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# Effect of Sodium Ion Addition on Copper Selenide/Chitosan Film Towards Electrical and Shielding Efficiency Improvement

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**ABSTRACT**

The operation of electronic devices can be disrupted by unwanted electromagnetic signals, affecting its operation. Deploying electromagnetic shielding is a viable solution to minimize the impact of electromagnetic interference (EMI). The conventional methods of electromagnetic shielding use metal gaskets to safeguard sensitive electronic components, which have drawbacks of cost and weight. Hence, electromagnetic shielding polymer can be an alternative to replace metal gaskets. This work investigates the effect of sodium ion (Na) addition to copper selenide/chitosan (CuSe/Ch) film for electromagnetic shielding applications. The shielding polymers were produced using solution casting methods, while the CuSe was synthesized using the chemical coprecipitation method. Impedance spectroscopy and two port waveguide methods were used to characterize the prepared polymer's electrical properties and shielding efficiency. The results indicate that Na incorporation in the CuSe/Ch film resulted in a 47 % decrease in bulk resistivity and increased DC conductivity from $6.07 \times 10^{-6}$ S/cm to $3.69 \times 10^{-5}$ S/cm. The AC conductivity of films containing Na demonstrates a similar level of conductivity at lower frequencies, followed by a sharp increase at higher frequencies, indicating a more substantial influence of Na at higher frequencies. Higher absorption shielding efficiency ($SE_A$) and lower reflection shielding efficiency ($SE_R$) were achieved by introducing Na into the CuSe chitosan film. The Na/CuSe/Ch film shows higher total shielding efficiency at an average of 20 dB, equivalent to 99 % of the EM power shield.

**Keywords:** *Electromagnetic interference, EMI shielding, conducting polymer, impedance spectroscopy*

## 1. INTRODUCTION

Electromagnetic interference (EMI) is an unwanted signal that can interfere with the regular operation of electronic equipment and lead to malfunctions. EMI shielding can be employed to help reduce the interference effects. EMI shielding was made of materials, traditionally metal, that protect sensitive electronic parts based on reflection, absorption, and multiple reflections of incident EM waves [1]. Metal as EMI shielding has weight, corrosion, and rigidity disadvantages. Various shielding materials, including composites, polymeric matrixes, and textiles, have been studied to overcome the disadvantages [2-3].

Shielding polymer offers an advantage over conventional methods, such as ease of fabrication, lightweight, flexible, and corrosion resistance [4-5]. The polymer can be made into an EMI shielding material by tailoring its electrical parameters. This includes adjusting the polymer conductivity, permittivity, and permeability. The most common technique to modify a polymer's electrical parameter was mixing conductive fillers such as metal powders, carbon-based material or a mixture into the polymeric matrix [6]. However, higher loading can affect the polymer's mechanical properties [7]. Modifying a polymer's electrical parameter can also be made intrinsically by changing the polymer matrix [8].

This work examined the effect of the sodium ion (Na) addition on the CuSe/Ch polymer film on its shielding efficiency. Na has gained interest in various energy storage applications, such as capacitors and batteries, due to its abundance and environmentally friendly [9]. Adding Na to the CuSe/Ch film will produce an ion-electron polymer structure, increasing its conductivity while minimizing CuSe loading. The electrical and shielding effects between the two films will be compared. The effect of electrons from the CuSe/Ch film and ion-electrons from the Na/CuSe/Ch film will be studied. The results show that adding Na improves the overall electrical properties by $2 \times 10^{-5}$ S/cm and increases total shielding efficiency by 1 %.

## 2. METHODOLOGY

Chitosan with medium molecular weight (75–85% deacetylation, Mw 190,000–310,000 Da) and acetic acid (99% purity) were purchased from Sigma-Aldrich (Burlington, USA). Na standard solution (1000 mg/L) was purchased from Fischer Scientific (Hampton, New Hampshire, USA). All chemical reagents employed during chemical coprecipitation to make the CuSe nanoparticles powder, such as $CuCl_2.2H_2O$ (Fisher Scientific), Se metal powder (HmbG Chemicals), and NaOH (Fisher Scientific), were of analytical grade and were used without further purification.

