Dielectric Behavior of Medical PMMA Polymer Filled With Copper Nanobud Particles

Ismail Ibrahim Marhoon*[1], Amer Hameed Majeed[2], Mohammed Ali Abdulrehman[3]

[1,2,3] Materials Engineering Department / Mustansiriyah University, Baghdad, Iraq

* E-mail: isibmr@uomustansiriyah.edu.iq

Abstract

In this paper, the influence of weight fraction and frequency on dielectric features of polymethylmethacrylate filled with Copper nanobud particles has been investigated. Copper nanoparticles (Cu-NPs) have been synthesized by chemical reduction method. The resultant Copper nanoparticles were characterized by UV-Vis spectroscopy and X-ray diffraction (XRD). Results show that the Cu-NPs have bud shapes, and their average particle size obtained from the XRD study is 53.78 nm. For the resultant composite materials, the dielectric behavior of composite materials reinforced with 5%, 10%, 15%, and 20% weight fractions of Copper nanobud particles and frequency ranges of 50, 250, 10^3, 10^4, 10^5, and 10^6 Hz at 25 °C were investigated. Results reveal that the dielectric constant, dielectric loss factor and dissipation factor increased with the increase in weight fraction of Copper nanobud particles as a result of their high conductivity. The dielectric constant, dielectric loss and dissipation factor have decreased with the frequency increase. Such dielectric parametric investigations are useful to understand their application limitations not only for electronic apllications but also for feasible medical uses.

Keywords

Nano-Copper particles, nanobuds, weight fractions, frequency, dielectric properties, composite materials, PMMA

1. Introduction

Conductive polymer composites are lightweight materials and they can combine the characteristics of electrically conductive metals with polymer capability. These composites are used in various applications such as acoustic emission sensors, angular acceleration accelerometers, integrated decoupling capacitors, electronic packaging, electromagnetic frequency interference shields, and antistatic devices [1-4]. The mixture of various fillers and fibers with polymer matrices can produce different composite materials with significant dielectric properties for electronic application [5-7]. Conductive polymer composites recently received increased attention due to their interesting electrical and electronic properties. One type of these composite materials is particulate-filled polymer matrix conductive composite, which comprises a polymer matrix with a second dispersed phase that is typically either a few non-metallic elements such as carbon or metal-based fillers (micro and nano) [8-11]. The actual use of filled polymers strongly depends on the capability of the filler particles to homogeneously disperse through the matrix [12]. The interface features between the polymer matrix and filler particles also intensely influence the performance and characteristics of these conductive composites [13]. One of the main features of filled composite materials is that their dielectric properties can be extensively altered by selecting the conductivity of filled components and the size and shape of the polymeric matrix [14]. Alumina, titania, Copper oxide, lithium fluoride, nickel salt, graphite, aluminum, and lead titanate have been commonly used in to fill various polymer matrices. Thus, composites with enhanced electrical property responses have been synthesized [15-22].

The efficiency of Copper as an active agent with low toxicity is mainly relevant in the antibacterial treatment and has been documented for a long time [23, 24]. Copper is still a desirable applicant for future conducting materials due to its low cost and abundance. However, recent studies demonstrate that Copper nanoparticles are oxidized from the surface under conditions of room temperature [25, 26]. The problems of oxidation and aggregation can be avoided using numerous protecting agents, such as polymers and organic ligands [27, 28].

Polymethylmethacrylate (PMMA) can be used for medical applications since they are physiologically harmless components and they are not attacked by molds and enzymes due to its low capacity for water absorption. PMMA has a high degree of compatibility with humanoid tissue. For, instance, it can be used in the production of rigid intraocular lenses that are implanted in the eye at for cataracts treatment. PMMA polymer materials are utilized due to their rigidity and strength to produce sensors, electromagnetic frequency interference shields, medical transplant components and antistatic devices. The addition of metal powders to PMMA polymer increases its electrical and thermal conductivity [23, 24].

Dielectric studies are useful to understand physical state of biological water, proton transport, and the difference between normal and tumorous tissue. Knowledge of the dielectric properties under specified frequencies is very important for medicinal applications in diagnostic and therapeutic medicine [29, 30].

