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ARTICLE

Enhanced Thermal and Dielectric Properties of Copper Oxide Nanoparticles Blended Polyisoprene Antibiofilm

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Abstract: In order to improve the properties of polyisoprene (natural rubber), a small quantity of copper oxide (CuO) nanoparticles was incorporated using a mechanical method. Copper oxide nanoparticles were synthesized by the simple chemical reaction between copper acetate and oxalic acid. 0.4 g of the prepared copper oxide nanoparticles was impregnated into the isoprene. The structural properties of nanoparticles confirmed the monoclinic crystal system with a = 4.685Å, b = 3.423 Å, c = 5.132 Å, $\alpha = \beta = 90^{o}$, $\gamma = 99.52^{o}$, and V = 81.17 $Å^3$, whereas the copper blended rubber exhibited a lower ordered crystalline structure with an interplanar distance of 2.1567 Å along the (0 2 0) orientation. The dislocation densities of isoprene with varied copper oxide and copper oxide were found to be $2.5932 \times 10^{22}\ m^{-2}$ and $1.12665 \times 10^{15}\ m^{-2}$, respectively. The polyisoprene matrix with a higher dislocation density confirms its hardest nature. The thermal stability increased by adding a lower quantity of copper oxide nanoparticles into the rubber matrix, reaching about 390 °C. The dielectric constant and loss of the materials were studied at various frequencies and temperatures. The dielectric properties were found to vary with the incorporation of copper oxide nanoparticles. The outstanding antibacterial actions against *Staphylococcus Aureus* bacteria were also identified.

Keywords: Natural rubber, Lattice strain, Thermal stability, Antibacterial activity.

Introduction

In the past decade, there has been a surge in research efforts focused on the development of polymer materials, which are highly organic and eco-friendly. The prospect of getting polymers from naturally occurring sources like polyisoprene, otherwise called natural rubber, has opened new possibilities for developing various everyday products, including containers, shoes, tires, rubber bands, tubes, and construction parts [1, 2]. Natural rubber polymer is essential in daily life due to its widespread use as a raw material in household, medical, and industrial products such as tubes, tires, coatings, and gloves. Recent developments in polyisoprene by metal oxide, rare earth complexes [3-5], and biomaterials have made it possible to tailor different properties of rubbers, especially their mechanical, thermal, and electrical properties in terms of strength, flexibility, and ease of processing for various engineering applications [6]. Natural rubber, with the chemical formula cis-1,4-polyisoprene, is an important organic ligand exhibiting unique coordination abilities of the double bond. Its flexibility limits its resistance to heat and ozone attack [7]. The demand for nanomaterial-metal complexes with natural rubber has attracted attention due to their thermal stability of bioinorganic models [8], such as elasticity, resilience, efficient heat dispersion, abrasion resistance, and heat resistance [9-10].

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The remarkable characteristics of copper oxide (CuO) nanoparticles, low production cost, non-toxicity, and narrow band gap have drawn a lot of attention. These distinctive characteristics make them effective materials for a wide range of applications in solar energy conversion, adsorbents, gas sensors, superconductors, supercapacitors, lithium-ion batteries, and catalysts [11-13]. Numerous reports have proven CuO nanoparticles' antibacterial efficacy against the Gram-positive and Gram-negative pathogens. Bacteria-associated infections are the most serious cases. The literature has described a variety of surface-coated polymer-based medical implants with bactericidal properties. Polyisoprene-based polymers are noted for their special activity against pathogenic bacteria [14]. However, there are a few medical reports on medical products made using natural rubber, namely production of surgical gloves, condoms, urinary catheters, and other things [15]. The biomaterials have great promise because of their mechanical qualities, high elasticity, and capacity to form films [16].

To find a way to produce isoprene-incorporated copper oxide nanoparticles with unique physical and biological properties, this paper investigates the preparation and characterization of such composites. Natural rubber latex collected from the southern part of India was incorporated with the copper oxide nanoparticles and characterized. The structural parameters were analyzed by X-ray diffraction (XRD) and EDAX analysis. To evaluate the enhancement of natural rubber performance by copper oxide addition, thermal performance was tested using thermal analysis under a nitrogen atmosphere, and dielectric properties were studied using an LCR meter. Infections due to microorganisms play a significant role in mankind and industry. This paper also discussed the antibiofilm activity against *Escherichia coli, Staphylococcus aureus,* and *Pseudomonas aeruginosa.* Overall, the activity of copper oxide nanoparticles affects the physical and biological properties of isopropene.

Materials and Methods

Materials

Analytical-grade chemicals such as copper(II) acetate monohydrate [Cu $(CH_3COO)_2$. H_2O], oxalic acid ($C_2H_2O_4$), and formic acid (CH_2O_2) were used in the synthesis process. Natural rubber, chemically known as polyisoprene latex, was collected from the southern part of India and used directly without further purification. Double-distilled water was used as the solvent throughout the preparation process.

Preparation of Copper Oxide Nanoparticles

Copper oxide nanoparticles were prepared through a simple one-step chemical reaction between copper acetate monohydrate and oxalic acid. An aqueous solution was prepared by dissolving 0.4 mol of copper acetate monohydrate in 50 mL of distilled water. Similarly, 0.4 mol of oxalic acid was dissolved in 50 mL of distilled water to form a separate solution. A chemical reaction takes place during the mixing of copper acetate and oxalic acid solution at 40 °C under magnetic stirring for 3 hours, during which a precipitate formed. The resulting precipitate was centrifuged and washed twice with distilled water to remove any unreacted precursors. The obtained copper oxalate precipitate was then dried in a hot-air oven at 100 °C for 5 hours. Finally, the dried powder was calcined in a muffle furnace at 500 °C for 2 hours to obtain copper oxide nanoparticles.

