

**EFFECT OF PEG – CAPPED METAL OXIDE NANOFILLERS  
ON THE ANTISTATIC PROPERTIES OF NATURAL  
RUBBER COMPOSITES**

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In partial fulfillment of the requirements for the award of*

*Master Degree in CHEMISTRY*

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2021-2023

# **BHARATA MATA COLLEGE**

## **THRIKKAKARA**



### **CERTIFICATE**

*This is to certify that the project report entitled “**EFFECT OF PEG – CAPPED METAL OXIDE NANOFILLERS ON THE ANTISTATIC PROPERTIES OF NATURAL RUBBER COMPOSITES**” is a bonafide work carried out by **MERIN JOY**, M.Sc. Pharmaceutical Chemistry, under my supervision and guidance and that no part of this has been submitted for any degree, diploma or other similar titles of recognition under any university.*

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## **DECLARATION**

I, **MERIN JOY** hereby declare that this project report entitled “***EFFECT OF PEG – CAPPED METAL OXIDE NANOFILLERS ON THE ANTISTATIC PROPERTIES OF NATURAL RUBBER COMPOSITES***” is an authentic work carried out during my course under the guidance of Dr. JINSA MARY JACOB, Department of Chemistry, Bharata Mata College, Thrikkakara.

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# **EFFECT OF PEG – CAPPED METAL OXIDE NANOFILLERS ON THE ANTISTATIC PROPERTIES OF NATURAL RUBBER COIMPOSITES**

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## **ABSTRACT**

The present study investigates the effect of incorporating different metal oxide nanofillers on the antistatic properties of natural rubber composites. Three different types of PEG-capped metal oxide nanofillers namely copper oxide (CuO), zinc oxide (ZnO), and titanium dioxide (TiO<sub>2</sub>) were synthesized using a hydrothermal method and characterized using powder X-ray diffraction and scanning electron microscopy. The nanofillers were then incorporated into natural rubber latex while compounding. The resistivity of the resulting natural rubber composite films was evaluated by using van der Pauw method. The results showed that the addition of various metal oxide nanofillers changed the antistatic properties of the natural rubber composite. The antistatic properties were found to be dependent on the type of metal oxide nanofillers employed. The results of this study will be beneficial for the development of antistatic rubber materials for diverse industrial applications.

**Keywords:** natural rubber, PEG, Copper oxide, Zinc oxide, Titanium oxide, resistivity, antistatic, XRD, SEM

## **References**

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## CHAPTER 1

### INTRODUCTION

Natural rubber is one of the main agricultural products of the rubber industry. It is used in tile floor, gloves, pillows and mattresses, medical etc. Natural rubber can be found in the genus *Hevea*, which is composed of two components: rubber (cis- 1,4- poly isoprene) and non-rubber components (sugar, proteins, salts, phospholipids etc). Rubber is a strategically important plant- derived polymers, having been used as a raw material in more than forty- four thousand products including over four hundred medical devices. Currently, the only commercial source of rubber is derived from the natural rubber tree named *Hevea brasiliensis* which is harvested from the state of Brazil. The milky fluid name natural rubber latex is obtained from the tree contains a variety of growth promoting substances including proteins, lipids, carbohydrates and other inorganic and organic compounds. There is no other synthetic material from plants which can be replace, to date.

Its molecular structure is complex and its molecular weight is high (>1 million Daltons), thus providing it with a high level of performance that cannot be easily replaced by artificial polymers. There are different fillers used to reinforce the natural rubber to improve its mechanical as well as electrical properties including resistance, tensile strength, hardness, abrasion resistance, tear resistance.



The rubber industry has seen a surge in the use of fillers in recent years, with the aim of improving mechanical properties, increasing production efficiency and decreasing the cost of rubber products. There are three main categories of fillers, which can be divided into reinforcing, semi reinforcing and non-reinforcing ones. The effectiveness of reinforcing filler depends on a variety of elements, including the size of the particles, the surface area of the filler and its shape.

Filler surface treatments can be employed to enhance the mechanical characteristics of polymer composite materials. The various treatments employed result in distinct properties of the treated fillers, including particle sizes and shapes, surface area and functional groups, which are directly related to their performance in polymer composites.

In order to further enhance the properties of existing polymer materials, numerous types of inorganic filler have been extensively studied and used. The size and dispersion properties of inorganic particulates have a significant impact on the overall properties of polymer composites. The use of nanometric fillers on polymer materials is a promising avenue for property alteration. Some nano-filler formulations have demonstrated remarkable improvements in polymer performance due to their high surface area compared to traditional fibers or particles.

Rubber is a widely used polymer material due to its high degree of deformability and its ability to be reversed. However, due to its low modulus and strength, an additional reinforcing phase is required for the practical applications of rubber materials. The full reinforcing effects of nano-fillers are reduced due to their size and volume, and the incorporation of these fillers into rubber in order to achieve advantageous mechanical and physical properties is becoming increasingly important.

Vulcanized natural rubber is an example of a material that has undergone an acidic coagulation process, washing with water and then processing into



sheets. The process of vulcanization, which involves the addition of sulphur, accelerator and other compounds results in the formation of three dimensional networks. As a result of this process, the rubber is able to become more elastic and strong. This elasticity is attributed to the strain induced crystallization phenomenon. Furthermore, natural rubber has a high level of strength and elasticity at break, which can be attributed to its uniform microstructural structure. The crystallites that form the network structure and the alignment of the chains towards stretch further explain the remarkable mechanical properties. Natural rubber extracted from trees by tapping and are used to chemically modify bitumen. Natural rubber has been successfully used for decades to produce tires and gloves as well as for the construction of buildings and roads. Medical rubber gloves are designed to provide a high level of performance due to their resilient, elastic and abrasion- resistant nature. Additionally, they are designed to be effective in reducing the amount of heat that Accumulates under friction as well as being break resistant. Furthermore, they should be able to retain the wear's fine tactile sensation and provide a barrier against pathogens.

Commercial natural rubber is a widely used material in various applications, such as adhesives and tyres as well as in the production of surgical gloves and coating for health equipment and accessories. Additionally, natural rubber is used in coatings for floor covering products and transportation vehicle accessories. The process of filling in rubber has a long history, dating back to the Amazon Indians who used black powder in latex to enhance the light aging properties of the rubber. The majority of fillers used in natural rubber are derived from carbonized organic compounds, with zinc oxide being used originally as a whitening pigment. Depending on the rubber applications, the properties of the elastomer are adjusted with varying particle sizes and surface energy. Recently, much attention has been paid to the effects of fillers containing nano sized particles on the natural rubber and synthetic rubber.

