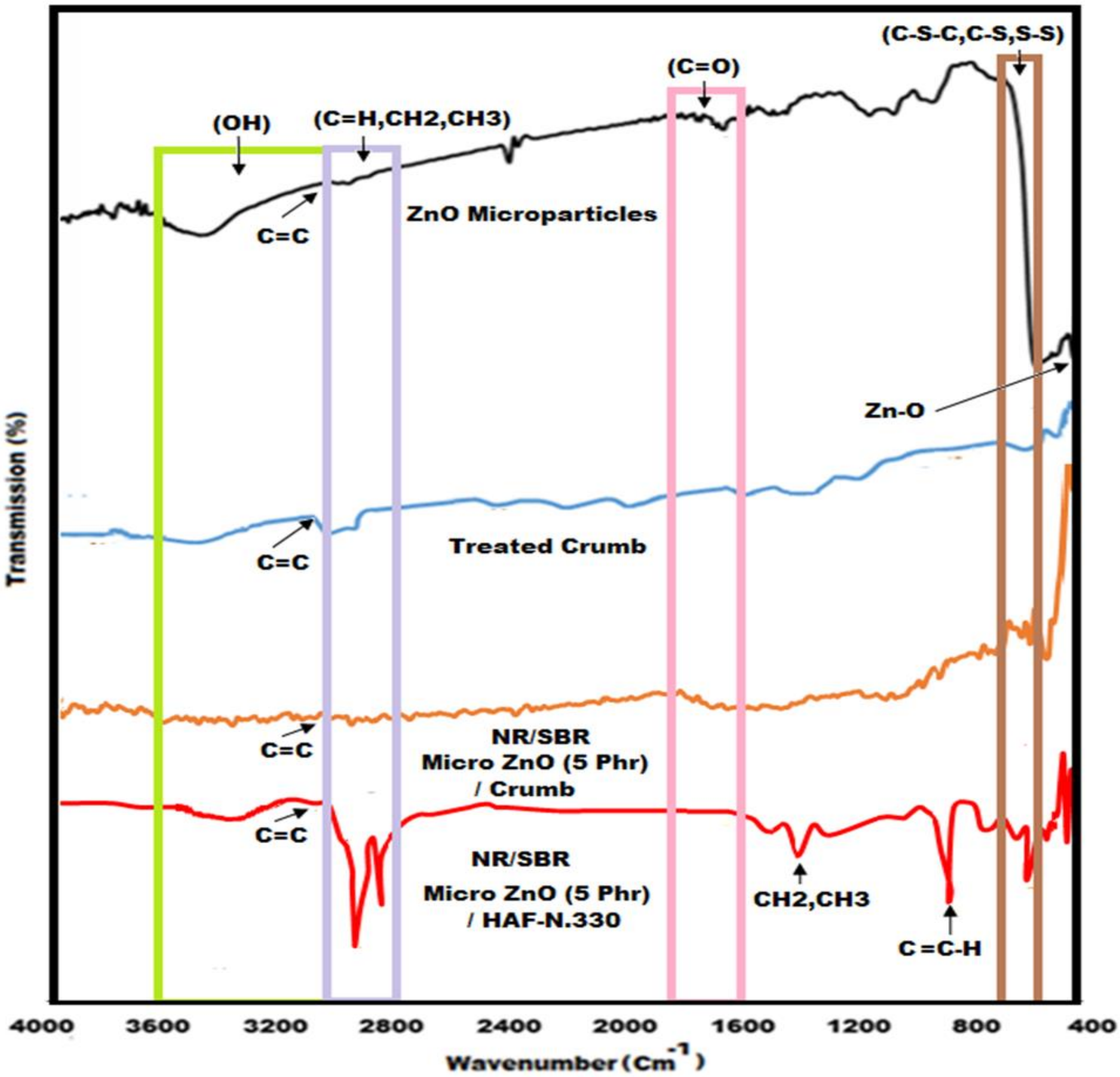


Figure (4.5): shows the FTIR spectra of micro ZnO particles, treatment crumbs rubber, and NR / SBR compound filled with micro ZnO (5 Phr) / crumb, and NR / SBR compound filled micro ZnO (5 Phr) / HAF-N.330