Fabrication of Heterogeneous Copper Oxide Nanoparticle-Blended Polyisoprene

Natural rubber latex, consisting primarily of carbon and hydrogen, was collected from the southern part of India. Copper oxide (CuO) nanoparticles were incorporated into the natural rubber latex by a simple mechanical method and fabricated into layered sheets using a two-roll milling machine. Initially, 500 mL of viscous natural rubber latex was mixed with 250 mL of distilled water and stirred thoroughly for about 10 minutes. Subsequently, 5 mL of formic acid and 0.4 g of CuO nanoparticles were mechanically blended with the latex mixture. The prepared latex solution was allowed to stand at room temperature for approximately 5 hours to facilitate coagulation. The coagulated heterogeneous CuO–polyisoprene mixture was then processed using a two-roll milling machine to form sheets of the desired thickness. The resulting sheets were left at room temperature for about 15 days to ensure complete removal of residual moisture.

Result and Discussion

X-Ray Diffraction Analysis

Investigation on phase, crystalline nature, and structure of the synthesized copper oxide nanoparticles and copper oxide blended polyisoprene was done using an X-ray diffractometer with a wavelength of 1.54060Å and with the TOPS software package. The XRD pattern of copper oxide nanoparticles obtained from the chemical synthesis is shown in Fig. 1.

The development of CuO, an inorganic compound, was confirmed by the XRD analysis. CuO exhibited a sharp, intense peak at 2θ = 22.812°, indicating a highly ordered crystalline structure with an interplanar distance of 3.89520 Å along the (0 2 1) orientation. The peaks of CuO nanoparticles, with d-spacing values **(**Å) of 1.93735, 1.79541, 2.14025, 1.94659, 2.32205, 2.48627, 1.76953, 1.77606, and 3.89520, correspond to the planes (1 1 2), (1 5 1), (1 3 1), (1 1 3), (1 3 0), (0 4 2), (3 1 1), (-2 0 2), and (0 2 1), according to the International Centre for Diffraction Data (ICDD) Card No. 41-0254. The highly intense peaks indicate that the prepared nanoparticles belong to the category of monoclinic crystal structure with a CuO phase, without the formation of any additional peaks due to the probable Cu_2O and $Cu(OH)_2$ impurities. Therefore, it was confirmed that the synthesized nanoparticles are in CuO phase with the lattice parameters a = 4.685Å, b = 3.423 Å, c = 5.132 Å, $\alpha = \beta = 90°$, $\gamma = 99.52°$, and V = 81.17 Å^3. These results are in close agreement with the findings reported by Nasihat *et al.* [17].

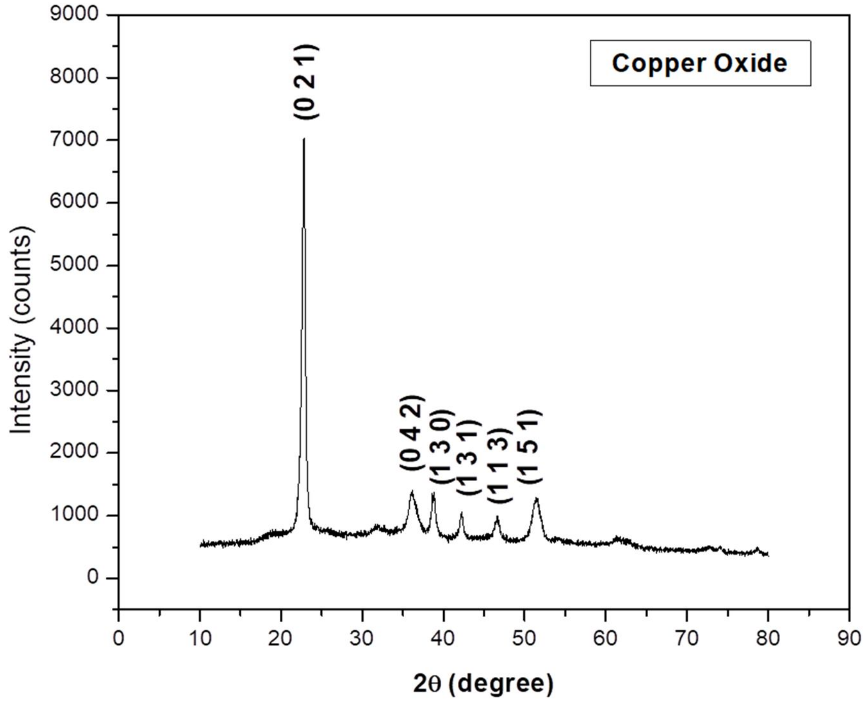

FIG. 1. XRD pattern of copper oxide nanoparticles.

