1 Noor A. Hameed

2 Alaa Raad Hussein

Electrical and Thermal Properties Enhancement of Carboxymethyl cellulose Composite Films Reinforced by Chromium Chloride

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Abstract: - Pure (CMC) polymer films and CrCl3 salt reinforcement was prepared using solution casting method. The salt was added to the CMC at various weight ratios of (1, 5, 9, and 13) wt%. The electrical (dielectric) and thermal properties were investigated for all samples. On the other hand, salt weight ratio effects on electrical (i.e., dielectric) and thermal characteristics of (CMC-CrCl3) composite films were examined at room temperature. When frequency increased, a reduction in the dielectric constant and rise in the A.C electrical conductivity were revealed for all composite films. In contrast, the A.C electrical conductivity and dielectric constant were increased as long as the salt weight ratio increased. A significant increase in the thermal conductivity coefficient of (CMC-CrCl3) composite films was revealed as the salt weight ratio increases. Generally, the dielectric constant, ionic conductivity and dielectric loss were increased as the metal salt content increase confirming the increment of the ion concentration. However, the results indicate the possibility of using these composite films in devices that require stability of the dielectric properties at high frequencies.

Keywords: Polymer composite, Carboxymethyl Cellulose (CMC), Chromium Chloride (CrCl3), Electrical Properties, Thermal Properties.

I. INTRODUCTION

Polymers especially biodegradable type has considered recently by researchers as an alternative to the synthetic polymers produced from petrochemicals industry [1, 2]. Less research woks were conducted on the battery applications specifically sodium-based biopolymer electrolytes for Na-ion [3]. However, the low sodium resources cost and its availability placed it as a suitable candidate to replace lithium-ion based batteries [4, 5].

The modification of the polymer electrolytes in terms of mechanical, optical and electrical properties, are required to plasticizing, or doping with variety of inorganic salts or nano fillers [6, 7]. On the other hand, chitosan, pectin, cellulose, gelatin, agar and starch who are natural polymers can be used potentially as polymer hosts for the diverse solid polymer electrolytes [8]. The properties improvement of these electrolytes' polymer can be conducted by the aid of plasticizers such as carbonate, glycerol, propylene and etc. [9].

Most of the research work performed on the natural polymers were utilized either ammonium-based salts or lithium. In which these materials resulted in conductivity lower than practical applications level requirement [10]. However, to reach better level of conductivity, a utilization of the Carboxymethyl cellulose (CMC) is a suitable choice. This natural polymer is a cellulose polymer derived from plants with additional properties such as water soluble, polyanionic and polysaccharide polymer [1]. So, a selection of CMC in this investigation was related to its biodegradability, non-toxicity and able to form films [12]. In addition to that, CMC alone as a natural polymer has low ionic conductivity, therefore, its required salt doping to improve the ionic conductivity to be utilized in the applications of energy storage device [13]. In the current research work, the dopant Chromium Chloride was inculcated in the CMC matrix to develop complex polymer electrolytes (CMC-CrCl3). Based on that, the effect of salt on the dielectric constant and thermal properties were investigated.

II. MATRIX MATERIAL PROPERTIES

The type of material that used as a matrix to prepare the composite was polymer called Carboxymethyl cellulose (CMC) manufactured by a German Company provided cellulose and chromium chloride. Its chemical formula is $CrCl_3$ which has a purple crystal form and larger solubility in distilled water. its average molecular weight of about (158.35 g/mol).

A solution casting process was used to make polymer electrolyte sheets of CMC doped with chromium chloride ($CrCl_3$). The solvent was distilled water used to make CMC-$CrCl_3$ at various weight ratios ((0, 1, 5, 9, 13) wt %). Then, vigorous stirring was performed after few hours to ensure homogenous mixture. The mixture then cast in glass Petri-dishes to achieve the matrix.

III. PURE (CMC) POLYMER FILM PREPARATION AND $CrCl_3$ SALT REINFORCEMENT

The pure (CMC) polymer films and its reinforcement $CrCl_3$ salt was made by casting method using specific glass molds. All molds that used in the experiment were cleaned up from any dust and dirt then they were fixed on a flat surface.

[1]Department of scientific Affairs, University of Diyala, Diyala 32001, Iraq. Noor.amer.hameed@uodiyala.edu.iq

[2] BioMedical Engineering Department, Al-Khwarizmi College of Engineering, University of Baghdad, 10070 Al Jadriya, Karrada, Baghdad, Iraq. alaa.r@kecbu.uobaghdad.edu.iq

The films were prepared firstly by mixing (1g) of (CMC) polymer to make a homogeneous solution with (15ml) of distilled water at 80°C for 1 hour using a magnetic stirrer. The produced solution was poured in the mold and let to full evaporation of the solvent to yield the required film. During the mixing procedure performing above, the salt $CrCl_3$ at certain percentages of ((1, 5, 9, and 13) wt%) was added. The addition of the salt was combined with extra addition of 15 ml of distilled water and at the same condition.