Accordingly, this study deals with the effect of the nanobud-Copper additive and the frequency of alternating current on dielectric properties of PMMA composite. The dielectric properties of PMMA polymer nanobud-Copper composite materials have been studied for practical medical applications at frequencies below 1 MHz.
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2. Materials and Methods

2.1. Chemicals and materials

L-ascorbic acid (CDH Chemicals, purity: 99%) and isonicotinylhydrazide (INH) were provided by Sandoz Corporation. On the other hand, Copper (II) sulfate pentahydrate (purity: 99%) and sodium hydroxide (purity: 97.5%) were supplied by Thomas Baker Corporation. Polyvinylpyrrolidone K30 (Ourchem Sinopharm Chemical Reagent, purity: 98%–99%) and all chemicals were used as supplementary without purification. The chemical reactions of these materials were carried out by using distilled water from our lab. Polymer components of PMMA, which comprise PMMA particles, were provided by VERACRIL Corporation. PMMA has a particle size of 75 mm, a density of 1.25g/cm^3, and purity of 90%–99%. The initiated methacrylate monomer (IMM) self-curing base resin was provided by Duracryl Plus and manufactured by Spofa Dental.

2.2. Synthesis of Bud-Shaped Cu-NPs

The Cu-NPs were synthesized by the chemical reduction method [23] using precursor Copper sulfate pentahydrate, as shown in Figure 1. In the usual procedure, the aqueous solution of $CuSO_4.5H_2O$ was prepared by dissolving 0.25 gm in 1 L deionized water and was added to a polyvinylpyrrolidone (PVP) $(C_6H_9NO)_n$ K-30 solution of 10 gm/L to provide an excellent covering agent to prevent precipitation and agglomeration of the particles. PVP has been frequently employed in the chemical synthesis of metal nanoparticles as stabilizers. Then, the solution of 20 gm/L NaOH was added drop by drop to adjust the pH of the solution to 7. The reaction mixture was continuously stirred for 60 minutes. L-Ascorbic Acid $(C_6H_8O_6)$ 0.034 M, which is an antioxidant and a mild reducing agent, was prepared by dissolving 6 g of L-ascorbic acid in 1 L deionized water and stirring at 25°C temperature for 60 minutes. The mixture was heated and maintained at 65°C for approximately 15 minutes. The ascorbic acid was added as a drop to the reaction mixture. The color of the solution changed to light yellow as shown in Figure 2a, thereby indicating the seed formation of nano-Copper. Then, the isonicotinylhydrazide $(C_6H_7N_3O)$ solution

with a concentration of 137.14 mg/L was slowly added to the solution. The color of the reaction mixture was transformed to reddish brown as shown in Figure 2b, thus signifying the formation of Copper nanobuds. Heating and stirring were maintained for 60 min to promote the growth of nanobuds. The resultant solution was then centrifuged for 15 minutes. Finally, the product was washed with ethanol and dried in air.
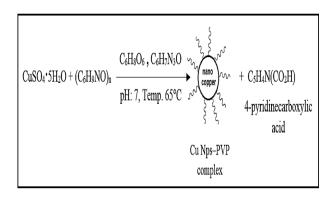

Figure 1: Illustration of synthesis of Bud-Shaped Cu-NPs. Copper sulfate reacts with PVP to form a complex that is reduced by L-ascorbic acid and isoniazid consequent in 4-pyridinecarboxylic acid $C_5H_4N(CO_2H)$ and Bud-Shaped Cu-NPs.
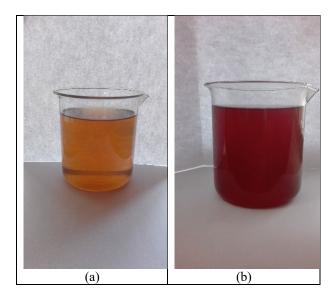

Figure 2: Different steps of Copper Nano-buds particle synthesis solution, (a) light yellow solution after addition L-ascorbic acid; (b) reddish brown solution after addition INH to the previous solution

2.3. Composite preparation

PMMA materials were used in the present work as matrix and the Copper nanobuds as a filler particle to attain a weight amount of Copper nanobuds and PMMA polymer powder by using electronic balanced with an accuracy of four digits. The weight percentages of Copper nanobuds are 0 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, and 20 wt.%. The

PMMA+Cu nanobud composite powder mixtures are combined by hand, and the homogenizing of powder mixture was tested by microscopic examination. The composite powder was then placed in a disc shape mold with a diameter of approximately 23 mm and a thickness of about 4.6 mm. The IMM is added to (PMMA+ Cu nanobuds) the composite powder mixture by 2:1 volume ratio. The mixture of different weight percentages of Cu-NPs was then compacted at a temperature of 100 °C under a pressure of 10 MPa for approximately 10 minutes to obtain coherent final disc sample shape. Then, it was cooled at 25 °C and released from the mold as shown in Figure 3. The coating unit, Cressington sputter coater (108 autos), was used for deposition of thin film gold electrode on both sides of each sample to improve the electrical properties of the sample surface.