The diffraction pattern of the mechanically prepared heterogeneous copper oxide nanoparticles blended with natural rubber polyisoprene is depicted in Fig. 2. Copper oxide nanoparticles blended with polyisoprene reveal that a broad peak at 2θ = 20.02109° experiences a lower ordered crystalline structure with an interplanar distance of 2.1567 Å along (0 2 0) orientation. Abraham *et al.* [18] found that the diffraction pattern of pure natural rubber displays an A-type amylose allomorph identified by a broad peak at 2θ= 17.9° and a strong peak at 25.07°. They also proved that adding nanocellulose to the natural rubber makes the shift towards a higher two theta value. This shift is due to the closely packed arrangement of copper oxide and natural rubber matrix. Therefore, the polymer matrix has no perfect crystal system, which in turn leads to the broadening of the peaks. This broadening also indicates a larger crystallite size of the polymer compared to the copper oxide nanoparticles.

Since polyisoprene is a cis-1,4 polymer, it is typically amorphous in nature. However, upon the addition of 0.4 g of copper oxide nanoparticles, a slight improvement in crystallinity was observed, as confirmed by the diffraction peak at 2θ = 20°. This result is consistent with the findings of Pazhooh *et al.* [19], who analyzed natural rubber containing a low concentration of copper nanoparticles and found that the copper peaks were less intense than those of pure natural rubber. This reduction in peak intensity can be attributed to the overlap of copper and carbon peaks that occurs when trace amounts of CuO nanoparticles are mechanically incorporated into the natural rubber matrix [20].

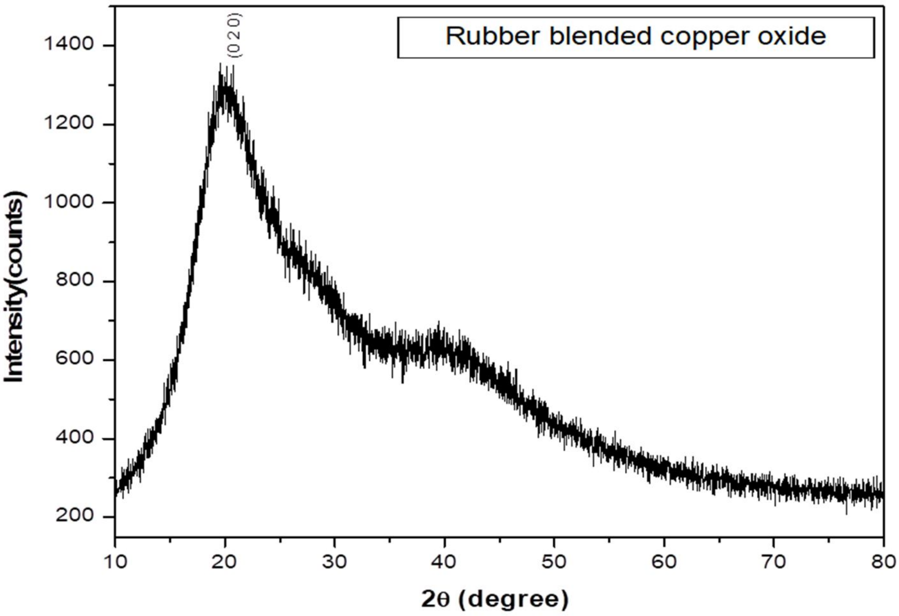

FIG. 2. XRD pattern of as-prepared rubber-blended copper oxide.

Additionally, the crystallite sizes of the chemically prepared CuO nanoparticles and the mechanically prepared rubber-blended CuO were calculated using Scherrer's equation [21] for the intense peaks:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where λ is the wavelength of the X-ray, θ is the angle of diffraction, and β is the full-width half-maximum.

The crystallite sizes obtained from the X-ray diffraction analysis of CuO and isoprene varied CuO were found to be 29.79 and 161.03 nm, respectively. Furthermore, the particle size of the CuO nanoparticles derived from diffraction analysis was correlated with the scanning electron microscopic image data shown in Fig. 3.

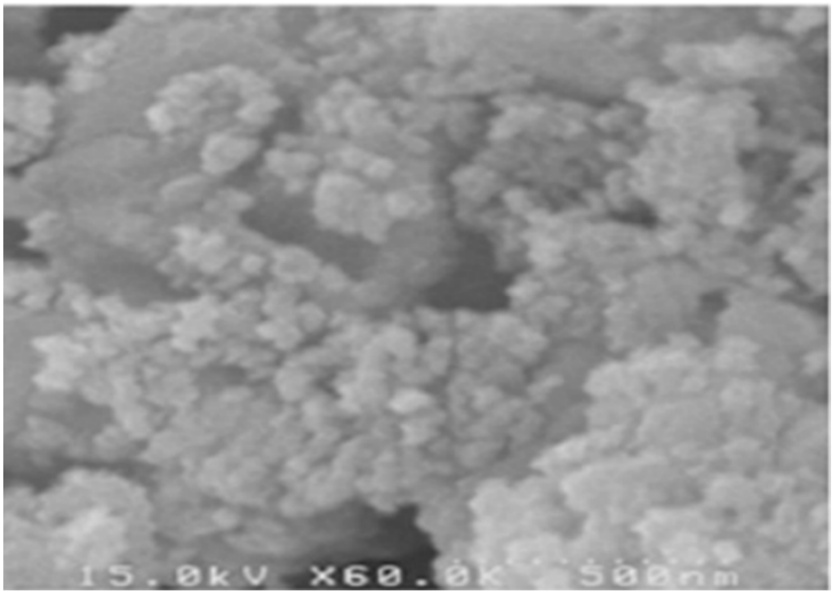

FIG. 3. SEM image of CuO Nanoparticles.