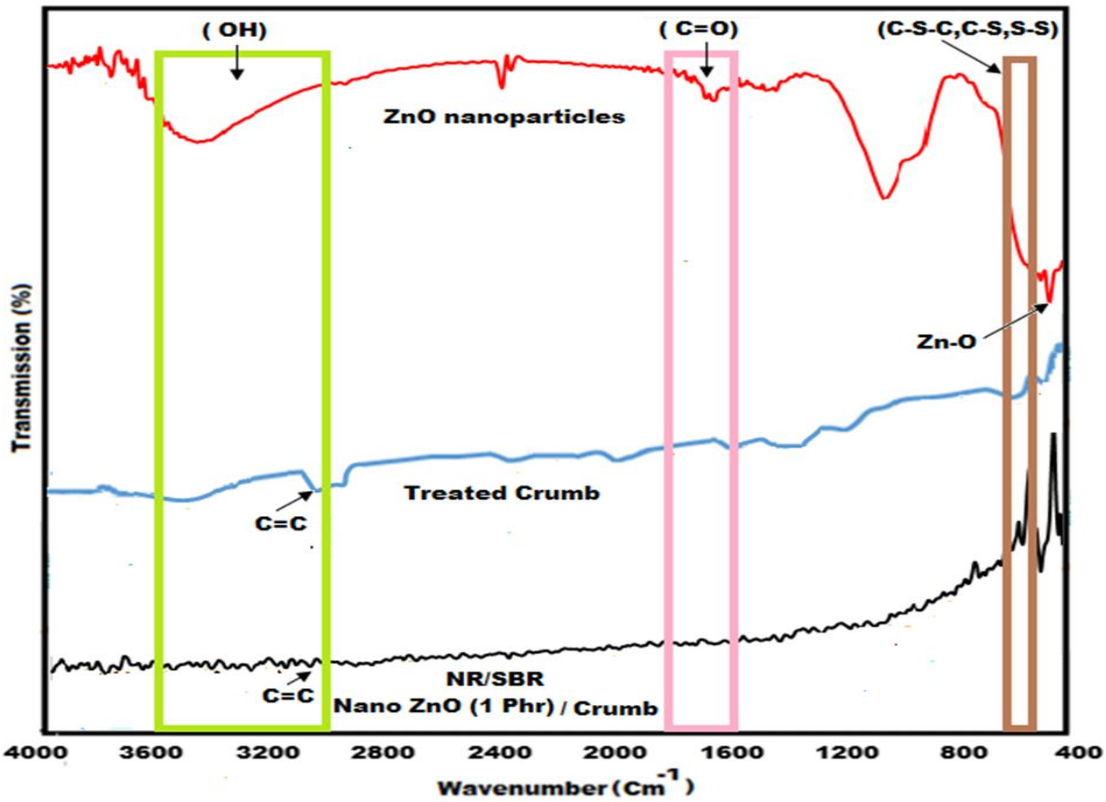


Figure (4.6): shows the FTIR spectra of Nano ZnO particle, treatment crumb rubber, and NR/ SBR compound filled with Nano ZnO (1 Phr) / crumb.

4.6 Mechanical Properties and Compression Set

The tensile strength test depends on the material and test conditions such as temperature, humidity, and sample geometry. The tensile strength of rubber materials is determined according to ASTM D 412. properties mechanical such as "strength of tensile, elongation at break and modulus of elasticity", which shown in Figure 4.7, Figure 4.8 and Table 4.2 depend on rheological properties such as viscosity, maximum torque and curing rate index. The results of the curing properties of the NR/SBR compound proved that the compounds that contain tire crumbs with the presence of Micro particle of ZnO exhibit the least cure rate index and require more cure time in addition to having less maximum Torque. In the case of the NR/SBR compound, which used the nanoparticle of ZnO with the presence of the treated tire crumbs, it gave better results compared with micro particle of ZnO with treated crumb rubber ,which given the

SEM images proved that the nanoparticle of ZnO regularly dispersion without clumping, especially when using 1 Phr. On the other hand, the use of carbon black (HAF-N.330) instead of crumb rubber led to an increase in the viscosity of the rubbers compound and reduced the cure time with the scorch time to a minimum value besides increasing in the maximum torque with curing rate index (CRI) [95] . NR/SBR compound filled by carbon black (HAF-N.330) had highest mechanical properties. Based on the above results, we note that the increment in mechanical properties is due to the effect of the particle size of zinc oxide with maintaining the same quantities of tire crumbs. The increment in strength tensile, elongation at break, and elasticity modulus are 9.6 %, 13.6%, and 13.85% respectively. While the increment in mechanical properties is due to the effect of changing the carbon black instead of the tire crumbs with maintaining the size and the amount of zinc oxide are 637.313%, 258.73%, and 105.67% respectively.