IV. RESULTS AND DISCUSSION

A. Dielectric Measurements

The measurement of the dielectric constant (ε') was performed in a frequency range of (1MHz-5MHz) for all (CMC) polymer films and $CrCl_3$ salt films.

Fig. 1 Shows the dielectric constant for all types of composite films. Large ε' value was revealed at low frequencies and then decreased significantly with increasing frequency. This attributed to the dipoles phenomenon that works on aligning and arranging the molecules at low frequency in the current flow direction of the two poles. Meanwhile, the adequate time that gained at low frequency becomes short at high frequencies, in which the alignment of the molecules in the direction of the external electric field becoming less comparing to the arrangement at low frequency [14]. On the other hand, the dielectric properties such as AC conductivity ($\sigma_{a.c}$), dielectric constant and dielectric loss provide information about the distribution of charges in the presence of an electric field in a polymer electrolyte [15, 16].
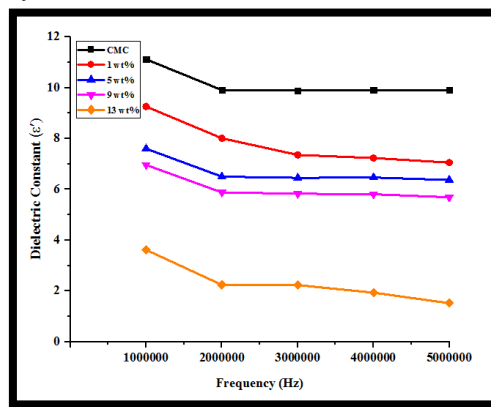

Fig. 1 Dielectric Constant of CMC Reinforced with $CrCl_3$

The dielectric properties can be given by the following equation:

$$\varepsilon_r(w) = \varepsilon' + i\varepsilon'' \tag{1}$$

where ε_r is the complex dielectric constant, ε' is the real part permittivity and ε'' is imaginary part permittivity, ε' and ε'' is given by:

$$\varepsilon'' = (t\ cp/A\varepsilon_0) \text{ and } \varepsilon'' = \varepsilon' \tan\delta \tag{2}$$

where t is the film thickness, A is the electrode area, CP is the electrolyte capacitance in parallel, ε_0 is the permittivity of free space and ($\tan\delta$) is the dielectric loss tangent. The real part permittivity ε' indicates how material is able to store energy, consequently the imaginary part permittivity is ability to dissipate energy. However, the dissipation of energy that occur in the composite was attributed to the conduction or as it can be said dipole migration.

Fig. 2 Shows the frequency response of the imaginary part permittivity (ε'') for all salt concentrations of the CMC-$CrCl_3$ samples. High ε'' was observed at low frequency and then gradual decrease as frequency increase to reach a plateau response when frequency reached higher value. The dipoles at lower frequency were capable of following the field direction due to high ε' and ε'' values, this related to the electric polarization [17]. However, this following up of the field direction that reduced dramatically at higher frequency, and all dipoles becomes incapable of reorient themselves as the field direction changes. So, it resulted approximately constant values of ε' at higher frequencies [18]. As it known that ε' is linked directly to the energy storage capacity of the polymer electrolyte. Therefore, increasing dielectric constant resulting in increasing electric flux density; in which enables the sample to have large electric charge quantities for a long period of time at low frequency.
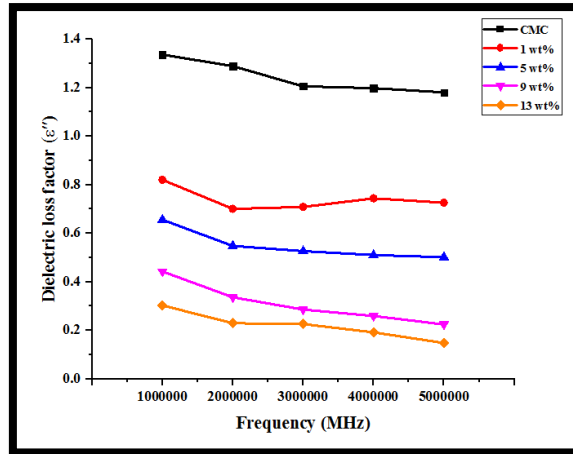
Fig. 2 Dielectric loss factor as a function of frequency of CMC Reinforced with $CrCl_3$