Although natural rubber has various applications, it has a tendency to generate static electricity when exposed to other materials. This buildup of static charges can result in the formation of high electrostatic voltages or even fires. As a result, there is an increasing focus on the development of antistatic rubber, or natural rubber that is conductive. The primary approach to improve the electrical properties of natural rubber is the use of conductive metal oxide nanosized fillers such as copper oxide or zinc oxide. Nanofillers have been gaining considerable attention due to their excellent properties which can be achieved by the use of smaller amounts than micrometric particles.

### **1.1. NANOPARTICLES**

The properties of natural rubber can be enhanced by incorporating various nanoparticles. Nanoparticles are materials composed of either inorganic or organic molecules with diameters ranging from 1 to 100 nanometers (depending on the terminology used), though there are examples of nanoparticles that are several hundred nanometers in size. These materials possess a variety of novel properties compared to the majority of the materials. Nanotechnology has gained a lot of attention in recent years due to its applications in biomedicine, electronics, agriculture and industry. Scientists have been continuously working to improve the effectiveness and extend the use of nanoparticles to various areas by altering their chemical and physical properties. Nanoparticles have been proposed to provide the desired properties with a low filler load and low density, as well as good chemical resistance and excellent electrical properties. Carbon based fillers such as carbon fibre, carbon nanotubes, graphene have been incorporated in to natural rubber elastomers taking in to account the synergic effect of the conductive filling and elastomer. Nano fillers including SiO<sub>2</sub>, layered silicates and metal oxides have been incorporated into various polymers to enhance the properties of the elastomer including strength, barrier strength, thermal resistance, permeability and electrical conductivity. The

interaction of the filler with the rubber is a key factor in the reinforcement of the elastomers, and a good dispersal of the filler within the rubber is essential for the final properties.

In our work, we used metal oxide nano fillers to enhance the antistatic properties of natural rubber which pave a path to various applications including medical as well as industrial. Copper oxide (CuO), Zinc oxide (ZnO) and Titanium dioxide (TiO<sub>2</sub>) are the three nano fillers used in natural rubber. There is a requirement to control particle size, shape, dispersibility in proper solvents and stability of the nanoparticles before introducing in to the sample.

There are several methods for the synthesis of nanoparticles efficiently to produce stable, controlled shape, well dispersed and biocompatible metal oxide nanoparticles. Hydrothermal synthesis, thermal decomposition, sonochemical synthesis, co-precipitation are some of the synthetic routes of nanoparticles.

Nanoparticles with controlled shape and size are crucial to study the antistatic properties of natural rubber. Among the all synthetic routes of nanoparticles, the hydrothermal method is most efficient to maintain the crystalline features of nanoparticles.. It helps for the successful growth of nanoparticles.

## **1.2. PEG CAPPED METAL OXIDE NANOFILLERS**

Polyethylene glycol is used as the capping agent for the nanoparticles like ZnO, CuO, and TiO<sub>2</sub>. The PEG encapsulation give arise to an influence on the morphology of nanoparticle structure as well as the crystalline nature. The antistatic properties of natural rubber on introducing the PEG capped nanofillers get improved when compared to the neat film of natural rubber. In this study we discuss the effect of PEG capped nanofillers on the antistatic properties of natural rubber.

The formation of macromolecules bonds of PEG with the –OH group present on the surface of the nanoparticles. This can be interact with PEG

through hydrogen bonding. Presence of capping agents helps to stabilize the nanoparticles in solutions which are biologically available.

**ZnO** is able to be grown in to a variety of spherical shapes such as nanorods, nanocups, flowers, spherical, nanotubes etc. due to its preferential growth in the (0 0 0 1). Nanoparticles with very small particle size have a very large surface to volume ratio. This gives them unique properties that are very different from the bulk counterparts. Infact, ZnO nanoparticles tend to aggregate while synthesizing due to their large surface energy with a large surface to volume ratio. This means that the surface of ZnO nanoparticle must be modified. Polymeric materials can be used to passivate the surface of nanoparticles. ZnO has been a most popular materials used in various devices including electrical, transparent films, photocatalysts etc. There is a possibility to divert the nanoparticles from nanoscale measurements due to the increased production and aggregation. To prevent the agglomeration we use capping agents.

**CuO** nanoparticles have been focus of research due to its semiconductive nature with distinct optical, electrical and magnetic properties and have been used for a variety of applications including supercapacitors and in near infra red filter technology, electrochemical cells, solar cells, gas sensors. Also in magnetic storage media, sensors in catalysis and semiconductors. Among them characterization and production of nanocrystalline semiconductors which is p-type have considerable attention. CuO have a speciality of narrow band gap among transition metal oxide semiconductors. In recent studies, because of its high dielectric constant CuO has a possibilities in the field of microelectronics . Size of particle and dielectric behavior broadly depend on the method of preparation and its conditions of CuO. Moreover it is used in biomedical applications because of its antimicrobial and biocidal properties. Narrow size distribution and high value of dispersion are the two characteristics of CuO nanoparticles.

**TiO<sub>2</sub>** nanoparticles have excellent optical transmittance and they are well known in photo catalysis and photo electrochemistry fields. They have high refractive index and possess chemical stability. Several methods are prevalent for the synthesis of TiO<sub>2</sub> nanoparticles. Basically, these nanoparticles have similar nature of n-type semiconductor with a broad energy gap. TiO<sub>2</sub> nanoparticles are also used in sensors, catalysis, ion exchange etc. Generating specific size and morphology for the nanoparticles by the controlled procedures give arise to significant applications.

### **1.3. CAPPING AGENT: POLYETHYLENE GLYCOL**

Capping agents play a critical role in the stabilization of nanoparticles, as they inhibit the excessive growth of the nanoparticles and prevent their coagulation or aggregation during colloidal synthesis. Capping ligands stabilize the interface between the nanoparticles and their medium of preparation, which is responsible for the specific structural properties of nanoparticles. These stabilizing agents play a fundamental role in the alteration of various properties of the nanoparticles. The steric effects of the adsorbed capping agents on the nanoparticle surface are responsible for such alterations in physical, chemical properties and antistatic properties. Polymers such as PEG, PPG as well as their copolymers are used in a lot of industrial settings. PEGs are generally used because of their low toxicity and it made to use as solvent , carrier, binding agent, capping agent, lubricant etc.