These results showed the relationship between the FTIR analysis, which showed a strong bonding between the carbon black particles and the polymer chains and the results of mechanical properties, FTIR analysis is a good method for assessing the mechanical properties of rubber, especially the tensile strength [96].

Table (4.2): *shows the results of tensile stress, modulus of elasticity (slope of stress- strain curves), elongation at break, and hardness of NR/SBR compounds.*

NR/ SBR samples	Tensile Stress (MPa)	Fitting Equation	Elongation at break (%)	Hardness (Shore A)
A	2.010±0.120	σ =2.0343 ε, R^2 = 0.962	90.83±2.36	74.88±0.981
B	14.82±2.310	σ =4.184 ε , R^2 = 0.974	325.83±13.25	77.88±3.192
C	2.203±0.340	σ =2.316 ε , R^2 = 0.987	103.17±12.06	75.48±1.473
D	2.013±0.307	σ =2.188 ε , R^2 = 0.982	98.5±29.8	75.04±1.28
E	2.083±0.240	σ =2.698 ε , R^2 = 0.989	110.5±10.76	74.72±0.996

A: Micro ZnO (5 Phr)/ Crumb; B: Micro ZnO (5 Phr)/ HAF-N.330 ; C: Nano ZnO (1 Phr)/ Crumb ; D: Nano ZnO (2 Phr)/ Crumb; E; Nano ZnO (3 Phr)/ Crumb; σ: Tensile stress, ε: Strain, R^2 : Correction factors of Fitting Equation , slope of fitting equation is the modulus of elasticity

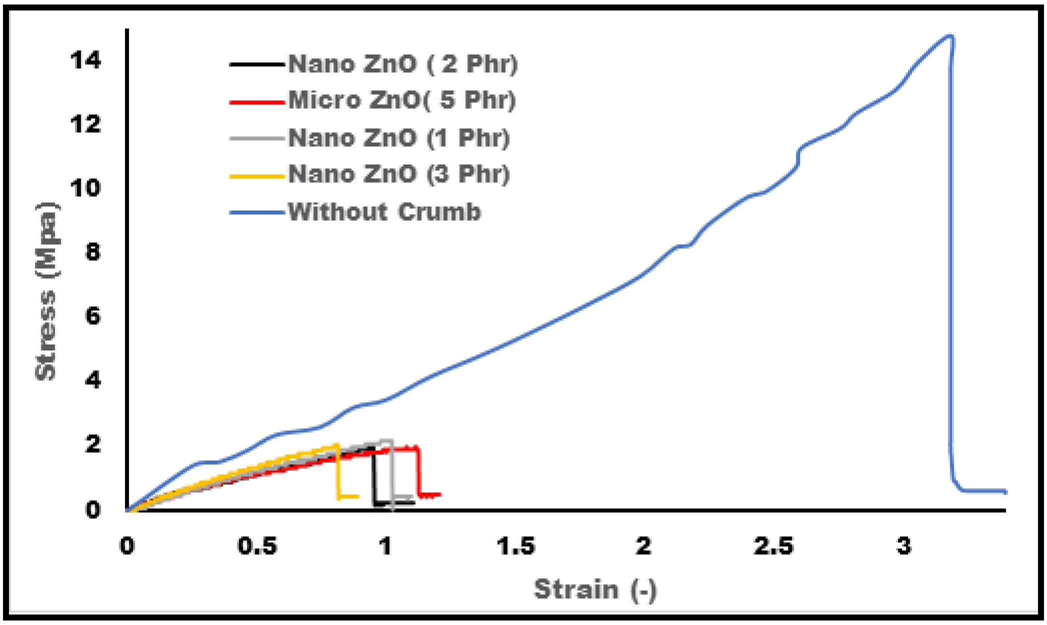


Figure (4.7): shows the stress-strain curves for NR/SBR compounds as Micro ZnO (5 Phr)/ Crumb, Micro ZnO (5 Phr)/ HAF-N.330, Nano ZnO (1 Phr)/ Crumb, Nano ZnO (2 Phr)/ Crumb, and Nano ZnO (3 Phr)/ Crumb.