The CuSe was synthesized using the chemical coprecipitation method [10]. Black precipitates were formed by completely dissolving Se metal powder into 12 Mol/l NaOH solution with $Cu^{2+}$ solution obtained from 0.03 mol $CuCl_2.2H_2O$ and stirred for 24 h to ensure a complete reaction. The black precipitates were centrifuged and washed with distilled water to remove the unreacted, unabsorbed, or excess selenium ions. The precipitate powder was dried at 70 °C for 24 h.

The CuSe/Ch film was prepared by dissolving 1 g of medium molecular chitosan flakes into 25 ml of 1% acetic acid solution and stirring until fully dissolved. CuSe (20 wt%) was dispersed into deionized water before being sonicated for 2 h. The prepared chitosan solution was then mixed with dispersed CuSe, and the solution was stirred to obtain a homogeneous solution before 1 wt% of glycerol was added. The final solution was directly cast and dried at 60 ˚C for 24 h. For the Na/CuSe/Ch film, 1 g of chitosan was dissolved into 25 ml of 100 mg/l of Na solution with 1% acetic acid. The 100 mg/l of Na solution was diluted from the standard solution in deionized water using the standard formula of $M_1V_1=M_2V_2$. The rest of the Na/CuSe/Ch film procedure follows the previously mentioned procedure.

The impedance spectroscopy was conducted using an electrochemical workstation (ZIVE SP1, WonA Tech) at frequencies of 0.1 to 100 MHz to obtain the complex impedance. The sample was placed in between parallel plate electrodes of 1 cm diameter. The Nyquist plot was obtained from the measured complex impedance. The conductivity value was calculated using Eq (1), where the $R_B$ value was obtained from the Nyquist plot, and t is the thickness of the film, while A is the area of the electrode.

$$\sigma = \frac{t}{R_B A} \quad (1)$$

The Tanδ of a material indicates the inefficiency of the material in storing energy; a lower dissipation factor indicates a more efficient insulator system. The Tanδ of the sample can be calculated using Eq (2).

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

The shielding efficiency was measured using the two-port waveguide technique. The measurement was done using Vector Network Analyzer (8720B Agilent Technology) at frequencies between 8 and 12 GHz. Complete two-port calibration was done before the measurement to eliminate system error and the effect of the thin supporting film used to ensure the sample was flat during measurement. The reflection ($SE_R$), absorption ($SE_A$), and the total value of the shielding efficiency were calculated from the measured S-parameter. The $SE_R$ and $SE_A$ as a function of the transmission and reflection were given by Eq (3) to (5) [11]. R is the reflectance, and T is the transmission associated with the S-parameter. If $SE_A$ is higher than 10dB, multiple reflections ($SE_M$) become very small and can be neglected.

$$SE_R(dB)=10\log_{10}\left(\frac{1}{1\text{-}R}\right) \quad (3)$$

$$SE_A(dB)=10\log_{10}\left(\frac{1\text{-}R}{T}\right) \quad (4)$$

$$SE_T(dB)=SE_R+SE_A \quad (5)$$

## 3. RESULTS AND DISCUSSIONS

### 3.1. Electrical Properties

Nyquist plot for CuSe/Ch and Na/CuSe/Ch is shown in Figure 1. It is observed that there was a semicircle in the higher frequency region with the spike at the lower frequency. The CuSe/Ch film shows a more apparent semicircle, while the Na/CuSe/Ch shows a less apparent of smaller semicircle. The more apparent semicircle in CuSe/Ch film was due to the bulk effect that reflects a parallel combination between bulk resistance ($R_B$) and capacitance of the film. The absence of the apparent semicircle in the film with Na/CuSe/Ch film suggests the film was more conductive, with a lower capacitance component. From the intercept of the semicircle and the spike, the bulk resistance ($R_B$) value can be obtained and shown in Table 1.