### **1.4. ULTRASONICATION**

The nanoparticles should be well dispersed in a medium. Nanoparticles like CuO, ZnO and TiO<sub>2</sub> in aqueous suspension is undergone ultrasonication method to investigate the behavior of aggregation and dispersion. The method of ultrasonic dispersion is an effective way for synthesizing concentrated and well dispersed suspensions of nanoparticles. The time or energy of sonication

reduce the particle size and helps to provide a better dispersion. This enhances the stability, thermal conductivity and reduce the viscosity. Also it prevent the nanoparticles from cluster formation.

The nanoparticles is ultrasonicated in our work to maintain the dispersive nature which aids the equal distribution of the nanoparticles on the surface of natural rubber films.

### **1.5. ANTISTATIC PROPERTY OF NATURAL RUBBER**

Natural rubber generates static electricity on rubbing with any surfaces. Static electricity thus generated by any mechanisms cause become a disturbance for the smooth functions especially in the field of medical, industrial and domestic purposes. Antistatic is term which represent the opposite action of static electricity. When we incorporate metal oxide nanofillers it reduce the generations of electrical charges by allowing easy flow of generating charges. Antistatic natural rubber gloves have applications in semiconductors industry and medical procedures. Metal oxide nanoparticles are a promising option for the development of antistatic rubber with improved performance and durability in various applications.

### **1.6. VANDER PAUW METHOD TO MEASURE RESISTIVITY**

There are various methods to determine the resistivity of a material. Among them van der Pauw method is most efficient and widely accepted method. It is used to find the resistivity of thin films. The method consists of four- probes to measure the resistivity. Numerical calculations confirm the correct version of the given equations for the suggested correction function which become similar to the graph. The equation was then experimentally tested by design of samples of various shapes and contact configuration. For easy, rapid and accurate correction factor estimation, tables of numerical values are provided with steps (0.1) and (1.0) for the  $R'/R''$  ratio range (1 to 200) .It is

recommended to use these tables rather than an imprecise estimation from graph or a recalculation of factor.

Apparatus describes a system that allows for the measurement of electrical transport properties for semiconductors over  $10^{12} \Omega$  resistance. The apparatus is based on a guarded version of the van der Pauw approach, which facilitates sample geometry and contact and allows for thin layer evaluation. The apparatus is user friendly, dependable and is constructed from commercially available components.

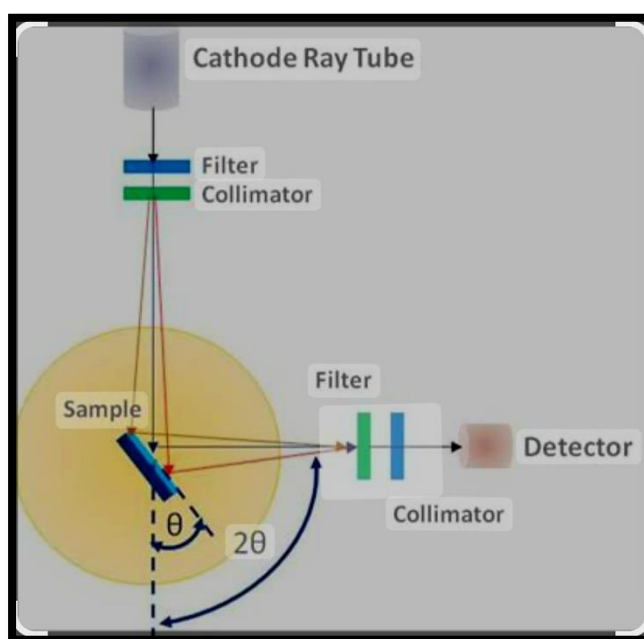


**Fig 1.1 van der Pauw apparatus**

## 1.7. CHARACTERIZATION TECHNIQUES

### (a) POWDER X- RAY DIFFRACTION

Powder X- ray diffraction (XRD) is used commonly for the characterization of particles which are in nanoscale. Powder XRD analysis of a sample provides essential information that complements various microscopic and spectrometric techniques, including phase determination, sample purity, crystal size and in certain cases morphology. Because powder XRD is a bulk technique, its information can be correlated with microscopic observations on a limited number of particles represent the bulk of the sample. However ubiquity and wide spread use, the information provided by the powder XRD for nanoscale material is not always fully utilized and in some instances, is misinterpreted.



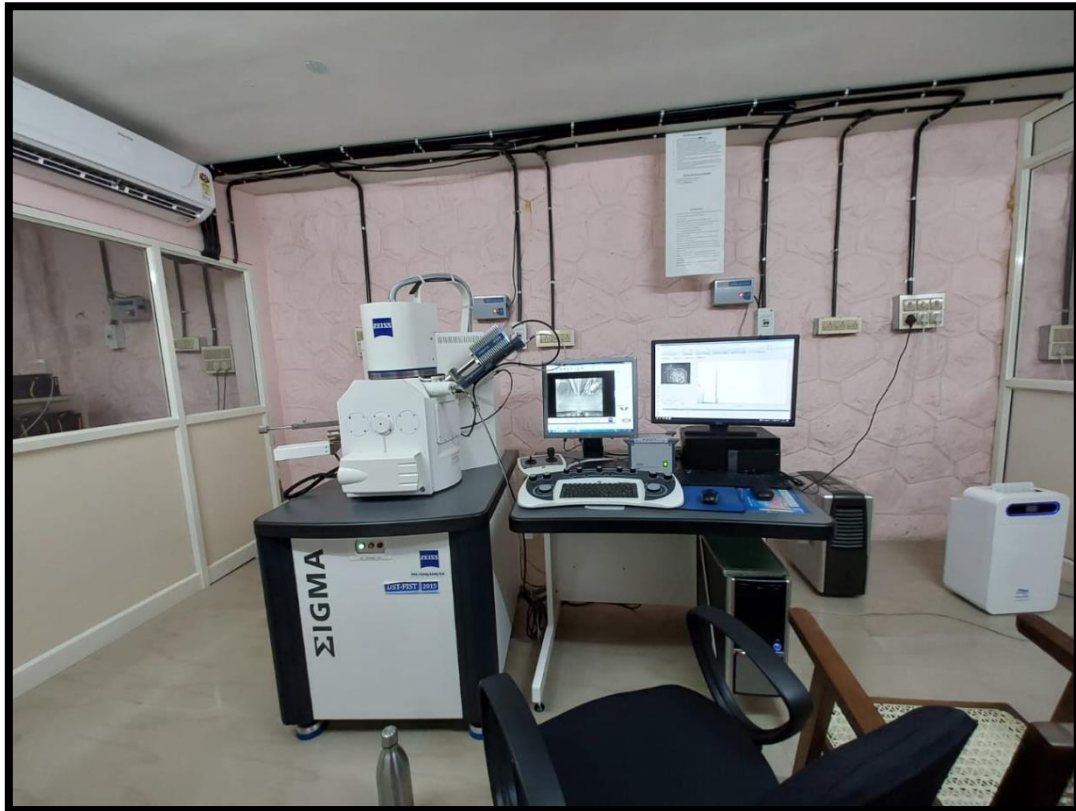
**Fig 1.2 Schematic representation of XRD**

The XRD peaks get broadened when the size of the crystal reduced from bulk to nanoscale. The Scherrer equation, quantitatively expresses the expansion of a peak at a specific diffraction angle. It is related to crystalline domain dimension by the width at half height of the peak. The Scherrer constant is usually expressed as 0.9, but can vary depending on the crystalline domain morphology. The X-ray wavelength is a variable that depends on the X-ray source used. Each peak is independent and should produce a uniform crystalline domain size, provided the sample can be approximated as a uniform, spherical molecule.