Dislocation density (δ), defined as the length of dislocation lines per unit volume of the prepared sample, was evaluated using the relation [22]:

$$\delta = \frac{1}{D^2} \qquad (2)$$

The number of particles per unit surface area (N) in the prepared samples was determined as:

$$N = \frac{d}{D^3} \qquad (3)$$

Lattice strain (ε), a measure of lattice dislocation, arises due to its crystal imperfections [23].

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad (4)$$

The dislocation density of the isoprene varied copper oxide was found to be higher (2.5932 x 10^{22} m^{-2}) compared to copper oxide (1.12665 x 10^{15} m^{-2}). The number of particles per surface area decreased for CuO nanoparticles (2.6443 x 10^{21} m^{-2}) compared to the isoprene-varied copper oxide (4.1760 x 10^{23} m^{-2}). Since dislocation is a crystallographic irregularity found inside the material, a higher dislocation density indicates greater hardness [24]; therefore, it was concluded that isoprene-varied copper oxide is harder than the copper oxide nanoparticles. Polymer mixed nanoparticles showed a higher lattice strain of 1.1318, while for the unmixed copper oxide, the lattice strain was 0.3519. Isoprene varied copper oxide with higher crystallographic irregularity and number of particles per unit surface area can be attributed to stronger covalent interactions between the carbon and hydrogen atoms in the polymer matrix. Elemental confirmation of the copper oxide nanoparticles was carried out with the EDAX analysis, as depicted in Fig. 4.

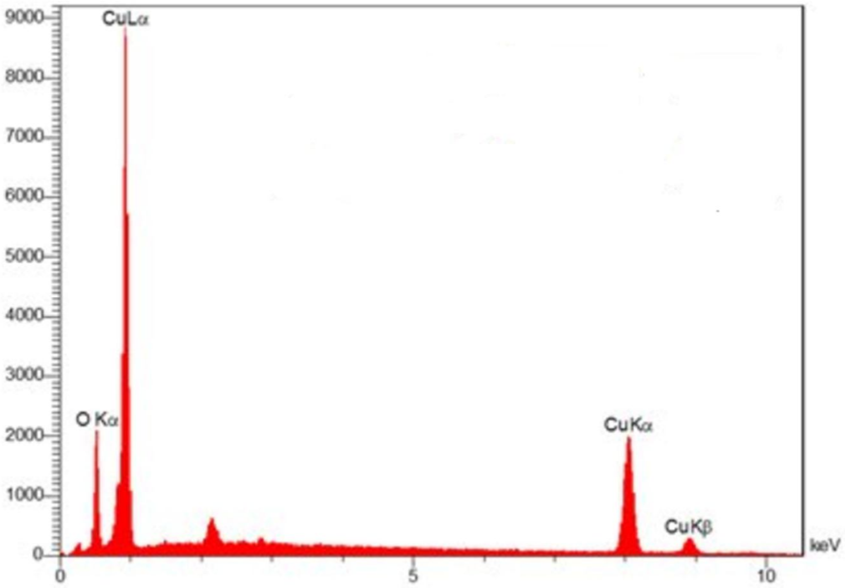

FIG. 4. EDAX spectrum of CuO nanoparticles.

From elemental analysis, it was identified that the elements copper and oxygen are present in the compound as the stoichiometric ratio of 1:1 with weight percentages of 53.55 and 46.45, respectively. The obtained atomic percentages of copper and oxygen were found to be 58.04 and 42.12, respectively.

Thermal Analysis

The thermal analysis of copper oxide nanoparticles and isoprene-varied copper oxide was performed at the temperature range of 0-1000 °C under a normal nitrogen atmosphere. The natural rubber matrix exhibits poor thermal conductivity compared to copper oxide nanoparticles. Thermogravimetric (TG) curves that determine mass loss over a temperature range for copper oxide nanoparticles and isoprene-varied copper oxide are shown in Figs. 5 and 6, respectively. It was noted that copper oxide experienced complete weight loss at 300 °C due to the liberation of oxygen molecules, whereas the rubber-blended copper oxide showed weight loss at about 392 °C. The thermal stability of isoprene molecules was reported in the temperature range of 200 –270 °C, during which both chain scission and cross-linking take place, by Bolland *et al.* [25]. In our case, due to the addition of copper oxide nanoparticles, the thermal stability of the polymer material improved. Thus, from the thermogravimetric analysis, it was confirmed that the prepared copper oxide and the isoprene-varied copper oxide retained their texture up to 300 and 395 °C, without decomposition below these temperatures.

