Ratio and Temperature Dependence of Dielectric Properties and AC Conductivity of Polyvinyl Alcohol / Iraqi Eggshell Composites

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Abstract

The polymer composites used in the present study were made of polyvinyl alcohol (PVA) as a matrix and *Iraqi eggshell* powder as filler. The eggshell powder was obtained from the waste of Iraqi chicken eggshell. The solution-casting method was used to prepare PVA/eggshell powder composite films with ratios (10, 30, and 50 wt %) of eggshell powder. The dielectric properties (dielectric constant, and power factor) and AC conductivity were investigated in the frequency range 100 kHz to 5 MHz at room temperature and different temperature (50, 70, 90, and 110 °C). It was found that the PVA sample and PVA samples containing 10% and 50% of eggshells had a dielectric constant that increases slightly with frequency up to 200 kHz, after which the decrease in the dielectric constant was very slight. While the sample of PVA containing 30% eggshell powder, the dielectric constant decreased slightly with increasing frequency. By studying the behavior of dielectric constant as a function of eggshell additives it was fond that the sample containing 50% of the eggshell powder has lowest values of the dielectric constant while the sample containing 10% of the eggshell powder has the highest values. The power factor decreased at a very small rate with increasing frequency and generally, the addition of eggshells led to a decrease in the power factor. At frequencies greater than 1MHz, it was found that the sample containing 10% eggshells has the highest conductivity while the samples containing 30% eggshells has lowest values. About the effect of temperature on the studied properties it was found that the dielectric constant and power factor generally increased with increasing temperature. Also, the values of the dielectric constant for samples containing 50% eggshell powder were lower than the other samples. It is generally found that the conductivity increased with frequency. At different temperatures it was found that sample containing 10% eggshells powder has close values of electrical conductivity. Generally, the samples had the highest conductivity at a temperature of 110 °C.

Key Words: PVA, Iraqi Chicken Eggshell Powder, Ratio, Temperature, Dielectric Properties, AC Conductivity.

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Introduction

Numerous studies have shown that chicken eggshell is considered as an aviculture byproduct that has been recognized as one of the global environmental problems, especially in countries that are interested in developing egg production (Hassan & Aigbodion, 2015). In the U.S. alone, about 150,000 tons of this material is disposed in landfills (Shuhadah *et al*, 2008). In Iraq, the yearly production of eggshell waste is about 23,000 tons (Veerabrahmam & Prasad, 2021).

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The general composition of eggshells, which varies according to each species, is a protein lined with mineral crystals, usually of a calcium compound such as calcium carbonate, these characteristics be eligible eggshell as a good candidate for bulk quantity, low-cost, lightweight and low load bearing composite utilizations, such as the automotive industry, homes, offices, trucks, and plants (Hassan *et al*, 2012). Many industrial wastes can be used as additives to other materials (such as polymers), and this means reducing the impact of these wastes. Eggshell is an example of this type of waste. In addition, the physical properties of a specific polymer can be controlled by changing the type of filler used, its concentration, method of penetration and interaction with the polymer chains (Omed & Bakhtyar, 2011). PVA can be manufactured in film form with promising applications can be easily done by solvent casting method. This synthesis technique is very useful for adding of different fillers materials or dopant into a PVA matrix to improvise or control properties such as thermal, morphological, photoluminescence, optical (Khan *et al*, 2019). PVA has many applications such as electronic devices, synthetic biomedical devices, membrane applications, drug delivery systems, electrochromic appliances, packaging, and textile applications (Deshmukh *et al*, 2016; Mohanapriya *et al,* 2017; Mohanapriya *et al*, 2016; Deshmukh *et al* 2017; Abdulkadir *et al*, 2021). A wide range of filler has been added to PVA to enhance or modify dielectric, optical, mechanical and gas separation properties (Reddy *et al*, 2019; Zheng *et al,* 2020; Karthik *et al*, 2020; Sanaa, 2021). Due to these many properties, PVA was chosen as a host matrix in this study by investigating the behavior of dielectric properties (dielectric constant, power factor) and conductivity at room temperature and different temperature within range of frequencies from 100 kHz to 5 MHz of PVA /eggshell composites.