The crystalline domain dimension does not always correspond to particle size. Polycrystalline particles are polycrystalline because they contain multiple crystalline domains; however when the crystalline domain diameter calculated by Scherrer equals the average diameter of the particles determined by any other particle size determining methods, to indicate that the particle is single crystals, not polycrystalline. Powder XRD provides useful information and it is a straight forward method.

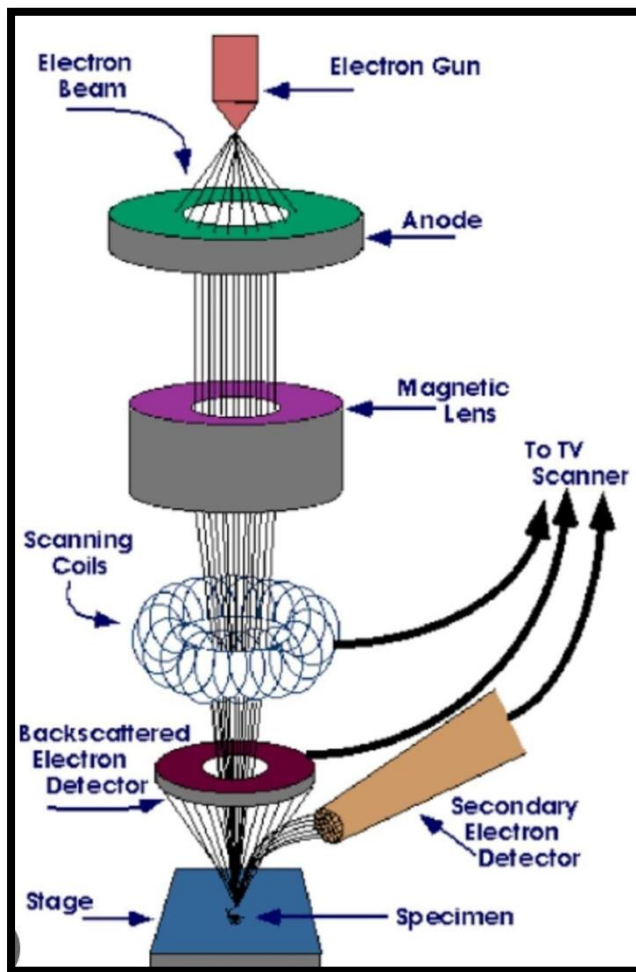
### **(b) FIELD EMISSION SCANNING ELECTRON MICROSCOPY**



**Fig 1.3 FESEM apparatus**

Field Emission Scanning Electron Microscopy offers topographic and elemental data at magnifications of upto 10x and 300,000x with an almost

limitless depth of field. Compared to conventional scanning electron microscopy, FESEM produces sharper and less electrostatically skewed images with spatial resolution as low as 1.5 nanometers, three to six times higher. The field emission cathode in a scanning electron microscope electron gun enables the production of narrower probing beams at both low and high electron energies, resulting in enhanced spatial resolution and reduced sample charging



and contamination. This is especially useful for applications that necessitate the highest magnification. Field Emission scanning electron microscopy (FESEM) is a type of microscope that operates with electrons, which have a negative charge, rather than light. The electron beams are emitted from the field emission source, and the object is scanned in a zigzag pattern. This is in contrast to thermionic electron microscopy (SEM), which relies on potential gradients to emit the beams.

**Fig 1.4 Schematic representation of FESEM**

The electron source is typically a one-tungsten filament, with a sharp pointed tip. FESEM can be used for a variety of purposes, such as cross section analyses of semiconductor devices, the determination of thickness and uniformity of coating, the measurement of small contamination features, and elemental composition measurements.

**CHAPTER 2**  
**AIM AND OBJECTIVES**

**AIM:**

**To determine the effect of polyethylene glycol capped metal oxide nanofillers on the antistatic properties of natural rubber.**

**OBJECTIVES:**

- i. To prepare polyethylene glycol (PEG) capped copper oxide, zinc oxide and titanium dioxide nanoparticles using hydrothermal method.**
- ii. Characterization of nanoparticles using powder XRD and SEM.**
- iii. Preparation of natural rubber latex composite films using the synthesized nanoparticles as filler.**
- iv. Measurement of resistivity of NR composite films using van der Pauw method.**

**CHAPTER 3**  
**EXPERIMENTAL METHODS**

**3.1. MATERIALS**

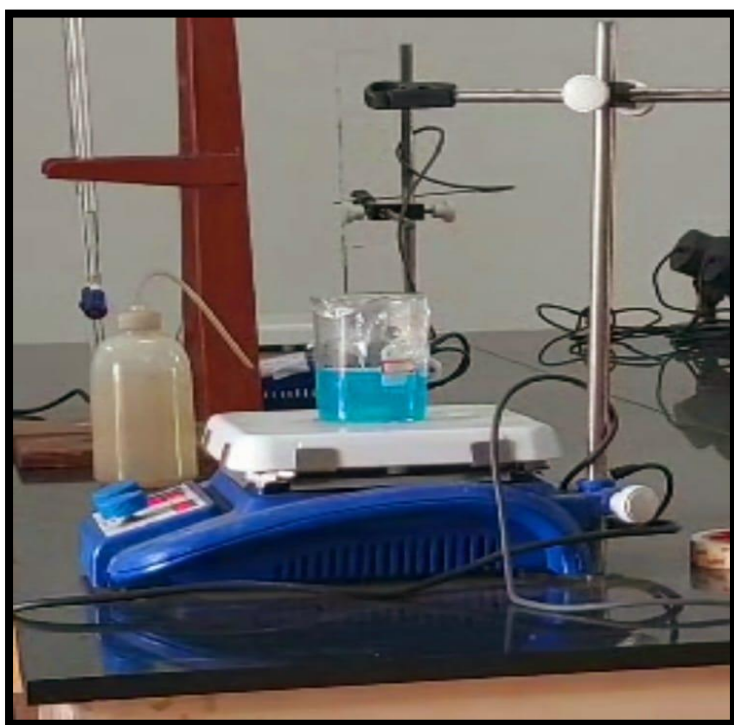
The solvents and reagents which were of pure in quality used in the method were obtained from commercial suppliers.