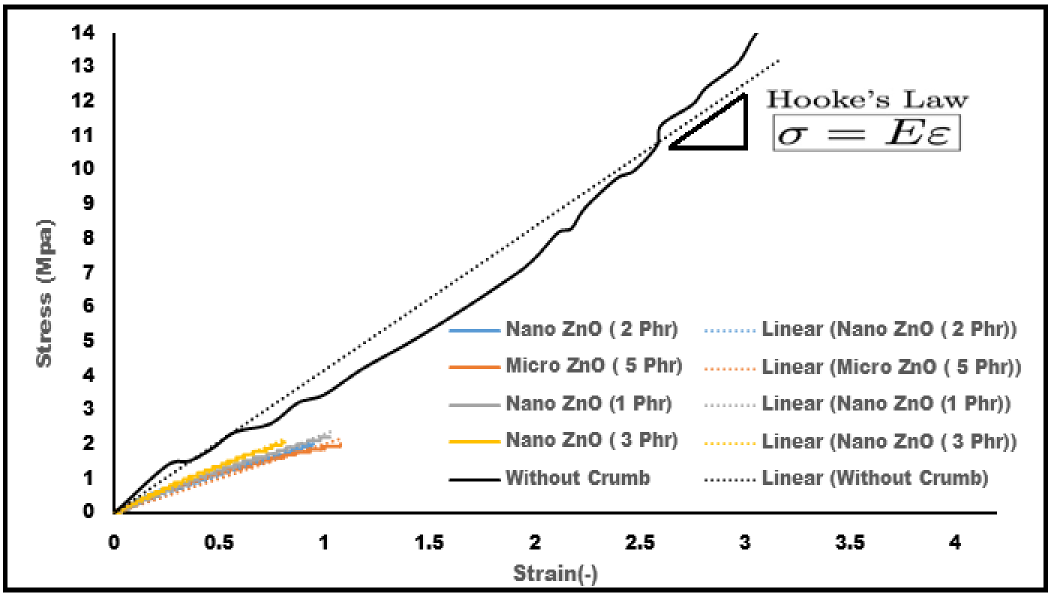


Figure (4.8): shows the slopes (modulus of elasticity) of stress-strain curves according to Hooke's law for NR/SBR compounds as Micro ZnO (5 Phr)/ Crumb, Micro ZnO (5 Phr)/ HAF-N.330, Nano ZnO (1 Phr)/ Crumb, Nano ZnO (2 Phr)/ Crumb, and Nano ZnO (3 Phr)/ Crumb.

The hardness is closely related to the tensile strength, where the hardness represents the penetration resistance of the rubber samples. This resistance increases with the increasing the density of crosslinks and interaction between the functional groups of the fillings and the polymeric chains .In addition of, the same behavior for relation between the modulus of elasticity and hardness for NR/SBR compounds .

Generally, used the crumb leads to 4.05% reduction in hardness of rubber compounds compared with used the carbon black as filler [97], these results are appearance in Table 4.2. The compression set is one of the important properties of rubber compounds to determine the possibility of restoring the rubber sample to its original thickness after removing the load from it. Where the rubber sample is compressed to a specific deformation under a specified period of time, the resulting value from this examination expresses the percentage of the NR/SBR samples fail to recover their original thickness. Table 4.3 showed the results of compression set , sample Micro ZnO (5 Phr)/ Crumb having a compression set 90.47 %, the sample only recovered 9.52% of its uncompressed thickness , while Micro ZnO (5 Phr) / HAF-N.330 having compression set 61.9% the sample only recovered 38.1% of its uncompressed thickness . In addition of, the nanoparticle of zinc oxide, lead to improvement of the thickness recovery percentage. [98]

Table (4.3): showed the results of compression set.