In general, decreasing (ε' and ε'') with increasing salt concentration attributed to the increase the number of available ions in the sample in which effect the conductivity of the sample. It is worthy noted that the value of ε' at (5 wt%) salt concentration has a tiny higher than (9 wt%) salt concentration which related to unknown effect. On the other hand, the dielectric loss is high at lower frequency region which considered high also at heavy CMC doped because of the much charge carriers number revealing to the dipoles free motion of within the polymer electrolyte. based on dielectric loss factor, the AC conductivity can be calculated by using:

$$\sigma_{a.c} = w\, \varepsilon_0\, \varepsilon'\, \tan\delta \qquad\qquad (3)$$

where $w = 2\pi f$ is the angular frequency of the applied AC field. The variation in the value of the dielectric parameters with salt concentration such as A.C conductivity shown in Fig. 3, indicating the frequency dependent are sensitive to both concentration of the carrier and to the dipoles present in the sample. the highest percentage of salt (13 wt%) has maximum conductivity in which its higher than, of (9 wt%) salt, related to the large decrease in the interchain distance [19].
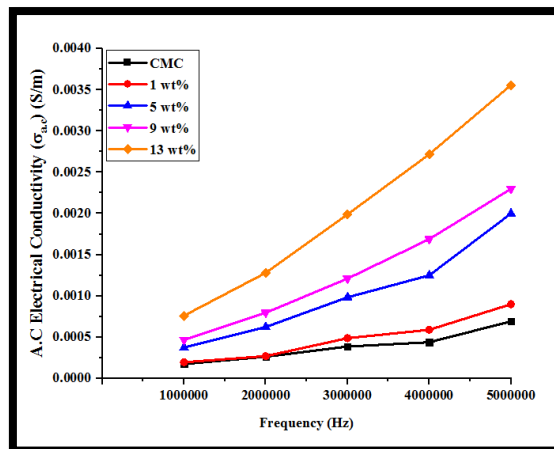

Fig. 3 AC Conductivity of CMC Reinforced with $CrCl_3$

B. Thermal Properties
1. Thermal Conductivity Coefficient

The use of Chromium Chloride is to increase the transport carriers and increase thermal conductivity. As it is known that polymer is a heat and electricity insulation material. However, it was reinforced by different weight ratios of Chromium Chloride that considers responsible for the transfer of thermal energy in the conductive materials. Fig. 4 shows a significant improvement in the thermal conductivity values of the composite films (CMC-$CrCl_3$) compared to pure (CMC) films. The preferred value of the composite films of (13 wt%) reinforced equals to 0.0199 w/m.oK which is explain the regular distribution in the polymer matrix. The thermal conductivity of the pure CMC matrix material compared to the reinforced matrix material is low (0.0123W/m°K). This increment in the thermal conductivity related to $CrCl_3$ reinforcement materials that have higher thermal conductivity than the thermal conductivity of polymer. Table 1 shows the values of the thermal conductivity coefficient for all polymer composite films [20, 21].
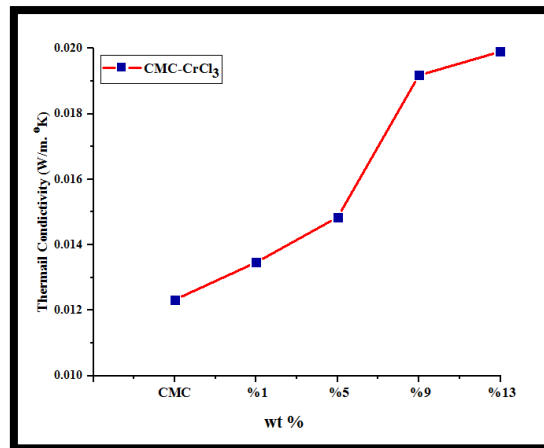
Fig. 4 Thermal Conductivity Coefficient of CMC Reinforced with $CrCl_3$

TABLE I
THERMAL CONDUCTIVITY COEFFICIENT OF POLYMER COMPOSITE FILMS

wt % of $CrCl_3$	K (W/m.°K)
CMC	0.01233
1%	0.01346
5%	0.01484
9%	0.01918
13%	0.0199

V. CONCLUSIONS

Dielectric and thermal characteristics of a two types of a materials pure CMC and reinforced CMC by using $CrCl_3$ up to 13 wt% were investigated.

The increase in the dielectric constant and the dielectric loss with increasing the weight ratios of which is attributed to the increase in the polarization of the interface. Decrease in the dielectric properties with increasing frequency for all concentrations at low frequencies, while at high frequencies, the dielectric properties do not depend on frequency and remain constant, which indicates the possibility of using these composite films in devices that require stability in the dielectric properties at high frequencies. By increasing the weight ratios, the thermal conductivity coefficient increases due to the increase in lattice vibrations within the polymer structure.

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