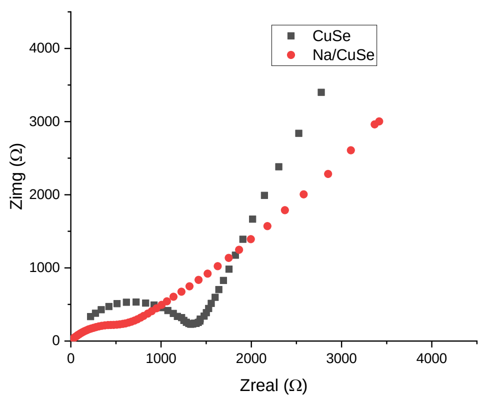


**Figure 1.** Nyquist plot for the CuSe and Na/CuSe in chitosan film.

Table 1 shows the bulk resistance and conductivity value of the films. Adding Na into the CuSe film causes a drop in the bulk resistance value from 896.96 Ω to 442.18 Ω. This subsequently will increase the conductivity of the film. The film's conductivity increased from 6.07 × $10^{-6}$ for the CuSe/Ch film to 2.68×$10^{-5}$ S/cm with the addition of the Na ions. Higher conductivity of the polymer will contribute to producing higher $SE_R$.

**Table 1** Thickness, bulk resistance, and DC conductivity of the CuSe and Na/CuSe in chitosan film

| Film | Thickness (mm) | Bulk Resistance, $R_B$ (Ω) | DC Conductivity (S/cm) |
|---|---|---|---|
| CuSe/Ch | 0.171 | 896.96 | $6.07 \times 10^{-6}$ |
| Na/CuSe/Ch | 0.152 | 442.18 | $3.69 \times 10^{-5}$ |

The AC conductivity of the films was calculated and shown in Figure2. The CuSe/Ch film shows an almost constant value throughout the measured frequency, with an average value of $9.37 \times 10^{-7}$ S/cm recorded. Adding Na into the CuSe/Ch film increased the AC conductivity and was more noticeable at higher frequencies (>1000 Hz). This indicates that the Na ions are activated at a higher frequency. The rises in the AC conductivity at higher frequencies can also be associated with rises in the value of dielectric loss (ε") due to the presence of the freer carrier (Na) in the film. The AC conductivity is a function of ε" and was given by $\sigma_{ac}=\omega c_o \varepsilon''$, where the ε" is associated with conduction current.

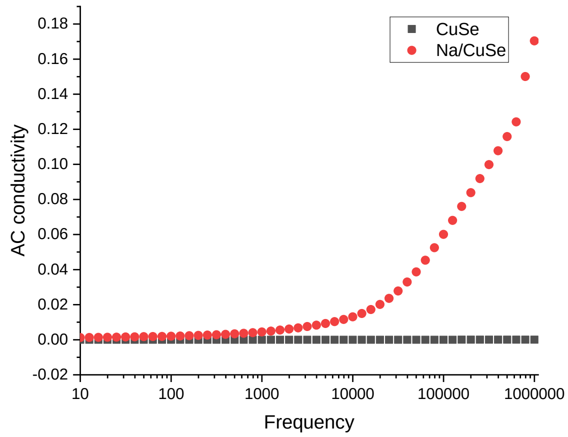


**Figure 2.** AC conductivity of the CuSe and Na/CuSe chitosan film.

The variation of Tanδ as a function of frequency for the two films is shown in Figure 3. The Na/CuSe/Ch film produces a higher Tanδ value than the CuSe/Ch film, with both films producing an almost similar pattern. The higher value of Tanδ in the Na/CuSe/Ch film corresponds to the conductivity where the Tanδ can also be given as Tanδ= σ/2πfε′. As Na/CuSe/Ch film recorded higher conductivity, it will translate to a higher Tanδ value. The Tanδ max was not observed within the measurement frequency range in both films. However, it can be estimated from the graph that the maximum peak shifted towards the lower frequency side with the addition of Na ions into the film. The shift of the maximum peaks towards lower frequency suggests a longer relaxation time. A higher Tanδ value can contribute to higher $SE_A$ as the polymer with higher Tanδ has a higher ability to store energy.