Experimental Work

The samples used in this research were prepared by using polymer as a basic material and Iraqi eggshells as an additive. The eggshell was collected, then washed and dried, after which it was ground using an electric grinder, with a grinding time of three hours. Then the powder obtained from the grinding process was sieved using a sieve with a diameter of 25 micron. The solution-casting method was used to prepare PVA/eggshell powder composite films with ratios (10, 30, and 50 wt %) of eggshell powder. The required amount of PVA powder was dissolved in distilled water (DW) at 80°C for 2 hr. The PVA solution was then continuously stirred with a magnetic stirrer for 2 hr then the desired amounts of eggshell powder were added. The final solution is placed in a Petri dish in a dust-free chamber to allow the solvent to slowly evaporate in air at room temperature for seven days. The thickness of the resulting samples ranged from 0.06 to 0.17 mm.

The dielectric properties (dielectric constant $\varepsilon^{/}$ and power factor tan δ) AC conductivity σ were measured by using a Hioki 3532 LCR Hi tester from 1000 Hz to 5 MHz at room temperature and different temperature (50, 70, 90, and 110°C). The dielectric constant ($\varepsilon^{/}$), AC conductivity $\sigma_{(\omega)}$, and power factor (tan δ) were calculated by using the following equations (Bhat *et al*, 2004):

$$\varepsilon/= \frac{C_p d}{(\varepsilon_0 A)}$$

$$\sigma = \frac{d}{(R_p A)} \text{ (ohm.m)}^{-1}$$

$$\tan\delta = \frac{1}{R_p 2\pi f C_P}$$

Where d is the thickness of the sample, A is the area of the electrodes: $A= \pi r^2$, and ε_o is the free space permittivity (8.854×10^{-12} F/m).

Result and Discussion

Fig.1 shows the change of the dielectric constant with frequency at room temperature for composites consisting of PVA with additions of eggshell powder. It is clear that the PVA sample and samples containing 10% and 50% of eggshells have a dielectric constant that increases slightly with frequency up to 200 kHz, after which the decrease in the dielectric constant is very slight. In the sample containing 30% eggshell powder, the dielectric constant decreases slightly with increasing frequency. Increasing the dielectric constant with an increase in frequency indicates that the polarization of the samples increases due to the accumulation of charges on the electrodes, that is, the increase in the interfacial polarization of the electrodes or the increase in the possibility of molecules or dipoles to align with the change in the applied field (Tsangaris *et al*, 1998; Psarras *et al*, 2007). This is the reason for the slight increase in the dielectric constant of some samples from 100 kHz up to the frequency of 200 kHz. Also, for all samples it is noticed that the decrease in dielectric constant with frequency is very little. The reason for decreasing the dielectric constant with frequency is due to the inability of the dipoles to align with the change in the applied field and thus the decrease in polarization (Chatchai *et al*, 2013). Regarding the effect of increasing the percentage of eggshells, it is noted from the figure that the lowest values of the dielectric constant are for the sample containing 50% of the eggshell powder and the highest values for the sample containing 10% of the eggshell powder. It is noticed that the dielectric constant increases when adding 10% of the eggshell powder, but the continuous increase in the percentage of filler led to a decrease in the dielectric constant. In other words, the values of the dielectric constant decreased with the increase of the eggshell powder from 10 to 50%. The reason for this may be attributed to the fact that the addition of eggshell powder caused the inhibition of the movement of the dipoles to align with the change in the applied field, which means the lack of polarization, i.e., the dielectric constant.

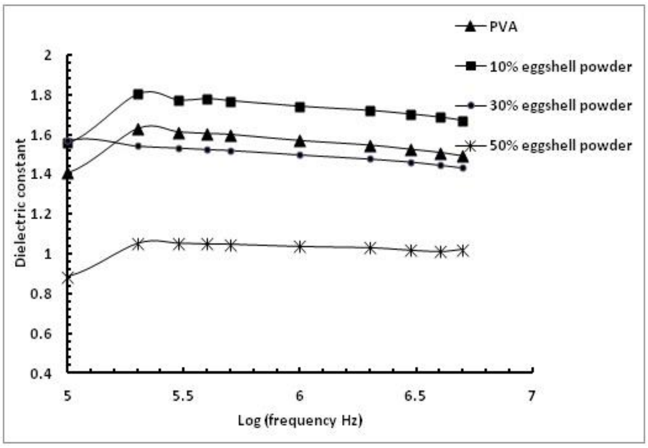

Figure 1. Dielectric constant plot of PVA/eggshell powder composites at different frequencies and filler concentrations