Figure 3: Dielectric test specimens at a different weight fraction

2.4. Characterization

The following studies have characterized the Copper nanoparticles. The UV-Vis spectra were recorded on a GENESYS UV-Vis spectrophotometer. UV-Vis stands for absorption or reflectance spectroscopy in ultraviolet-visible spectral region. It uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the involved materials.
Atoms and molecules undergo electronic transitions in this region of the electromagnetic spectrum. Absorption spectroscopy is corresponding to fluorescence spectroscopy, in that fluorescence is related with transitions from the excited state to the ground state, whereas absorption processes transitions from the ground state to the excited state.

Powder X-ray diffraction (XRD) analysis was carried out on a Shimadzu labx-XRD 6000 unit with a Cu- Kα radiation at a scanning speed of 8°/min, a sampling pitch of 0.02°, and a preset time of 0.15 s. X-ray powder diffraction (XRD) stands for a speedy analytical method principally employed for phase detection of a crystalline material and can offer information on unit cell dimensions.

2.5. Measurement of composite properties

The Debye–Scherrer equation was used to estimate the size of crystallite as follows:
$$D = K \lambda / \beta \cos \theta \qquad (1)$$
Where D is the average size of Cu-NPs,
K: dimensionless shape factor 0.94 for spherical crystallites,
λ: wavelength of Cu K-α1 (1.54056 °A),
β: full width at half maximum (0.16590),
θ: diffraction angle.

The precision LCR meter device (Gwinstek LCR8000G) was used to measure the capacitive (C_P), while the dissipation factor (tan δ) and values were recorded from the electronic screen [31]. The dielectric constant (ϵ') and dielectric loss factors (ϵ'') can be obtained from these values using Equations 2 and 3, respectively. These measurement investigations for 50, 250, 10^3, 10^4, 10^5, and 10^6 Hz are at room temperature [32].
$$\epsilon' = C L / \epsilon_o A \qquad (2)$$
where ϵ' is the dielectric constant, L is the thickness of the dielectric sample in cm, A is the cross-section area in cm^2, and ϵ_o is the vacuum permittivity (8.854×10^{-14} F/cm)

$$\epsilon'' = \tan\delta \times \epsilon' \qquad (3)$$
Where ϵ'' is the dielectric loss factor, and tanδ is the dissipation factor.

3. Results and discussion

In the present research, Cu nanobuds have been prepared through a chemical reduction method using Copper sulfate pentahydrate as a precursor.

3.1 UV-Vis Spectrum of Cu Nanobuds

Figure 4 demonstrates the UV-Vis spectrum of Cu nanobuds. The characteristic plasmon absorption band for Copper nanobuds was observed at 574.8 nm indicated to undergo bathochromic with the size increase. For Cu-NPs, the surface plasmon resonance band was found to be approximately 560–570 nm [33, 34]and was indicated to undergo hypsochromic with size decrease [30]. In general, the hypsochromic and surface plasmon resonance is affected by the particle size distribution when the particles are spherical. Therefore, the band observed at 574.8 nm is suggested to be attributed to the Copper nanobuds.
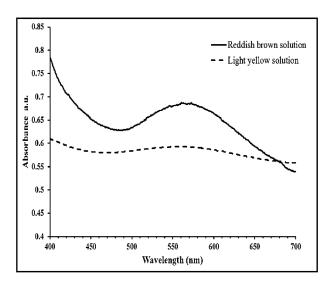
Figure 4: UV-Vis spectrum of Cu nanobuds particles synthesis solution, (a) light yellow solution after addition L-ascorbic acid; (b) reddish brown solution after addition INH to the previous solution at room temperature

3.2 XRD of Cu Nanobuds

In Figure 5, the XRD of Cu nanobuds exhibits a peak at 44.14° and 76.87°, thereby matching planes {111} and {220} of the face-centered cubic structure of Cu-NPs. However, the 63.94° {220} plane shows a trace of impurities of cuprite (Cu_2O) and these resultant peaks are agree with Smapath et al. [23]. All possible Cu nanobud peaks are allocated by using match software in comparison with those defined in the PDF No. 00-004-0836. Using Equation 1, the size of the crystallite is approximately 53.78 nm, which may indicate a high surface area and the ratio of surface area to volume of the Cu nanobuds.
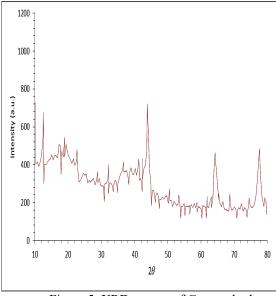