NR/SBR samples	T_0 (mm)	T_s (mm)	T_r (mm)	Cs (%)	ER (%)
A	11.5	9.4	9.60	90.5 %	9.52%
B	11.5	9.4	9.78	61.9%	38.1%
C	11.9	9.4	10.1	72%	28%
D	11.8	9.4	10	75%	25%
E	11.5	9.4	9.78	81.9%	18.1%

A: Micro ZnO (5 Phr)/ Crumb; B: Micro ZnO (5 Phr)/ HAF-N.330 ; C: Nano ZnO (1 Phr)/ Crumb ; D: Nano ZnO (2 Phr)/ Crumb; E; Nano ZnO (3 Phr)/ Crumb E R %: Elastic recovery; Cs%: Compression set; To: Initial height; T r: recovery height; T s: Spacer height

4.7 Anti-microbial properties

The antibacterial properties of NR/ SBR composites were investigated after putting the samples with 6 mm diameter in agar plates against S. aureus (Gram-positive) and E. coli (Gram-negative). Figure 4.9 shows the antibacterial zone of inhibition of the NR/SBR samples as Micro ZnO (5 Phr)/ Crumb, Micro ZnO (5 Phr)/ HAF-N.330, and Nano ZnO (3 Phr)/ Crumb respectively. There is high inhibition zone for Micro ZnO (5 Phr)/ Crumb sample exhibited against S. aureus (Gram-positive) and lower than inhibition zone of this sample against E. coli (Gram-negative) compared with the Micro ZnO (5 Phr)/ HAF-N.330 which exhibited very low inhibition zone against S. aureus (Gram-positive) and no inhibition zone against E. coli (Gram-negative). The surface of zinc oxide needs to be modified as more dispersion of nanoparticles occurs inside the rubber chain and leads to homogeneity of the compound without agglomeration. The decrease in the size of the nanoparticles causes an increase in the specific surface area, which increases the enhancement of the surface interaction of the particles. ZnO penetrates the walls of the bacterial cells and disintegrates them and aggregates In the cytoplasm of the cell where it binds with vital molecules and thus causes cell death [99]. This study discussed the role of treated crumb for increased the hydrophilicity of rubber surface by decreased the water contact angle with the mechanical properties [100], which lead to more inhibition zone against E. coli and S. aureus.

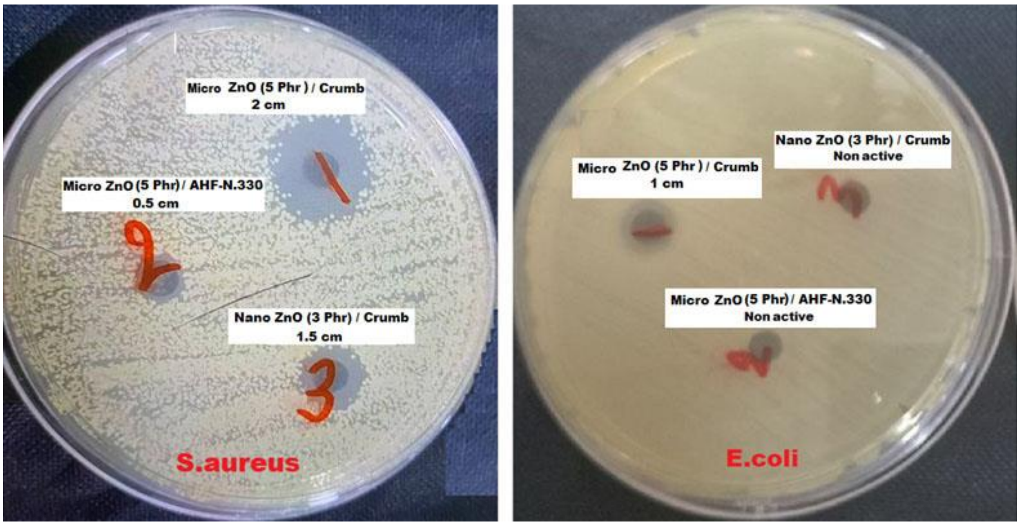


Figure (4.9): Antibacterial zone of inhibition of the NR/SBR samples as Micro ZnO (5 Phr)/ Crumb, Micro ZnO (5 Phr)/ HAF-N.330, and Nano ZnO (3 Phr)/ Crumb against S. aureus and E. coli.