It is noticed from Fig. 2, with the exception of the addition of 30% of the eggshells, the addition of eggshells led to a decrease in the power factor. This is consistent with the behavior of the dielectric constant, that is, the increase in the addition of eggshells powder decreased the polarization, and this means that the addition of 10% and 50% of the eggshells powder led to a decrease in the response of the dipoles, which means a decrease in the dielectric constant. For the sample containing 30% eggshells, the power factor increases with increasing frequency up to 5 MHz. It is generally observed from Fig. 2 that the power factor decreases at a very small rate with increasing frequency. This is due to the inability of the dipoles to align with an external electric field, which means that the energy absorbed by the dipoles decreases. As previously indicated, as the frequency decreases, the dielectric constant will increase. This can be interpreted by taking into account the time available for molecular dipoles to align the field. At lower frequencies, dipoles have enough time to follow the applied electric field and align with it, which leads to larger values of permittivity or power factor (Campo, 2008).

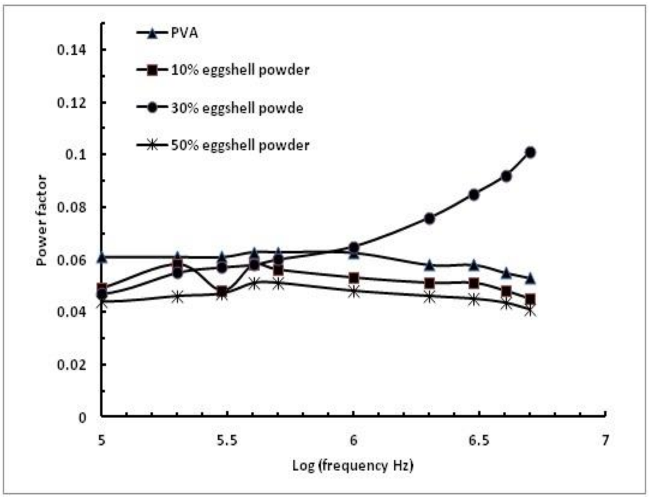

Figure 2. Power factor plot of PVA/eggshell powder composites at different frequencies and filler concentrations

Variation of electrical conductivity with frequency for the range from 100 kHz to 5MHz for different percentages of eggshell powder additions is shown in Fiq. 3. It is clear that all samples have close values of electrical conductivity up to frequency 1 MHz. At frequencies greater than 1MHz, it is clear that the highest vales of conductivity for samples containing 10% eggshells and the lowest values for samples containing 30% eggshells. An increase in the frequency of the applied electric field leads to an increase in the displacement of ions. An increase in frequency indicates that more energy is being expended on the charge carrier. The charge carrier hopping or tunneling is increased with increasing frequency (Bin Dahman *et al*, 2017). Thus, the AC conductivity increases with increasing frequency.

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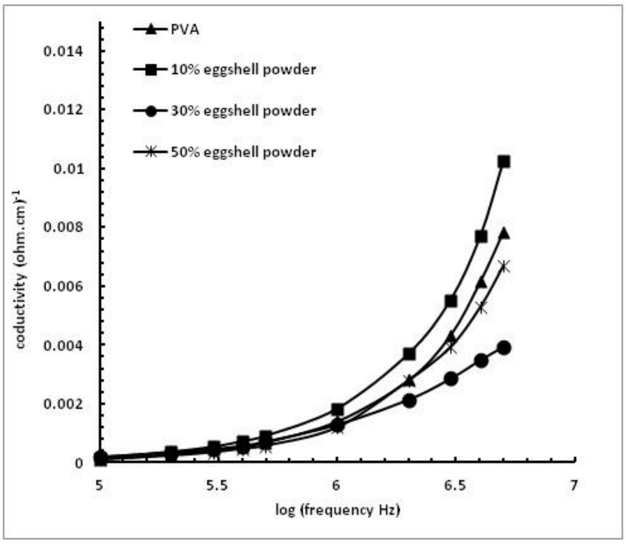

Figure 3. Electrical conductivity plot of PVA/eggshell powder composites at different frequencies and filler concentrations

