Dielectric and dynamic mechanical properties of Rochelle salt / PVA composites

E O Taha1* and G M Nasr2
1 Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt
2 Department of Physics, Faculty of Science, Cairo University, Giza 12613, Egypt
*Email: 1eman.omar2006@gmail.com; 2rrrrrgmail@yahoo.com

Abstract. A new type of PVA composites containing Rochelle salt was prepared using the casting method. The electrical, Dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) tests were performed on 0, 20, 30, and 50 weight% PVA based Rochelle salt to identify the effect of salt on the electrical, thermal and mechanical properties of composites. The results showed that the dielectric properties of composites were greatly improved by the addition of salt. The dielectric constant by 28.5%, 98.4% and 236.5% for composite contents 20 wt%, 30 wt% and 50 wt% Rochelle salt, respectively. The observations of dynamic mechanical analysis indicated that the adding of salt reduces both the storage modulus and affect the glass transition temperature of the composites. Moreover, the thermal stability and char yield of the PVA composites were highly affected by the Rochelle salt content.

1. Introduction
A massive number of polymers and polymer blends such as polymethyl methacrylate (PMMA), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), PVP-PVA, polyethylene dioxythiophene: polystyrenesulfonate-polyvinyl alcohol and polypyrrolepolo(ethylene glycol) have been used as dielectric layers recently [1-5]. Mixing physically two or more polymers with inorganic materials in order to create polymer composites with modern, specific properties is one of the most effective ways to improve dielectric behaviour. [4 6 ]. The dielectric, electrical and mechanical properties of the material composites are important for its applications in electronic devices [7]. Numerous articles on PVA composites were reported. For instance, the studies on the dielectric properties of PVA-InTiO [8] and PVA-Al2O3 [9] have been reported by Sugumaran et al. Also, PVA/ BaTiO3 by Tuncer et al. [10] and PVA/ Al2O3 by Nigrawal et al. [11]. The studies on the mechanical properties of Reduced graphene oxide (RGO) doped PVA has been reported by Aslam et al. [12] and PVA/ Cellulose nanofibrils (CNF) nanocomposite has been reported [13].

In this sense, PVA composites are attractive for electrical applications because of their relatively high dielectric strength, high flexibility, lightweight and better chemical stability [14,15]. Morsi et al. [16] examined the structural properties and the dielectric behavior of polystyrene (PVA)/ carboxymethyl cellulose (CMC) blend filled different contents of biosynthesized Au nanoparticles to be used for radio/audio frequency operating microelectronic devices. Anlin Golda et al. [17] have prepared a novel Bi1,Sm2FeO3/PVA nanocomposite film with enhanced dielectric properties to be used in the development of transient electronics of microwave devices. Ghoshal et al. [14] have investigated dielectric properties of PVA composites filled different concentrations of the alizarin red and have confirmed its potentially used in optical filtering and flexible optoelectronic applications.
This work also aimed to enhance the dielectric behaviour of the PVA matrix by means of incorporating different concentrations of Rochelle salt in the PVA matrix in addition to improve mechanical properties PVA composites by increase its flexibility to be able to use in applications like organic flexible electronic devices.

2. Experimental Methodology

2.1. Materials and sample preparation
Polyvinyl alcohol (PVA) powder [Sigma- Aldrich] was dissolved in double distilled water at 80 °C and stirred for 4 h in order to ensure uniform dispersion. The Rochelle salt (Potassium sodium tartrate tetrahydrate, KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}•4H\textsubscript{2}O) was papered by mixing the two ingredients; potassium bitartrate (KHC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}) and Sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) in distill water at temperature approximately 55 °C. To prepare Rochelle salt/ PVA composites, different weight percentages (0, 20, 30 and 50 wt. %) are added to the above solution of PVA in water and stirred for 1 h. The mixture was then cast in a glass dish and the sample was left to dry for a week at room temperature.

2.2. Characterizations
Dielectric properties were measured with a Hioki 3532-50 LCR Hitester in frequency range from 50 Hz to 5 MHz. Dynamic mechanical analysis (DMA) was conducted on a Triton Instruments, running in the tension mode at frequency of 1 Hz over the temperature range from -50 to 80 °C at a scanning rate of 5 °C/min. The thermal stability was performed using Thermogravimetric Analysis (TGA) - Mettler Toledo where the samples were heated in N\textsubscript{2} atmosphere from room temperature to 600 °C with 20 °C/minute heating rate.

3. Results and Discussion

3.1. Dielectric properties
Complex dielectric constant as function of frequency (f) is represent by equation: \(\varepsilon^*(f) = \varepsilon'(f) - \text{i}\varepsilon''(f)\). The real part \(\varepsilon'(f)\) is the relative dielectric constant and the imaginary part \(\varepsilon''(f)\) is the dielectric loss. The relationship between the imaginary and the real part \(\frac{\varepsilon''}{\varepsilon'}\) is called “dissipation factor” and denoted by \(\tan \delta\) which referring to the angle between the voltage and the charging current [18].