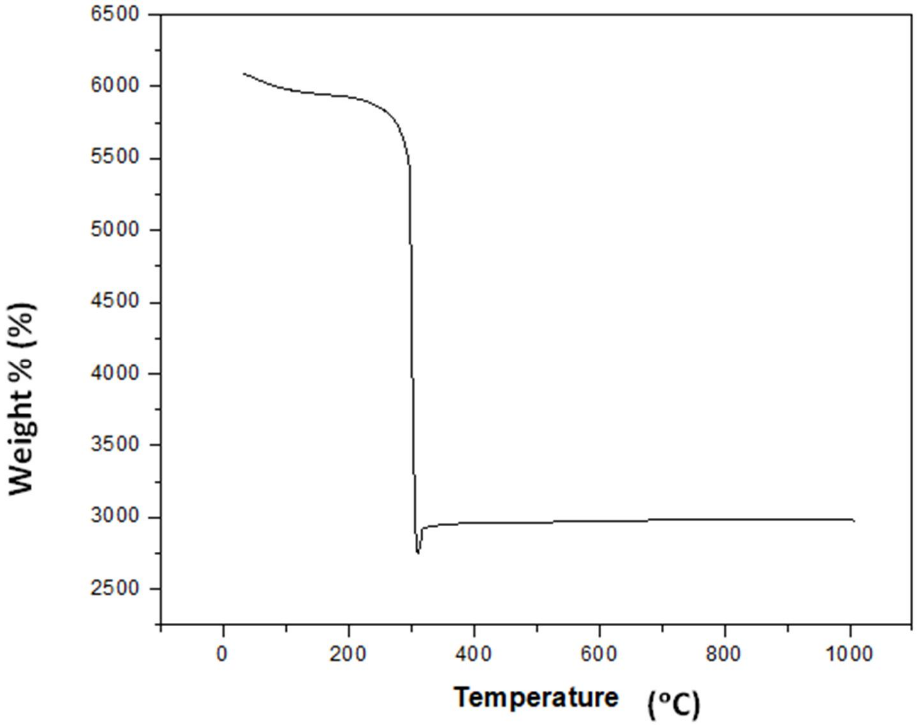

FIG. 5. TG curve for copper oxide nanoparticles.

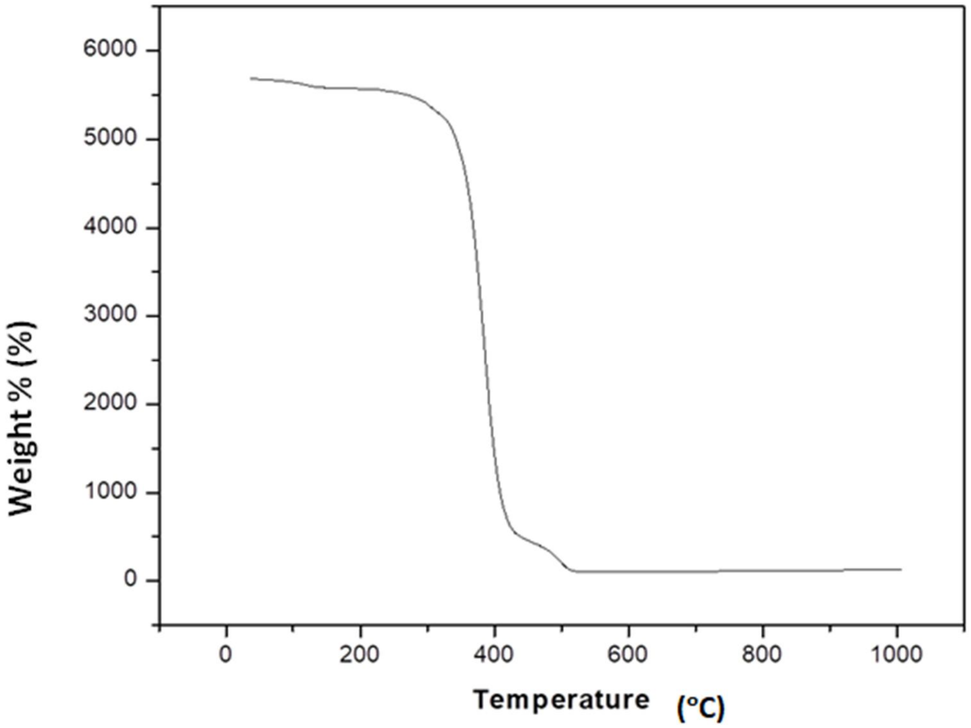

FIG. 6. TG curve of the rubber-blended copper oxide.

Differential thermal analysis (DTA) of copper oxide nanoparticles and isoprene-varied copper oxide was performed at the temperature range of 0-1000 °C under a normal nitrogen atmosphere. DTA determines the chemical degradation due to the exothermic and endothermic peaks over a temperature range. Phase transitions for copper oxide nanoparticles and isoprene-varied copper oxide are given in Figs. 7 and 8, respectively.

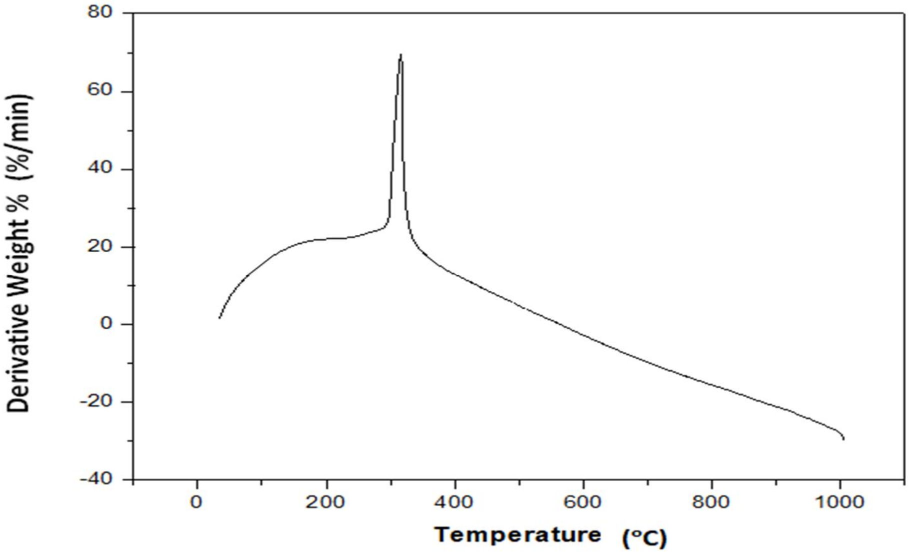

FIG. 7. DTA curve of copper oxide nanoparticles.