Fig. 4 (A, B, C, D) shows the change of the dielectric constant with temperature for different additives of eggshells powder. It is clear that the dielectric constant generally increases with increasing temperature and for additives 10%, 30% and 50%, within a range of frequencies from 100 KHz to 5 MHz This is due to the fact that the increase in temperature leads to breaking the bonds between the polymeric chains, which gives more space for the polar groups to align with the change in the applied field, and this means an increase in the polarization or the dielectric constant (Young, 1989; Sinha *et al*, 2015). The figure also shows that samples without additives and samples containing 10% eggshell powder have close values of the dielectric constant at a temperature of 50°C and 70°C. Also, the values of the dielectric constant for samples containing 50% eggshell powder are lower than the other samples for temperatures from 50°C to 110°C and for frequencies from 500 KHz to 5MHz. The reason for this may be attributed to the fact that the addition of eggshell powder caused the inhibition of the reorientation of the dipoles towards with the external electric field, which means the lack of polarization, i.e., the dielectric constant.

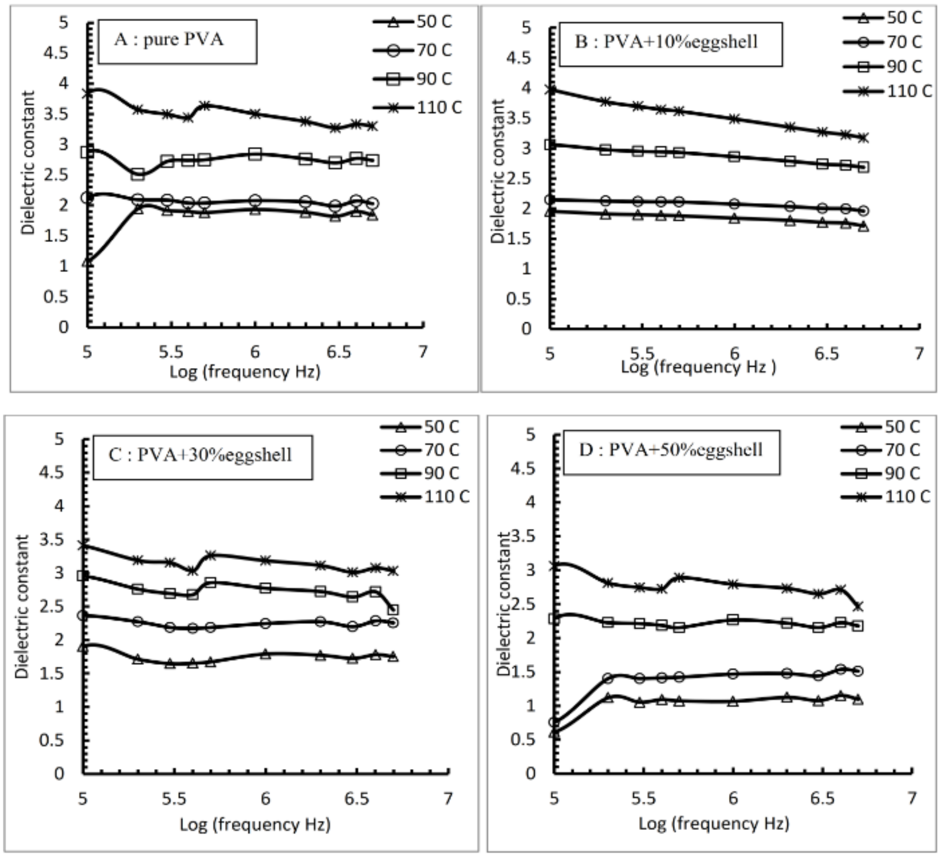

Figure 4. (A, B, C, D): Variation of dielectric constant with temperature for different additives of eggshells powder

Fig. 5 (A, B, C, D) show the effect of temperature on the power factor of samples containing 10%, 30% and 50% additions of eggshell powder for the range of frequencies from 100 kHz to 5 MHz. In general, it is clear that the power factor increases with temperature from 50 to 110°C. At the temperature of 90 ᵒC and 110 ᵒC, it was observed that some peaks appear, which represent the greatest energy absorbed by the applied electric field at certain frequencies. Change in power factor with frequency and temperature may be attributed to the movement of charged carriers and relaxation mechanism of the material. Both dielectric constant and power factor gradually increase with increasing temperature and increase towards lower frequencies. At higher temperatures, the rotation of the dipoles and molecular motions become easier, which speeds up the response to the applied electric field (Suat *et al,* 2016).

