Conduction mechanism and dielectric properties of pure and composite resorcinol formaldehyde aerogels doped with silver

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Abstract. Pure and composite Resorcinol–Formaldehyde (RF) aerogel samples were prepared by sol-gel process using KOH as a catalyst and doped with silver nanoparticles at different concentrations (1.2×10⁻⁴, 2.4×10⁻⁴, 3.6×10⁻⁴, and 4.8×10⁻⁴ wt.% at catalyst ratio 0.024 wt.%). DC electrical conductivity \( \sigma_{dc} \), AC electrical conductivity \( \sigma' \), and the dielectric properties of the prepared samples have been measured at different frequencies and temperatures. The results show that \( \sigma' \) increases with increasing frequency. The values of \( \sigma' \) range from ~10⁻⁴ Ω⁻¹m⁻¹ to around unity at room temperature. The analysis of the results of \( \sigma'(\omega,T) \) reveals that the large overlapping polaron (OLP) is the most favorable mechanism to describe the conduction mechanism in these samples. The behavior of the dielectric constant with the frequency of these samples is normal, where it decreases with increasing frequency, while the behavior of dielectric loss tangent tanδ exhibits a peaking behavior at relatively higher temperature.

Keywords: RF aerogels, porous materials, composite materials, conduction mechanism, dielectric constant.

1. Introduction
Composites are two or more materials combined on a macroscopic scale to form a useful material, and exhibit the best qualities of their constituents and often some qualities that neither constituent possesses. The synthesis of nano scale composite materials has attracted a great deal of attention due to their physical and chemical properties which are suitable for a wide range of industrial applications [1]. The properties of these materials depend strongly on the size, distribution and specific concentration of metal clusters within the host porous matrix as well as the properties of the support [2, 3]. Because of their unique properties such as low density, high surface area continuous porosity and high cross linking structure, aerogels are widely used as thermal insulation, nuclear particle detection, light-guides, electronic device [4, 5], super-capacitors [6], battery electrodes [7], adsorbents for gas separation [8, 9], catalysts supports [10, 11], electrode material for double layer capacitors [12, 13], and energy storage device [14]. The objective of this work is to investigate the dielectric properties and the conduction mechanism of a novel composite material, made of RF aerogel doped with silver nanoparticles at different concentrations.

2. Material and methods
Pure aerogel was prepared by adding resorcinol (C₆H₄(OH)₂) with formaldehyde (HCHO) with molar ration 1:2. Potassium hydroxide (KOH) was used as a catalyst (0.024 wt. %). After stirring the solution for one hour by magnetic stirrer, the solution was poured into glass tube which sealed by high temperature flame. Then the samples were stored in an oven at 90°C for a week. Then the samples were placed in acetone bath. Finally, the samples were supercritically dried using supercritical dryer, type-Quorum Technologies E3100 Series. A silver nano particles were prepared by dissolving AgNO₃ in the
water under the action of NaOH as a catalyst. Then a dark brown precipitate of Ag₂O was formed immediately. Ag₂O precipitate was dispersed in a sodium dodecyle sulfate solution to form a colloidal. Finally the colloidal of Ag₂O was reacted with a solution of formaldehyde to produce a silver nano particle colloidal. After preparing nano-silver colloidal, it has been added to pure aerogel during the preparation process of RF aerogel at different Ag concentrations (1.2×10⁻⁴, 2.4×10⁻⁴, 3.6×10⁻⁴ and 4.8×10⁻⁴ wt. %). The samples were poured in tube glass and left in an oven for one week at 90°C then they were cut in a disk shape using a diamond saw, and place in the acetone path before the final step, the supercritical drying. After preparing the sample, they have been characterized using FTIR spectroscopy, UV-Vis spectroscopy, and scanning electron microscopy. The electrical conductivity, σ dc, was measured at different temperature using an electrometer (Keithley model 617). The frequency and temperature dependence of dielectric constant, ε ′, AC electrical conductivity, σ ′, and dielectric loss tangent, tanδ, was determined using an an RLC meter (type HIOKI 3532-50).

3. Results and Discussions

DC and AC electrical conductivities were measured for pure and composite RF aerogels doped with different concentration of silver (1.2×10⁻⁴, 2.4×10⁻⁴, 3.6×10⁻⁴ and 4.8×10⁻⁴ wt. %). The measurements were carried out in the temperature range from room temperature ~25°C up to 200°C and cover the frequency range from 100 Hz to 5MHz for AC electrical conductivity. The frequency dependence of the measured AC conductivity, σ ′, at different selected temperatures is shown in figure 1. It is shown that σ ′ increases with increasing frequency. Also the values of AC electrical conductivity at room temperature increase with increase of Ag content. The values of these samples vary from 3×10⁻⁸ to 10 Ω⁻¹m⁻¹. The behavior of σ ′ for the investigated samples can be expressed by the relation [15]

\[ \sigma_{ac}(\omega) = \sigma'(\omega) - \sigma_{dc} = A \omega^s, \]

where, A is a constant depending on temperature, \( \omega \) is the angular frequency (=2\pif), \( \sigma_{ac}(\omega)=A\omega^s \) is the pure AC conductivity arises due to the bound charges [16], and the frequency exponent, s, can be determined by the relation; \( s = (d\ln(\sigma_{ac}(\omega)))/d(\ln(\omega)) \).