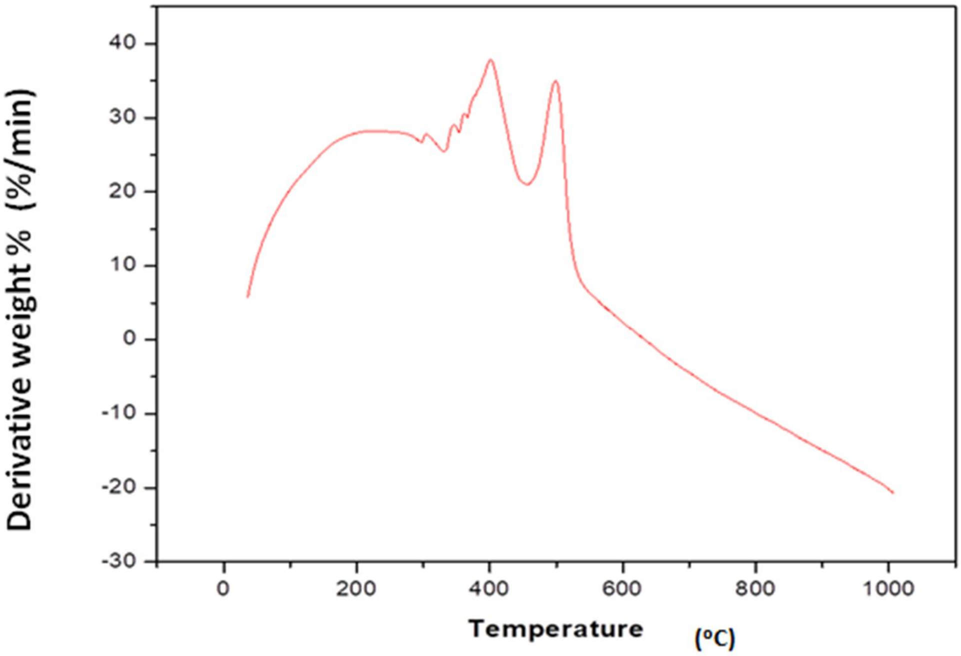

FIG. 8. DTA curve of rubber-blended copper oxide.

In the DTA curve, a sharp exothermic peak for copper oxide nanoparticles was identified at 300 °C, due to the absolute liberation of oxygen molecules. The final product left behind due to the increase in temperature is copper. From the DTA curve of rubber-blended copper oxide, it was known that the prepared material experienced two exothermic peaks: at 392 and 495 °C. These exothermic peaks are due to the liberation of H_2O and C_5H_6 molecules. There may be a phase transition from CuO to Cu at the transition temperature of 300 °C.

Dielectric Studies

The Dielectric constant of the rubber-blended copper oxide was recorded using a high-precision LCR meter at various frequencies. The dielectric constant of the prepared samples was calculated using the relation:

$$C=\frac{\varepsilon_0 A}{d} \tag{5}$$

To fetch the information about the material's ability to store energy due to the relaxation process, the dielectric constant of isoprene-varied copper oxide was measured as a function of frequency shown in Fig. 9. Various temperature values and dielectric constant of rubber-blended copper oxide are summarized in Table 1.

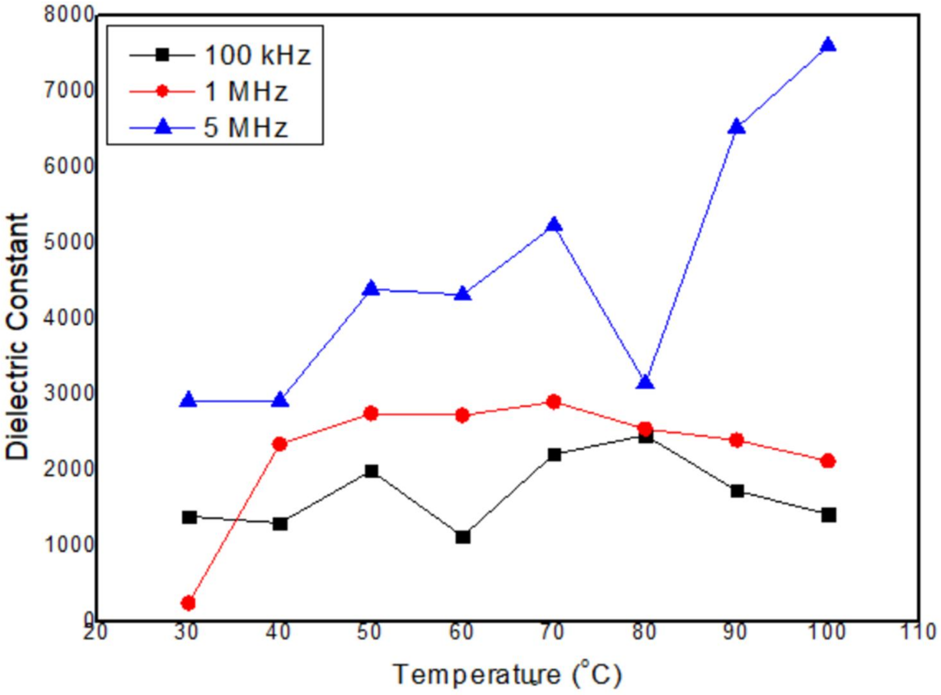

FIG. 9. Dielectric constant of rubber-blended copper oxide.