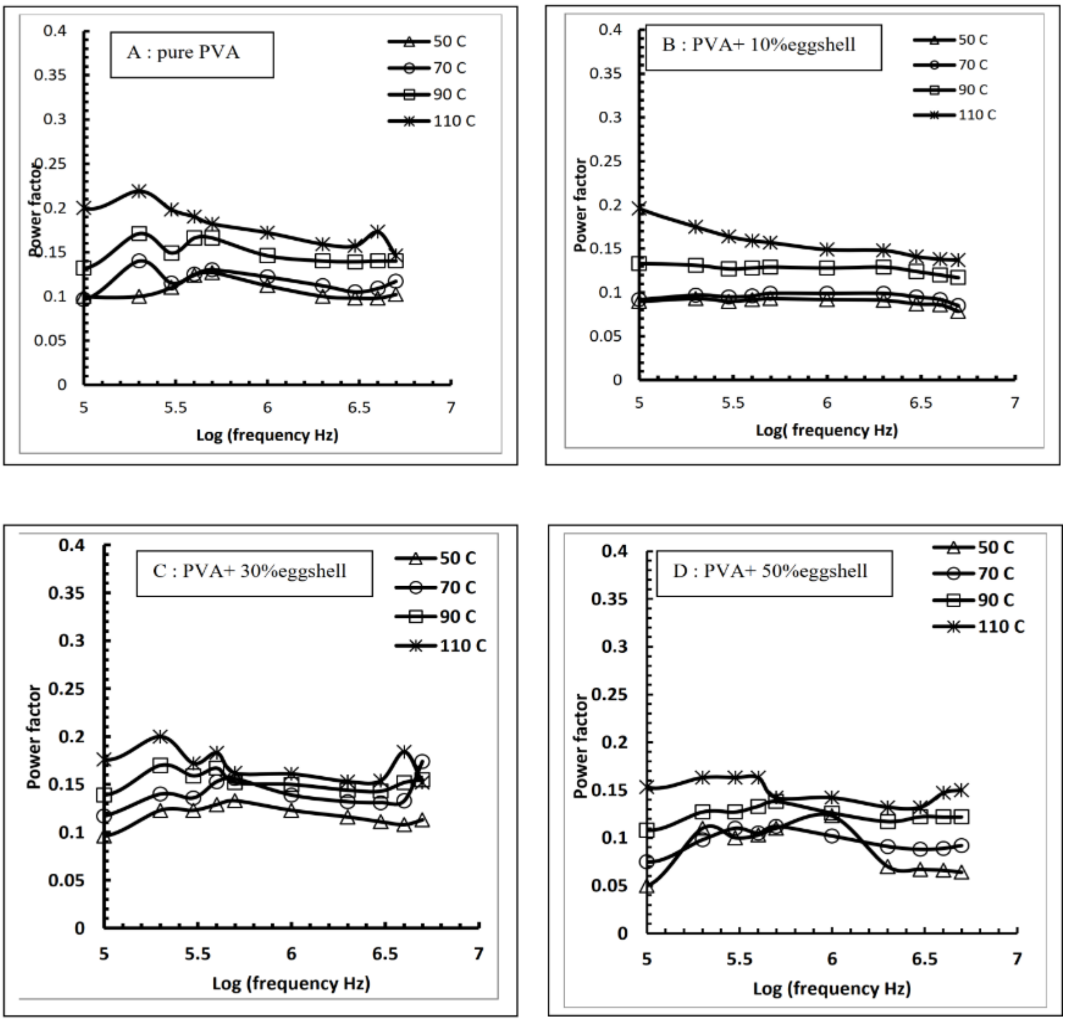

Figure 5. (A, B, C, D): Variation of power factor with temperature for different additives of eggshells powder

Figure 6 (A,B,C,D) show the change of AC conductivity within the frequencies range from 100 kHz to 5 MHz at different percentages of eggshell powder additions at temperatures 50, 70, 90 and 110ᵒC. It is generally clear that the conductivity increases with the increase in the applied frequency. This is due to the fact that an increase in the frequency of the applied electric field leads to an increase in the displacement of ions. An increase in frequency indicates that more energy is being expended on the charge carrier. The charge carrier hopping or tunneling is increased with increasing frequency (Bin Dahman *et al*, 2017). Thus, the AC conductivity increases with increasing frequency. Regarding the effect of temperature, the sample containing 10% eggshells powder has close values of electrical conductivity at different temperatures. The values start to vary gradually when adding 30% of the eggshell powder, and when adding 50%, the values are clearly different and the samples have the highest conductivity at a temperature of 110ᵒC.