Figure 5: XRD pattern of Cu nanobuds

3.3 Frequency Effect

The effect of frequency and weight fraction on the dielectric constant ϵ', dielectric loss factor ϵ'', and dissipation factor tanδ for all samples at room temperature is shown in Figures 6–8. The results reveal that the dielectric constant ϵ', dielectric losses factor (ϵ''), and dissipation factor (tan δ) are decreased with the increase in frequencies. Such a result can be related to the permittivity of dielectric materials, which depends on the movement of charges and dipoles. Therefore, when dielectric materials are subjected to an alternation of the electric field, the field direction changes. Furthermore, with each electric field reversal direction, the dipoles attempt to reorient with a new field direction in a process that requires some finite time. These interfacial dipoles have less time to orientate into the direction of the applied electric field that changes direction with time. The intensity of the alternating electrical field is represented by the frequency range of applied voltage, where the frequency affects the dipole alignment of the dielectric material. Therefore, dielectric relaxation is revealed to include orientation polarization. Figure 7 shows a dielectric loss as a function of the frequency of Copper nanobud composites. The figure shows that when the applied field has low frequency, the dielectric loss is high and decreases with increasing frequency. This decrease is related to the reduction in the charge polarization influence when the frequency increases. These findings are in agreement with reported results in [30, 35].
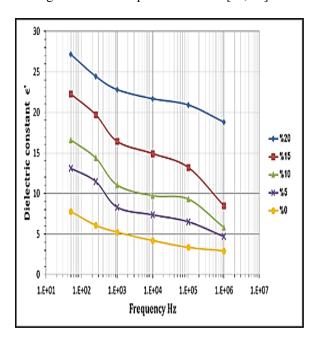

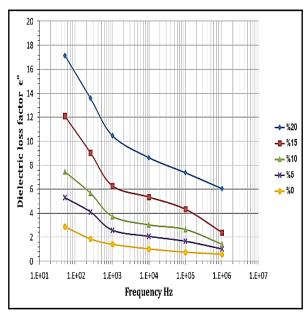Figure 6: Variation of dielectric constant (ϵ') with log frequencies

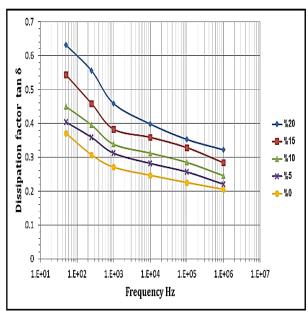Figure 7: Variation of dielectric loss factor (ϵ'') with log frequencies

Figure 8: Variation of dissipation factor (tan δ) with different frequencies.

3.4 Weight Fraction Effect

The effect of different weight fractions of Copper nanobuds was investigated in the present work. The results showed that weight fractions of Copper nanobuds affected the dielectric properties of the resultant composite materials. The dielectric properties for the samples of 0%, 5%, 10%, 15%, and 20% are shown in Figures 6–8.

Compared to the electrical conductivity of Copper which is 5.98×10^7 S/cm, the dielectric constant of PMMA is 2.8–4, and its electrical conductivity is 10^{-14}–10^{-15} S/cm. Therefore, increasing the weight fraction of Copper

nanobuds at constant frequency results in the increase in dielectric constant. The maximum value of dielectric losses and dielectric constant reached 17.14 and 27.15, respectively at 20 wt.% with 50 Hz. The increase in dielectric constant and dissipation factor values with the increase in weight fraction of Copper nanobud particles was due to the interfacial polarization. When the prepared composite material samples are placed in an electric field, the charged particles of the nanobuds interact with the applied field. Therefore, if the material is a conductor, then the free electrons transfer to the nearby positive electrode. Besides, when no electric field exists, the free electrons remain within the material. If a material is non-conducting in another term dielectric, then the electrons are only locally displaced because they are bound to individual atoms. The local displacement polarizes the material. For the low weight fraction, when the frequency is increased to 10^6 Hz, the dielectric loss is approximately constant. This condition is attributed to the mechanisms of other types of polarization that occurs at high frequencies. These findings are in agreement with reported results in [35].

4. Conclusion

The effect of weight fraction and frequency on dielectric properties of polymethylmethacrylate filled with Copper nanobud particles has been investigated in this paper. The prepared Copper nanobuds were characterized by UV-Vis spectroscopy and XRD. The results show that the Copper nanoparticles have bud shapes, and their average particle size obtained from the XRD study is 53.78 nm. The presence of UV-Vis absorption peak at 574.8 nm is attributed to the formation of Copper nanobuds. When frequency increases, the dielectric loss factor (ϵ'') and dielectric constant (ϵ') are diminished. By contrast, the dielectric loss factor and dielectric constant increase as the weight fraction increases. Besides, the dissipation factor (tan δ) has a similar behavior to that of dielectric constant and dielectric loss factors in terms of frequency and weight fraction of Copper nanobud particles. The dielectric parametric investigations are advantageous to realize their application limitations not only for electronic apllications but also for practicable medical uses. Additional future work can be done by investigating particle size dependent study on the performance of medical PMMA polymer filled with copper nanobud particles.

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