- 1) Copper(II) acetate monohydrate ( $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ )
- 2) Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )
- 3) Polyethylene glycol 6000
- 4) Titanium isopropoxide ( $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ )
- 5) Glacial acetic acid
- 6) Sodium hydroxide (NaOH)
- 7) Potassium hydroxide (KOH)
- 8) Methanol
- 9) Natural Rubber(NR) latex
- 10) 50% ZnO (activator)
- 11) 50% ionol (antioxidant)
- 12) 50% ZDC (accelerator)
- 13) 50% Sulphur (vulcanizing agent)

## **3.2. SYNTHESIS OF CuO, ZnO AND TiO<sub>2</sub> NANOPARTICLES**

### **HYDROTHERMAL METHOD**

The method used for synthesizing CuO, ZnO and TiO<sub>2</sub> is hydrothermal method. 10 Mm (0.19965g) of copper acetate monohydrate was added to 1% glacial acetic acid. (1mL glacial acetic acid in 99 mL distilled water) containing 0.05g of polyethylene glycol 6000. The mixture was agitated with a magnetic stirrer for 24 hours. Sodium hydroxide solution was added drop wise till the pH becomes 12 and magnetically stirred for half an hour. Afterward, the solution was transferred carefully in to a Teflon- lined autoclave and kept in the oven at 100°C for 7 hours. Then keep the autoclave to cool at room temperature. Centrifuge at 5000 rpm for 20 minutes, discard the supernatant liquids. Collect the resultant precipitate by the method of filtration. Wash the precipitate using distilled water until we get a pH value of 7. Then kept in oven to dry the precipitate. At 100°C for 24 hours. Follow the same method for synthesizing ZnO and TiO<sub>2</sub>. There is an exception for TiO<sub>2</sub> that it should be dissolved in methanol as first step before the addition of glacial acetic acid solution.



**Fig 3.1 Hydrothermal method.**

**a) Mixture for synthesizing CuO NPs is kept on magnetic stirrer for agitation**

**Fig 3.2**

**b) Mixture for synthesizing CuO**

**After the dropwise addition of NaOH pH becomes 12.**

**Colour changes from blue to green**



**Fig 3.3 Synthesized CuO, ZnO and TiO<sub>2</sub> nanoparticles**

### 3.3. PREPARATION OF NR-CuO, NR-ZnO AND NR-TiO<sub>2</sub> NANOCOMPOSITE FILMS



**Fig 3.4 Nano composite films**

The NR composites were prepared by the following procedure. Natural rubber was used in the form of latex. The nanofiller dispersion (0.25% each) was added to the latex while compounding in the form of a dispersion. Natural rubber latex was mixed with potassium hydroxide, followed by ZnO, ionol, nanofiller dispersion, ZDC and sulfur. All ingredients were added either in the form of a dispersion or solution to avoid coagulation. After each addition, the mixture was stirred in a magnetic stirrer for five minutes. The resultant mixture was cured for 24 hours and then poured into Petri dish and films were developed by keeping in the oven overnight at 100°C. The formulation used for compounding is given in Table 1.

**Table 1 Compounding formulation for NR composite**

Ingredients	Weight
NR	10 g
KOH	0.2999 g
50% ZnO (activator)	0.1199 g
50% ionol (antioxidant)	0.1199 g
Nanofiller	0.25%
50% ZDC (accelerator)	0.0899 g
50% Sulfur (vulcanizing agent)	0.1199 g