TABLE 1. Dielectric constant of rubber-blended copper oxide.

S.No.	Temperature °C	Dielectric Constant		
		100KHZ	1MHZ	5MHZ
1.	30	1384.8823	239.0045	2909.3859
2.	40	1296.1698	2338.7530	2909.9540
3.	50	1989.2723	2740.8252	4386.0697
4.	60	1120.1541	2717.8252	4311.2523
5.	70	2202.8671	2894.9051	52223.3162
6.	80	2453.6110	2539.7295	3138.5718
7.	90	1723.8111	2390.6545	6511.8203
8.	100	1412.4371	2115.3394	7586.6919

In rubber-blended copper oxide, the dielectric constant was measured at three different frequencies: 100 kHz, 1 MHz, and 5 MHz. From the dielectric studies, it was noticed that the maximum value of dielectric constant occurred at higher temperatures and 5MHz. The highest value of the dielectric constant was observed at a higher frequency of about 5 MHz. The variation in dielectric constant is attributed to the polarization mechanisms, including electronic, ionic, orientation, and space charge [26]. Ionic polarization in the copper oxide nanoparticles-varied polyisoprene arises mainly from the movement of copper, carbon, hydrogen, and oxygen ions present in the polymer matrix. Dielectric loss measured at 100 kHz and 1 MHz with varied temperature remained almost constant; therefore, the material at this particular frequency can be utilized as a filter. Orientation polarization results from the polar oxygen in the polyisoprene chain, which causes asymmetry in the cross-linked bonds. As the temperature and frequency simultaneously increase, the dipoles of Cu and O enhance the dielectric properties.

The dielectric loss curve and the corresponding dielectric parameters of the rubber-blended copper oxide are given in Fig. 10 and Table 2, respectively.

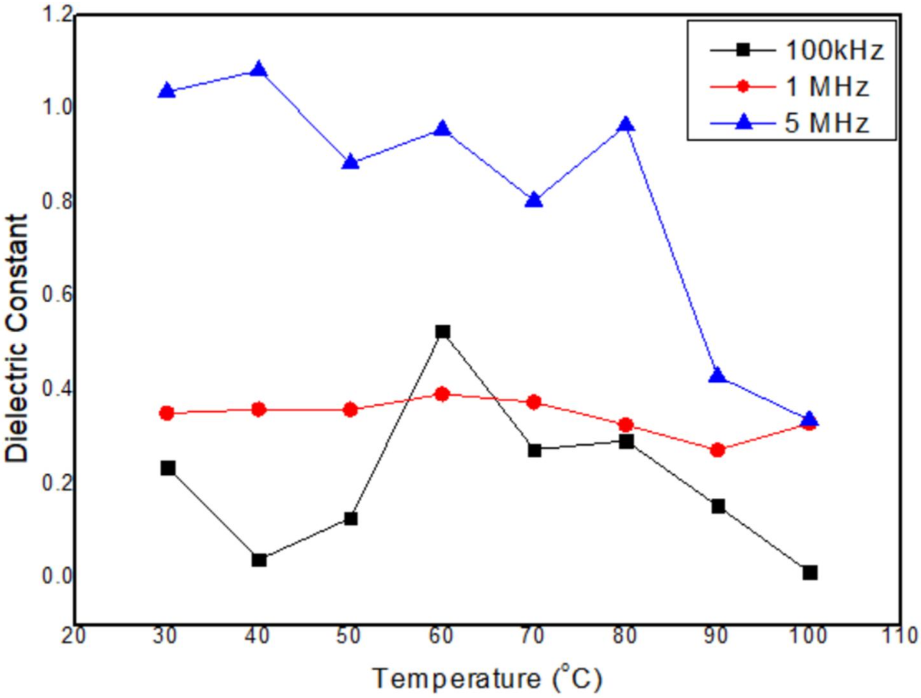

FIG. 10. Dielectric loss of rubber-blended copper oxide.

TABLE 2. Dielectric loss parameters of rubber-blended copper oxide.

S.No.	Temperature (°C)	Dielectric Loss		
		100HZ	1MHZ	5MHZ
1.	30	0.23605	0.35071	1.0359
2.	40	0.03901	0.35887	1.0814
3.	50	0.12775	0.35865	0.8837
4.	60	0.52638	0.3914	0.9562
5.	70	0.27347	0.37423	0.8044
6.	80	0.291946	0.32608	0.9641
7.	90	0.15365	0.27239	0.429
8.	100	0.01317	0.32924	0.3364

When an a.c. voltage is applied to the isoprene-varied copper oxide sheet, a fraction of the electrical energy is absorbed while the remainder is lost in the form of heat; this loss corresponds to the dielectric loss [27]. From the dielectric measurements, it was identified that at 100 kHz, fluctuations in dielectric loss occurred due to polarization effects. At 1 MHz, the dielectric loss remains nearly constant, suggesting that the material can function effectively as a filter. At 5 MHz, a decrease in dielectric loss was observed. From an application perspective, materials with a monoclinic crystal structure and higher dielectric constants at elevated temperatures and frequencies are suitable for use as frequency filters [28, 29].