The change in the dielectric permittivity, \(\varepsilon'\), and the dielectric loss, \(\varepsilon''\), versus frequency of Rochelle salt/PVA composites is shown in figure 1 (a, b) for three concentrations of the Rochelle salt (RS) (20 wt%, 30 wt% and 50 wt%) at room temperature. Dielectric permittivity and dielectric loss reach high values in the low frequency region, which decrease with the increasing frequency. This behavior demonstrates a process of relaxation attributable to an interfacial polarization, known as the Maxwell-Wagner-Silars effect, which is a phenomena of accumulation of charges on interfaces in heterogeneous media. [18]. Also, figure 1 (a, b) shows that the \(\varepsilon'\) of the PVA composite increased from 63 for pure PVA at frequency 50 Hz to 212, 125 and 81 for composite contents 50 wt%, 30 wt% and 20 wt% Rochelle salt (RS), respectively, which represents an increase in dielectric constant by 236.5%, 98.4% and 28.5% for composite contents 50 wt%, 30 wt% and 20 wt% RS, respectively. This increase might be due to the high dielectric constant of RS which approximately is 2000 at room temperature [19] resulting the accumulation of carriers at the internal surface of a PVA matrix producing interfacial polarizations. The dielectric losses are also influenced by the concentrations of Rochelle salt (RS) in the PVA and increased from 104 for pure PVA at frequency 50 Hz to 395, 541 and 455 for composite contents 50 wt%, 30 wt% and 20 wt% Rochelle salt (RS), respectively.
Figure 1. The frequency dependence of (a) dielectric permittivity, $\varepsilon'$, and (b) the dielectric loss, $\varepsilon''$ of Rochelle salt / PVA composites.

Figure 2 shows AC conductivity for the Rochelle salt / PVA composites as frequency function. The values of conductivity show great dispersion of frequencies. Conductivity corresponds to constant values within the low frequency range and sometimes increases slowly with frequency, whereas it shows an exponential frequency dependence at high frequency. The conductivity tends to be following the universality rule stated in the following Eq.:

$$\sigma_{AC} (f) = \sigma_{DC} + A f^s$$

where $\sigma_{DC}$ is the DC limiting value of conductivity, $f$ the frequency, $A$ a fitting parameter and $s$ frequency exponent parameter related to the under test material. The value of $s$ could be calculated from the slope of a plot of log $\sigma_{AC}$ versus log $f$. The values of $s$ were found to be 0.69 for pure and 50 wt% composites and 0.61 for 20 wt% and 30 wt% composites.

AC conductivity sums all processes of dissipation, including dipolars and real ohms due to migration charges for the carrier. The field alternation is sluggish at low frequencies, allowing charges inside the composite to drift over large distances. The insulating existence of the host material imposes heavy restrictions on this movement, thereby contributing to low conductivity values. As frequency rises, field alternation becomes faster, and charges cannot migrate over long distances. Charges can, therefore “jump” between neighboring conductive sites and thus contribute to the overall conductivity reported.

Figure 2. The frequency dependence of conductivity of Rochelle salt / PVA composites.
3.2. Dynamic mechanical properties

The temperature impact of Rochelle salts / PVA composites is illustrated in figure 3(a) on the storage module at 1 Hz frequency. When the temperature rose in the first glassy region, the storage Module decreased in three distinct areas of all PVA composites; due to the reduction in segmental mobility, the Module exhibited the highest module values in the first glassy region. The modulus dramatically reduces the transition temperature of the glass (T_g) for the second transition region. In the third rubbery region, due to the high mobility of polymer chains and their energy dissipation, the modulus has low values. The storage modulus value for purity PVA was higher than all composites (4.9 GPa at 10 °C), and with the increase in Rochelle salt (RS) the storage modulus decreases.

Figure 3(b) shows a variation of the damping parameter ($\tan \delta$) for various Rochelle salt / PVA composites. The temperature of the glass transition (T_g) is a temperature at which maximum parameter of peak damping is attained. The $\tan \delta$ can shift to a higher temperature by increasing the content of Rochelle salt. The values of T_g are 29.7 °C, 26.4 °C, 41.3 °C and 46.9 °C for pure PVA, 20 wt% RS, 30 wt% RS and 50 wt% RS, respectively. For 30 wt% RS and 50 wt% RS composites the peaks appear between -18 °C and -24 °C are the Curie points of RS [20].

Figure 3. Temperature dependence of (a) storage modulus and (b) $\tan \delta$ of Rochelle salt / PVA composites.

3.3. Thermal Properties:

Thermogravimetric Analysis (TGA) test was utilized to investigate the thermal stability of Rochelle salt / PVA composites (figure 4). The decomposition temperature of pure PVA is approximately 217 °C and it shifted towards higher temperatures as concentrations of RS increase. The decomposition temperatures of composites content 20 wt% RS, 30 wt% RS and 50 wt% RS are approximately 231 °C, 236 °C and 258 °C, respectively. Moreover, The Char residue is a significant affected by RS content and increases with RS content and its values are 13 mg, 22 mg and 25 mg for 20 wt%, 30 wt% and 50 wt% RS / PVA composites, respectively.

4. Conclusions

In this paper, 20 wt% RS, 30 wt% RS and 50 wt% RS were well dispersed in the PVA matrix and used to fabricate Rochelle salt / PVA composites using the casting method. The dielectric, dynamic mechanical and thermal properties were examined. The results showed that the dielectric properties of Rochelle salt / PVA composites were improved with increase Rochelle salt content. The dielectric constant increases by 236.5%, 98.4% and 28.5% for composite contents 50 wt%, 30 wt% and 20 wt% RS, respectively. The results also showed that the storage modulus and the glass transition temperature were significantly affected by adding of Rochelle salt where the storage modulus decreases with Rochelle salt and the elasticity of all PVA composites increases. Moreover, the thermal stability of the
Rochelle salt/PVA composites was also highly affected by the Rochelle salt content. The decomposition temperatures are approximately 231°C, 236°C and 258°C for 20 wt% RS, 30 wt% RS and 50 wt% RS PVA composites, respectively.

Figure 4. TGA graph of Rochelle salt / PVA composites

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