**Fig 3.5 Chemicals used for compounding ( accelerator, vulcanizing agent, activator, antioxidant, KOH )**





**Fig 3.6**  
Natural rubber along with compounding chemicals and nanofillers (here ZnO) is kept on magnetic stirrer

**Fig 3.7**  
After stirring the mixture is transformed in to petri dish

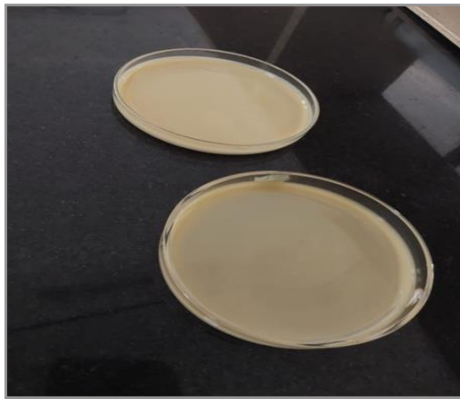


**Fig 3.8**  
**Petri dish**  
**containing the**  
**mixture**



**Fig 3.9**  
**Keeping the petri dish**  
**containing mixture in**  
**oven for developing NR**  
**films.**





**NR- ZnO FILMS**  
**( CREAM COLOUR )**

**NR- TiO<sub>2</sub> FILM**  
**( MILKY WHITE )**

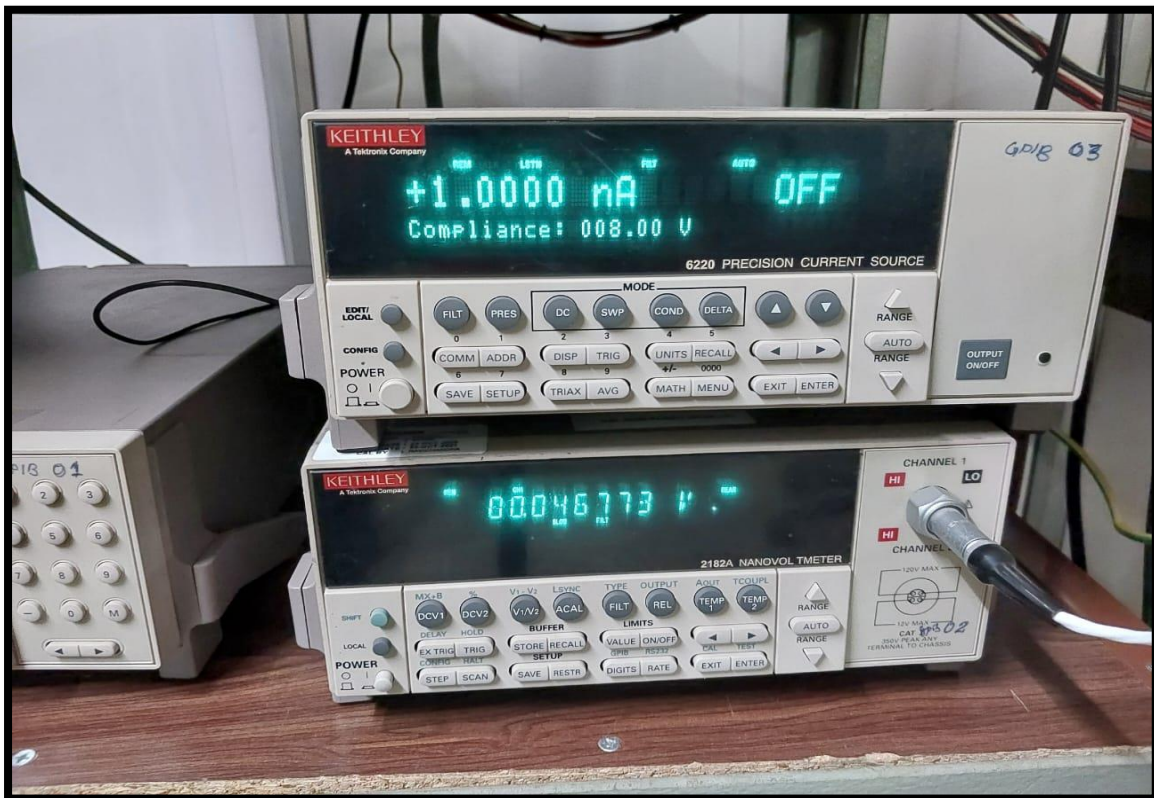


**NR- CuO FILMS**  
**( BROWN COLOUR )**



### 3.4. MEASUREMENT OF RESISTANCE OF NR COMPOSITE FILMS

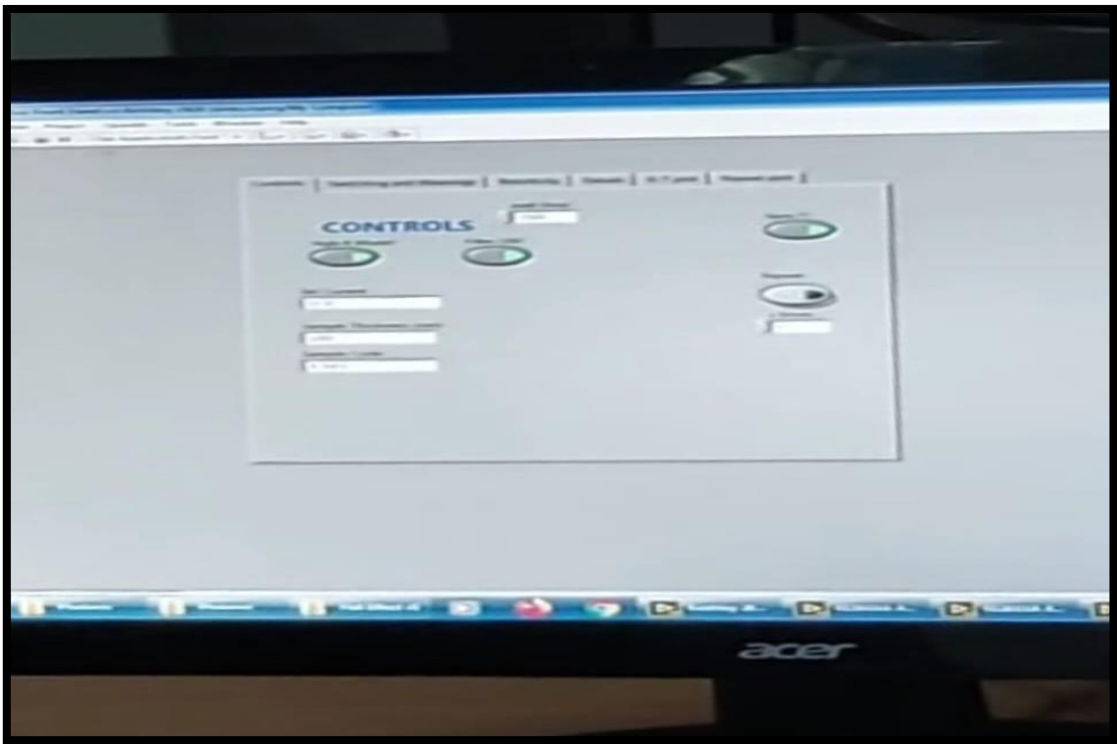
The van der Pauw method was used to measure the sheet resistance of NR films, providing valuable information regarding the electrical properties of the films. This involves a precision technique, in which four metallic contacts are kept on the surface of the NR film. A constant current source is connected to two contacts, while the other two are connected to a voltmeter



**Fig 3.10 van der Pauw readings**



**Fig 3.10(a) Four – probe of van der Pauw apparatus**



**Fig 3.10(b) Out put device showing resistivity by van der Pauw method.**

## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1. X- RAY DIFFRACTION (XRD)

The powder XRD patterns obtained for CuO, TiO<sub>2</sub> and ZnO samples are given in Fig. 1. For CuO, all the diffraction peaks are due to monoclinic structure of CuO (JCPDS card no. 48-1548) with 2 theta values and corresponding diffraction planes such as 35.7 (002), 38.9 (111), 48.7 (202), 58.3 (202), 61.7 (113), 66.3 (311) and 68.3 (220).

For TiO<sub>2</sub>, the most intense peak at 27.5 indicates the (110) plane of rutile phase (JCPDS card no. 21-1276) and the peaks at 48.1 and 62.3 arise due to the (200) and (204) planes of anatase phase.

Analysis of the diffraction pattern of ZnO clears that all the peaks are due to the wurtzite phase (JCPDS Card no 36-1451) with no peaks of any other phases. The diffraction peaks and related planes are given as 31.8 (100), 34.4 (002), 36.3 (101), 47.6 (102), 56.7 (110), 62.9 (103) and 68.1 (112).

The XRD patterns thus proved the existence of pure metal oxides in all the three samples with no other impurities. The CuO and ZnO are phase-pure also. We have got sharp XRD peaks for CuO and ZnO indicating that these two metal oxides are crystalline in nature.