Antibacterial Studies

The antibacterial activity of copper oxide nanoparticles and rubber-varied copper oxide films was evaluated against bacterial strains, including *Escherichia coli, Staphylococcus Aureus,* and *Pseudomonas aeruginosa*. The agar disc diffusion (Kirby-Bauer) method was employed, in which bacterial strains were swabbed onto the agar medium using sterile cotton. The test discs were placed on the surface of the medium, allowed to diffuse for 5 minutes, and then incubated at 37 °C for 24 hours. The antibacterial activity was assessed by measuring the diameter of the zone of inhibition (ZOI). The ZOI produced by the copper oxide nanoparticles against *Escherichia coli, Staphylococcus Aureus,* and *Pseudomonas aeruginosa* bacterial strains is shown in Fig. 11 and summarized in Table 3.

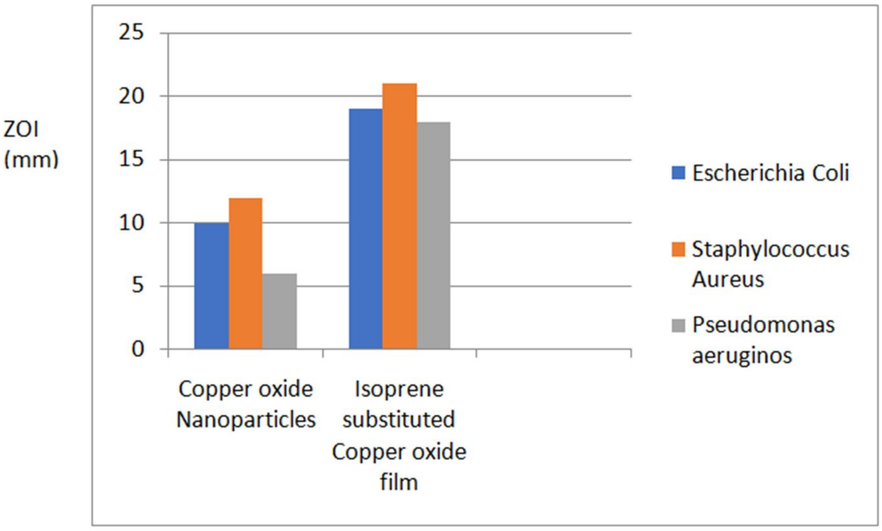

FIG. 11. Antibacterial activity chart.

TABLE 3. Diameters of the ZOI produced by the samples against the microbes.

S.No.	Microbes	Positive control levofloxacin	Zone size in diameter (mm)	
			Copper oxide nanoparticles	Isoprene-substituted copper oxide film
1.	Escherichia coli	27	10	19
2.	Staphylococcus aureus	22	12	21
3.	Pseudomonas aeruginosa	25	6	18

From the studies, it was confirmed that the copper oxide nanoparticles and isoprene-substituted copper oxide film exhibit high antibacterial activity against *Staphylococcus aureus* bacteria, with a ZOI diameter of 12 and 21 mm, respectively. In contrast, the antibacterial activity of copper oxide against *Escherichia coli* and *Pseudomonas* aeruginosa was relatively low, with ZOI values of 10 mm and 6 mm, respectively. For the isoprene-substituted copper oxide film, the antibacterial activities against *Escherichia coli* and *Pseudomonas aeruginosa* were 19 and 18 mm, respectively. According to the literature [30-32], natural rubber itself exhibits notable antibacterial properties. Therefore, the natural rubber-varied copper oxide nanoparticles film can be utilized as an anti-biofilm material to prevent infections caused by *Staphylococcus aureus* bacteria.

Conclusion

In summary, natural rubber-varied copper oxide nanoparticles with excellent thermal and dielectric properties were successfully prepared by incorporating a low content of copper oxide nanoparticles. A simple chemical method was employed to synthesize CuO nanoparticles and fabricate the natural rubber-varied copper oxide anti-biofilm. Structural variations arose due to the isoprene polymer. The crystallite sizes of copper oxide nanoparticles and isoprene-varied copper were found to be 29.7924 and 161.03515 nm, respectively, which was further confirmed by scanning electron microscopy. Compared to copper oxide nanoparticles, dislocation density, lattice strain, and the number of particles per unit surface of the polymer matrix increased widely. This is due to the higher cross-linkage between carbon and hydrogen molecules. Thermal analysis proved that the stability of copper oxide is about 300 ^{o}C, but the incorporation of copper oxide into natural rubber enhanced the thermal stability of the composite to around 395 °C. The dielectric properties were also improved, indicating potential applications of the composite film in energy storage devices. The nanoparticles and composite films were evaluated for antibacterial activity against *Escherichia coli, Staphylococcus Aureus,* and *Pseudomonas aeruginosa* bacterial strains. Copper oxide-varied natural rubber film is an excellent antibacterial agent and can be utilized as an anti-biofilm, which prevents infection against the *Staphylococcus aureus* bacteria. This study provides valuable insights for the design and fabrication of isoprene-varied copper oxide films for medical applications.

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