Chapter Five

Conclusions

and

Recommendations

5 .1 Conclusions

The most important of this thesis can be summarized according to the following important points:

- The mechanical properties of polymer mixtures decrease in the presence of tire crumbs compared to the presence of carbon black.
- scorch time properties decrease with the presence of tire crumbs, as well as the presence of zinc oxide microparticles, while they are the best in terms of scorch time and scorch speed in the presence of zinc oxide nanoparticles.
- crosslink density decreases with the presence of tire crumbs.
- FTIR results showed the presence of covalent bonds when using carbon black instead of tire crumbs.
- The SEM images confirmed the homogeneity of the rubber compounds in which 1phr of nano-zinc oxide was used.
- Bacterial resistance is better in the presence of tire crumbs with zinc oxide.

5.1 Recommendations

Some important recommendations for developing this study for future research work are as follows:

- Multiple loading levels of tire crumb rubber can be used and utilized in other engineering applications such as sports floor coverings.

- Use of other treatments for tire crumbs, ammonium or potassium hydroxide
- Use the crumb rubber as a de-vulcanizer of the rubber after mixed with water, oil, and chemicals
- Used the magnesium oxide with crumb rubber in NR/SBR compounds for antibacterial applications

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الخلاصة

في هذا العمل ، تمت دراسة إعادة استخدام فتات الإطارات كمواد مالئة واستخدمت كميات عديدة من جزيئات أكسيد الزنك كمنشط في مركبات المطاط الطبيعي / مطاط ستايرين بوتادين (NR / SBR) لإنتاج المطاط المقاوم للبكتيريا . الذي يستخدم في المقابض مقابض لكرسي متحرك أو سرير متحرك للمريض. تم عمل خمس عينات بما في ذلك ، Micro ZnO (5 P · h r) / Crumb (A) ، Micro ZnO (5 P · h r) / HAF-N.330 (B) ، Nano ZnO (1 P · h r) / Crumb (C) ، Nano ZnO (2 P h r) / Crumb (D) ، و Nano ZnO (3 P · h r) / Crumb (E). إطارات الفتات هي رخيصة الثمن وتساعد على زيادة تحلل مركبات المطاط مع زيادة قابلية البلل عن طريق تقليل زاوية التلامس مع الماء تم إجراء العديد من التحقيقات مثل خصائص المعالجة وكثافة الارتباط المتشابك ومورفولوجيا السطح مثل صور المجهر الإلكتروني المسح (SEM) والتلامس مع الماء الزوايا ، الخواص الميكانيكية (مجموعة الشد والصلابة والضغط). أثبتت النتائج أن عينة مركبات المطاط (ب) كان لها أعلى إجهاد شد 14.82 ميجا باسكال ، وكان معامل المرونة 4.184 ميجا باسكال ، والاستطالة عند الكسر 325.83٪ نتيجة لعزم الدوران العالي 67.78 (Ib-In) وكانت كثافة الارتباط المتشابك (0.57 مول / سم ^{3}). مع تشتت جيد لجزيئات HAF-N.330 في مصفوفة مطاطية. إلى جانب ذلك ، كان مظهر الروابط قويًا في اختبار (FTIR) ، بينما كان ظهور الروابط الضعيفة في عينة مركب المطاط (أ) التي كان لها إجهاد شد 2.01 ميجا باسكال ، وكان معامل المرونة 2.03 ميجا باسكال ، والاستطالة عند الكسر 90.83٪ نتيجة لذلك من عزم الدوران العالي 52.77 (Ib-In) وكثافة الارتباط المتشابك (0.436 مول\سم^3) مع تشتت منخفض من فتات المطاط في مصفوفة مطاطية ويتضح أن التجنب والشقوق الدقيقة تعتمد على صور SEM. وفقًا للنتائج أعلاه ، مركب المطاط (أ) يؤدي إلى نشاط مرتفع ضد بكتريا S. aureus و E. coli وكانت منطقة التثبيط 2 سم ضد S. aureus و 1 سم للإشريكية القولونية.

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل

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قسم هندسة البوليمرات والصناعات البتروكيماوية

تنشيط مطاط الاطارات بواسطة جزيئات أكسيد الزنك النانوية لتحسين أداء المركبات المطاطية

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من قبل

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