The diffraction pattern of TiO<sub>2</sub> includes broad peaks which means the extent of crystallinity is very less or it is amorphous in nature. This is due to the low-temperature synthesis strategy\_\_that we have followed. The average crystallite size of the metal oxides has been calculated using the **Debye-Scherrer formula.**

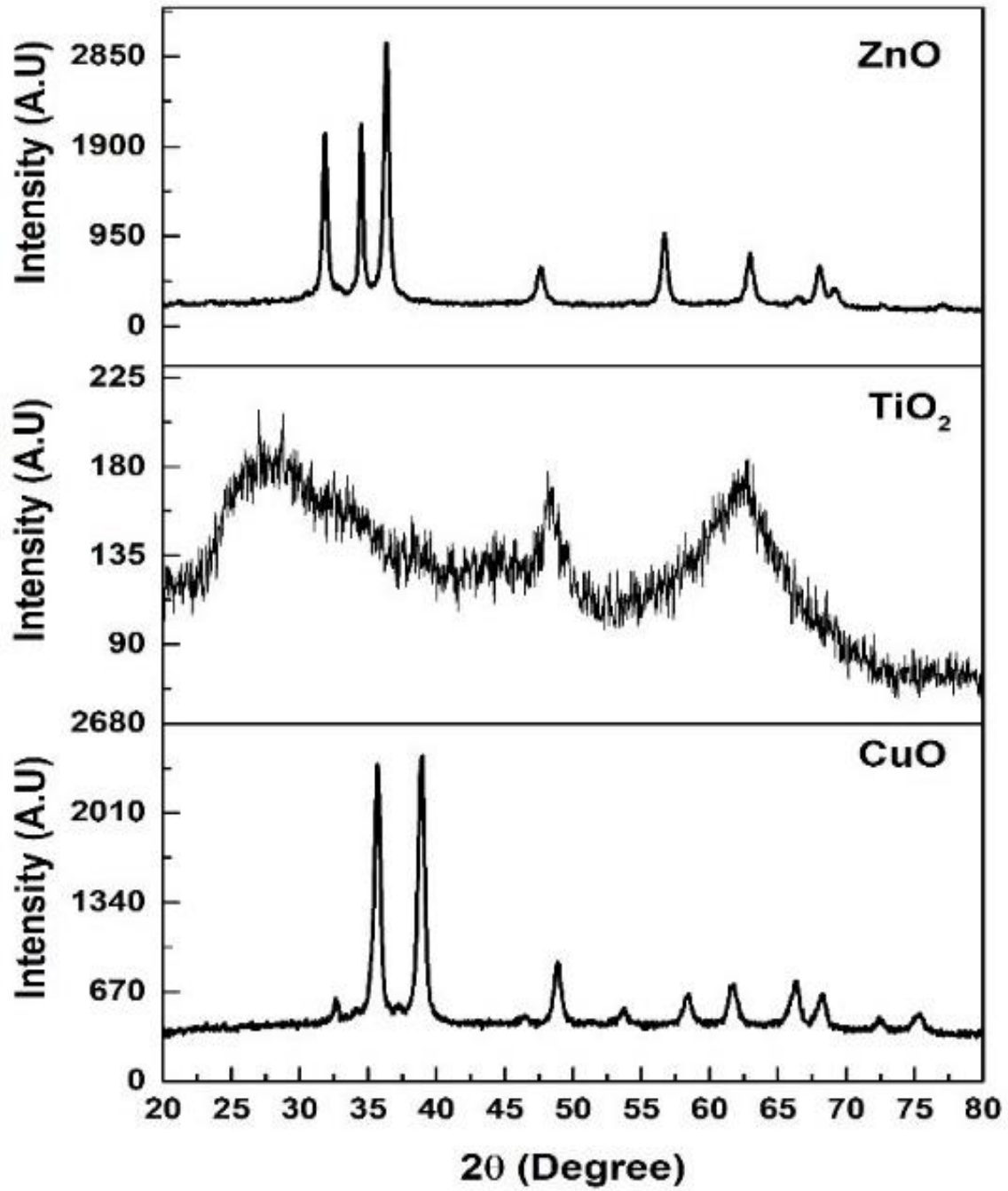
$$D = \frac{K\lambda}{\beta \cos\theta}$$

where

- **D** is the crystallite size
- **K** is a dimensionless constant and it may vary from 0.89 to 1.39 depending on the precise geometry of the scattering substances (here it was taken as 0.94)
- $\lambda$  is the wave length of X-ray (1.5406Å for Cu K $\alpha$  radiation)
- $\beta$  is full width at half maximum of the XRD peak
- $\theta$  is the diffraction angle and it is obtained from the  $2\theta$  value of the peak with maximum diffraction intensity in the XRD pattern.

The average crystallite size obtained for CuO and ZnO nanoparticles is 16.6 and 21.8 nm, respectively.

For TiO<sub>2</sub>, due to the amorphous nature of the sample, the crystallite size could not be accurately calculated from the XRD pattern.