Figure 2 shows the variation of DC conductivity (σ dc) with the temperature as 10³/T, for pure and composite RF aerogel doped with silver at different concentration. The results show that the DC electrical conductivity of aerogel samples decreases with increase of temperature till a certain temperature after which, the conductivity increases with further increase of temperature. This means that the DC electrical conductivity behaves as semiconductor at relatively low temperature region and exhibit a metallic behavior at relatively high temperature region. The values of DC electrical conductivity vary from 2×10⁻⁸ to 10⁻⁵ Ω⁻¹m⁻¹ which are less than AC conductivity in the order 10⁻³. In order to explain the behavior of \( \sigma_{ac}(\omega) \), with both temperature and frequency, different theoretical models have been proposed to correlate the conduction mechanism of AC conductivity with s(T) behavior [16-17]. The classical barrier model for single electron hopping between two localized states over a potential barrier separating the sites as well as the correlated barrier hopping (CBH) model suggested that s should decrease with increasing the temperature. The quantum mechanical tunneling (QMT) model implies that s is temperature independent. In the case of small polaron (SP) model, s should increase with increasing the temperature. Finally, the large overlapping polaron (OLP) model suggested that s should decrease with increasing the temperature up to a certain temperature, after that s increases with further increase of the temperature [15]. Figure 3 shows the behavior of the exponent, s, with the temperature for all samples. It should note that the behavior of s(T) exhibits a minimum value for all samples with the temperature. Therefore, the results shown in figure 3 suggest that the large overlapping polaron (OLP) conduction mechanism is the most favorable mechanism to describe the conduction mechanism for the samples under investigation.

The dielectric constant ε ′ and loss tangent tanδ were measured in the temperature range from room temperature ~25°C up to 200°C and cover the frequency range from 100 Hz to 5MHz. The Variation of dielectric constant ε ′ with the frequency at various temperatures for some RF aerogel doped with silver at different concentrations are shown in figure 4. It is shown the behavior of the dielectric constant is normal, i.e., ε ′ decreases with increasing frequency. The same behavior was observed for other polymers [18]. The dispersion in both σ ′ and ε ′ reveals a strong correlation between the AC electrical conductivity and the dielectric constant in these materials.
Figure 1. The frequency dependence of AC conductivity $\sigma'$ at different temperatures for RF aerogel doped with silver at different concentrations.

Figure 2. The temperature dependence of DC conductivity for pure and composite RF aerogels doped with silver.

Figure 3. Variation of the frequency exponent, $s$, with the temperature $T$ (K) for RF aerogel doped with silver.

Figure 4. The frequency dependence of $\varepsilon'$ at different temperatures for some RF aerogel doped with silver.

Figure 5. The frequency dependence of $\tan \delta$ at different temperatures for RF aerogel doped with silver.
It is well known that the complex dielectric constant \( (\varepsilon^* = \varepsilon' + j\varepsilon'') \) of the medium vary with the angular frequency \( \omega \) according to the following equation [19]: \( \varepsilon^* = \varepsilon_\infty + \left[ (\varepsilon_\infty - \varepsilon_\tau) / (1 + j\omega\tau) \right] \), where \( \tau \) is the relaxation time, \( \varepsilon_\infty \) is the static field dielectric constant, and \( \varepsilon_\tau \) is the high-frequency (optical) dielectric constant of the material. The real part of the complex dielectric constant \( \varepsilon' \) can be expressed as \( \varepsilon' = \varepsilon_\infty + \left[ (\varepsilon_\infty - \varepsilon_\tau) / (1 + j\omega^2\tau^2) \right] \). This equation gives an explanation for the decrease of the dielectric constant with the frequency. From the other hand, the behavior of dielectric constant with the frequency can be explained on the fact that the hopping of the charge carriers can not follow the frequency of the external applied electric field beyond a certain frequency value [20].

The imaginary part of the dielectric constant \( \varepsilon'' \) represents the dielectric loss through the material. A very important quantity is the dielectric loss tangent; \( \tan\delta \) which measures directly the phase difference due to loss of energy within the sample at a particular frequency, \( \tan\delta \) is given by \( \tan\delta = \varepsilon''/\varepsilon' \). The Variation of dielectric loss tangent (\( \tan\delta \)) with the frequency at different temperatures for RF aerogels doped with silver is shown in figure 5. It observed that dielectric loss tangent exhibits a peaking behavior at relatively low temperature. The peak is shifted toward a higher frequency with increasing the temperature. By increasing temperature the peaking behavior disappears and the dielectric loss tangent increase rapidly with the frequency.

4. Conclusion
Different samples of the RF-aerogels doped with silver nanoparticles were prepared by the sol-gel process using KOH as catalyst. DC electrical conductivity, \( \sigma_{dc} \), AC electrical conductivity, \( \sigma' \), dielectric constant, \( \varepsilon' \), and dielectric loss tangent, \( \tan\delta \) were measured for all prepared samples. The measurements were carried out in the frequency range from \( 10^2 \) to \( 10^6 \) Hz and at different temperature from 300 to 475 K. The results can be concluded as follows; the values of \( \sigma' \) are higher than those of \( \sigma_{dc} \) for all samples; \( \sigma' \) increases with increasing frequency; \( \sigma_{dc} \) exhibits a semiconducting behavior at relatively lower temperature region, while it exhibits a metallic behavior at relatively higher temperature region; Large overlapping conduction mechanism is the predominant conduction mechanism in these materials; \( \varepsilon' \) exhibits a normal behavior with the frequency, where it decreases with increasing frequency; \( \tan\delta(\omega) \) increases with increasing frequency at relatively lower temperature range, while it exhibits a peaking behavior at relatively higher temperature region. The peaks are shifted towards lower frequency with increasing temperature.

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