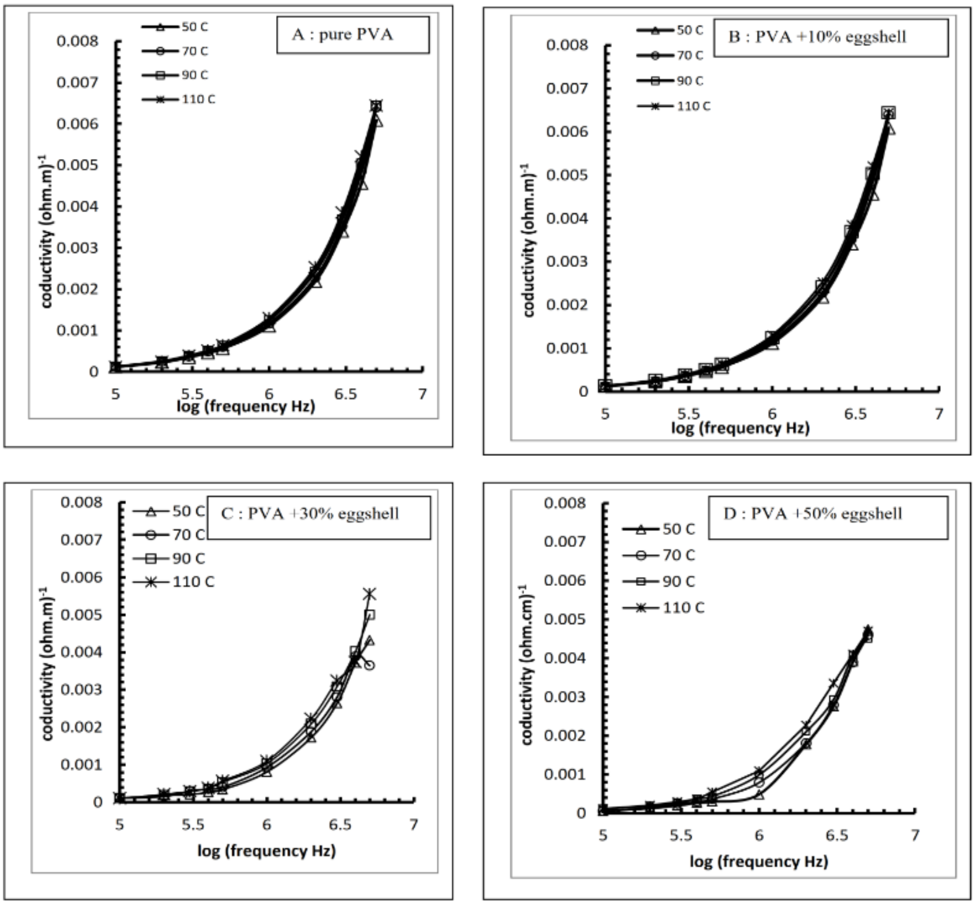

Figure 6. (A,B,C,D): Variation of AC conductivity with temperature for different additives of eggshells powder

Conclusion

The current study aims to use the eggshell powder (from the Iraqi chicken eggshells) as additives to the PVA polymer. The dielectric properties and AC conductivity were studied as a function of the additions ratios and for a range of frequencies from 100 kHz to 5 MHz at temperatures 50°C, 70°C, 90°C and 110°C. It was found that the dielectric properties and AC conductivity change with the additions of eggshell powder within the studied frequencies. For example, it was found that adding 30% of eggshell powder to the PVA gave the polymer, at frequencies greater than 1 MHz, the highest values of power factor and the lowest values of conductivity, while the values of the dielectric constant were not affected much in the case of room temperature measurements. On the other hand, both the dielectric constant and the power factor have the lowest values when adding 50% eggshell powder. In addition, it was generally concluded that increasing the temperature causes an increase in the dielectric constant and power factor for all the added percentages of eggshell powder. Also, in the case of adding 10% of eggshell powder, it was found that at the measurement temperatures of 50°C and 70°C, the dielectric constant values were close. As for the electrical conductivity, it was not significantly affected by the temperature change when adding 10% of eggshell powder at different measurement temperatures.

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