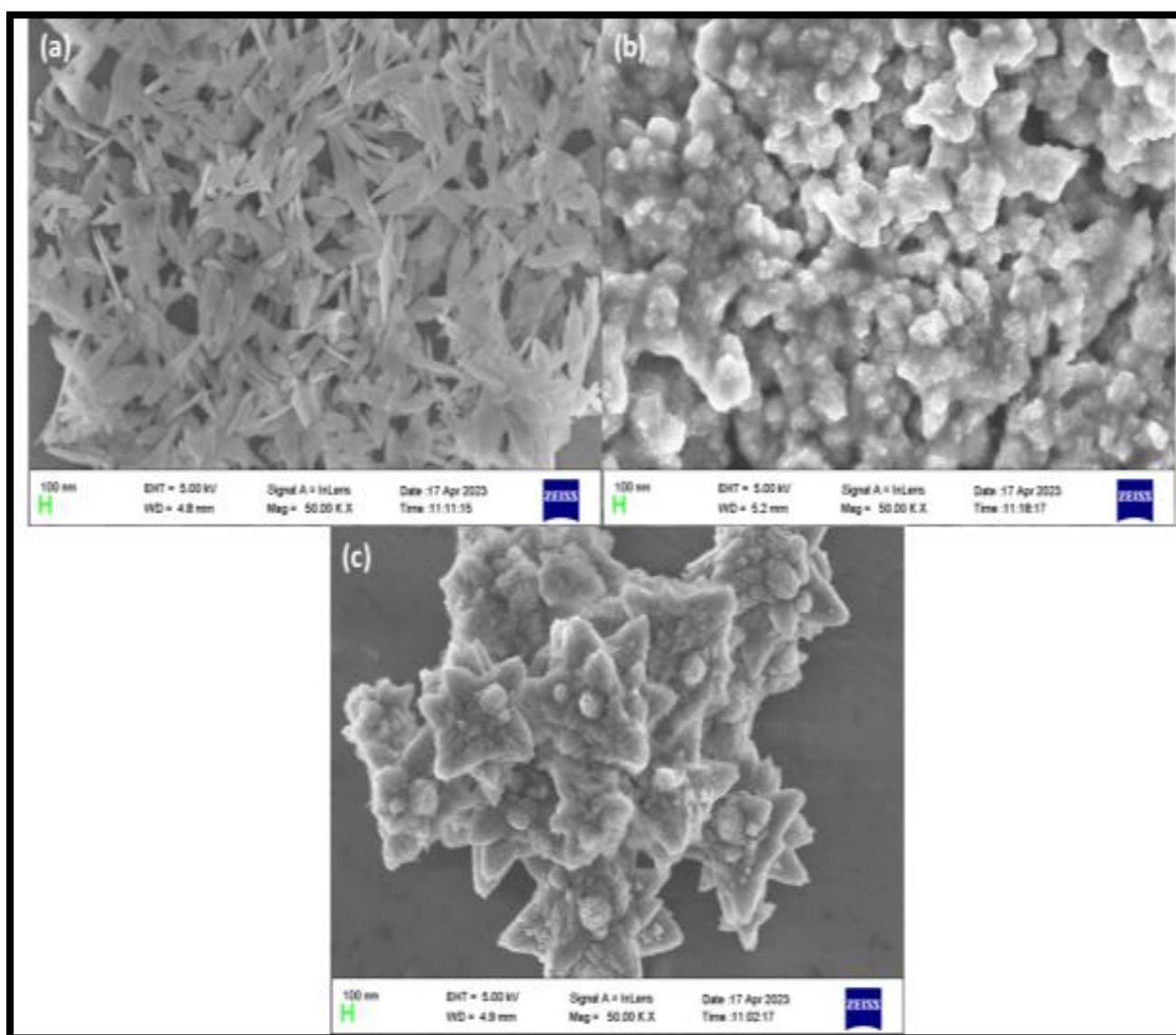


**Fig 4.1.** The XRD peak patterns of ZnO, TiO<sub>2</sub> and CuO



## 4.2. SCANNING ELECTRO MICROSCOPY (SEM)

The FESEM surface morphological images of the samples ZnO, TiO<sub>2</sub> and CuO are represented in Fig. 2 (a-c) respectively. From the figures, it is clear that the morphology looks like grains for CuO NPs, corals for TiO<sub>2</sub> NPs, and flowers for ZnO NPs

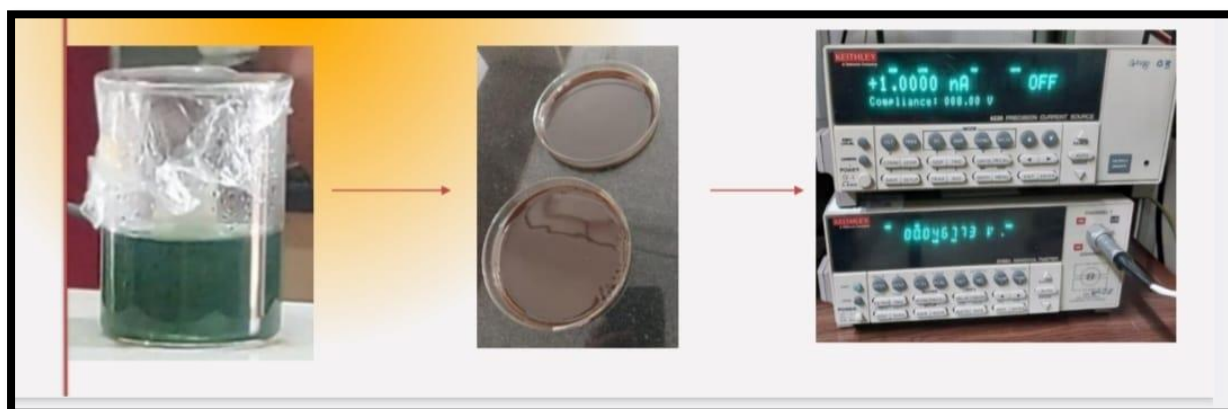


**Fig. 4.2 SEM micrographs of: (a) CuO, (b) TiO<sub>2</sub>, (c) ZnO**

### 4.3. SHEET RESISTANCE OF NR COMPOSITE FILMS

The sheet resistance values of various NR composite films are shown in the following Table. From the values, it is clear that the lowest sheet resistance was exhibited by CuO-NR films which imply that copper oxide nanoparticles considerably improve the antistatic properties of natural rubber film.

FILMS	FILLER%	SHEET RESISTANCE (Ohm/cm <sup>2</sup> )
NEAT NR	0	$8.09 \times 10^8$
CuO-NR	0.25	$5.86 \times 10^7$
ZnO-NR	0.25	$3.29 \times 10^9$
TiO <sub>2</sub> -NR	0.25	$6.35 \times 10^8$



**Fig 4.3 simple representation of methodology**

## CHAPTER 5

### CONCLUSIONS

**In this study, we synthesized and characterized three types of PEG-capped metal oxide nanofillers: copper oxide (CuO), zinc oxide (ZnO), and titanium dioxide (TiO<sub>2</sub>) using a hydrothermal method. The CuO nanoparticles exhibit a grain-like structure, TiO<sub>2</sub> nanoparticles resemble coral formations, while ZnO nanoparticles take the form of beautiful flower-like structures. The nanofillers were then incorporated into natural rubber latex during compounding. To assess the impact of these metal oxide nanofillers on the natural rubber composite, the resistivity of the resulting composite films was measured using the van der Pauw method. The results implied that copper oxide nanoparticles considerably improve the antistatic properties of natural rubber film. The findings of this study will help to engineer antistatic rubber composites with enhanced performance and suitability for diverse uses.**

**CHAPTER 6**  
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## **CHAPTER 4**

### **CONCLUSION**

- We have reported the molecular docking of five drugs (chloroquine, hydroxychloroquine, ivermectin, remdesivir and favipiravir) against SARS-CoV-2 S glycoprotein. All the above showed very good binding affinity with SARS-CoV-2 S glycoprotein, out of which ivermectin (-13.88 KCal/mol) showed the best binding affinity to SARS-CoV-2 S glycoprotein.
- We have analyzed the drug-likeness properties of all the five drugs. The analysis revealed that all the drugs are orally bioavailable and readily absorbed by the body.
- All the five drugs have got very good absorption, distribution, metabolism and excretion parameters. The drugs chloroquine, hydroxychloroquine and remdesivir are nontoxic. But ivermectin and favipiravir shows slight toxicity.

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