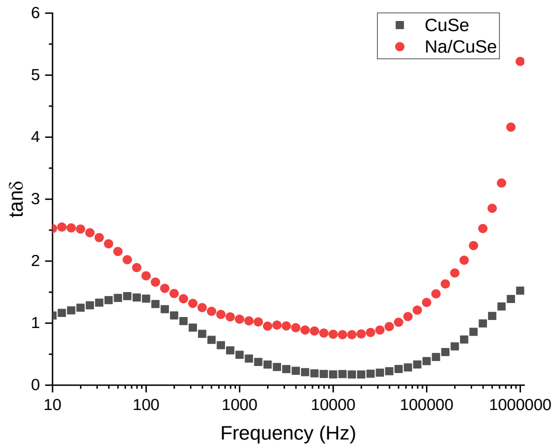


**Figure 3.** The Tanδ of CuSe and Na/CuSe in chitosan film.

### 3.2. Shielding Efficiency

Figure 4 shows the $SE_A$ as a function of frequency for the two films. The Na/CuSe/Ch film shows higher $SE_A$ than the CuSe/Ch film. The $SE_A$ for Na/CuSe/Ch film recorded an average of 16.4 dB $SE_A$, while CuSe/Ch film produced an average of 13.82 dB. The higher $SE_A$ for Na/CuSe/Ch film can be attributed to the higher conductivity in the film. When the EM wave passes through any shielding material, some of the energy will be absorbed, causing decreases in amplitude. This absorption loss occurs due to the interaction between the dipoles in the shielding material and the EM waves. This interaction produces induced current and causes ohmic loss in the shielding material. Eq (7) gives the $SE_A$ as a material properties function. It indicates that the $SE_A$ is a function of the material thickness (t) and conductivity (σ). If the $SE_A$ is higher than 10dB, $SE_M$ can be neglected.

$$SE_A=-8.68t\left(\sigma\ \frac{\omega\mu r}{2}\right)^{1/2} \quad (7)$$

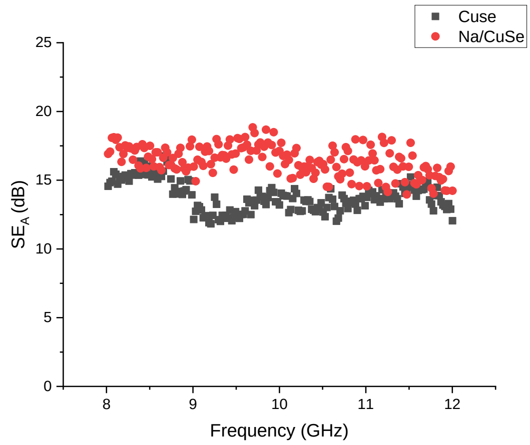


**Figure 4.** The absorption shielding efficiency of the CuSe and Na/CuSe in chitosan film.

The $SE_R$ value of the CuSe/Ch and Na/CuSe/Ch film was observed in Figure 5. $SE_R$ can be related to the film's electrical properties by Eq (9), where σ is conductivity and $\mu_r$ is the permeability. From the equation, shielding material with higher conductivity will produce higher $SE_R$. The addition of Na ions increased the conductivity of the film. Based on Eq (9), the Na/CuSe/Ch film is supposed to show a higher $SE_R$ than the CuSe/Ch film. However, the CuSe/Ch film produces a higher $SE_R$ value than the Na/CuSe/Ch film in this work. The Na/CuSe/Ch polymer recorded an average of 3.12 dB of $SE_R$, while the CuSe/Ch polymer produced 4.9 dB.

$$SE_R = -10\log_{10}\left(\frac{\sigma}{16\omega_c\varepsilon_o\mu_r}\right) \quad (9)$$

Apart from conductivity, $SE_R$ is also a function of impedance mismatch between the propagating wave and the film surface. The CuSe/Ch film might produce higher reflection due to higher surface impedance than the Na/CuSe chitosan film. Adding Na into the chitosan will cause the Na ion to attach itself to the OH- group of the chitosan monomer. This mainly happens in the bulk of the material, which improves the bulk resistance but not precisely the surface impedance of the film.

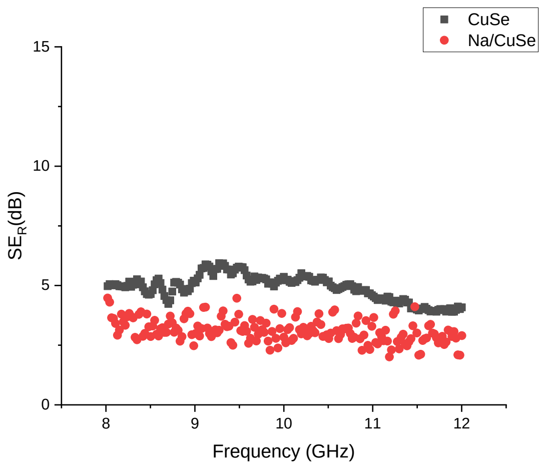


**Figure 5.** The reflection shielding efficiency of the CuSe and Na/CuSe in chitosan film.

The total shielding efficiency as a function of the frequency of the two films is shown in Figure 6. The average recorded $SE_T$ value for CuSe/Ch film was 18.77 dB. In contrast, Na/CuSe/Ch film has a higher average value at 20 dB. The $SE_T$ value recorded equals 98 % and 99 % power shield for CuSe/Ch film and Na/CuSe/Ch film, respectively. The addition of Na ion improved the total shielding efficiency by 1%. The $SE_A$ value for both films is also higher than the measured $SE_R$ value, indicating absorption as the primary mechanism in shielding for both polymers.

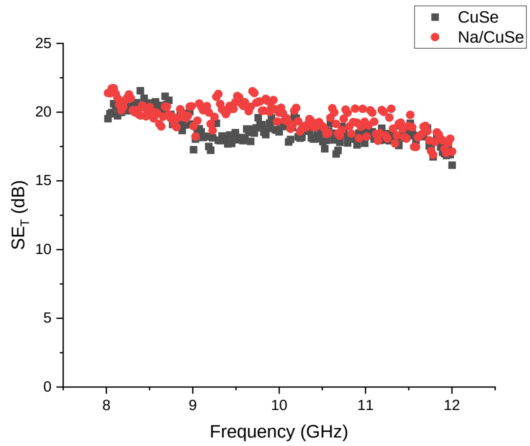


**Figure 6.** The total shielding efficiency of CuSe and Na/CuSe in chitosan film

## 4. CONCLUSION

The addition of Na ions improves the electrical parameter of the Na/CuSe/Ch film. Adding Na into the CuSe/Ch film reduced the $R_B$ by 454.78 Ω and increased the DC conductivity by 30.83 × $10^{-6}$ S/cm. The AC conductivity of the Na/CuSe/Ch film shows exponential increment at a frequency above 1 MHz, indicating that the Na was activated at a higher frequency. The overall Tanδ value of the Na/CuSe/Ch shows a higher value, with $Tan\delta_{max}$ being outside the measurement range for both films. The improvement in the electrical parameter increased the film $SE_A$ but decreased the $SE_R$ value. The $SE_T$ of the two films was comparable, where Na/CuSe/Ch produced 20 dB shielding equivalent to 99.95 % EM energy shield.

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